

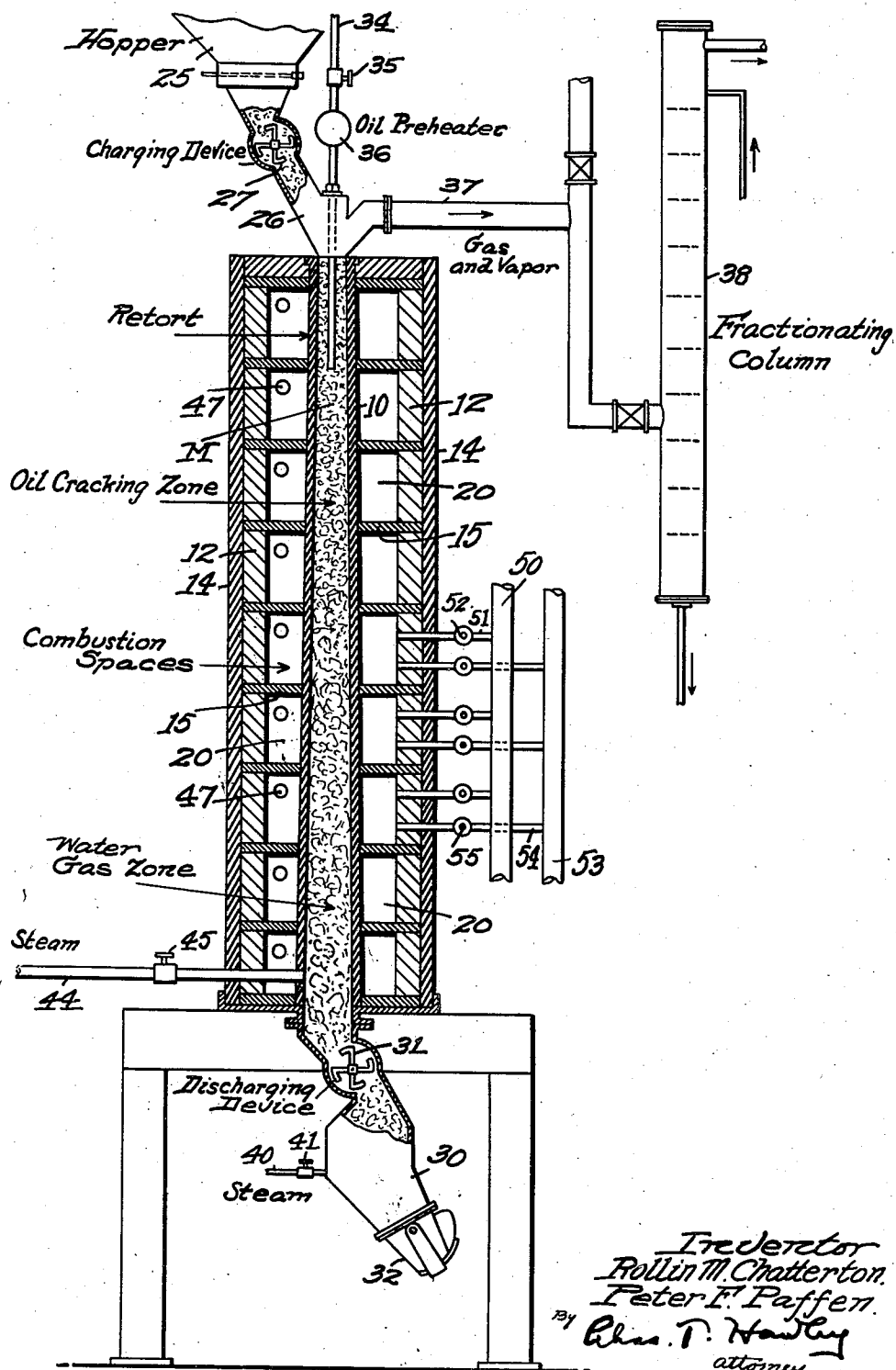
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R. M. CHATTERTON ET AL

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CONTINUOUS PROCESS OF MAKING CARBURETED WATER GAS

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Inventor
Rollin M. Chatterton
Peter F. Paffen
By
Chas. T. Hawley
attorney.

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CONTINUOUS PROCESS OF MAKING
CARBURETED WATER GAS

Rollin M. Chatterton, Malden, and Peter F. Paffen, Cambridge, Mass., assignors to Fuel Research Development Corporation, Boston, Mass., a corporation of Massachusetts

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This invention relates to a process of gas manufacture by which the net cost of carbureted water gas may be substantially reduced.

