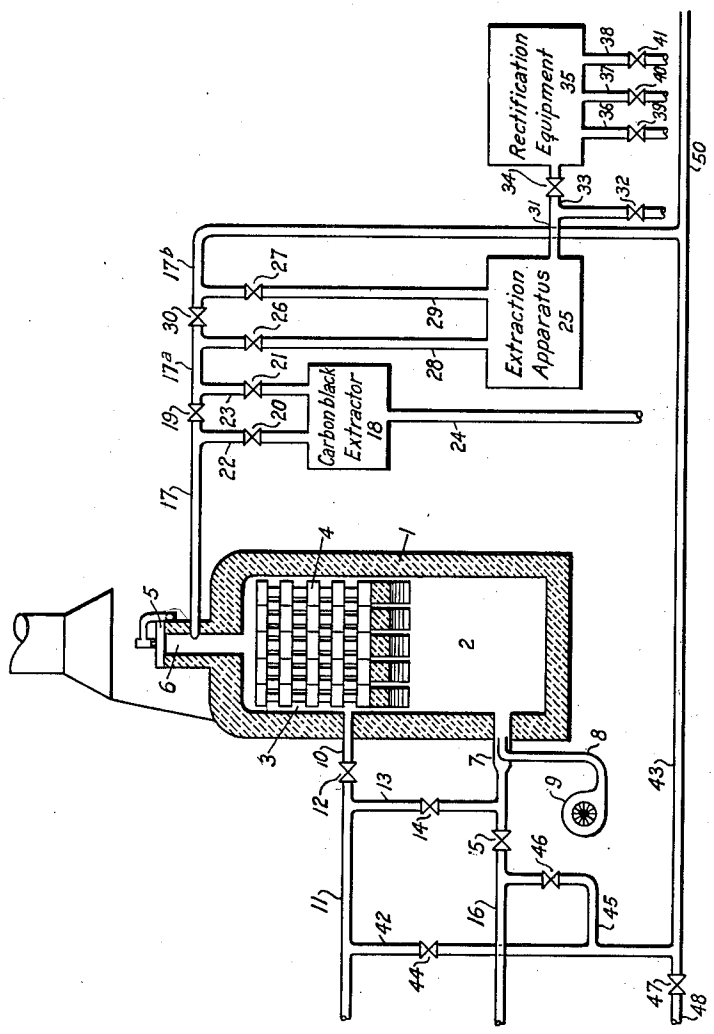
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PROCESS FOR THE PYROLYTIC CONVERSION OF NORMALLY GASEOUS ALIPHATIC HYDROCARBONS

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INVENTOR
L. S. Gregory
BY
Robt. E. Barry
ATTORNEY

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LON S. GREGORY, OF TULSA, OKLAHOMA, ASSIGNOR TO PHILLIPS PETROLEUM COMPANY, OF BARTLESVILLE, OKLAHOMA, A CORPORATION OF DELAWARE

PROCESS FOR THE PYROLYTIC CONVERSION OF NORMALLY GASEOUS ALIPHATIC HYDROCARBONS

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The present application is a continuation in part of my application, Ser. No. 250,184, filed January 28, 1928.

This invention relates to a process for cracking gaseous hydrocarbons, such as occur in natural gas, so as to produce from the natural gas, liquid hydrocarbons and gases suitable, either with or without enrichment, for burner and other purposes.

As natural gas occurs it is a mixture of hydrocarbons, principally the hydrocarbons of the methane series. Due to the fact that natural gas possesses a higher calorific value than is necessary for the usual burner design, natural gas is sometimes reformed for the purpose of reducing its calorific value to municipal standards. In large industries engaged in the reforming of natural gas no effort is made to produce and conserve the liquid hydrocarbons. The production of benzol alone from this source would have been of considerable benefit to the public because benzol as a component motor fuel greatly enhances the antiknock properties thereof.

