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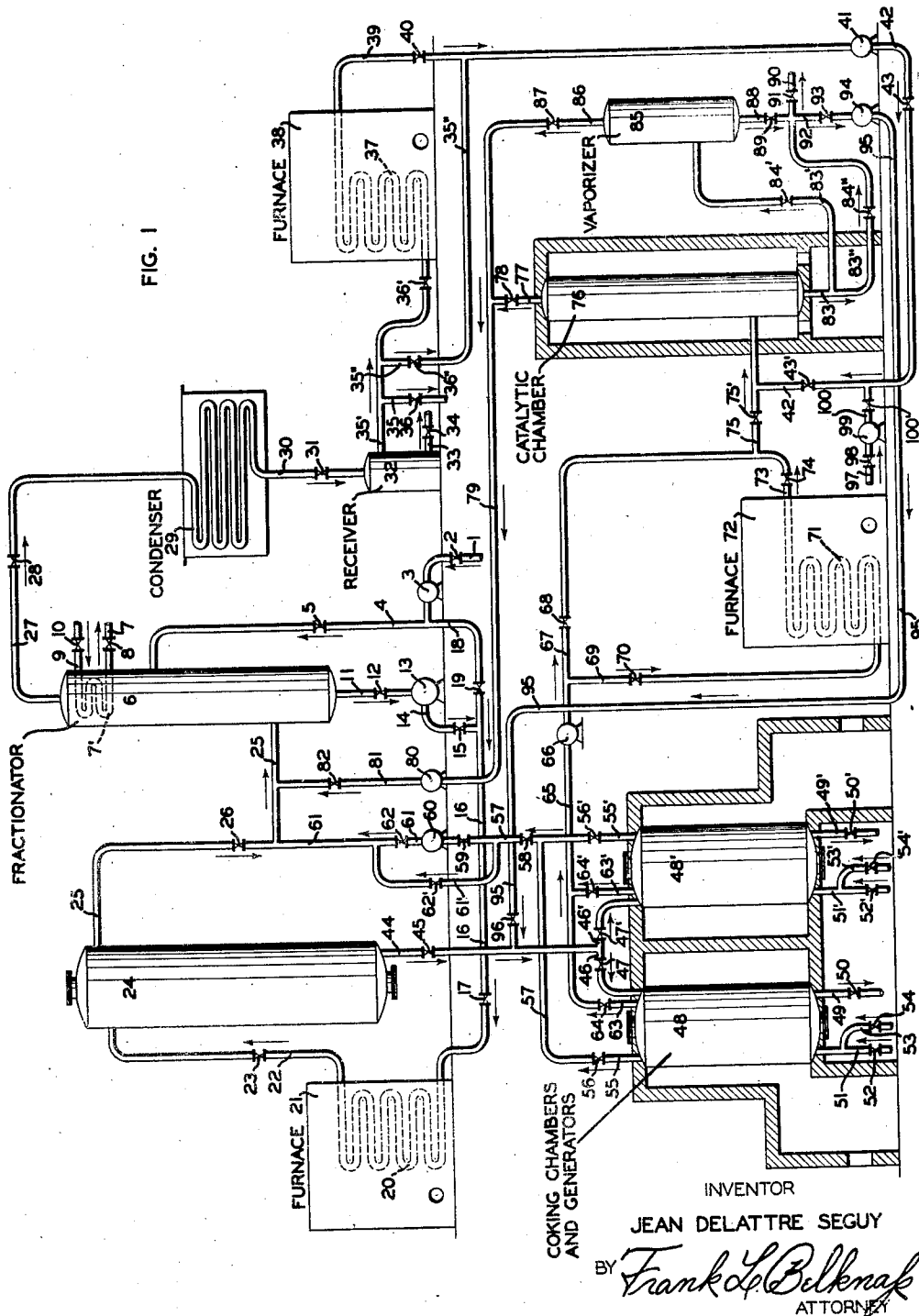
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2,039,459

