

THE COMPOSITION AND FUEL VALUE OF NATURAL GAS

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The composition and fuel value of natural gas by Francis C. Phillips

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FRANCIS C. PHILLIPS

**THE COMPOSITION
AND FUEL VALUE
OF NATURAL GAS**

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GEOLOGICAL SURVEY OF PENNSYLVANIA.

J. P. LESLEY, STATE GEOLOGIST.

*Supplement of
Francis C. Phillips*

THE COMPOSITION AND FUEL VALUE
OF
NATURAL GAS.

By **PROF. FRANCIS C. PHILLIPS.**

WESTERN UNIVERSITY, ALLEGHENY CITY.

Extract from Annual Report for 1886.

UNIV. OF
CALIFORNIA

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UNIV. OF
CALIFORNIA

The Chemical Composition of Natural Gas.

BY FRANCIS C. PHILLIPS,
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Introduction.

Natural gas, as obtained from several of the most productive fields in Pennsylvania, according to the analytical data presented in this report, consists chiefly of the hydrocarbons of the paraffin series, together with nitrogen, a small proportion of carbon dioxide and traces of oxygen. Free hydrogen was found in minute quantity in Speechley gas. It is possible that by employing many thousand cubic feet of gas, traces of other constituents might be discovered. Inasmuch as the composition of natural gas possesses an interest for those who are not familiar with the strictly chemical aspect of the question, a few preliminary statements as to the more characteristic properties of its chief constituents will no doubt prove of value in this connection.

Hydrogen is obtained as a gas by the action of dilute sulphuric acid upon zinc. It is also produced during the putrefaction of vegetable matters buried under stagnant water. Its specific gravity is 0.069234 as compared with

NOTE.—Prof. Phillips has spent considerable time in the study and practical investigations of gaseous fuels, and at my request he was commissioned in the early part of the year to make analyses of the natural gas from eight of the most prominent pools in the State, and one analysis of the Fredonia gas in New York.

The first systematic investigation as to the composition of natural gas in the State, was made by the Geological Survey in 1875, the results of which were published in a Report on the Use of Natural Gas in Iron Manufacture, in 1876. Since 1883, when the use of natural gas for fuel became more general, numerous analyses of the different gases have been made by a number of chemists. The wide differences in the composition of the gases as shown by these analyses were so great that Prof. Phillips exercised more than special care in the collection of his samples and in the method of determining the individual constituents of the gases. All analyses were made in duplicate.

C. A. ASHBURNER,
Geologist in Charge.

air. One cubic meter weighs 0.089593 kilogram. One cubic foot weighs 39.12 grains. Hydrogen is odorless and tasteless. It takes fire at a bright red heat, and more readily than other constituents of fuel gases.

Hydrogen in burning generates 34180 heat units per unit weight burned. The product of its combustion is water.

In fuel gases hydrogen may occur in two very different forms.

In its *free* or *uncombined* state, it is often reported in the analyses of natural gas, and constitutes generally from 30 per cent. to 40 per cent. by volume of ordinary coal gas, being a product of the destructive distillation of coal at very high temperatures. The presence of a large proportion of *free* hydrogen in a gas fuel causes it to burn with a relatively small admixture of air, since one volume of hydrogen requires only one-half volume of oxygen, or two and one-half volumes of air for complete combustion. The hydrogen flame is non-luminous.

In *combination with carbon*, in the form of hydro-carbons, hydrogen constitutes about one-fourth by weight of the combustible portion of the natural gas now being used as fuel in Pennsylvania.

These hydro-carbons, which represent approximately nine-tenths by volume of natural gas, are divided into two classes: Paraffins and Olefines. Of the paraffins, the best known and most abundant is methane (C_1H_4) consisting of 25.03 per cent. hydrogen, and 74.97 per cent. carbon by weight.

Methane is, like hydrogen, a product of the destructive distillation of coal, and consequently constitutes a large proportion of ordinary coal gas. It is also produced with hydrogen when plants decay at the bottom of rivers and swamps, and hence its older name of marsh gas. Methane, when pure is odorless, and not poisonous. Its specific gravity is 0.55297. One cubic meter weighs 0.7148 kilogram. One cubic foot weighs 312.36 grains. It is converted into a liquid under a pressure of about 2700 lbs. per square inch at 12° F., or at 263° below zero F., under atmospheric pressure. Methane requires twice its volume of oxygen or ten

volumes of air for its complete combustion, and the products are carbon dioxide and water vapor.

The Hukill well, Lyon's run, south of Murrysville, as already stated, yields this gas in a nearly pure condition. Methane contains *in one cubic foot, two cubic feet of hydrogen*, and hence in the union of the carbon and hydrogen, a considerable condensation occurs. Methane is the typical and best known member of a large group of hydro-carbons, which exhibit a remarkable resemblance in chemical relationships. The following list includes several of the most important :

Methane,	$C H_4$
Ethane,	$C_2 H_6$
Propane,	$C_3 H_8$
Butane,	$C_4 H_{10}$
Pentane,	$C_5 H_{12}$
Hexane,	$C_6 H_{14}$
Heptane,	$C_7 H_{16}$
Octane,	$C_8 H_{18}$
	$C_n H_{2n+2}$

The first four hydro-carbons are gases, but are more and more easily condensable to the liquid form in proportion as the amount of carbon is greater. The higher paraffins are solid. Common "paraffin wax" contains several of the highest members. While Methane ($C H_4$) constitutes from 50 per cent. to 90 per cent. or more of Pennsylvania natural gas, Ethane, ($C_2 H_6$), the next member of the series occurs in smaller quantity. Concerning the higher members, Propane, ($C_3 H_8$), and Butane, ($C_4 H_{10}$), very little is as yet known, but there is reason to think that they are of common occurrence. Pentane, ($C_5 H_{12}$), is found in the lightest distillates from petroleum, and the higher members are found in abundance in crude oil. It may be said concerning the gaseous hydro-carbons of the series that they possess higher specific gravity, fuel value and illuminating power, and also stronger odor in proportion as the percentage weight of carbon is greater.

