

May 25, 1948.

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2,442,093

PYROLYSIS OF FLUID HYDROCARBONS

Filed June 18, 1945

2 Sheets-Sheet 1

FIG. 1.

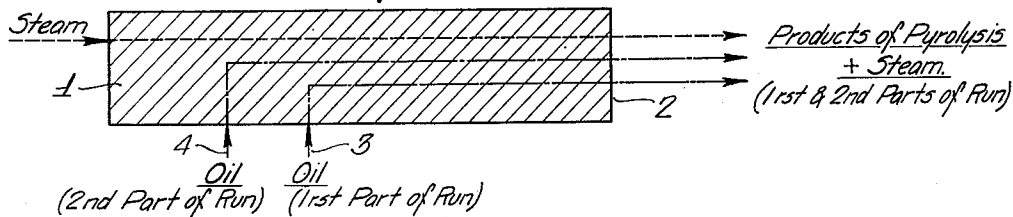


FIG. 2.

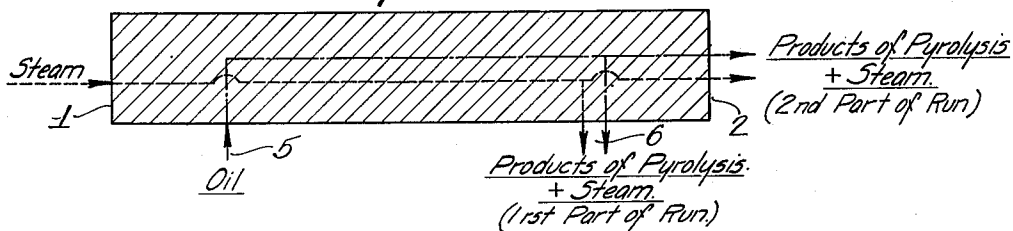


FIG. 3.

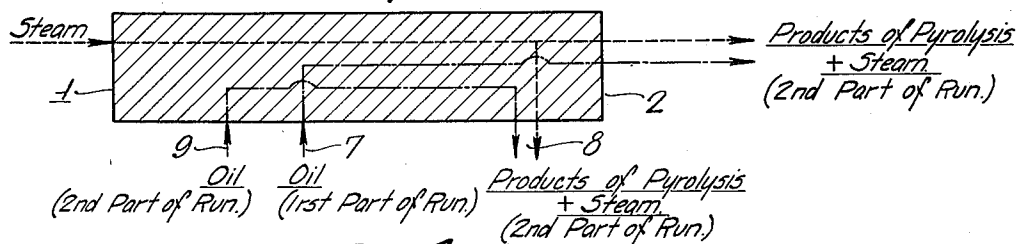


FIG. 4.

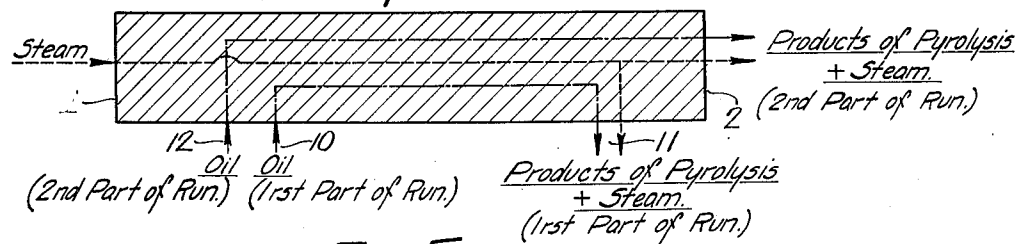
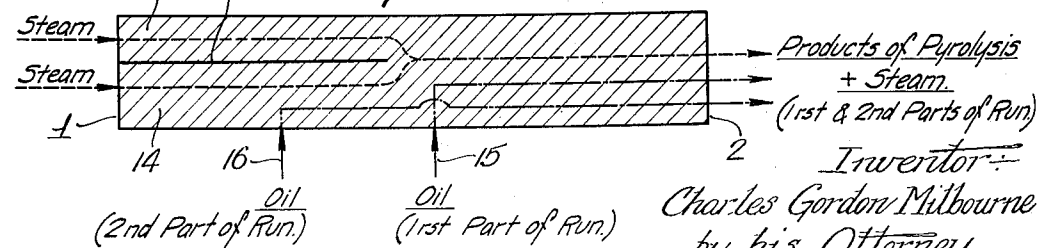


FIG. 5.