PROCESS FOR TREATING HYDROCARBONS

Filed Dec. 14, 1932

2 Sheets-Sheet 1



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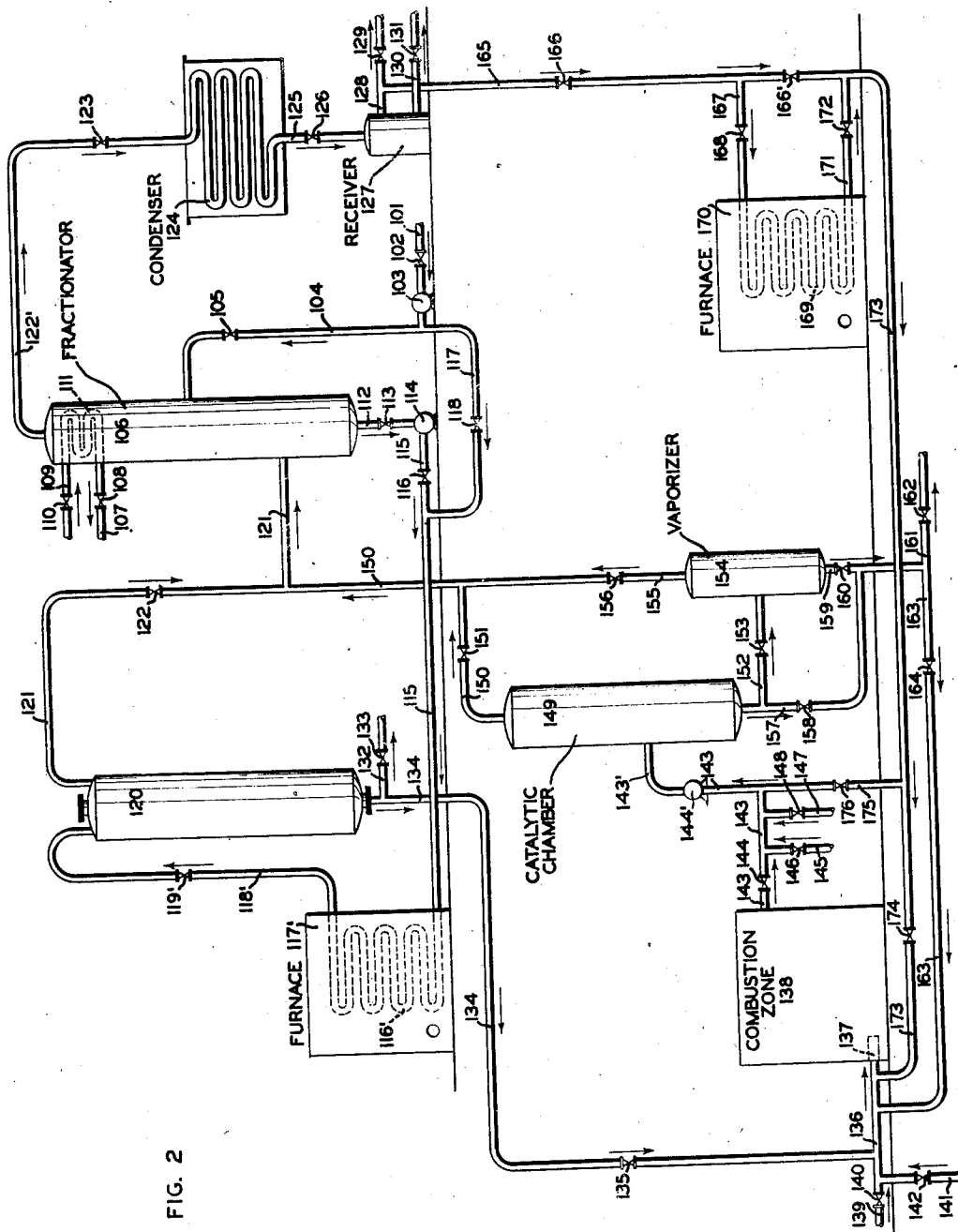


FIG. 2

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PROCESS FOR TREATING HYDROCARBONS

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Application December 14, 1932, Serial No. 647,076

6 Claims. (Cl. 196—49)

This application is a continuation in part of my co-pending applications, Serial Nos. 463,061 and 463,062, filed June 23, 1930.