Gas for public service distribution is commonly produced at the present time by one of two major processes, either the coal gas process or the carbureted water gas process. Each of these processes has been in use without substantial change for many years, and the thermal limitations of the processes apparently prevent any substantial lowering of the net production cost of gas made by either of these processes. But by the use of our invention, as hereafter described, by-products of much increased value and importance are produced, and the by-product credits are so increased that the net production cost of commercial gas is substantially lowered.

It is the general object of our invention to provide an improved process by which carbureted water gas having the usual commercial heating value may be continuously produced from low-grade hydrocarbon oil and steam.

A further object of our invention is to provide an improved process for continuously making carbureted water gas, by which process valuable by-products are also produced and rendered commercially available.

We also provide an improved process for the continuous manufacture of carbureted water gas, in which the operating conditions and the resultant reactions can be effectively controlled and uniformly maintained.

Apparatus suitable for the carrying out of our improved process is shown in the drawing, which is a front elevation, partly in section, of an externally heated retort and associated mechanism suitable for use in practicing our invention.

Referring to the drawing, we have shown an elongated vertical retort 10, the internal cross section of which gradually increases downward to permit easy and continuous downward movement of materials charged thereto. The retort 10 may be made of a heat-resistant metal or of any suitable refractory or heat-resistant material, and is mounted in spaced relation within a heating chamber 12, commonly made of fire-brick and provided with an outer metal casing 14.

The furnace 12 is preferably provided with a series of horizontal partitions 15 by which the annular space between the retort 10 and the furnace 12 is divided into a series of combustion spaces 20 in which heat is provided by circulation of externally produced hot combustion gases, or by burning producer gas or any other suitable and available gas, and in each case with separate

control of the heat conditions in each combustion space 20.

For illustrative purposes, a gas feed pipe 50 is shown, having branch connections 51 to each combustion space, and each connection being controlled by a valve 52. An air supply pipe 53 is also shown, which pipe is connected through branch pipes 54 and valves 55 to the separate combustion spaces. In this way, the gas and air supply in each space 20 may be separately and accurately controlled and a desired temperature uniformly maintained. Any low-grade fuel gas or hot combustion gases may be supplied through the pipe 50.

The retort 10 is filled with a suitable fragmentary solid material M, such as calcined clay, broken fire-brick or coke, which material is carefully sized and is substantially refractory and heat-resistant under the conditions of operation. This material M may be supplied from a hopper 25 through a pipe 26 and charging device 27. At the lower end of the retort, the material M is delivered to a receptacle 30 by a discharging device 31, and may be removed therefrom through a spout 32 at such intervals as may be desired.

Suitable actuating mechanism (not shown) is provided for the charging device 27 and the discharging device 31, and these devices are preferably operated in predetermined speed relation, so that a slow but continuous downward movement of the material M in the retort 10 will take place, while at the same time the retort 10 will be continuously maintained substantially full of the charged material.

An oil feed pipe 34 projects downward into the upper part of the retort 10 and is provided with a control valve 35 and preferably also with an oil preheater 36. A discharge pipe 37 is connected to the upper end of the retort 10.

The gases and oil vapors produced in the retort 10 are removed through the pipe 37 to a fractionating column 38, which in turn may be connected with any suitable mechanism for separating the liquid and gaseous products and for condensing the various liquid products or distillates.

A pipe 40 with a valve 41 is provided for introducing steam into the discharge receptacle 30 to cool the discharged material, and a pipe 44 with a valve 45 is provided for introducing superheated steam at the lower end of the retort 10.

Having described a form of apparatus suitable for the carrying out of our improved process, we will now describe the operation and ad-

vantages of our invention in the manufacture of carbureted water gas and associated by-products.

The retort 10 is first filled with fragmentary solid refractory or heat-resistant material M, and the retort is heated by the circulation or production of hot gases in the combustion spaces 20, suitable provision being indicated at 47 for removal of the waste gases.

When the material M in the retort 10 has been heated to a desired temperature, oil is introduced through the pipe 34, which pipe projects downward into the retort in the cooler upper portion thereof. This oil may be preliminarily heated in the preheater 36, which increases the amount of oil which can be vaporized and cracked in a given time. As the oil leaves the pipe 34, it trickles downward over the heated refractory material M and absorbs heat from the material over which it flows. Vaporizing and cracking of the oil then takes place, commonly with the deposit of a substantial amount of oil carbon on the material M.