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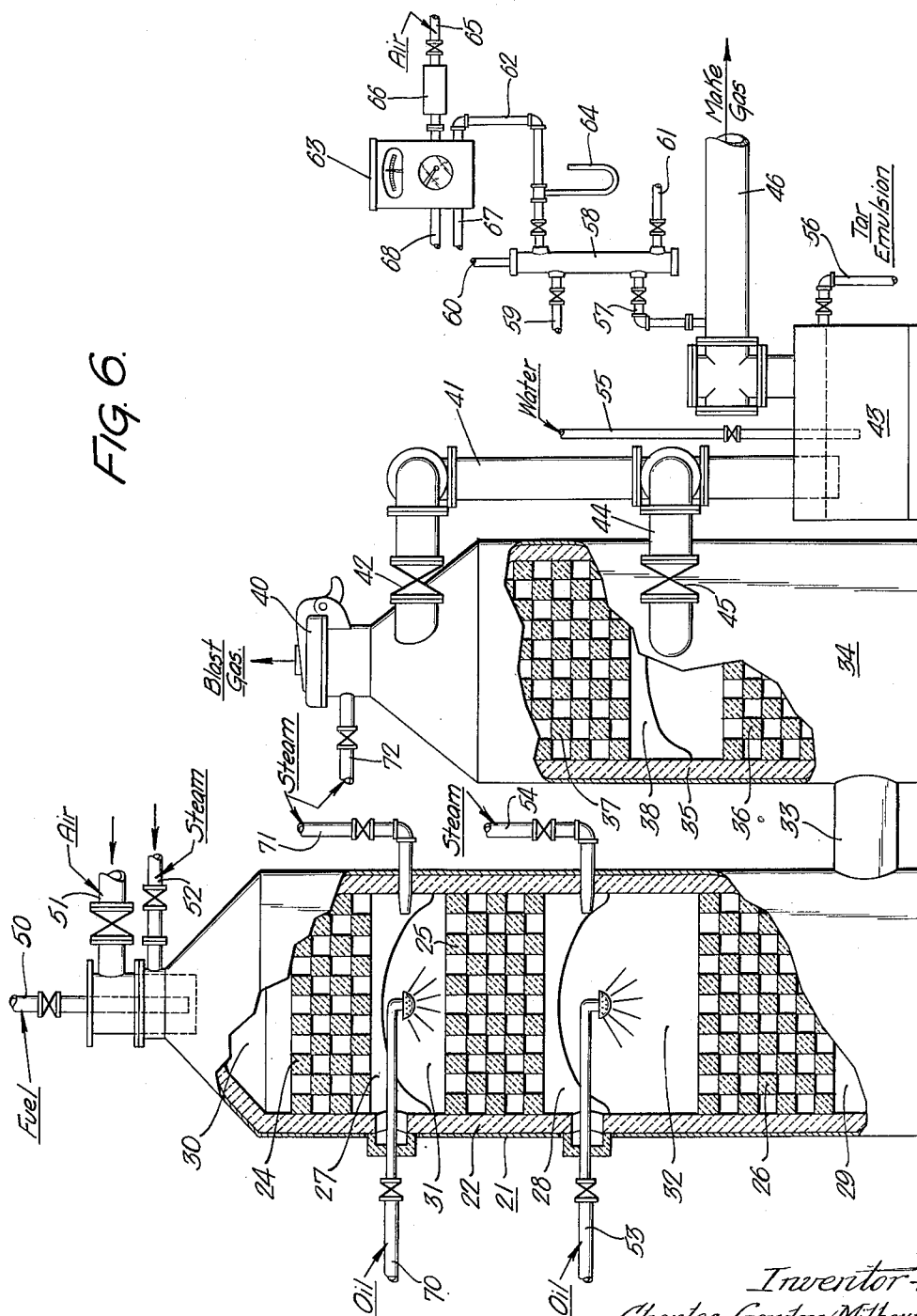
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2 Sheets-Sheet 2

FIG. 6.



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UNITED STATES PATENT OFFICE

2,442,093

PYROLYSIS OF FLUID HYDROCARBONS

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Application June 18, 1945, Serial No. 600,041

4 Claims. (Cl. 196-61)

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The present invention relates to the manufacture of combustible gas by a cyclic process, which involves the pyrolysis of fluid hydrocarbon material, and in which heat is stored in a gas making path, during a heating period of the cycle, by the passage of hot combustion gases there-through; and in which the stored heat is subsequently utilized for the pyrolysis of the fluid hydrocarbon material, by its passage through the heated path, during a gas making period of the cycle.

Typical of such cyclic processes for the manufacture of combustible gas are the well known cyclic oil gas processes, carburetted water gas processes, and hydrocarbon gas reforming processes.

Typical of the fluid hydrocarbon material pyrolyzed in such processes are crude petroleum oil and fractions thereof, such as naphtha, gas oil, fuel oils and residuums; natural gas; refinery oil gas; and sometimes tars derived from the pyrolysis of petroleum oil or coal. Some of these materials contain non-hydrocarbon components in addition to their hydrocarbon constituents.

The invention, for convenience, will be described in connection with the employment of crude petroleum oil or a fraction thereof, which for convenience will be referred to generally as oil, although it is to be understood that the invention is applicable to the pyrolysis of other fluid hydrocarbon material.

The invention, also for convenience, will be described in connection with the introduction of the oil to the cyclically heated gas making path in the liquid phase for vaporization therein, although it is to be understood that the invention is applicable to processes in which the oil is vaporized, for example in a continuous tube still, before its introduction into the cyclically heated path.

In the cyclic manufacture of oil gas, a gas set comprising a vessel or vessels, provided with a refractory lining or linings and with refractory checker brick, is heated during the heating period of the cycle, termed the "blow," by the combustion of fuel such as oil, tar or combustible gas, and by the passage of the resulting hot combustion products through the vessel or vessels, thereby raising the refractory lining or linings and checker brick to elevated temperatures and storing heat therein to provide a path of stored heat.

After the "blow" has been terminated, a "run" is made in which oil is sprayed into the gas set in the presence of a diluent gas, such for example as steam, and vaporized therein, the resulting oil

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vapors being passed along the path of stored heat with the steam and cracked therein by the stored heat to produce oil gas.

The cycle also includes steps for purging products of combustion to the atmosphere, and for purging oil gas to storage.

In the manufacture of carburetted water gas, an ignited bed of solid fuel, in a generator, is blasted with air and raised to a high temperature. The resulting blast products are burned with secondary air, and their heat stored in the refractory lining and checker brick of a carburetting vessel or vessels, producing a path of stored heat. After the blast, termed the "blow," a water gas "run" is made in which steam is passed through the highly heated fuel bed, generating blue water gas, which together with the excess steam is passed along the path of stored heat in the heated carburetting vessel or vessels, in which the blue water gas is carburetted with oil, which is sprayed into the set, vaporized, and the vapors cracked by the stored heat in the presence of the blue water gas.

Purging steps are performed in the cycle to purge blast products to the atmosphere, and to purge carburetted water gas to storage.

In normal cyclic oil gas and carburetted water gas practice, by far the larger part of the petroleum oil, which customarily comprises the less costly fractions of the crude such as gas oil and heavy residuums, finds its way into fixed gas or in other words into gases which are liquefied with difficulty, such as hydrogen, methane, ethylene, and possibly other gaseous paraffines and olefines. Nevertheless a certain portion of the oil is used up in the production of tar, drip oil and lower temperature condensates, the quantity of the later recovered depending upon the final temperature to which the gas is reduced before delivery to a gas holder for distribution.

The tar, drip oil and lower temperature condensates contain a wide variety of hydrocarbons, the number and quantity of which vary with the final temperature to which the gas is subjected.

