Jan. 17, 1939. L. D. FORWARD 2,144,488

PROCESS OF CRACKING HEAVY HYDROCARBON OILS

Filed July 21, 1926 3 Sheets-Sheet 1

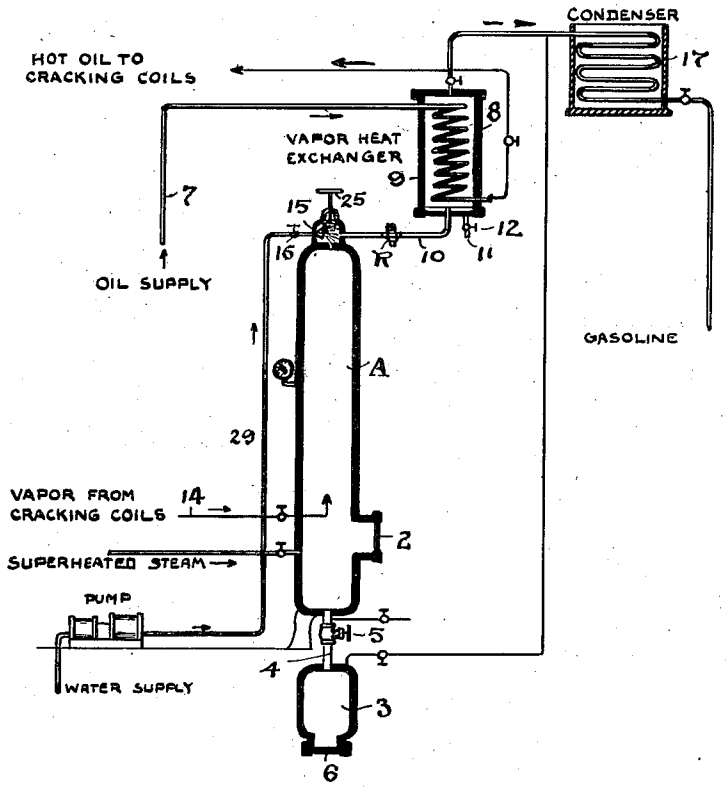
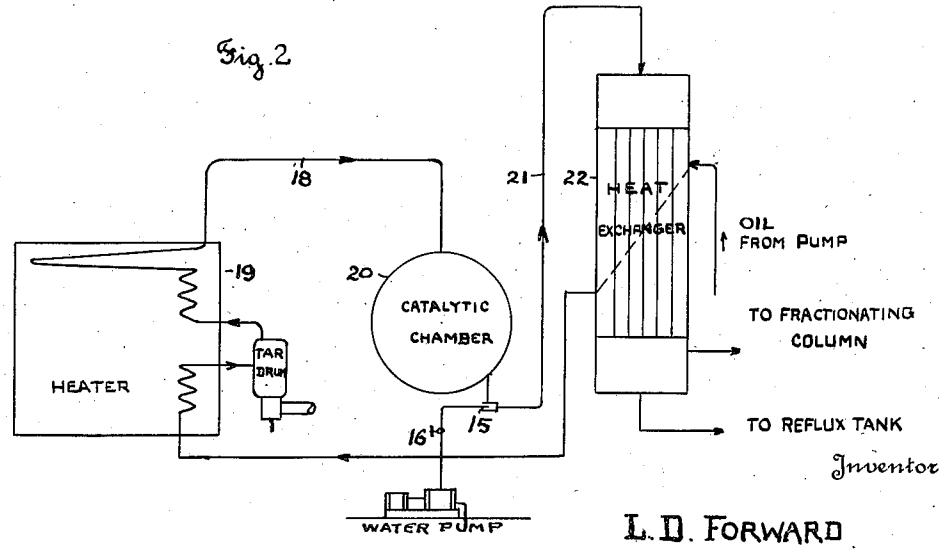


Fig. 1.

Fig. 2.