When the apparatus is in continuous operation, the temperature in the oil cracking zone indicated in the upper part of the retort will commonly range from 1200° F. to 1600° F., while the temperature in the water gas zone in the lower part of the retort will be substantially higher and will commonly range between 1750° F. and 1950° F. The lower temperature limit of production of water gas in any substantial proportion is well above the upper temperature limit of the oil cracking operation as carried out under our improved process. The provision of separately controlled combustion chambers 20 permits the temperature to be effectively maintained at a desired point in each different portion of the retort.

The refractory material discharged to the receptacle 30 is still highly heated and contains more or less deposited carbon. Steam is admitted through the pipe 40 to the receptacle 30 to cool the discharged material and to conserve heat, and also to prevent the carbon deposited on the material from taking fire and being immediately consumed on exposure to air.

The injected steam becomes highly heated by the heat absorbed from the discharged material, and this hot steam then passes directly upward into the retort, where it comes in contact with the descending material M and deposited carbon in the water gas zone and supplies a part of the heat required for the water gas reaction.

Conditions are thus extremely favorable for producing water gas, and such gas is produced in substantial quantities by the reaction of the highly heated steam on the deposited oil carbon. This carbon which is deposited on the material M is in a finely divided state and is highly reactive.

As the highly heated water gas travels upward in the retort, it supplies additional heat to vaporize and crack the oil which has flowed down over the refractory material in the oil cracking zone. The oil vapors are cracked in the upper part of the retort under such conditions that substantial quantities of liquid by-products are produced which are relatively more valuable than the oil fed to the cracking zone of the retort, together with oil gas in sufficient amount to enrich the water gas to the required thermal standard for commercial distribution.

If the cooling of the discharged material in the receptacle 30 does not provide sufficient highly heated steam for the water gas reaction, addi-

tional hot steam may be introduced through the pipe 44.

An outstanding feature of our improved process is the ease and accuracy with which temperature conditions can be controlled, and the uniformity with which they may be maintained in all parts of the apparatus. As a result of maintaining uniform temperature conditions, we are able to produce uniform by-products having predetermined and desired properties.

Our improved process thus has a very important advantage over all intermittent processes in which wide fluctuations in retort temperatures are unavoidable, and in which these variations recur during each cycle of the process.

As the oil is discharged from the pipe 34 and descends over the filling material, a comparatively cool core is formed along the axis of the retort, which extends downward a greater or less distance. The length of this cool core is determined in part by the rate at which oil is fed to the retort and should not extend too far down, or unvaporized oil will be discharged into the receptacle 30.

As the oil vapors emerge from the cool core and expand with increased temperature, they pass up through the heated refractory material M toward the outlet at the top of the retort. The path of least resistance for the oil vapors and also the highest temperatures are found along the inner face of the retort wall. As the oil vapors pass upward through the heated filling material in the presence of heated water gas and superheated steam, conditions for rapid cracking of the oil vapors are extremely favorable.

Any oil carbon freed by the cracking operation and deposited on the material M passes downward therewith and is partially consumed in the water gas reaction. Any excess carbon not used in this reaction is discharged with the refractory material to the receptacle 30. When removed therefrom, the carbon may be separated from the refractory material by screening and is then available for boiler fuel, while the refractory material itself may be returned to the hopper 25 for further use in the retort 10.

The cracking of the oil vapors under the described conditions, with the retort substantially at atmospheric pressure, results in the production of hydrocarbons of superior values and largely in the aromatic series, such as benzene and toluene. Relatively high-boiling products, such as naphthalene and anthracene, which are solids at ordinary temperature, are also produced, together with non-condensable gases comprising hydrogen, methane and paraffinic and olefinic hydrocarbons.

By adjusting the rate of downward travel of the filling material M, and by controlling the temperature conditions in the different parts of the retort 10, oil of widely varying characteristics may be successfully cracked. Extended experiments have shown that the low-priced oil, such as Bunker C oil having a gravity of 12° A. P. I. or less, may be cracked to advantage, as it not only yields excellent oil gas and valuable aromatics, but also a large amount of carbon to be utilized in making water gas which is immediately enriched by admixture of the oil gas produced in the upper zone of the retort.

The value of the by-product credits produced by our improved continuous process is much higher than with the usual intermittent process, in which the principal by-product is a heavy, viscous and low-priced water gas tar. The by-

products of our process, on the other hand, are suitable for the production of more valuable products such as blending agents, solvents, wetting agents and lubricants.