Thermal decomposition of natural gases has been effected on a considerable scale in the production of carbon black but with no effort to produce and conserve the liquid hydrocarbons.

It has been a matter of scientific knowledge that paraffin hydrocarbons, when subjected to the proper thermal conditions, can be decomposed, or cracked, or reformed so as to produce in definite amounts, hydrocarbons which are normally liquid such as benzol, toluol, xylol, and still heavier hydrocarbons. In the reforming of the natural gas in order to reduce its calorific value, as to "municipal standards" a greater or less increase in volume is effected.

The industrial significance of this invention, and the meaning of "municipal standards" will be understood from the following:

Before the present extensive development of the petroleum industries, municipal gas was made from the distillation of soft coal in closed retorts. The heating value of that kind of gas ran fairly uniformly about 530 B. t. u. per cubic foot, and in consequence, all apparatus using it as fuel was designed to regulate on that basis.

With the introduction of water gas, known technically as—"blue gas"—whose thermal content runs about 290 B. t. u. to the cubic foot, it was soon discovered that the apparatus installed to use the older soft coal gas would not operate satisfactorily with such a lean supply, and the practice began of enriching it with some petroleum product to raise its heat value to range from 530 B. t. u. to 560 B. t. u. per cubic foot, as representative standard practice on which all contracts for the supply of gas was based.

This enrichment of municipal supplies of gas, like all other industrial processes, has recently been subjected to a searching analysis as to economy and efficiency, and it became apparent that the use of raw petroleum products, either liquid or gaseous, was not the best way to accomplish the result aimed at. In the case of the addition of richer gas to raise the thermal content, it was seen that the by-product gases released in the fractional distillation of petroleum, previously burned under the steam boilers, or even allowed to escape unused to the atmosphere from still and condenser vents, could be applied with even better results than raw material gases or concentrates, containing easily condensible liquids that often clogged up the mains. This invention is particularly directed to utilize such enriching gases in the most economical and efficient way. It takes gases, which, while sufficiently rich in thermal content, to raise the B. t. u. value of the municipal supply to the right figure, contain compounds deleterious for such a purpose, and frees the gas of such compounds, at the same time effecting a simultaneous refining and extraction of both the enriching gas or a finished gas and the by-product compounds derived therefrom.

With the foregoing in mind, the present invention has for one of its principal objects the provision of a process for the dual purpose of reforming the hydrocarbons of natural gas or mixtures or derivatives thereof, and the production of liquid hydrocarbons.

Another object is to provide a process which

may be continuous in contradistinction to those processes where there are intermittent "blow periods" for the primary purpose of bringing a chamber or chambers to the desired temperature, or the intermittent shutting off of the supply of one or more of the gas producing agents.

A further object of the invention is to provide a process suitable to the particular characteristics of the natural gas and other materials available in various localities and suitable to the requirements of different industries or municipalities as to the resulting gas and its calorific value, particularly the by-product gases of refineries.

A still further object of the invention is to provide a process whereby carbon block may be incidentally produced and separated from the products, and other by-products may be obtained which are in great demand as solvents and as base materials in the industries using organic materials, also liquids designed to impart anti-knock properties to motor fuels.

Other objects and advantages of the invention will appear in the following detailed description taken in connection with the accompanying drawing, forming a part of this specification and in which drawing is shown, by way of example, somewhat diagrammatically, suitable apparatus for carrying out the process.

In the drawing 1 designates a suitable furnace containing a combustion chamber 2 and a mixing and reaction chamber 3, the furnace in the example shown having checkerwork brickwork 4 and a lid 5 for an opening 6 through which pass the waste products of combustion of initial heating, it being understood that the preferred process being continuous after initial heating of the mixing and reaction chamber 2, the lid 5 remains closed. A conduit 7 is open to the combustion chamber 2 and, with air entering as by conduit 8 from blower 9 to support combustion, supplies fuel to maintain the necessary temperature of reaction.