As an example hydrocarbons such as benzene, toluene, xylene, naphthalene, anthracene, indene, styrene, methyl styrene, cyclopentadiene, isoprene, piperylene, butadiene, etc., might be detected in small quantities or recovered in substantial amounts. All of these hydrocarbons are valuable, the unstaured resin forming compounds perhaps more so than the others, because under normal gas manufacturing conditions small quantities only are produced.

From the standpoint of the manufacture of gas

for distribution, these cyclic processes have been developed to a high degree of efficiency. However, from the standpoint of securing high yields of selected individual hydrocarbons, while the employment of a cyclic operation of their general character is highly desirable, the usual methods of operation are not so satisfactory.

In securing high yields of many valuable individual hydrocarbons from petroleum oil, a severity of pyrolysis is required which inevitably results in the production of a very considerable quantity of carbon or at least of hydrocarbon material which is extremely poor in hydrogen. If a continuous process such as tube cracking is employed, the deposition of this carbon on the interior of the tubes presents operating difficulties, besides in some cases exerting an undesired catalytic effect upon the course of the pyrolysis.

In cyclic processes of the general character of those above, the continual recurrence of the heating period affords regular and frequent opportunity for burning off any deposited carbon, preventing its accumulation and providing a substantially carbon free path of pyrolysis at the beginning of each gas making "run."

In the usual methods of operating these cyclic processes for the production of gas for distribution, however, even should the required conditions for a high yield of a given hydrocarbon of good quality be accidentally attained in a portion of the gas making path, and during a portion of the gas making "run," other portions of the gas making path and other portions of the gas making "run" may provide cracking conditions far removed from those which are desirable from the standpoint of production of the desired hydrocarbon material.

In the heating step of the cycle, in establishing temperature conditions approximating the desired temperature conditions in the downstream portion of the path of the heating gases suitable for effecting the desired pyrolysis therein, it is extremely difficult to avoid setting up temperature conditions in the upstream portion of the heating path, which are entirely too severe for the desired pyrolysis.

During the gas making "run," due to the fact that the stored heat in the path of pyrolysis is being continually abstracted in the vaporization of the oil and the pyrolysis of the resulting vapors with consequent cooling of the heat storage material, there is a continual shift, during the run, toward pyrolysis conditions of decreased severity as the "run" proceeds, which is indicated by the swing, with respect to time, of observed temperatures at various points in the gas making path.

The swing in pyrolysis conditions, throughout the gas making "run," may be decreased by the employment of refractory heat storage material of relatively high heat conductivity as compared with that of the usual fire clay brick, such for example as bricks of bonded silicon carbide or carborundum. Such refractory material has the capability of rapidly transferring heat from the outside surface to the interior during the "blow," and from the interior to the outside surface of the brick, during the "run," thereby maintaining more uniform surface temperatures.

Short cycles with short "runs" also tend to lessen the swing in pyrolysis conditions attendant upon operations with any given oil input rate. There is a practical limit to the shortening of cycle time, however, in that, with continued shortening, valve operations begin to take up a disproportionate portion of the cycle. The

time occupied by purges may also be disproportionate, or if it is not, an undue contamination of the make gas with combustion gases, or an undue loss of make gas to the atmosphere may take place.

The present invention is directed to the provision of a novel cyclic process of the above general character in the performance of which a greater uniformity of pyrolysis may be effected and greater yields of desired valuable hydrocarbons in good quality secured.

According to the present invention, during the first portion of the run, only a portion of the entire path of stored heat established during the blow is employed as the path of pyrolysis, and during the run the path of pyrolysis is shifted longitudinally within the path of stored heat in such manner that the succeeding portion of the run is conducted under pyrolysis conditions more closely approximating in pyrolyzing effect those existing in the path of pyrolysis at the beginning of the run, than did those existing in the path of pyrolysis immediately before the shift.

Stated otherwise, during the run after the pyrolysis conditions existing in the path of pyrolysis at the beginning of the run have been moderated due to the cooling action of the pyrolysis upon that portion of the path of stored heat employed as the path of pyrolysis, the path of pyrolysis is shifted lengthwise within the path of stored heat, so as to alter the pyrolysis conditions in the direction of greater intensity of cracking and so as to approximate more closely the intensity of the cracking effected at the beginning of the run, whereby greater uniformity of cracking is attained.

The shift of the path of pyrolysis within the path of stored heat during the "run" may be made in a number of ways depending, among other things, upon the temperature conditions set up in the path of stored heat during the "blow," upon the particular portion of the path of stored heat employed during the initial part of the run, and upon the degree of compensation in pyrolysis conditions to be effected by the shift of the path of pyrolysis.

The restoration of pyrolysis effect produced by the shift of the path of pyrolysis during the run may be obtained by shifting the path of pyrolysis so as to compensate for reduced temperature conditions by increased time of contact, or by shifting the path of pyrolysis so as to operate during the succeeding portion of the run with substantially the same temperature and time of contact as at the start of the run, or even by shifting the path of pyrolysis so as to operate under more severe temperature conditions and with shorter time of contact, than those obtaining at the start of the run.

The shift in the path of pyrolysis within the path of stored heat may be conveniently made by shifting either the point of admission of the oil to the path of stored heat, or the point of exit of the products of pyrolysis therefrom, or both.

Other features of the invention reside in the steps, combination of steps, sequence of steps, and in the construction, combination, and arrangement of parts, all of which together with other features will become more apparent to persons skilled in the art as the specification proceeds, and upon reference to the drawings, in which

Figures 1 to 5 are diagrammatic flow sheets illustrating the process of the present invention.

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Figure 6 is an elevation partly in section, illustrating, somewhat diagrammatically, an oil gas set adapted for employment in the process of the present invention.

The invention will be more particularly described in connection with the manufacture of oil gas, although it is applicable as before stated to other processes in which fluid hydrocarbon material is pyrolyzed.

Referring to Figures 1 to 5:

In all of the Figures 1 to 5, the path of stored heat established during the blow portion of the cycle is indicated by the shaded rectangle having an upstream end at 1 and a downstream end at 2.