In the production of carbureted water gas by the usual intermittent process, further lowering of the net production cost depends chiefly on reducing the cost of the raw materials used, while with our new continuous process the net production cost of the water gas is substantially reduced by increasing the value of the by-products. A relatively small portion only of the oil supplied is used to enrich the water gas, and the remaining and larger portion of the oil is used in the production of liquid by-products of much increased value. It will be noted that the only gas-making materials essential to the success of our improved process are the low-grade oil introduced through the pipe 34 and the steam introduced through the pipe 40 or the pipe 44.

The chemical composition and properties of the by-products produced by our improved process are modified by the temperature maintained in the cracking zone, by the length of time the oil vapors remain in the cracking zone, and by the chemical composition of the cracking oil. Changes in the composition of the retort wall and in the retort filling material may also have important effects on the nature of the by-products.

The control and maintenance of uniform temperature conditions in our improved process are particularly important, as some 90% of the by-product credits in money value, comprise oils having a boiling range between 100° F. and 700° F. Such oils cannot be produced in substantial amounts and of uniform quality under the widely varying temperature conditions of the intermittent water gas processes.

While we have described our improved process as being adapted to produce commercial gas having the usual standard heating values, our process is very flexible and may be used to advantage in producing other grades of gas if so desired. If a lighter gas oil is substituted for the heavy Bunker C oil, a gas which is high in hydrogen and methane and which will have a heating value of from 850 to 1,000 B. t. u. per cubic foot may easily be produced. On the other hand, by a different modification of conditions, fuel gas of relatively low heating value may be produced for industrial purposes. In each case, by-products rich in aromatic hydrocarbons will be produced, and the net production cost of manufacture will be correspondingly low.

The rates of feed of the charging device 27 and of the discharging device 31 are so adjusted relative to the oil feed, that the deposited carbon will be removed fast enough to prevent clogging of the retort.

When heavy oil is used, the amount of carbon deposited is usually more than is needed to produce the amount of water gas which can be enriched by the oil gas produced in the associated vaporizing and cracking operations. The amount of water gas produced may be controlled in part by adjustment of the temperature in the water gas zone.

The liquid by-products recovered by our improved process amount to 40% to 60% by weight of the oil fed to the retort and contain up to 70% of aromatic hydrocarbons.

The words "refractory material" as used in the claims are intended to designate such materials as coke, calcined clay, broken fire brick, chromite, bauxite, etc. which are infusible and chemically

unchanged under the described conditions of operation.

The words "upright retort" as used in the claims are intended to define a retort so positioned that the solid refractory material charged to the retort will move downward therein by gravity.

The term "water gas" as used in this specification and in the following claims is intended to define a combustible gaseous mixture produced by the reaction of steam on highly heated carbon, and consisting essentially of hydrogen and carbon-monoxide, both in substantial proportions.

Having thus described our invention and the advantages thereof, we do not wish to be limited to the details herein disclosed, otherwise than as set forth in the claims, but what we claim is:

1. The continuous process for making carbureted water gas in a retort, using oil and steam as the initial reacting materials and relying primarily on external heat for bringing about the gas-making reactions, which comprises feeding fragmentary solid refractory material which does not enter actively into the gas-making reactions to the upper part of a retort, externally and continuously heating said retort and the refractory material therein, progressively feeding oil to the heated refractory material in the retort and cracking said oil in an oil-cracking zone, thereby producing oil gas and vapors and oil carbon, which carbon is deposited in and on said refractory material, progressively moving said heated refractory material and the carbon deposited thereon downwardly through said retort, continuously reacting on a portion at least of said deposited carbon by steam admitted to a lower water-gas-producing zone in said retort, continuously passing the resulting water gas upwardly through the refractory material in the retort and mixing said water gas with the oil gas and vapors formed in the cracking zone to form a carbureted water gas of increased heating value, progressively removing said carbureted water gas, oil vapors and any excess steam from the upper part of said retort, and progressively discharging the refractory material and any unreacted carbon from the lower end of the retort.