The gas (for instance, natural gas composed mainly of constituents lighter than pentane) to be subjected to thermal decomposition enters the mixing and reaction chamber 3, as through conduit 10. A conduit 11, in communication with the source of such gas has connection as through valve 12, with conduit 10, and the fuel supplied to the combustion chamber may also be such gas, entering conduit 7, as by conduits 11 and 13, the latter valve controlled as at 14. A fuel differing from the gas to be subjected to thermal decomposition, may be supplied to the combustion chamber 2, as by closing valve 14 and opening a valve 15 interposed between the conduit 7 and a conduit 16 having communication with the source of such different fuel or a mixture of such fuels may be supplied to the combustion chamber 2 as by partially opening valves 14 and 15.

Combustion chamber 2, and mixing and reaction chamber 3 are so designed that the free space in the latter serves as the only means of exit for the products of combustion obtained in the former. Chamber 3 is maintained, solely by the heat generated in chamber 2, at such temperatures as guarantee optimum conditions for maximum yield of the products desired. It has been ascertained that the products of combustion can be commingled with the gases in the reaction chamber 3 without materially affecting the gas cracking reaction.

The mixed gases leave the chamber 3 through opening 6 and a conduit 17. If the conditions maintained in chamber 3 are such as to produce carbon black in any appreciable amount such may be removed by shunting the gases from conduit 17 through a carbon black extractor 18 as by closing a valve 19, between conduit 17 and a section 17^a thereof and opening valves 20 and 21 in conduits 22 and 23, respectively between the conduits 17 and 17^a, and extractor 18, the valve 19 being intermediate the points of connection of these conduits 22 and 23 with the conduits 17 and 17^a. The extractor 18 may be any suitable equipment for removing carbon black, as water equipment including water sprays or bag separators, the carbon black or water or aqueous liquid passing from the extractor 18 through conduit 24. When the nature of the materials treated and the operating conditions maintained in the furnace 1 are such as to reduce the volume of carbon black and tar produced to harmless amounts, the extractor 18 may be by-passed by closing valves 20 and 21 and opening valve 19.

The gases (denuded of carbon black and tar if found necessary or desirable), may pass from conduit 17^a to extraction apparatus 25 as through valves 26 and 27 in conduits 28 and 29 respectively which latter have communication with conduits 17^a and 17^b at opposite sides of a valve 30 which joints the latter. The apparatus 25 may be any suitable equipment for removing liquid hydrocarbons, such as compression and cooling or absorption equipment. The liquids resulting from the apparatus 25 may be considered the final liquid product and withdrawn through conduit 31, valve controlled as at 32, or may be led as through conduit 33, valve controlled as at 34, to rectification equipment 35 where it may be separated into a number of liquid products which may be drawn off as through conduits 36, 37 and 38, valve controlled as at 39, 40 and 41.

The extraction equipment 25 may be bypassed by closing valves 26 and 27 and opening valve 30, as when it is desired to maintain the calorific value of the reformed gases

at a higher level than would be the case if the liquid hydrocarbons were extracted.

The gas leaving conduit 17b may be enriched by gas from source 11 as through conduits 42 and 43, the former, valve controlled as at 44; or from fuel at source 16 as by conduit 45 valve controlled as at 46; or by means of an outside enriching agent entering conduit 43, as through valve 47 from a source in communication with conduit 48.

The gas leaving conduit 17b enters a conduit 50, with which conduit 43 has communication for the admixture of any enriching agent, and conduit 50 may have communication (not shown in the drawings) with conduit 16, when it is desired to use a portion of the reformed gas as a fuel in combustion chamber 2.

It is preferred to use a different gas for fuel and enriching agent, (when such enriching agent is deemed necessary or desirable) than is introduced into the reaction chamber 3 as through conduit 10. To accomplish this, valves 14, 44 and 47 would be closed and valves 12, 15 and 46 opened. It may be desirable to use the same gas as raw material, fuel and enriching agent under which condition valves 12, 14 and 44 would be opened and valves 15, 46 and 47 closed. Where liquid hydrocarbons are the only end sought, no enricher would be necessary and valves 44, 46 and 47 would be closed and the source of fuel obtained either through valves 14 or 15.

