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CRACKING OF HYDROCARBON OILS

Filed June 26, 1930

2 Sheets-Sheet 1

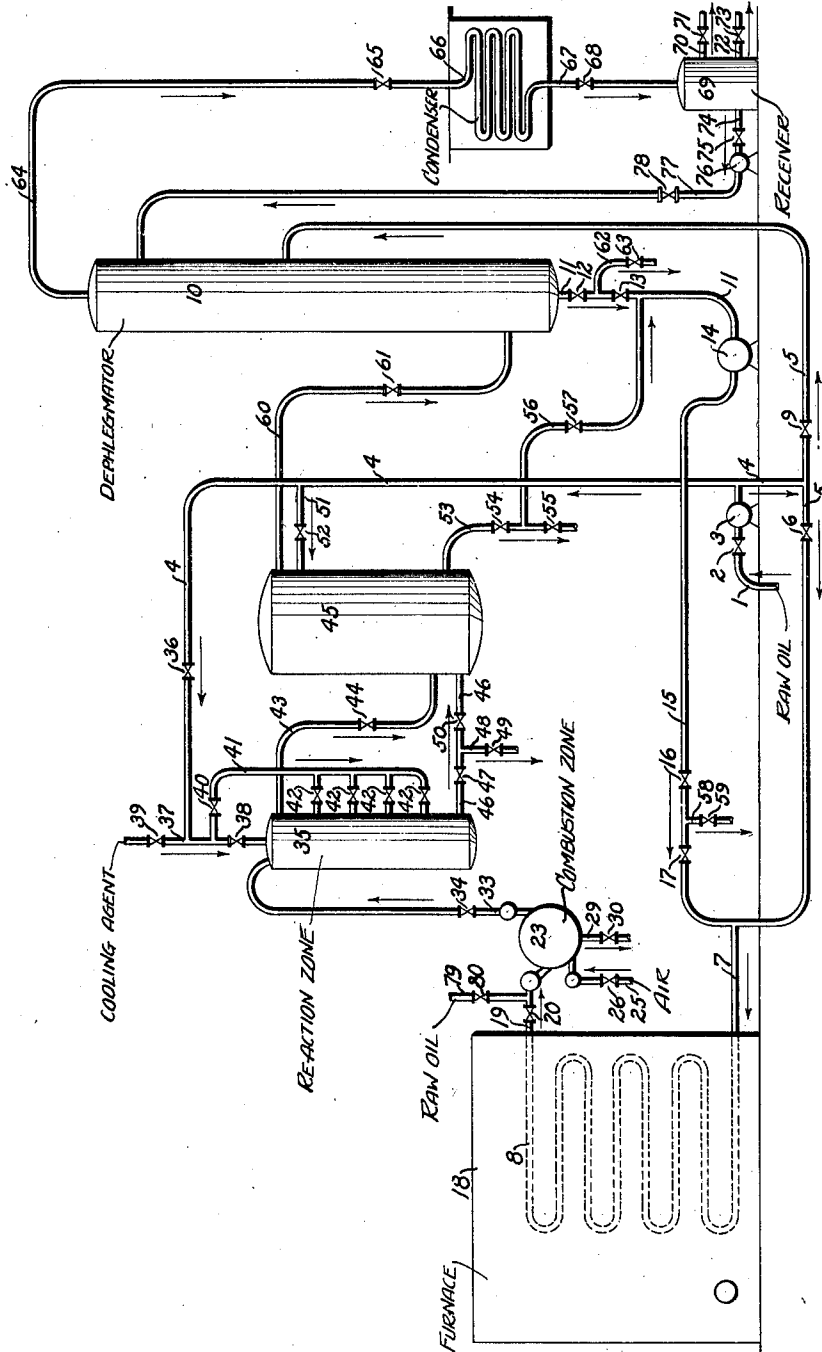


FIG. 1

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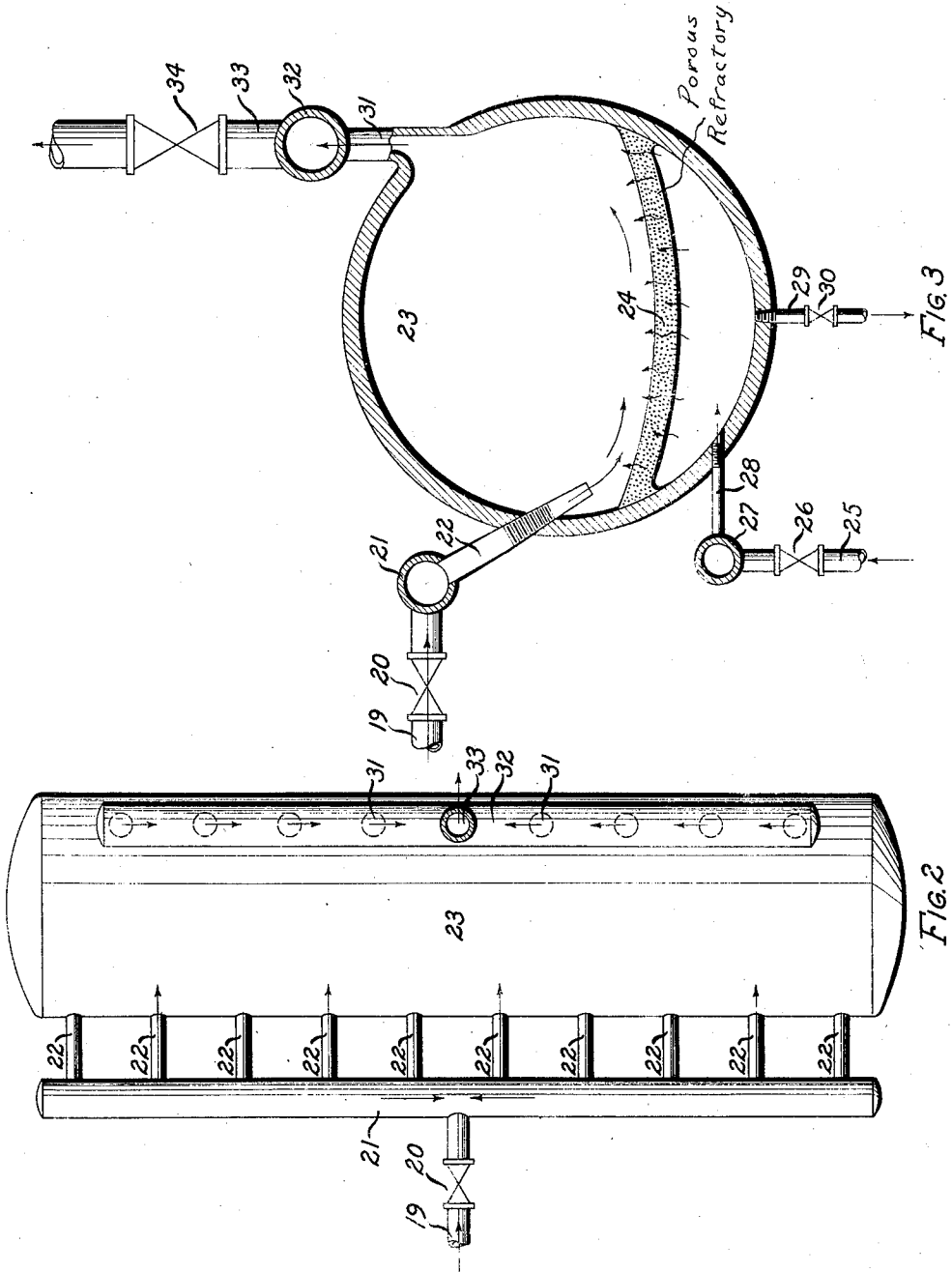
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## UNITED STATES PATENT OFFICE

1,960,608

## CRACKING OF HYDROCARBON OILS

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3 Claims. (Cl. 196-65)

This invention relates to the conversion of relatively high boiling hydrocarbon oils into substantial quantities of more desirable products of lower boiling ranges and specifically embodies a process and apparatus in which the reaction time is properly correlated with the reaction temperature thus producing, when working at temperatures now in commercial use, higher yields of desirable products for a given gas loss or, vice-versa, a lower gas loss for a given yield of desirable products.