In the operation diagrammatically illustrated in Figure 1, during the first part of the gas making "run," oil is introduced to the path of stored heat at 3, which is downstream from 1, while a diluent gas such as steam is introduced at 1, the products of pyrolysis and steam leaving the path of stored heat at 2.

During the later portion of the gas making run, and after the moderation of excessive temperatures in the stream portion of the path of stored heat by the cooling effect of the steam, the admission of the oil is shifted upstream to 4, the products of pyrolysis and steam still leaving the path of stored heat at 2.

It will be seen that the path of pyrolysis in the first portion of the "run" extended within the path of stored heat from 3 to 2, while in the second portion of the "run" the path of pyrolysis was shifted so that it extended from 4 to 2. The time of the shift and the degree of the shift and other conditions are chosen so that while the pyrolysis conditions existing in the longer path from 4 to 2 at the time of the shift are somewhat more severe than those existing at the time of the shift in the shorter path from 3 to 2, they closely approximate in effect the conditions of pyrolysis existing in the shorter path at the outset of the "run." A measure of the intensity of the cracking effected in the several portions of the run may be obtained by a comparison of the density relative to air of the gas produced in the several portions of the "run," as will be more particularly described hereinafter.

In the operation diagrammatically illustrated in Figure 2, during the first portion of the "run," the oil is introduced to the path of stored heat at 5, a diluent gas such as steam being introduced upstream at 1. The products of pyrolysis and steam leave the path of stored heat during the first portion of the run at 6 which is up stream from 2.

During the later portion of the "run," with the oil and steam admissions unchanged, the point of removal of the products of pyrolysis and steam is shifted downstream to 2.

During the first portion of the "run," the path of pyrolysis extended within the path of stored heat from 5 to 6, while during the latter portion of the "run" it was shifted so as to extend from 5 to 2.

As in the previous operation, the time, degree and other conditions of the shift are chosen so that the pyrolyzing effect of the longer path of pyrolysis, while somewhat more severe than that of the shorter path of pyrolysis at the time of the shift, closely approximates the pyrolyzing effect of the shorter path at the outset of the "run."

In the operation diagrammatically illustrated in Figure 3, during the first portion of the "run,"

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the oil is introduced downstream at 7, while a diluent gas such as steam is introduced at 1. The resulting products of pyrolysis and steam leave the path of stored heat at 2.

During the second portion of the "run," after the upstream portion of the path of stored heat has been sufficiently cooled by the passage of steam therethrough, the admission of the oil is shifted upstream to 9, and the point of removal of products of pyrolysis and steam shifted upstream to 8.

In this case, the path of pyrolysis in the latter part of the "run" extending from 9 to 8 may be longer, shorter or the same length as the path of pyrolysis in the first portion of the run extending from 7 to 2. In any case, other conditions such as temperature, rate of oil and steam admission, etc., are such as to produce a pyrolyzing effect in the path of pyrolysis from 9 to 8 somewhat more severe than that existing in the path of pyrolysis from 7 to 2 at the time of the shift, but closely approximating pyrolyzing effect of the pyrolysis conditions in the path from 7 to 2 at the outset of the "run."

In the operation diagrammatically illustrated in Figure 4, during the first portion of the "run," oil is introduced to the path of stored heat at 10, while a diluent gas such as steam is introduced at 1. The products of pyrolysis and steam leave the path of stored heat at 11.

During a later portion of the run, oil is admitted to the path of stored heat at 12, which is upstream from 10, and downstream from 1, steam continuing to be admitted at 1. During this portion of the "run," the resulting products of pyrolysis and steam are taken off at 2, which is downstream from 11.

As in the case of the previously described operations, the shift in the pyrolyzing path, during the "run," is to compensate for moderation of pyrolyzing conditions during the earlier portion of the "run" and to secure greater uniformity of cracking.

In Figure 5, the operation is similar to that of Figure 1 except that the upstream portion of the path of stored heat is divided by partition 13a into two parallel portions 13 and 14.

During the first portion of the "run" oil is admitted to the path of stored heat downstream at 15, with steam supplied at 1 to either or both of the parallel portions 13 and 14, the resulting pyrolysis products and steam being taken off at 2.

During a later portion of the "run" the oil admission at 15 is terminated and oil admitted at 16, which is upstream from 15 and downstream from 1. Steam is admitted at 1 to both parallel portions of the path of stored heat 13 and 14, the steam admitted through portion 14 providing a diluting medium in the oil vaporization zone as well as carrying heat from the upstream end of the path of stored heat into the path of pyrolysis. The steam admitted through 13 carries heat from this portion of the path of stored heat into a downstream portion of the path of pyrolysis, by-passing the upstream portion of the path of pyrolysis. Appropriate proportioning of the steam admitted through 13 and 14 provides a further control of the uniformity of cracking.

The resulting pyrolysis products and steam during the later portion of the "run" are taken off at 2 as before.

The greater time of contact of the longer path of pyrolysis from 16 to 2 as compared with that from 15 to 2, compensates for lower temperature conditions, with a result that the intensity of

pyrolysis effected at the beginning of the "run" is substantially restored, thereby securing increased uniformity.

In the operations diagrammatically illustrated in Figures 1 to 5, steam may be admitted to the path of stored heat simultaneously with the oil, at the same point or points as the oil.

Also, if desired, the upstream admission of the oil to the path of stored heat, during the latter part of the run, in the operations of Figures 1, 3, 4 and 5 may be at 1, the upstream end of the path of stored heat instead of somewhat downstream therefrom as shown in these figures, providing however that in such event the temperature conditions in the shifted path of pyrolysis are not excessive.

In the operations of Figures 1, 3, 4 and 5 the admission of the steam upstream at 1, during the earlier portion of the "run" carries heat into the downstream portion of the path of stored heat, which is then being employed as the path of pyrolysis, thereby reducing the swing in pyrolysis conditions therein, due to the cooling effect of the pyrolysis. Reference is made, in this connection, to Patent No. 2,372,197, dated March 27, 1945, to Edwin L. Hall.