This invention refers more particularly to the treatment of heavy hydrocarbon oils at elevated temperatures and pressures to produce therefrom lighter and more valuable hydrocarbon oil fractions.

More specifically the present invention is concerned with processes wherein hydrocarbon oils or other liquid bituminous materials are subjected to pyrolytic conversion conditions to produce motor fuels, the by-products of the conversion reactions, to-wit, heavy residual products (either solid or liquid) and gases, being utilized directly and efficiently as base materials for the production of further quantities of low boiling hydrocarbons by synthetic processes.

One of the chief problems in the production of gasoline by cracking heavy hydrocarbon oil mixtures is that of increasing the yield of desired low boiling fractions to render the process more economical. The limit of yield in most commercial cracking processes is reached when the residual products consist either of coke or extremely high viscosity liquids, the latter requiring special handling when utilized as fuel oil on account of their heavy consistency and tendency to contain suspended carbonaceous particles which clog the ports of burners. It has been appreciated by those familiar with the cracking process for some time that if fixed gases could be caused to recombine with the residuals that further quantities of motor fuel might be produced. However, this combination is only effected with difficulty due to the stable character of the two by-products and attempts to utilize this possibility have met with very little success from a commercial standpoint.

The present invention is concerned with a process by the operation of which the undesirable by-products from the cracking process may be economically utilized for the production of increased amounts of low boiling gasoline fractions, the particular features of the process being hereinafter fully disclosed.

In one specific embodiment the invention comprises cracking hydrocarbon oils at elevated temperatures and pressures to produce gasoline, solid or liquid residues, and fixed gases, condensing and collecting the gasoline, suitably treating the residue and fixed gases with oxidizing gases and steam to produce proportioned mixtures of carbon monoxide and hydrogen, subjecting said gas mixtures to catalytic influences to produce increased

yields of hydrocarbons, and subjecting the products from the catalytic step to fractionation together with the products from the primary cracking step.

To assist in describing operations characteristic of the process of the invention the attached diagrammatic drawings, Figs. 1 and 2, have been provided, which show, by the use of conventional figures, arrangements of apparatus in which the process may be conducted.

Referring to Fig. 1 of the drawings, a plant layout is shown in which the cracking stage may be carried to the production of solid residuals. Line 1, containing control valve 2, indicates a supply line for whatever heavy hydrocarbon oil may be chosen for treatment in the process. Such an oil may be the heavier residual portions of petroleum resulting from a primary fractionation thereof, heavy distillates from the same source or analogous hydrocarbon mixtures from other natural or artificial bituminous materials such as coal tars, shale oils, asphalts, etc. These charging oils may be taken by charging pump 3 and discharged through a line 4, containing a control valve 5, into a fractionator 6 which receives conversion products from both the cracking step and the synthetic conversion step, the raw oil introduced coming into direct contact with the reaction products, assisting in their fractionation by its cooling action and being itself preheated and stripped of light fractions. To further assist in efficiently fractionating the products entering the fractionator, a cooling coil 7 may be provided near the top of this coil having inlet line 8, containing a control valve 9, for the admission of any suitable cooling fluid such as oil, water or steam and a line 7, containing control valve 8, for the rejection thereof.

The mixture of preheated and stripped charging oil and refluxes from the fractionator may be led from the bottom thereof through a line 11, containing control valve 12, taken by a high pressure pump 13 and discharged in turn through a line 14, containing a control valve 15, and a line 16, containing control valve 17, to a heating element 20. To permit the diversion of any or all of the charging oil around the fractionator and its direct feed to the heating zone a by-pass line 18, containing control valve 19, is preferably provided so that different rates of feed to the fractionator may be employed and the dephlegmating action better controlled. During passage through heating element 20, which may be of any suitable type disposed to receive heat from a furnace 21, the temperature and pressure are

brought to the optimum point for producing desired conversions and the products of the heating are then preferably discharged through a transfer line 22 having interposed therein a control valve 23 and enter a chamber 24 which constitutes an enlarged vaporizing or reaction zone in which the reactions of conversion initiated by the heating may be permitted to progress to substantial equilibrium. Conditions are preferably so regulated, however, that the formation of coke is substantially prevented and the residual products which are withdrawn through line 44 and valve 45 have sufficient fluidity to be handled as liquids. The treatment of these liquids will be described presently.