By the use of our process we are able to employ relatively high conversion temperatures without suffering the gas losses which normally accompany high temperature cracking and so may derive the benefits from high temperature cracking, such as high conversion rates and a light distillate product high in anti-knock value and suitable for sale as premium motor fuel, without paying the penalty of high losses heretofore demanded by this type of process.

We have found that the excessive production of gas usually accompanying cracking processes employing temperatures of about 925° to 1050° F. or thereabouts is due primarily to too long a time of exposure of the hydrocarbons to the cracking temperature.

We have also found that, aside from the time and temperature relation, the pressure employed has a separate effect. Thus, for a given temperature and corresponding proper reaction time for a given conversion to gasoline per pass through the reaction zones, the proportion of noncondensable gas is decreased by increasing the reaction pressure. Our process, therefore, preferably employs pressures higher than those ordinarily used in high temperature cracking and to maintain the proper relation between the reaction time and the reaction temperature we provide means of controlling both of these variables.

We may use any of the well known methods of controlling the reaction temperature and may further provide a novel means of generating a portion of the heat required for conversion by the direct combustion of a portion of the hydrocarbon material undergoing treatment and more particularly combustion of the carbon formed during the cracking reaction. We may also control a temperature in the reaction zone by introducing cooling material such as raw oil charging stock for the process into direct contact with the heated materials undergoing conversion. By introducing a sufficient quantity of cooling material at a sufficiently low temperature we may arrest the cracking reaction at any

point, thus providing a means of controlling the reaction time as well as the temperature. Also, other means of controlling reaction time such as properly proportioning the size of the reaction zones may be employed.

In the drawings, Fig. 1 is a diagrammatic side elevational view of one form of apparatus in which the invention may be carried out.

Fig. 2 is an enlarged plan view of the combustion zone.

Fig. 3 is a still further enlarged transverse sectional view through the combustion chamber illustrated in Fig. 2.

Referring to the attached Fig. 1, which is a diagrammatic illustration, not drawn to scale, of one of the many forms of apparatus in which are incorporated the improvements embodied by our invention, raw oil introduced through line 1 and valve 2 to pump 3 may be fed through lines 4 and 5 and valve 6 into line 7 and thence through heating element 8 or may be fed through valve 9, in line 5, into dephlegmator 10 where it is preheated by direct contact with the ascending vapors which it assists to fractionate in this zone and may pass together with the reflux condensate from said vapors through line 11 and valves 12 and 13 to pump 14 which feeds the combined feed through line 15 and valves 16 and 17 into line 7 and thence through heating element 8 together with that portion, if any, of the raw oil supplied directly to the heating element through line 5 and valve 6. If desired, any portion or all of the raw oil may be introduced to the system through line 79, controlled by valve 80, by a suitable pump (not shown).

Heating element 8 is located in any suitable form of furnace 18 and the oil passing through this heating element may be subjected to any desired temperature under the desired pressure conditions and may thence pass through line 19 and valve 20 into combustion zone 23 where it may further be heated by introducing air or other oxidizing materials through line 25 and valve 26 in such a manner, as will be more fully described later, as to cause the combustion of coke deposited from the heated hydrocarbons undergoing conversion and also combustion of a portion of said hydrocarbons, if desired. Liquid which may collect within zone 23 at the beginning of the operation may be removed through line 29, controlled by valve 30. The conversion products in zone 23 may be removed as vapors through line 33, controlled by valve 34, and enter reaction chamber 35.

Raw oil charging stock supplied by pump 3 and fed through line 4 and valve 36 into line 37 may enter reaction chamber 35 through valve 38 to assist in cooling the vapors, introduced into this zone through line 34, to the desired reaction temperature. Extraneous cooling materials, such as another oil, steam, hydrogen or hydrogen-containing materials, may be introduced to line 37 through valve 39 and may be fed into reaction chamber 35 through valve 38 or may be diverted from line 37 through valve 40 and line 41 and fed into the reaction chamber 35 at any, all or any combination of a plurality of points through valves 42. It will be understood that raw oil alone or in combination with any of the cooling materials mentioned or any other suitable cooling medium may also be introduced through any of the valves 42 into chamber 35. Hydrogen, or hydrogen-containing gases, if used either alone or in combination with other materials aside from their cooling action employed to regulate the reaction temperature, may induce hydrogenation in the hydrocarbon vapors in chamber 35, thus substantially increasing the production of light distillate products from the system and more completely saturating certain unstable reaction products.