In the operation of the present invention, as exemplified in the operations of Figures 1, 3, 4 and 5, this passage of steam may have the further function of moderating, during the earlier portion of the "run," temperature conditions in the upstream portions of the path of stored heat in and adjacent to the zone of combustion, which are excessive from the standpoint of oil vaporization and pyrolysis, so that when the point of introduction of the oil is shifted upstream, the temperature conditions in this upstream portion of the path of stored heat are no longer too severe for use as a portion of the path of pyrolysis.

Referring to Figure 6:

21 generally indicates an oil gas generator provided with the refractory lining 22. In the generator chosen for illustration, there are provided three refractory checkerbrick masses 24, 25, and 26 suitably supported on arches 27, 28, and 29 respectively, and, together with the lining, forming the combustion space 30, and the oil vaporization spaces 31 and 32. Below checkerbrick 26, the generator is in communication by way of connection 33 with the superheater 34, provided with the refractory lining 35.

In the superheater chosen for illustration, there are provided two checkerbrick masses 36 and 37, suitably supported by arches, one of which is shown at 38.

The superheater is further provided with the stack valve 40, and with the gas offtake 41, which is provided with valve 42, and which leads to the wash box 43. The superheater may be provided with the additional gas offtake 44, provided with valve 45, which leads from the space between checkerbrick masses 36 and 37 to the offtake 41 and thence to the wash box. From the wash box, gas offtake 46 leads to condensation, gas purification, and gas storage apparatus.

In an operation of Figure 6, chosen for illustration and similar to that diagrammatically illustrated in Figure 1, during the "blow," with stack valve 40 open and valve 42 closed (valve 45 is also closed, if connection 44 and valve 45 are provided), fluid fuel such as crude petroleum oil, fuel oil, residuum oil, tar or combustible gas is admitted to the combustion space 30, through fuel supply means 50, and burned with air supplied through air supply means 51. The hot com-

bustion gases traverse the combustion space 30, the checkerbrick 24, oil vaporizing space 31, checkerbrick 25, oil vaporizing space 32, and checkerbrick 26. From the generator base, the hot combustion gases pass through connection 33 to the superheater 34, and through the superheater checkerbrick to the stack valve 40, and thence to the atmosphere.

During the "blow" the refractory linings and checkerbrick of the vessels are heated to a high temperature and heat stored therein.

The path of stored heat, so produced, extends from the combustion chamber 30, through checkerbrick 24, vaporization chamber 31, checkerbrick 25, vaporization chamber 32, and checkerbrick 26 of the generator, and through the checkerbrick masses 36 and 37 of the superheater, with the highest temperature conditions being established in combustion chamber 30 and checkerbrick 24 and lower temperature conditions in vaporization chamber 31, checkerbrick 25, vaporization chamber 32, checkerbrick 26 and the superheater checkerbrick 36 and 37.

When the desired temperature conditions for the oil vaporization and pyrolysis in the selected downstream portion of the path, that is, for illustration, in the generator below the arches 28 and in the superheater, have been set up, the heating is terminated by shutting off the fuel supply through 50 and the air supply through 51.

A purge may now be made with steam supplied at 52, purging combustion products out through stack valve 40.

The stack valve 40 may then be closed, valve 42 opened (valve 45 remaining closed if provided), and the gas making "run" begun.

The admission of steam through steam supply 52 is continued, while simultaneously oil is sprayed into the vaporizing chamber 32, through oil supply means 53. Additional steam may be simultaneously supplied, if desired, through steam supply means 54.

The oil is vaporized in the lower portion of the generator, in the presence of the steam, at least a part of which is heated in passing down through checkerbrick 24 and 25 into the vaporizing chamber 32. The steam and the resulting oil vapors pass through the generator checkerbrick 26 and the superheater checkerbrick 36 and 37, in which the desired pyrolysis of the oil hydrocarbons is effected.

The resulting oil gas passes through the gas offtake 41 to the wash box 43, and thence through offtake 46 to storage, condensing, purification, and fractionation apparatus (not shown) for the removal and separation of impurities and valuable constituents therefrom.

The washbox is illustrated as continuously supplied with water through connection 55, so as to maintain a body of sealing liquid, in the wash box, at a level sufficiently high to seal the end of connection 41, and to prevent the return of gas to the set during the "blow," but insufficiently high to prevent the ready passage of the oil gas to the offtake 46 during the "run."

The oil gas is cooled in the wash box, and a considerable quantity of tar containing valuable hydrocarbons is condensed therefrom. This tar is continuously removed with sealing water in the form of an emulsion, through connection 56.

As the gas passes through the gas offtake 46, it may be continuously sampled, the sampled gas passing through connection 57 to the scrubber-cooler 58. The scrubber-cooler 58 is illustrated as provided with the supply means 59 of

a cooling and scrubbing liquid such as water.

As the gas sample passes upward through the scrubber-cooler, it is scrubbed and cooled to remove entrained tar particles or other entrained material, and to cool the gas to a definite selected temperature indicated by thermometer 60. The removed entrained material and any condensate produced by the cooling leaves the scrubber with scrubbing and cooling liquid through connection 61. Other means for removing entrained particles such as the use of packing with or without scrubbing might be employed.

The cleaned and cooled gas sample passes through connection 62 to the relative density register 63. The pressure of the gas may be controlled by valves to maintain a desired pressure approximating atmospheric and indicated by the manometer 64.

The gas passes through the relative density register 63, in which its density is compared with that of air, which is drawn in through connection 65, by way of the drier 66. The gas sample and the comparison air leave the register by way of connections 67 and 68 respectively. The relative density register may be arranged to continuously indicate and record the density with respect to air of the produced oil gas at chosen standard conditions of temperature and pressure, for example at 60° F. and slightly above atmospheric pressure.

An example of a type of relative density register which may be advantageously employed is that known commercially as "Ranarex."

The relative density of the gas, so determined, may be employed as a measure of the intensity of the pyrolysis effected in the several portions of the "run."