2. The continuous process for making carbureted water gas in a retort using oil and steam as the initial reacting materials and relying primarily on external heat for bringing about the gas-making reactions, which comprises feeding fragmentary solid refractory material which does not enter actively into the gas-making reactions to the upper part of an upright retort, externally and continuously heating said retort and said refractory material, progressively admitting oil to the heated refractory material and cracking said oil in an oil-cracking zone in said retort, thereby producing oil gas and vapors and oil carbon, which carbon is deposited in and on said refractory material, progressively moving said heated refractory material and the carbon deposited thereon downwardly by gravity through said retort, continuously reacting on a portion at least of said deposited carbon in a lower water-gas-producing zone in said retort by steam admitted to said retort, continuously passing the resulting water gas upwardly through the refractory material in the retort and mixing said water gas with the oil gas and vapors formed in the oil-cracking zone to form a carbureted water gas of increased heating value, progressively removing said carbureted water gas, oil vapors and any

excess steam from the upper part of said retort, the steam for the water gas reaction being admitted at the lower part of said retort and thereby cooling said refractory material and the unreacted carbon before discharge from said retort, and discharging the cooled refractory material and unreacted carbon from the lower end of the retort.

3. The continuous process for making carburated water gas in a retort at substantially atmospheric pressure, using oil and steam only as the initial reacting materials and relying on external heat for bringing about the gas-making reactions, which comprises progressively feeding fragmentary solid refractory material which does not enter actively into the gas-making reactions to the upper part of an upright retort, externally and continuously heating said retort and the refractory material in said retort, progressively feeding oil to the heated refractory material and cracking said oil in an oil-cracking zone in said retort at a substantially uniform selected temperature in the temperature range between 1200° F. and 1600° F., thereby producing oil gas, oil vapors containing a large proportion of aromatic hydrocarbons, and oil carbon which is deposited in and on said refractory material, separately controlling the oil feed, progressively moving said heated refractory material and the carbon deposited thereon downwardly through said retort, continuously reacting on a portion at least of said deposited carbon by steam admitted thereto in a lower water-gas-producing zone, continuously passing the resulting water gas upwardly through the refractory material in the retort and mixing said water gas with the oil gas and vapors formed in the cracking zone to form a carburated water gas of increased heating value, progressively removing said carburated water gas, oil vapors and any excess steam from the upper part of said retort, progressively discharging the refractory material and the unreacted carbon from the lower end of the retort, and coordinating the rate of feed of refractory material to the top of the retort with the rate of discharge of the refractory material and unreacted carbon from the lower end of the retort.

4. The continuous process of manufacturing carburated water gas in a retort, using oil and steam as the initial reacting materials and relying primarily on external heat for bringing about the gas-making reactions, which comprises passing fragmentary solid refractory material which does not enter actively into the gas-making reactions axially downwardly by gravity through an elongated vertical retort, selectively and externally heating different horizontal zones of said retort and the refractory material therein to different predetermined temperatures, progressively feeding oil to said heated refractory in said retort, vaporizing and cracking the oil in contact with the heated refractory material in an upper oil-cracking zone in said retort and in the presence of water gas, thereby producing oil gas and oil vapors and carbon, which carbon is deposited in and on said refractory material, said carbon and said refractory material being progressively transferred by gravity from the cracking zone to a lower water-gas zone in said retort, continuously supplying steam in said water-gas zone to react with at least a part of said deposited carbon to produce water gas, enriching said water-gas with oil gas and vapors formed in the oil cracking zone to form a carburated water gas, progressively removing said enriched

water gas, oil vapors and any excess steam from the upper end of said retort, and highly heating said steam when admitted to the retort by heat recovered from the refractory material and the unreacted carbon remaining thereon before said latter elements are discharged from said retort, thereby conserving recoverable heat therefrom.

5. The continuous process of making carburated water gas and hydrocarbon products which are predominantly aromatic in character, in a retort and relying primarily on external heat for bringing about the gas-making reactions, which consists in continuously cracking petroleum oil at substantially atmospheric pressure and at relatively high temperature and in an atmosphere of heated water gas in a retort filled with a moving mass of solid fragmentary refractory material which does not enter actively into the gas-making reactions, thereby producing oil gas and oil vapors containing a large proportion of aromatic hydrocarbons, externally and continuously heating said retort and the refractory material therein, depositing the carbon produced by cracking the oil in and on said refractory material, transferring said heated material and said deposited carbon by gravity to a lower water-gas zone in said retort, continuously supplying steam to react with a part of said carbon to form water gas, which water gas, with any excess steam, rises through the oil cracking zone and mixes with the oil gas and vapors from the cracking operation to produce a carburated water gas of an increased heating value, progressively removing the carburated water gas, oil vapors and any excess steam from the retort and recovering the predominant aromatic hydrocarbons from the gaseous mixture, and removing the refractory material and the unreacted carbon from the lower end of said retort.