Temperature and pressure ranges cannot be exactly defined since those required will be dependent upon the character of the combined feed to the heating element and the degree of conversion required. In general, temperatures of from 850 to 1050° F. more or less may be employed and superatmospheric pressure from about 100 to 500 pounds per square inch. Vaporous products from the reaction zone may be conducted through vapor line 25, containing a control valve 26, and enter fractionator 6 along with vapors from lines 61 and 81, these vapors originating in a manner which will later be more fully described.

Vapors from fractionator 6 which are preferably of approximate gasoline boiling point range may be passed through a vapor line 27, containing a control valve 28, and be condensed during passage through a condenser 29 of proper design, uncondensable gases and gasoline then being conducted through a line 30, containing control valve 31, to a receiver and separator 32. Liquid products may be removed through line 33, containing control valve 34, and gases through line 35', which has branch line 35, containing control valve 36, for the ultimate disposal of such portions of process gases as are not needed and branch line 35'', containing control valve 36'', for the transfer of fixed gases directly to the second or synthetic stage of the process. Line 35' contains a control valve 36' which permits the reheating of the fixed gases by heating element 37 disposed in a furnace 38, the reheated gases then being caused to travel through a line 39, containing a control valve 40, to the second stage of the process which will be described more at length in succeeding paragraphs.

The liquid residuals from reaction zone 24 are released to coking chambers under reduced pressure in which they are further heated if necessary to insure the production of coke of proper quality. The residuals passing through line 44 and valve 45 which receive liquid increments from the synthetic stage from line 95 as will be presently described, may be passed, preferably with pressure reduction, to any one of a group of multiple coking chambers, designated as 48 and 48', respectively. Branch line 46, containing control valve 47, permits the introduction of the liquids to chamber 48 and line 46', containing control valve 47', permits their introduction to chamber 48'. The coking chambers are shown positioned in a furnace setting to permit of their external heating if necessary.

In the first or coking stage hydrocarbon vapors may be released to pass through line 55, containing control valve 56 or 55', containing control valve 56', and pass through line 57, containing control valve 58, line 61', containing control valve

25, in case coking has been effected without pressure reduction or the pressure in the reaction zone has been reduced sufficiently through valve 26. When pressure in the coking chambers has been reduced to a point lower than that obtaining in line 25, these vapors will necessarily be recompressed before entering the fractionator (since the latter is preferably maintained at the same approximate pressure as the reaction zone) and to effect this object a valve 59 may be opened while valve 62' is closed and the low pressure vapors admitted to a compressor 60 which is of a capacity adapted to raise the pressure to the desired degree to permit their passage through valve 62 and line 61 to line 25 leading to the fractionator. Coking chambers 48 and 48' are provided with liquid draw lines 49 and 49', respectively, containing valves 50 and 50', for withdrawing liquid accumulations if necessary.

When any one chamber has been filled with coke to the proper point the stream of liquid products from the reaction zone is preferably diverted to another chamber and the coke accumulation in the first chamber is subjected to the controlled and alternate action of air and steam to produce mixtures of carbon monoxide and hydrogen to be used in the synthetic conversion step following. For the admission of steam, lines 51 and 51', respectively, containing valves 52 and 52' are provided. Correspondingly, lines 53 and 53', respectively, containing valves 54 and 54' are provided for the admission of air. As in the usual water gas plants the coke bed may be preliminarily blasted with air to bring its mean temperature to approximately 2000° F. during which period the gases produced are best released from the system and utilized as fuel since they will consist primarily of oxides of carbon and of steam, these mixtures not being suitable for the subsequent syntheses. After the air blasting, steam may be turned in in place of the air to effect the usual water gas reactions.

As a matter of economy the low heating value producer gases formed during the blasting period may be utilized to heat chambers that are in the coke-forming stage.