As another example, the reformed gas issuing from conduit 17b may be used as a fuel, delivered to conduit 7, with the valve 14 opened during the starting period.

During the starting period, the valve 12 is closed, the cupola lid 5 opened, and the fuel in combustion chamber 2 used to heat the chamber 3, to the desired temperature. When this temperature is reached the lid 5 is closed, the valve 12 opened and the gases from chambers 2 and 3 must therefore find exit from the furnace through conduit 17.

As a specific example of the operation of this process 4 volumes of a mixture of paraffin hydrocarbons or natural gas having a calorific valve of 2200 B. t. u.'s per cubic foot have been introduced into the reaction chamber 3, while the latter was at substantially atmospheric pressure. In the particular apparatus employed, 1 volume of fuel gas (1450 B. t. u's per cubic foot), and 13.8 volumes of air were necessary to effect suitable temperatures of about 1400° F. in reaction chamber 3. The effluent gases in conduit 17 occupied 24.5 volumes, had a calorific value of 310 B. t. u.'s per cubic foot and contained 0.2 of a gallon per thousand cubic feet of desirable liquid hydrocarbons, principally benzol.

In commercial operation, the reaction chamber should be maintained at a temperature within a range of 1250° F. to 1750° F. and the higher the temperature, the faster should be the rate of flow of reaction gases through the same. The time of exposure of the products of the reaction will come within a range of 0.002 minutes to 10 minutes, depending on the temperature maintained, the character of the gas treated and the products desired.

The relation between temperature and exposure time for gases consisting largely of propane and butane has been determined, and is embodied in the following empirical formula,

$$T = 1245 - 180 \log_{10} t$$

wherein T = cracking temperature in degrees Fahrenheit and t = time in minutes during which the gas is maintained at the temperature T, subsequent to a rapid heating to that temperature, with rapid cooling upon expiration of cracking period t. A several fold increase in exposure time above that calculated by the formula results in little increase in yield of volatile oils, but tar and carbon formation are thereby increased and the gas depleted in calorfic value.

In regard to said formula, it may be stated that experiments were conducted with the object of determining the role of cracking time as well as temperature in producing an optimum yield of benzol. A gas of the composition

Methane	18.6%
Propane	44.7%
Butane	36.7%
	100.0%

was submitted to cracking in a non-catalytic silica tube under conditions suitable for the production of benzol. The experiments were conducted at atmospheric pressure and the carbon, tar, benzol and gases were separately measured. The effect of time and temperature on benzol yield is shown in the following table, in which time is expressed in minutes and benzol yield in gallons per thousand cubic feet of gas:

Table—Effect of time of cracking on benzol yield at several temperatures,

Time	Yield
1292° F.	
.5	1.5
1.1	1.7
3.5	1.8
1382° F	
.28	1.8
.38	2.1
2.6	2.1
1562° F.	
.012	1.7
.031	1.9
.066	1.8
1742° F.	
.003	2.1
.006	1.9

At a given temperature, the yield of benzol was observed to increase gradually as the cracking time increased, until a virtually maximum yield was developed. A several fold increase in time beyond the minimum necessary to develop a virtually maximum yield caused little change in benzol yield, but tar formation was increased, of necessity through depletion of the gas. The increase in temperature increased the reaction velocity without greatly influencing the sequence of changes taking place during cracking. The maximum yield of benol was roughly constant throughout the rather wide temperature range studied within the time range appropriate to and unique for each temperature.

The data of the table show the minimum time required to obtain a substantially optimum yield of benzol at several temperatures within a rather wide range. The values are approximately 0.5 minutes at 1292° F., 0.2 minutes at 1382° F., 0.012 minutes at 1562° F., and somewhat less than 0.003 minutes at 1742° F.