6. The continuous process for converting essentially non-aromatic fluid hydrocarbons into gases which are substantially olefinic and liquids which are predominantly aromatic and olefinic and solids which are aromatic, which consists in cracking the said essentially non-aromatic fluid hydrocarbons at substantially atmospheric pressure and in an atmosphere essentially containing highly heated steam and water gas by introducing the fluid hydrocarbon into a retort primarily externally heated and through which a mass of solid fragmentary heated refractory material is moving downward and the said highly heated steam and water gas are moving upward, cracking the fluid hydrocarbon to oil gas, vapors and oil carbon, depositing the carbon as it is formed in the cracking operation in and on the mass of refractory material, progressively removing the refractory material with the deposited carbon downward from the cracking zone and into a lower zone where water gas is made by reacting on the deposited carbon with steam admitted at the bottom of the retort, said steam also cooling the refractory material and the carbon deposited therein and thereby conserving heat, causing said water gas, and steam which has been highly superheated in the water gas zone, to flow up through the retort to the cracking zone, said water gas and any excess steam thereafter passing out of the top of the retort mixed with the predominantly aromatic and olefinic oil gases and vapors, and from which mixture aromatic and olefinic products are subsequently recovered by conventional methods of condensation absorption and fractionation, and

said cooled refractory material and unreacted carbon being removed from the lower end of the retort.

7. The continuous process of manufacturing aromatic and olefinic hydrocarbons from essentially non-aromatic fluid hydrocarbons by a cracking operation and relying primarily on external heat for bringing about the cracking reaction, which comprises feeding fragmentary solid refractory material which does not enter actively into the cracking reaction to the upper end of a retort, externally and continuously heating said retort and the refractory material therein sufficiently to bring about an oil-cracking reaction at a relatively high temperature and substantially at atmospheric pressure, feeding said non-aromatic fluid hydrocarbons to said retort and continuously vaporizing and cracking the same in contact with the heated refractory material in a cracking zone in said retort, thereby producing oil gas and vapors and carbon which is deposited in and on said refractory material, progressively transferring the deposited carbon with said refractory material from the cracking zone to a lower water-gas zone in said retort, continuously supplying heated aqueous fluid in said water-gas zone to react with a part of said deposited carbon to produce water gas, passing said water gas up through the cracking zone and mixing said water gas with said oil gas and vapors, discharging said refractory material and the unreacted carbon from the lower end of said retort, progressively removing the carbureted water gas and oil vapors from the upper end of said retort, and condensing and removing the condensible aromatic and olefinic hydrocarbons from said mixed gases and vapors.

8. A continuous process for converting essentially non-aromatic fluid hydrocarbon mixtures into gases of high caloric value which are rich in olefinic hydrocarbons and to liquids predominantly aromatic and olefinic in character, which consists in cracking the said hydrocarbon mixture in an atmosphere of highly-heated water gas in a retort primarily externally heated and through which a mass of solid, fragmentary, re-

fractory material is moving downward and the said water gas and condensable vapors are moving upward, depositing carbon as it is formed in the cracking operation in the mass of refractory material, progressively removing the refractory material and the deposited carbon downward from the cracking zone into a lower zone where water gas is made by reacting on the deposited carbon with steam admitted near the bottom of the retort, causing said water gas to flow up through the retort to the cracking zone, said water gas and the volatile products of the oil-cracking operation passing out of the retort, and removing the refractory material and the carbon contained therein from the bottom of the retort.

9. A continuous process for converting essentially non-aromatic fluid hydrocarbon mixtures into gases of high caloric value which are rich in olefinic hydrocarbons and to liquids predominantly aromatic and olefinic in character, which consists in cracking the said hydrocarbon mixture in an atmosphere of highly-heated water gas in a retort primarily externally heated and through which a mass of solid, fragmentary, refractory material is moving from the entrance end toward the discharge end of said retort and the said water gas and condensable vapors are moving in the opposite direction, depositing carbon as it is formed in the cracking operation in the mass of refractory material, progressively removing the refractory material and the deposited carbon from the cracking zone to an adjacent zone nearer the discharge end of the retort and where water gas is made by reacting on the deposited carbon with steam admitted near the discharge end of the retort, causing said water gas to flow through the retort from the water gas zone to the cracking zone, said water gas and the volatile products of the oil-cracking operation thereafter passing out of the retort near the entrance end thereof, and removing the refractory material and the carbon deposited thereon from the discharge end of the retort.

ROLLIN M. CHATTERTON.
PETER F. PAFFEN.