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PROCESS OF CRACKING HEAVY HYDROCARBON OILS

Filed July 21, 1926 3 Sheets-Sheet 2

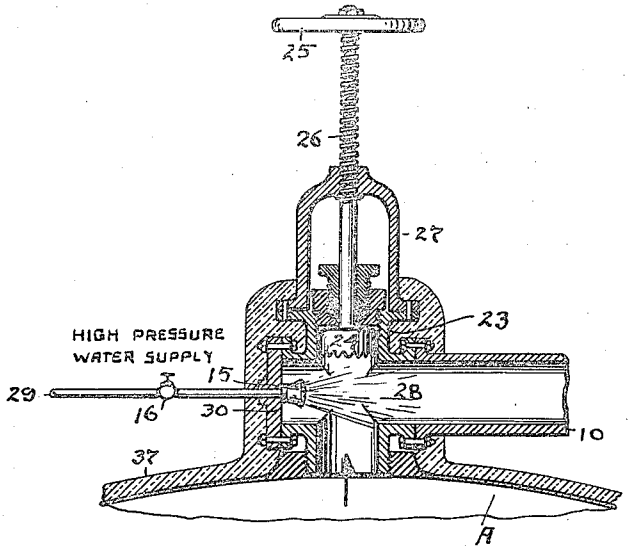
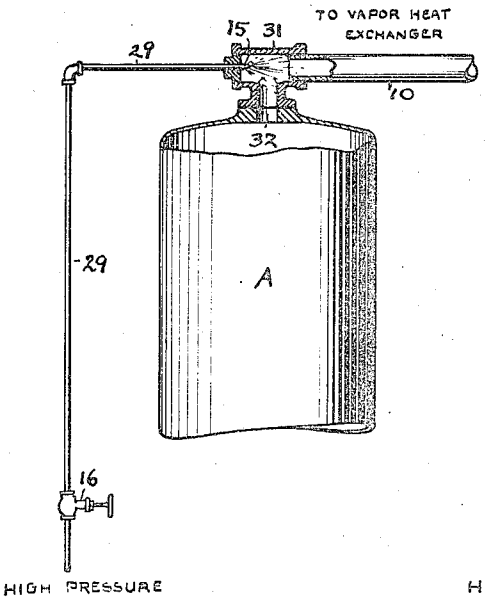


Fig. 3.

Fig. 4.



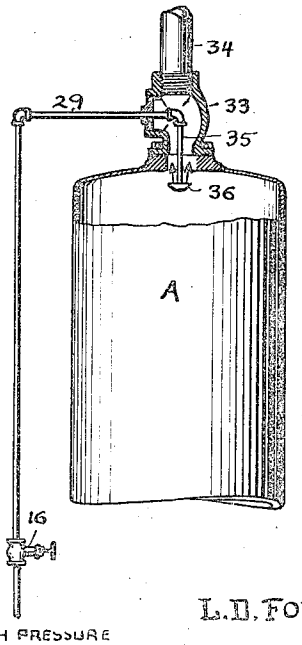


Fig. 5.