The water gas mixtures thus formed in the chambers may be passed through lines 63 or 63', respectively, containing valves 64 and 64', and enter a header 65 leading to a compressor 66. This compressor is preferably of a type adapted to produce high pressures upon gas mixtures of the order of 1000 to 3000 pounds per square inch, since good yields of low boiling hydrocarbons are frequently obtained when operating at these high pressures. Owing to the two facts that on the one hand the water gas mixtures coming from the coke chambers are usually at too high a temperature for efficient catalytic hydrocarbon synthesis and that on the other hand additional temperature rise occurs when these low pressure gases are compressed, it is in most cases advisable to cool the gases either prior to or after their recompression, though means for effecting this cooling are not shown in the present drawings. In addition, it is generally easier to design a compressor for cool than for hot gases.

The gases discharged from compressor 66 may pass to the catalytic chamber 76 by way of line 67, containing control valve 68, and line 75, containing control valve 75', if the temperature is at the right point or if necessary they may be reheated. To permit such reheating a heating element 71 may be disposed in a furnace 72 and

a line 69, containing a control valve 70, may serve to divert the gas stream through the heating element, line 73, containing control valve 74, connecting the heating element with line 75.

Prior to the admission of the water gas mixtures to the catalytic chamber other gases may be added from line 42. For example, if analyses have shown that the proportion of carbon monoxide to hydrogen is not right for obtaining the best results either gas may be pumped into the line until the correct proportion is obtained. For this injection either gas or a proportional mixture of both may be admitted to a pump 99 from a supply line 97, containing a control valve 98, and discharged through a line 100, containing a control valve 100', and through valve 43' in line 42. Reheated process gases may also be admitted through valve 43 in line 42, such gases having been brought to the required pressure by means of compressor 41.

Conditions are preferably regulated in catalytic chamber 76 to produce maximum yields of low boiling hydrocarbon products. In general as already stated, high pressures of the order of 1000 to 3000 pounds per square inch are advantageous along with moderate temperatures, for example, from 600 to 800° F. approximately. Another stipulation in case predominating yields of hydrocarbons instead of oxygen compounds are desired, is a ratio of carbon monoxide to hydrogen greater than unity or, in other words, an excess of carbon monoxide over the theoretical hydrogen equivalent. Catalysts are required though metals of a very diverse character may be employed such as chromium, cobalt, nickel, iron, manganese, molybdenum, titanium, cerium, osmium, palladium, zinc, etc. The oxides, sulfides and salts of these metals may also be employed.

The exact choice of conditions, catalysts, et cetera, will depend upon a variety of factors; particularly since the carbon monoxide-hydrogen mixtures may contain small amounts of residual nitrogen from the gas generators, though it is usually preferable to desulfurize the gases unless an efficient sulfide catalyst is found. Furthermore, the recycled process gases may be of variable composition so that again adjustment of conditions is necessary to secure best results.

Provision may be made for either heating or cooling the catalytic chamber to hold the temperature at an optimum point in any given case. In general the reactions involved are exothermic so that exterior cooling is generally necessary for good control.

Provision is made for discharging both vaporous and non-vaporized products from the catalytic chamber. The former may be released through a line 77, containing a control valve 78, into line 79 preferably with substantial reduction in pressure, line 79 leading in turn to compressor 80 which discharges through line 81 and valve 82 to vapor line 25 entering the fractionator of the process, so that the vaporized products from the catalytic chamber undergo fractionation to produce overhead gasoline fractions and refluxes which are reconverted in the primary heating stage.

Non-vaporized liquids from the catalytic chamber may be released through a line 83 and pass either through a line 83', containing control valve 84', to a low pressure vaporizer 85 or through a line 83'' and a control valve 84'' to a line 92. In the former event a certain amount of material vaporizable at the reduced pressure may be released in vaporizer 85 and pass through

line 86, containing control valve 87, into line 79 which was shown to lead ultimately to the process fractionator. In the event that the liquid products from the catalytic chamber are withdrawn through line 83'' and valve 84'' they may be either rejected from the process through line 90, containing control valve 91, or pass through line 92, containing control valve 93, to a pump 94 which has a discharge line 95 containing a control valve 96, and joining with line 44, thus permitting the return to the coking and gas generating stage of liquid residuals from either the catalytic chamber or the vaporizer since the latter has a bottom draw line 88 containing a control valve 89 which also leads to pump 94 through line 92 and valve 93.