As the gas making "run" proceeds, the temperature conditions in the vaporizing chamber 32 and in the checkerbrick 26 and the superheater are reduced due to the abstraction of heat for vaporization of the oil and for the cracking of the resulting vapors. This cooling is reduced in rate, however, by the passage into the vaporization chamber 32 of the steam admitted to the combustion chamber 30, through steam supply 52 and superheated in passage through the combustion chamber and the checkerbrick sections 24 and 25, while simultaneously cooling these upstream portions of the path of stored heat.

After a considerable portion of the gas making "run" has elapsed, for example after the expiration of 60, 70 or 80% thereof at the end of which time pyrolysis conditions in the path of pyrolysis have been moderated somewhat due to cooling of that portion of the path of stored heat by the pyrolysis, and providing also that at the end of which time, the temperature conditions in the portion of the path of stored heat upstream from the point of oil admission have been sufficiently moderated by the passage of steam therethrough, the admission of oil through supply means 53 is terminated (steam supplied through 54 may also be shut off).

During the succeeding portion of the run the path of pyrolysis is extended upstream in the path of stored heat by supplying oil through oil supply means 70 to vaporization space 31. Steam may be continued to be supplied to the combustion space 30 through steam supply 52 and additional steam may be supplied simultaneously to the vaporization space 31, through steam supply means 71.

The oil is vaporized and the resulting vapors cracked in passage through the vaporization space

31, checkerbrick 25, vaporization space 32, checkerbrick 26, and superheater checkerbrick 36 and 37, the resulting products of pyrolysis passing through offtake 41, to the wash box, the undensified gas passing through connection 46, as before. During its passage through connection 46, the gas may be sampled, scrubbed, cooled, and its relative density measured as before described.

A comparison of the relative density of the gas after the shift of the path of pyrolysis within the path of stored heat with the relative density of the gas produced at the outset of the "run," furnishes a measure of how closely pyrolysis conditions in the shifted path of pyrolysis approximate those existing in the original path of pyrolysis at the outset of the "run."

According to the present invention it is preferred to shift the path of pyrolysis during the "run" so that the change in pyrolyzing conditions during the "run" does not produce a swing during the "run" of more than 0.03 in relative density of the oil gas when measured, at 60° F. and slightly above atmospheric pressure, by the method above described or by an equivalent method.

More preferably this swing in relative density does not exceed 0.02 and still more preferably 0.01.

Those skilled in the art will understand that care should be taken, in comparing relative densities of the oil gas produced in the several portions of the "runs," to avoid the inclusion of significant proportions of other gases such for example as unpurged combustion gases from the "blow," or correction should be made therefor in order to calculate the swing in relative density which is due to changes in conditions of oil pyrolysis.

At the end of the run the supply of oil to vaporization space 31, through oil supply means 70 is shut off, and the gas set is purged, for example, by continuing the admission of steam thereto through steam supply 52, purging the pyrolysis products out of the set through offtake 41.

The steam may then be shut off and the cycle repeated.

It will be understood by those skilled in the art that the points of admission of oil and of steam in the respective portions of the "run," as well as the durations of the respective portions of the "run" may be so chosen that the pyrolyzing effect of the shifted path of pyrolysis, very closely approximates that of the original path of pyrolysis at the outset of the "run."

Within a very considerable range of variation, the influence of changes in temperature upon cracking intensity may be closely compensated for by appropriate change in the length of the pyrolyzing path.

Under certain conditions, it may be possible to move the point of oil admission upstream in the path of stored heat, and simultaneously move upstream the point of exit of the pyrolysis products from the path of stored heat, maintaining the length of the path of pyrolysis substantially the same as before, providing temperature conditions in the shifted path are appropriate.

For example in the later portion of the "run," the oil may be admitted to the vaporization space 31, through supply 70, while with valves 40 and 42 closed and valve 45 open, the products of pyrolysis are taken off from the superheater through offtake 44, without passing through the downstream checkerbrick 37. In such case, the

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upper portion of the superheater may be kept free of oil gas and purged by steam admitted at 72. This operation is in general similar to that diagrammatically illustrated in Figure 3.

During the later portion of the run, in either of the operations before described, if desired the oil may be admitted directly to the combustion space 30, providing temperature conditions therein and in checkerbrick 24 have been sufficiently modified.

It will be obvious to those skilled in the art that the apparatus of Figure 6 may also be readily employed with whatever modification may be necessary to effect any of the operations described in connection with Figures 2, 4 and 5.

An example of a cycle, employed in the operation of a 12.0 ft. diameter oil gas set somewhat similar to the apparatus of Figure 6, and having silicon carbide linings and checkerbrick downstream in the path of stored heat from the top of the downstream oil vaporizing zone, and the ordinary firebrick lining and checkerbrick upstream therefrom, is as follows.

[Cycle length, 1.9 minutes]

Per cent of cycle time	Operation
51.6	Air and fuel admission to combustion zone.
1.8	Soaking period.
2.8	Steam to combustion zone (purge).
23.4	Steam to combustion zone. Oil to downstream vaporizing zone.
2.5	Steam purge of downstream oil admission means.
6.5	Steam to combustion zone. Oil to upstream vaporization zone (combustion zone).
5.4	Steam to combustion zone (purge).
1.0	Expansion.
5.0	Air to combustion zone (air purge).

It will be seen that the total oil pyrolyzing time of the above cycle is less than 33 seconds, during approximately 78% of which, oil was admitted to the downstream vaporization zone, while the upstream vaporization zone was cooled by the passage of steam therethrough, and during the remaining 22% of which, the oil was admitted with steam to the upstream vaporizing zone, in this case the combustion zone. The products of pyrolysis were taken off from the superheater top in both portions of the pyrolyzing period, the operation being generally similar to one described in connection with Figure 1.

Of course, so short a cycle so highly subdivided is only practicable with efficient automatic valve operation.