Vapors from chamber 35 may be withdrawn through line 43 and valve 44 to reaction chamber 45. Unvaporized liquid may be removed from reaction chamber 35 through line 46 and valve 47 and may be removed from the system through line 48, controlled by valve 49, or may be introduced into reaction chamber 45 through valve 50, in line 46. When so desired the total products, liquid and vapor, from reaction chamber 35 may be withdrawn through line 46 and valve 47 and introduced into chamber 45 through valve 50, or a portion or all of the vapors may pass through line 43 and valve 44 to chamber 45, the remainder, if any, passing together with the liquid from chamber 35 through line 46 and valves 47 and 50 into chamber 45.

The reactions may be allowed to continue in chamber 45 at a temperature regulated by the introduction of raw oil from line 4 through line 51, controlled by valve 52. Preferably, sufficient raw oil is introduced into direct contact with material undergoing conversion in chamber 45 that the reaction is retarded to a sufficient degree to prevent over-cracking and the consequent excessive formation of gas and coke or other undesirable products. When required sufficient raw oil may be introduced into chamber 45 to completely arrest the reaction.

Separation of vapors and liquid occurs in chamber 45 and by the introduction of raw oil to this zone through line 51 and valve 52, as above described, that portion of the raw oil remaining unvaporized within the chamber may serve to dilute the residual liquid rendering it suitable in characteristics for commercial fuel oil. When fuel oil is not desired as one of the products of the system, the raw oil introduced into chamber 45 may still assist in preventing the formation of substantial quantities of heavy pitch and coke-like materials in the residual oil rendering it suitable for reconversion in the same or a separate process. The residual liquid from chamber 45 diluted or otherwise, as the case may be, is removed through line 53, controlled by valve 54, and may be withdrawn all or in part from the system through valve 55 in line 53, or may be diverted in any proportion through line 56 and valve 57 into line 11 to mix

with reflux condensate or combined feed flowing to pump 14 to be recycled through line 15, valves 16 and 17 and line 7 through heating element 8. A portion of the material passing through line 15 may, if desired, be removed from the system through line 58, controlled by valve 59.

Vapors from chamber 45 pass through line 60 and valve 61 into dephlegmator 10 where they are subjected to fractionation, their heavier portions passing through line 11 and valves 12 and 13 to pump 14, as already described. If desired, a portion of the reflux condensate from dephlegmator 10 may be diverted from line 11 and removed from the system through line 62, controlled by valve 63.

Fractionated vapors from dephlegmator 10 pass through line 64 and valve 65 to be subjected to condensation and cooling in condenser 66, the products passing through line 67 and valve 68 into receiver 69 where separation of condensed distillate and uncondensed gas is effected, the gas being released through line 70, controlled by valve 71, and the distillate being withdrawn through line 72, controlled by valve 73. A portion of the distillate from receiver 69 withdrawn through line 74 and valve 75 to pump 76 may be recirculated through line 77 and valve 78 to dephlegmator 10 to assist fractionation and to maintain the desired outlet temperature of the vapors from this zone.

Referring now to Figs. 2 and 3, which are, respectively, a plan view and a cross-section of combustion zone 23, both of which are diagrammatic and not drawn to scale. Heated hydrocarbons introduced through line 19 and valve 20 to manifold 21 are fed into combustion zone 23 through a plurality of nozzles 22. These heated hydrocarbons impinge upon a porous refractory plate 24 within combustion zone 23. Materials such as air, steam, or mixtures thereof, introduced through line 25 and valve 26 to manifold 27, are fed through a plurality of lines 28 into chamber 23 below the porous refractory plate 24. Under certain conditions, mixtures of air and hydrocarbon gases or vapors from the process or from any other source, or hydrogen-containing gases or vapors may be introduced into chamber 23 below the porous refractory plate 24. Sufficient pressure is maintained beneath plate 24 to force the oxidizing material through the perforations or porous openings in the plate. This oxidizing material effects the combustion of coke and other heavy pitch-like material deposited on the upper side of plate 24, and, if desired, may be introduced in sufficient quantity to effect the combustion of a portion of the hydrocarbon vapors within chamber 23. Chamber 23 is provided with a drain 29, controlled by valve 30. Hydrocarbon vapors and combustion products at the attained temperature are removed from chamber 23 through a plurality of vapor lines 31 into manifold 32 and may thence pass through line 33, controlled by valve 34, to further treatment.