Referring to Fig. 2, a modified arrangement of plant equipment is again shown diagrammatically, this arrangement permitting the utilization of gases and liquid residuals without subjecting the latter to a coking operation. In general, the operation of the cracking unit constituting the primary stage of the process is substantially the same as before but owing to minor differences it will be preferable to trace the flows.

Raw oil charging stocks of the same diverse character mentioned in connection with Fig. 1 may be supplied through a line 101 containing a control valve 102 to charging pump 103 which may discharge the charging oils either through a line 104, containing a control valve 105, to a fractionator 106 or through a line 117, containing a control valve 118, directly to the heating element which will be presently mentioned. Portions of relatively cold charging oil admitted to fractionator 106 assist in the dephlegmation of vapors undergoing fractionation and are stripped of their lighter fractions and preheated. The usual cooling coil shown as 111 may be provided in the top of the fractionator, this coil having an inlet line 109, containing control valve 110, for the admission of cooling fluids and a line 107, containing control valve 108, for their rejection. Heavier refluxes from the fractionator consisting of insufficiently converted intermediate fractions and preheated and stripped raw oil may be passed out of the fractionator through a line 112, containing a control valve 113, and discharged by a combined feed pump 114 through a line 115, containing a control valve 116. Line 115 leads to the usual heating element 116' disposed to receive heat from a furnace 117'. The heated products which have been treated under conditions substantially similar to those mentioned in connection with Fig. 1 may pass through a transfer line 118', containing a control valve 119', and enter reaction chamber 120 as before. Vapors from the reaction chamber may pass through a line 121, containing a control valve 122, and enter fractionator 106. Vapors from the secondary or synthetic conversion stage may be admitted through line 121 from line 150. Vapors of desired boiling point range leaving fractionator 106 may be subjected to the usual condensing and separating operation, such vapors passing through a line 122', containing a control valve 123, through a condenser 124 and a line 125, containing a control valve 126 to receiver 127 in which liquids and fixed gases separate. Line 130, containing control valve 131, is provided for the withdrawal of liquid fractions and line 128, containing control valve 129 is provided for the removal of gases that are not to be utilized further in the process.

Liquid residuals from reaction chamber 120 are preferably, withdrawn through a line 134, con-

taining a control valve 135, to treatment in the secondary or synthetic conversion stage of the process. For the removal of such portions of these liquids as cannot be advantageously treated a branch line 132, containing a control valve 133, is provided through which they may be withdrawn to storage or use as fuel. The essential difference between the operation now being described in connection with Fig. 1 and the one previously described in connection with Fig. 2 may be stated to consist in the fact that the liquid residuals instead of being coked and gasified to produce gas mixtures for synthetic conversion are subjected to the combined action of oxidizing gases and steam in what may be termed a gas generating or modified combustion step. The liquids from line 134 are preferably reduced in pressure as they pass through valve 135 and enter a header 136 terminating in an atomizer 137 at the entrance to combustion zone 138. Regulated amounts of oxidizing gases such as air or oxygen may be admitted to header 136 from a line 139 containing a control valve 140 and steam may be similarly admitted through a line 141, containing a control valve 142. Header 136 may also receive a portion or all of the fixed gases of the process from line 173, containing a control valve 174, and a portion of the non-vaporized liquids from the secondary stage from line 163.

The exact construction of combustion zone 138 is subject to considerable variation and as its exact character is not an essential feature of the present invention it has not been shown in detail. In general, its design will be similar to the types of apparatus that are employed in the manufacture of oil gas and may consist of chambers filled with inert material for the mixing of the reacting constituents and the entrainment of carbon or it may be of tubular design. In any event the portions of liquid and gaseous hydrocarbons, oxidizing gases and steam are adjusted to produce most nearly the mixtures of carbon monoxide and hydrogen which will serve to produce good yields of low boiling hydrocarbons in the synthetic step which follows.