The illuminating power of pure methane, artificially prepared, has been determined as 5.15 to 5.20 standard candles

per 5 cubic feet burned per hour. (Wright, Chemical News, 1885, p. 102.)

The second class of hydro-carbons found in gas and petroleum includes the Olefines. Of these the typical member is Ethylene or Olefiant gas, (C_2H_4). Ethylene is one of the products of the action of heat upon coal and various vegetable substances. It is a gas having a specific gravity of 0.96744. Condensable to a liquid at a temperature of 166° below zero F. According to Frankland its illuminating power is equal to 68 standard candles, and hence the name "illuminating hydro-carbons" often give to the group. One cubic foot in burning requires 3 cubic feet of oxygen, or 15 cubic feet of air. On account of their limited occurrence, olefines in many cases have no influence upon the fuel value of natural gas. They appear to be more abundant among the less volatile hydro-carbons of petroleum.

Whether hydrogen occurs in the *free state* in a gas fuel, or as a hydro-carbon, the product of combustion will invariably be water vapor, mixed in the latter case with carbon dioxide.

Carbon Dioxide, CO_2 . Well known as a universal product of decay, and as a gaseous furnace product, Carbon Dioxide, or Carbonic Acid is everywhere present, in the air, in water and in the soil and rocks.

A suffocating gas, having a specific gravity of 1.5241. 1 cubic meter weighs 1.9650 kilogram.

Condensable to a liquid under 780 lbs. pressure at 60° F.

Being incombustible its presence in gas (varying from a trace to 4 or 5 per cent.) tends to reduce to a corresponding degree the fuel value. Its presence may readily be shown by causing the gas to stream slowly through lime water, in which a milky deposit of carbonate of lime soon begins to form.

Nitrogen.—As a diluent of greater influence upon fuel value, we must regard nitrogen, on account of its occurrence in larger quantity. Constituting $\frac{1}{4}$ of atmospheric air, it is well known for its chemically indifferent character. In gas fuels it reduces the heating power in proportion to its quantity.

Gas from the Hukill well, Lyon's run, contained 2.02 per cent. while gas from Houston (near Canonsburg) contained 15.30 per cent. of nitrogen. Should the natural gas supply ever become seriously diminished, it is probable that a time will come when the actual calorific power will be an important factor in determining the market value. In that event the proportion of carbon dioxide and nitrogen, as well as the character of the hydro-carbons, will possess great interest for the gas companies and the consumers.

Oxygen being well known as the constituent of atmospheric air which is the active cause in all cases of combustion slow or rapid, its presence in natural gas would seem improbable. Contact of oxygen with the oxidizable elements of gas under high pressure would appear likely to cause its absorption and the formation of a corresponding amount of carbon dioxide or water. Nevertheless minute traces are constantly found and are indicated with great positiveness in gas as it flows directly from the wells and under high pressure. It has been experimentally shown that oxygen and nitrogen may be dissolved and held in mechanical solution by petroleum, and that oxygen is even more soluble in petroleum than in water. (St. Guiewosz, Reports of the Berlin Chemical Society, 1887, p. 188.)

For its liquifaction methane requires, as already stated, a pressure of at least 2,700 lbs. at common temperatures. Ethane is liquified under a pressure of 690 lbs. Carbon dioxide requires a pressure of 780 lbs.

Far greater pressures are needed for the liquifaction of oxygen, nitrogen and hydrogen.

It is a fact of much interest in this connection that in the case of methane, the principal constituent of natural gas, the pressure under which liquifaction takes place is about four times that found in the most productive gas wells.

If in the reservoir tapped by the well a pressure exists four times greater than that at the well mouth, it is probable that the expansion there resulting would cause a marked lowering of the temperature in the well.

It is commonly found however that the main leading from the well mouth does not possess a temperature much lower

than the air. From this it seems probable that methane cannot exist in a liquified state in the rocks.

The carbon dioxide and ethane, on the other hand, may occur constantly in liquid form in the rocks to which many of the wells penetrate.

Collection of Samples.

Glass vessels having a capacity of 250 to 400 cubic centimeters were carefully dried by a current of warm air, and in order to obtain the gas as nearly as possible free from moisture the following method was employed:

Glacial phosphoric acid, partially cooled from fusion, was drawn out into fine threads. A considerable number of such threads, in short pieces, could be pushed through the glass stopcocks, by which the vessels were closed, and left in the vessels which were then ready for the reception of gas samples. It is of importance to state that these vessels had been long in use for the same purpose and had been proved to be air-tight by thorough and repeated tests.

In collecting the samples several of these glass cylinders were connected in a series with the well or main by a short rubber hose, and gas allowed to flow for twenty minutes through them all.

The stopcocks were then closed in such a manner as to leave a slight excess of gas pressure in each vessel.

The stopcocks (which had previously been well greased with a mixture of tallow and wax) were then wound over and completely covered by fine cord, so that each resembled a ball of cord. The capillary ends of the cylinders were then closed by short pieces of thick rubber hose plugged with glass rods.

By this mode of wrapping all movement of the stopcocks during transportation on railroads is prevented.

The gas thus left in contact with the glacial phosphoric was gradually dried and ready for analysis on reaching the laboratory.

The common method of taking a gas sample in a glass cylinder having finely drawn out ends, which are to be sealed by a flame when the vessel is filled, is not applicable