The following temperatures were average observed temperatures through the cycle as measured by shielded iron-constantan thermocouples

Top of downstream vaporizing zone.....	1520
Middle of downstream vaporizing zone.....	1495
Base of downstream vaporizing zone.....	1595
Base of superheater.....	1535
Top of superheater.....	1395

In general, in such operations, the high combustion temperatures of the combustion zone, at the end of the "blow," were reduced to observed temperatures (by optical pyrometer) of the order of 1700° F. and lower, by the steam passing therethrough, during the first portion of the run, prior to the introduction of oil to the combustion zone. It was found that greatly improved uniformity of pyrolysis could be secured under these conditions of operation with very materially increased set capacities as compared with operations in which the path of pyrolysis was not shifted within the path of stored heat, during the run. Increases

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in capacities of the order of 30% and more may be so obtained without sacrifice of yield and quality of desired unsaturated hydrocarbon products.

In the practice of the invention, it has been found that variations of observed temperature through the set and through the cycle may be very materially reduced. For example, the observed temperature swing, throughout a cycle of the above length, in ° F. (shielded iron-constantan thermocouple) at the middle of the downstream vaporizing zone may be only 30° F. or less; at the bottom of the downstream vaporizing zone only 15° F.; in the lower superheater checkers only 14° F. or less; while in the middle of the superheater and in the top of the superheater, the observed temperature swing may be reduced to 0° F.

In operations without the shift in the path of oil pyrolysis during the run, but otherwise comparable, these swings were very much greater resulting in much less uniform cracking. For example, swings in the observed temperature of the downstream vaporizing zone were frequently of the order of 100° F. and more, even with a cycle of the above length and with the use of silicon carbide refractories. Likewise, the variation in temperature throughout the set is much less in the employment when the path of pyrolysis is shifted in accordance with the present invention.

In operations, in which neither the process of the above referred to patent to Edwin L. Hall nor the process of the present invention are employed, swings of observed temperatures of the order of 300-400° F. in the oil vaporization zone have been frequently encountered, while without the use of refractory heat storage material of relatively high conductivity as compared to that of ordinary firebrick, still greater swings in observed temperature may occur, even though a short cycle be employed.

The above temperatures are purely illustrative. Those skilled in the art will understand that the required intensity of pyrolysis varies widely depending upon the character of the fluid hydrocarbon material pyrolyzed and upon the particular hydrocarbon products desired.

For example, when unsaturated aromatic resin-forming hydrocarbon material in good yields and in good quality and other aromatic hydrocarbon material in good quality is desired, there is a preference for relatively severe conditions of pyrolysis and for a naphthenic oil, such as a crude petroleum oil falling within classes 5 to 7 and particularly class 7, when classified by the method of Bureau of Mines Report of Investigations R. I. 3279, or a fraction of such an oil. On the other hand, when highest yields of aliphatic or alicyclic conjugated olefines are particularly desired, milder pyrolysis conditions and a more paraffinic oil may be chosen.

It will be further understood that in cyclic operations of the character described, for the same intensity of cracking, the observed temperatures in different portions of the apparatus and in different portions of the cycle, as well as calculated times of contact therein, may vary widely depending, among other things, upon the particular apparatus and cycle employed and upon the particular method of measuring temperature. Some of the influential variables are the character of the fuel and the method of combustion, the character, quantity and arrangement of the heat storage material, the character, subdivision, and rate of input of the hydrocarbon material pyrolyzed, the character and quantity of the diluent

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gas, whether or not the hydrocarbon material is vaporized as well as pyrolyzed by the stored heat, and the length and subdivision of the cycle.

In the operations particularly described in the foregoing, the path of pyrolysis was shifted within the path of stored heat but once during the "run." Those skilled in the art will readily understand, that the path of pyrolysis may be so shifted a plurality of times, and that the manner of the shift need not be the same. For example the first shift of the path of pyrolysis during the "run" may be made by shifting the point of removal of the products downstream in the path of stored heat, without changing the point of oil admission, while the next shift may be made by moving the point of oil admission upstream in the path of stored heat, without changing the point of removal of the products.

Other modifications of the process and of the apparatus illustrated will occur to those skilled in the art without departing from the spirit of the invention. For example, it may be preferred, especially when "heavy oils" and residuums are employed, which yield particularly large quantities of coke on vaporization, to further subdivide the gas set, so as to provide separate shells for the upstream and downstream vaporizing zones either or both of which may be devoid of checkerbrick below the point of oil admission thereto. If the vessels are of large diameter, a central refractory pier may be provided in each otherwise empty vaporizing chamber.

The set may be further subdivided for other reasons, or on the other hand may be consolidated into a single shell.

Although it is preferred to flow the fluid hydrocarbon material through the path of stored heat in the direction of the flow of the heating gases, as above described, the invention may be applied in cases in which these flows are in opposite directions to each other.

From the foregoing, it will be obvious to those skilled in the art that the invention may be readily applied to the manufacture of carburetted water gas. For example, during the first portion of the up "run" the carburetting oil may be admitted into the path of stored heat downstream from the top of the carburetter, during a later portion of the up "run" the admission of the oil may be to the top of the carburetter, the carburetted water gas in each case being led from the set at the top of the superheater.

In comparing the relative densities of the carburetted water gas produced during different portions of the run, it should be remembered that the composition of the blue water gas component of the carburetted water gas varies with the temperature of the fuel bed, and that this affects the density of the carburetted water gas. Those skilled in the art will understand how to correct for varying blue water gas composition and will be able to employ the corrected relative gas density to control the uniform pyrolysis of the carburetting oil.

As in the case of oil gas manufacture, significant quantities of combustion products from the "blow" should be excluded from the carburetted water gases compared as to relative density, or the determined relative densities should be corrected for the presence of such combustion products.

The application of the invention to the reforming of such hydrocarbon gases as natural gas and oil refinery gas will likewise be readily under-

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stood by those skilled in the art without the necessity of detailed explanation.

In the foregoing, the equalization of pyrolysis conditions in the several portions of the path of pyrolysis, which may be in part overlapping, and in the several portions of the "run" by equalizing the density, relative to a standard gas such as air, of the gas produced therein has been described.

The same method of equalizing pyrolysis conditions may be applied in the case of pyrolysis carried out in a plurality of pyrolyzing paths arranged in parallel, such, for example, as a plurality of cyclically operated oil gas sets, the resulting pyrolysis products from which pass into a common conduit or common relief holder.