The gases from the combustion zone may be conducted through a line 143, valve 144 and pump or compressor 144', by means of which they are supplied, at high superatmospheric pressure, through line 143' into a catalytic chamber 149, which functions similarly to the chamber described in connection with Fig. 1. As before, carbon monoxide or hydrogen may be added to the gas mixture to obtain the desired ratio, a line 145, containing control valve 146, serving for the admission of carbon monoxide and line 147, containing control valve 148, serving for the admission of hydrogen or other reducing gases.

Recycled process gases may also be admitted from line 175, containing control valve 176. These gases which come from branch line 165, containing control valves 166 and 166', may be either pumped directly to line 175 through valve 166' and line 173, or may be controllably heated. In case they are heated they may be diverted through line 167 leading to heating element 169 disposed in furnace 170 by closing valve 166' and opening valve 168, the heated gases then being returned to line 173 through line 171, containing control valve 172.

The reactions occurring in catalytic chamber 149 are substantially the same as those occurring when mixtures are treated corresponding to those produced in the previously described operation and will not be further described. Vapors

from the catalytic chamber may be released through a line 150, containing control valve 151, and leading to line 121 as already mentioned. Residual liquids may be released through line 157, containing control valve 158, and may be returned directly to the controlled combustion zone by way of line 159, line 163 and control valve 164 or may be submitted to a flashing action under reduced pressure by passing them through a line 152, containing control valve 153, to a vaporizer 154. The vaporizer is provided with a vapor line 155, containing control valve 156 and joining with line 159. Heavy liquids from the vaporizer may be withdrawn through line 159, containing control valve 160, and also be returned to the controlled combustion zone. To permit the rejection of liquids from the second stage, a line 161, containing a control valve 162 is shown.

The operations of the process as disclosed may be varied over a considerable range and numerous examples of results obtainable might therefore be given. However, two will serve which show results obtainable by operations conducted in the general manner disclosed in connection with Figs. 1 and 2, respectively.

Referring to operations conducted substantially in accordance with those described in connection with Fig. 1 a Mid-Continent topped crude may be cracked in the primary stage to produce a yield of 60% of 425° F. end point gasoline along with 15% of refluxes which may be utilized for blending with raw oil charging stock for subsequent operation or disposed of as light fuel oil. There may be produced by outside coking approximately 55 pounds of coke per barrel of raw oil. By treating the coke with steam by the usual methods employed in water gas manufacture, namely, by alternate blasting with air and treatment with superheated steam at temperatures of from 1800 to 2000° F., a gas of the general character of water gas may be produced, in yield approximating 25% of the theoretical. When this mixture is treated at temperatures of approximately 700° F. and pressures of 1500 pounds per square inch in the presence of a composite catalyst consisting chiefly of finely divided iron and minor amounts of potassium or sodium carbonate, an additional yield of light compounds boiling within the range of motor fuel may be produced, which calculated back to a charging oil basis, may increase the overall yield of gasoline from the process by from 3 to 5%.

Operations upon the same charging oil may be conducted in accordance with the process described in Fig. 2, the residual liquids from the reaction chamber being treated with steam at high temperatures and approximately atmospheric pressure to produce a gas of the following approximate composition:

	Percent
Carbon dioxide	3
Illuminants	3
Oxygen	0.5
Carbon monoxide	13.5
Hydrogen	50
Methane	28
Nitrogen	2

By subjecting this gas mixture to conversion in the presence of selected catalytic mixtures comprising metals of the iron group such as, for example, nickel reduced at a relatively high temperature to render it of suitable efficiency, yields

of approximately 10% by weight of the gas may be produced at temperatures in the catalytic chamber of the order of from 500 to 600° F. and pressures of about 100 pounds per square inch.

5 This step may increase the overall yield of gasoline by approximately 2 to 3% which is of definite economic value.

10 It will be recognized that many types of operation are possible without departing from the scope of the invention and therefore it is to be understood that the specification and examples given are not to be used in the light of imposing limitations thereon.