These values may be used to determine a time-temperature relation which is expressed in a compact form by the equation

$$T=1245-180 \log_{10} t$$

in which T' is temperature in degrees Fahrenheit, and 't' is time in minutes. The time given by the formula is a minimum value for the formation of a substantially maximum yield of benzol.

In practice, a reaction time as much as several fold greater may be used without loss in benzol yield. Since the literature shows that the time consumed by the initial decomposition of gaseous paraffins to form gaseous olefines is only a small fraction of the total time found to be required for forming a yield of benzol, it is obvious that the same time-temperature relation is applicable to the treatment of gaseous olefines to form benzol and to all the simpler paraffins which decompose into gaseous paraffins and gaseous olefines. Methane, because of its great stability to heat is not converted into benzol under the above mentioned time-temperature conditions.

One of the chief benefits of this invention is the fact that by its means gas cracking reactions can be effected in a continuous operation so as to permit the recovery of a considerable volume of valuable liquid hydrocarbons. The optimum conditions necessary to obtain the maximum yield of the desired liquid hydrocarbon, or the desired mixture of liquid hydrocarbons, can readily be determined from the foregoing. It has been ascertained that within practical limits of pressure and rate of flow of gases through the apparatus these conditions do not materially influence the progress of the cracking reaction providing the temperature in the reaction chamber is maintained within a range of 1250° F. to 1750° F. Neither has the dilution of the reacting gases with the products of combustion a material effect on the progress of the gas cracking reaction

The process may be employed in the treatment of natural gas constituents which are gaseous at atmospheric temperature and pressure or it can be used with mixtures composed mainly of such constituents, for the purpose of producing substantial quantities of liquid hydrocarbons, and by substantial quantities I mean .5 of a gallon to each 1000 cubic feet of gas treated.

The invention is not limited to the use of an enriching agent or to any particular enriching agent in order to provide a reformed gaseous product of the desired calorific value, nor to the particular apparatus disclosed, which is susceptible of many modifications and in many instances to simplification as when the raw material, fuel and enriching agent are all from one and the same source.

It will be seen the improvements described relate, as noted, earlier in the specification, to that branch of refining known in the art as pyrolysis, or cracking, and researches have verified that these improvements can be applied successfully to all gaseous hydrocarbons, pure or mixed, the vapor pressure of which will be found in the range from 25 to 500 pounds per square inch; obviously, these mixtures may be limited, for certain purposes, as described in this specification, to such hydrocarbon mixtures as would be gaseous under ordinary conditions of temperature and pressure, i. e., those which have a boiling point of approximately 50 degrees F., at most, like members of the paraffin series up to pentane, as hereinbefore explained.

What is claimed is:

1. In a process for the pyrolytic conversion of normally gaseous aliphatic hydrocarbons to crude benzol, continuously passing said gaseous hydrocarbons through a chamber while maintaining said hydrocarbons at a temperature between 1250 and 1750° F. for an interval of time substantially as expressed by the formula

$$T=1245-180 \log_{10} t,$$

controllably commingling in said chamber the gases to be cracked with hot products of substantially completed combustion produced in situ with relation to said chamber for heating said hydrocarbons, and separating the crude benzol so produced.

2. In a process for the pyrolytic conversion of normally gaseous aliphatic hydrocarbons to crude benzol, continuously passing said hydrocarbons upwardly through a chamber while maintaining said gaseous hydrocarbons in the chamber at a temperature between 1250 and 1750° F. for an interval of time substantially as expressed by the formula

$$T=1245-180 \log_{10} t,$$

controllably commingling in said chamber said hydrocarbons with substantially insert gaseous products of combustion produced in the chamber at a point below the point of introduction of said hydrocarbons for heating the latter, and separating the crude benzol so produced.

LON S. GREGORY.