For example in the case of a plurality of oil gas sets such, for example, as that shown in Fig. 6, and connected in parallel to the same relief holder, the relative density, with respect to air, for example, of the make-gas passing from the wash box of each oil gas set, may be continuously measured and recorded as previously described, in connection with the description of the apparatus of Fig. 6, and the pyrolysis conditions within the individual sets adjusted in such manner that each of the sets produces oil gas of substantially the same desired relative density, within any desired degree of variation, tolerance, such for example, as that discussed in connection with the previously described equalization of pyrolysis conditions in different portions of the same set, during different portions of the "run."

Those skilled in the art will know how to adjust the various factors which control variation in the intensity of pyrolysis as between individual gas sets, which is reflected in variations in the density of the make-gas therefrom. Among the variables involved are the temperature conditions set up in the heating period in the various portions of the pyrolyzing path of the set, the time of contact during pyrolysis, and the effectiveness of contact between the material pyrolyzed and the heated surfaces in the gas set, the length and subdivision of the cycle, etc.

Assuming that other factors such as the disposition of heated surfaces and the character of heat conductive and heat storage refractory material are fixed, and that the rate of input, during the "run," of fluid hydrocarbons and accompanying diluent gas is the same, the intensity of pyrolysis may be increased or decreased by elevating or reducing temperature conditions set up during the "blow" by increased or decreased rate of fuel combustion or by employing longer or shorter heating periods.

With the same temperature and other conditions, the intensity of pyrolysis may be increased or decreased by increasing or decreasing the time of contact by reducing or increasing the rate of input of materials into the pyrolyzing path, such as, by decreasing or increasing the input of petroleum oil and steam to the generator.

It may be convenient to substantially fix all of the pyrolysis variables except one, for example, the rate of fuel combustion during a heating period of fixed length, and to control the intensity of pyrolysis, as measured by the relative density of the produced gas, by increasing the rate of heat input during the "blow" period in response to increase in said relative density, and decreasing the rate of heat input during the "blow" period, in response to decrease in said relative density.

However, control may be exercised by varying

other variables, as between sets, if desired, such as by varying the rate of input of the oil to be pyrolyzed, together with the accompanying steam, or other diluent gas. Control may also be effected by varying more than one pyrolysis variable, if desired,

The petroleum oil pyrolyzed may be introduced into the set in liquid or vapor form, as desired.

Other modifications will readily occur to those skilled in the art and may be made without departing from the spirit of the invention.

This application is a continuation-in-part of my copending application Serial Number 564,540, filed November 21, 1944, which has matured into Patent No. 2,393,333, dated January 22, 1946.

I claim:

1. A process for equalizing the intensity of pyrolysis effected in a plurality of fluid hydrocarbon pyrolyzing zones arranged in parallel flow relation one to another and discharging into a common gas storage zone comprising separately measuring the density of the gas produced in each of said zones during a pyrolysis "run," and in accommodation to the indications of such measurements separately adjusting the conditions of pyrolysis in each of said zones including separately timed shifting of the pyrolysis path traversed by the said fluid hydrocarbon in each of said zones during the pyrolysis "run" to produce gas in each of said zones of substantially the same density.

2. A process for equalizing the intensity of the pyrolysis cyclically effected in a plurality of petroleum oil pyrolyzing zones arranged in parallel flow relation one to another and discharging into a common gas storage zone, said pyrolyzing zones being heated by the passage of combustion gases therethrough during heating periods of the cycle and between heating periods being employed for pyrolysis of fluid hydrocarbons by passage therethrough of said fluid hydrocarbons in contact with heat storage material arranged therein during a pyrolysis "run" which comprises continuously and separately measuring under substantially the same conditions of temperature and pressure and after substantially the same degree of condensation, the gas produced during said pyrolyzing "runs" in each of said pyrolyzing zones, and in accommodation to the indications of such measurements separately adjusting pyrolysis conditions in said zones including separately timed shifting of the pyrolysis path traversed by the said petroleum oil in each of said zones during the pyrolysis "run" to cause the production of gas in each of said zones of substantially the same density when so measured.

3. A method for controlling the uniformity of products of pyrolysis produced in a plurality of cyclically operated oil gas sets connected in parallel to the same relief holder, the cycle comprising a heating period in which heat is stored in refractory heat storage material by the passage in contact therewith of hot combustion gases and an oil pyrolyzing "run" in which petroleum oil is

pyrolyzed by the stored heat in vapor phase and in the presence of steam, said oil gas sets each operating in a cycle of substantially the same length and subdivision, which comprises separately cooling the oil gas flowing from each set during the oil pyrolyzing "runs" of the cycle to substantially the same temperature under substantially the same pressure conditions, separately measuring the density of the gas in each stream so cooled under substantially the same conditions of temperature and pressure, and in accommodation to the indications of such measurements separately adjusting the rate of heat input to the several gas sets during the heating periods of the cycle in such manner that the density of the oil gas flowing from each set when so measured is substantially the same and with separate timing in the two sets shifting the pyrolysis path traversed by the said petroleum oil in each of the two sets during the pyrolysis "run."

4. A method for controlling the uniformity of products of pyrolysis produced in a plurality of cyclically operated oil gas sets connected in parallel to the same relief holder, the cycle comprising a heating period in which heat is stored in refractory heat storage material by the passage in contact therewith of hot combustion gases and an oil pyrolyzing period in which petroleum oil is pyrolyzed by the stored heat in vapor phase and in the presence of steam, said oil gas sets each operating in a cycle of substantially the same length and subdivision, which comprises separately cooling the oil gas flowing from each set during the oil pyrolyzing periods of the cycle to substantially the same temperature under substantially the same pressure conditions, separately measuring the density of the gas in each stream so cooled under substantially the same conditions of temperature and pressure, and in accommodation to the indications of such measurements separately adjusting the rate of petroleum oil input to the several sets during the pyrolyzing periods of the cycle and separately shifting the pyrolysis path traversed by the said petroleum oil in each of the sets during the pyrolysis periods of the cycle in such manner that the density of the oil gas flowing from each set when so measured is substantially the same.

CHARLES GORDON MILBOURNE.

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