I claim as my invention:

15 1. A process for producing low boiling liquids from heavy hydrocarbon oil which comprises cracking the oil in a cracking zone, separating the cracked oil into vapors and residue, treating such residue with air and steam at temperatures
20 adequate to form a gaseous mixture containing carbon monoxide and hydrogen, introducing said mixture to an independent zone maintained under synthesizing conditions of temperature, pressure, and catalysis, synthesizing the carbon
25 monoxide and hydrogen in said independent zone into condensible vapors under conditions controlled independently of the cracking zone, combining the vapors formed by the synthesis with those formed by the cracking, fractionating
30 the commingled vapors to condense heavier fractions thereof and supplying resultant reflux condensate to the cracking zone, and finally condensing the fractionated vapors.

35 2. A process for producing low boiling liquids from heavy hydrocarbon oil which comprises cracking the oil in a cracking zone thereby forming vapors and unvaporized oil, flash distilling the unvaporized oil by pressure reduction and reducing the same to coke, blowing the
40 coke with air and steam at temperatures adequate to form a gaseous mixture containing carbon monoxide and hydrogen, introducing said mixture to an independent zone maintained under synthesizing conditions of temperature,
45 pressure and catalysis, synthesizing the carbon monoxide and hydrogen in said independent zone into condensible vapors under conditions controlled independently of the cracking zone, combining the vapors formed by the synthesis
50 with those formed by the cracking, fractionating the commingled vapors to condense heavier fractions thereof and supplying resultant reflux condensate to the cracking zone, and finally condensing the fractionated vapors.

55 3. A process for producing low boiling liquids from heavy hydrocarbon oil which comprises cracking the oil in a cracking zone, separating the cracked oil into vapors and residue, treating such residue with air and steam at temperatures
60 adequate to form a gaseous mixture containing carbon monoxide and hydrogen, increasing the pressure on the gaseous mixture and synthesizing the carbon monoxide and hydrogen content thereof into condensible vapors in an

independent zone maintained under higher pressure than the cracking zone, combining the vapors formed by the synthesis with those formed by the cracking, fractionating the commingled vapors to condense heavier fractions thereof and
5 supplying resultant reflux condensate to the cracking zone, and finally condensing the fractionated vapors.

4. A process for producing lower boiling liquids from heavy hydrocarbon oil which comprises sub-
10 jecting the oil to cracking conditions of temperature and pressure and separating the same into vapors and residue, treating such residue with air and steam at temperatures adequate to form a gaseous mixture containing carbon monoxide
15 and hydrogen, increasing the pressure on said mixture and synthesizing the carbon monoxide and hydrogen content thereof into condensible vapors under higher pressure and at lower temperature than prevailing in the cracking step,
20 combining the vapors formed by the synthesis with the first-mentioned vapors and fractionating the resultant mixture to condense heavier fractions thereof, returning such condensed fractions to the cracking step, and finally condens-
25 ing the fractionated vapors.

5. A process for producing low boiling liquids from heavy hydrocarbon oil which comprises cracking the oil in a cracking zone to form vapors and unvaporized oil, flash distilling the unvapor-
30 ized oil by pressure reduction, treating resultant flashed residue with air and steam at temperatures adequate to form a gaseous mixture containing carbon monoxide and hydrogen, fractionating and condensing said vapors and sepa-
35 rating the incondensable gases therefrom, increasing the pressure on said gaseous mixture and introducing the same and a substantial portion of said incondensable gases into an independent zone, synthesizing the carbon monoxide and hy-
40 drogen content of the commingled gases into condensible vapors in the independent zone under conditions controlled independently of the cracking zone, and combining the vapors formed by such synthesis with the first-named vapors prior
45 to fractionation of the latter.

6. A process for producing low boiling liquids from heavy hydrocarbon oil which comprises cracking the oil in a cracking zone to form vapors and unvaporized oil, flash distilling the unvapor-
50 ized oil by pressure reduction, treating resultant flashed residue with air and steam at temperatures adequate to form a gaseous mixture containing carbon monoxide and hydrogen, fractionating and condensing said vapors, increasing
55 the pressure on said gaseous mixture and introducing the same into an independent zone, synthesizing the carbon monoxide and hydrogen content of said mixture into condensible vapors in the independent zone under conditions controlled
60 independently of the cracking zone, and combining the vapors formed by such synthesis with the first-named vapors prior to fractionation of the latter.

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