Instead of operating chamber 23 as outlined above under certain conditions, the following operations may be practiced: we may carry on the reactions in the chamber 23 by alternately admitting air or other oxidizing materials and decomposing hydrogen-containing gases or vapors either with or without steam, sufficient heat being developed during the oxidizing period to accomplish the necessary reactions during the following period.

It will be apparent that many different structural forms as well as modifications of the form shown may be employed as a combustion zone, for example, the plate 24 may take any desired shape and may be made of porous refractory material, high temperature resistant metallic alloys with suitable perforations or any other material suitable for the purpose.

Pressures up to 2000 pounds or more, per square inch may be employed within the system. Pressure may be substantially equalized throughout the system, or differential pressures may be employed between the various elements. Reaction temperatures employed in various parts of the apparatus may range from, say 700° to 1400° F., more or less. Preferably, however, the temperature of the materials discharged from heating element 8 are substantially increased in combustion zone 23 and are maintained at a somewhat lower temperature in chamber 35, being further cooled when required in chamber 45, if necessary, even to below cracking temperatures.

As an example of specific operating conditions and yields which may be obtained by our process operating at a temperature of about 1000° F., in the vapors leaving the combustion zone and with a substantially uniform pressure of 200 pounds per square inch throughout the system, a yield of approximately 55% of gasoline having an anti-knock value equivalent to a blend of 50% benzol and 50% straight run Pennsylvania gasoline is obtainable. Using air as an oxidizing agent in the combustion zone the resultant distillate shows an appreciable quantity of alcohols and other oxidation products.

We claim as our invention:

1. A hydrocarbon oil cracking process which comprises passing the oil in a restricted stream through a heating zone and heating the same therein to cracking temperature, discharging the heated oil into a combustion zone and separating vapors from residuum therein, depositing in the combustion zone the coke and carbon formed by cracking of the oil, injecting air into the deposited coke and carbon during the cracking operation to effect combustion thereof and to supply additional heat to the oil undergoing cracking, removing the mixture of vapors and combustion gases from the combustion zone and abruptly cooling the same to below cracking temperature by the injection of a cooling medium

thereto, and then recovering the desired cracked products from the cooled mixture of vapors and combustion gases by dephlegmation and condensation.

2. A hydrocarbon oil cracking process which comprises passing the oil in a restricted stream through a heating zone and heating the same therein to cracking temperature, discharging the heated oil into a combustion zone and separating vapors from residuum therein, depositing in the combustion zone the coke and carbon formed by cracking of the oil, injecting air into the deposited coke and carbon during the cracking operation to effect combustion thereof and to supply additional heat to the oil undergoing cracking, removing the mixture of vapors and combustion gases from the combustion zone and abruptly cooling the same to below cracking temperature by the injection of charging oil for the process into direct contact therewith thereby preheating the charging oil, dephlegmating the cooled mixture of vapors and combustion gases to separate insufficiently cracked fractions therefrom, supplying resultant reflux condensate and the preheated charging oil to the heating zone, and recovering the sufficiently cracked fractions from the dephlegmated mixture by final condensation.

3. A hydrocarbon oil cracking process which comprises passing the oil in a restricted stream through a heating zone and heating the same therein to cracking temperature, discharging the heated oil into a combustion zone and separating vapors from residuum therein, depositing the coke and carbon formed by cracking of the oil upon a relatively thin firmly fixed porous refractory member in the combustion zone, injecting air into the deposited coke and carbon from beneath said member and burning the deposited coke and carbon during the cracking operation while liquid oil and vapors are present in the combustion zone, removing the mixture of vapors and combustion gases from the combustion zone and abruptly cooling the same by direct heat exchange to below cracking temperature to prevent excessive cracking of the vapors, and then subjecting the cooled mixture of vapors and combustion gases to dephlegmation and condensation.

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