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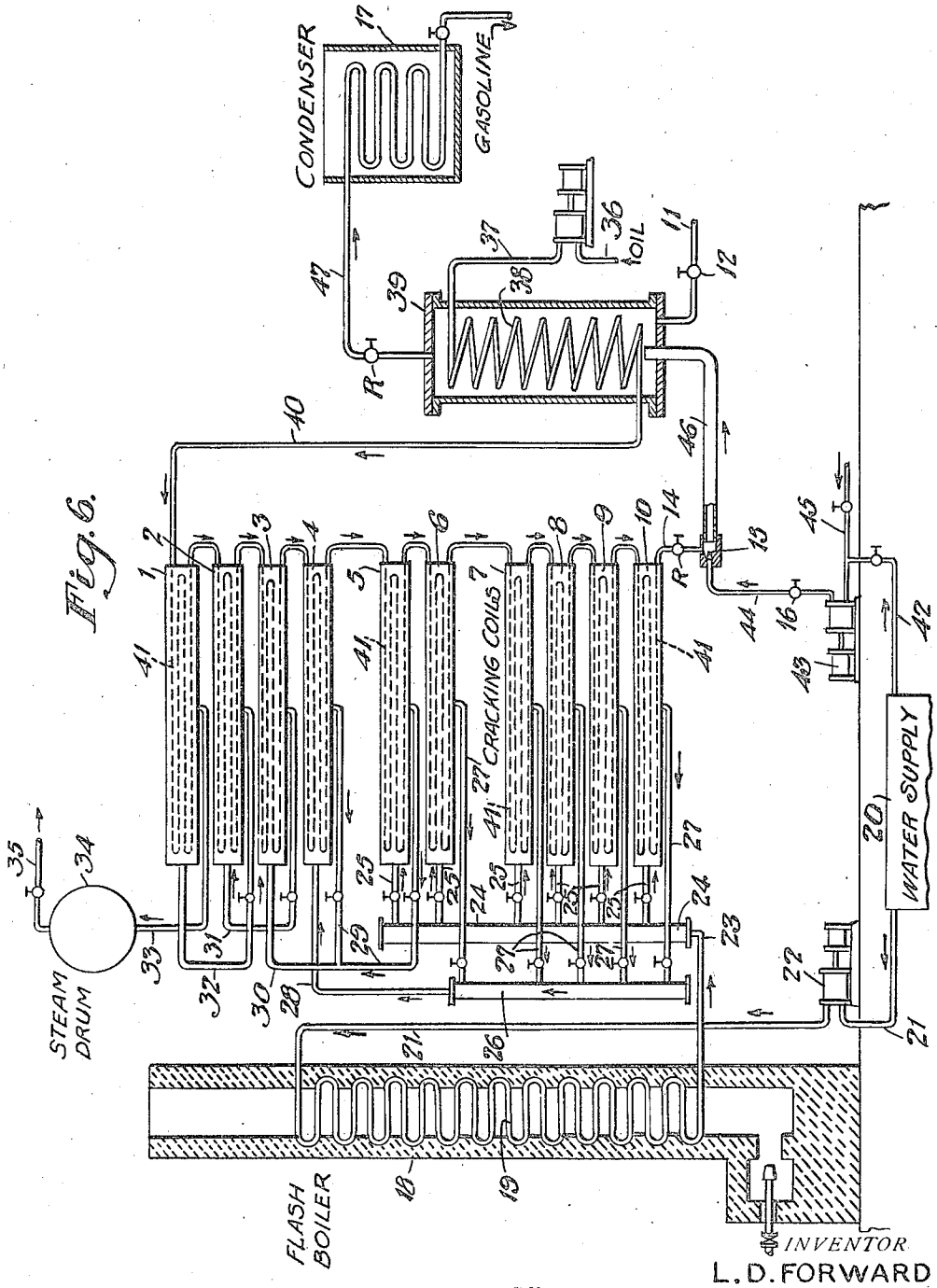
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Jan. 17, 1939. L. D. FORWARD 2,144,488

PROCESS OF CRACKING HEAVY HYDROCARBON OILS

Filed July 21, 1926 3 Sheets-Sheet 3

Fig. 6.



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2,144,488

PROCESS OF CRACKING HEAVY HYDROCARBON OILS

Louis D. Forward, New York, N. Y., assignor, by mesne assignments, to Forward Process Company, Dover, Del., a corporation of Delaware

Application July 21, 1926, Serial No. 123,829

8 Claims. (Cl. 196—61)

This invention has for its object improvements in the art of cracking heavy hydrocarbon oils for the production of lighter hydrocarbon oils therefrom, whereby such processes may be carried out continuously without the accumulation of free carbon, coke, or pitchy materials in any part of the system which materials would otherwise prevent efficient heat transfer to the oil undergoing the cracking treatment, and in general foul the apparatus eventually so that frequent shut downs for cleaning out would be required with consequent reduction in the overall capacity of the apparatus, together with loss in fuel due to the cooling and reheating of the system.

The present invention is particularly applicable to vapor phase cracking processes of the type described in the application of Chauncey B. Forward, Serial No. 682,477, filed December 24, 1923, but may be applied advantageously to other cracking processes in which heavy oils are cracked at high temperature and pressure to produce lighter and lower boiling point oils therefrom. In such processes for cracking petroleum oils or distillates by distillation under pressure the charging stock is heated to the cracking temperature by heat transfer from heating gases directly, or by some intermediate heat transferring substance, such as superheated steam, molten metal and the like, or by direct contact with electric heating units.

Where the oil being treated is kept in motion at high velocity and not subjected to an extremely high temperature, such as where the oil is passed through heating coils of relatively small cross section heated by superheated steam, tempered combustion gases, or other accurately controllable heating means, it has been found possible to raise the oil to and considerably above the cracking temperature, and to continue the operation for a prolonged period without the deposition of carbon in the heating zone. If the vapors liberated are then subjected to a digesting operation in an enlarged heat-insulated chamber or zone, either with or without the presence of a catalytic agent, an additional percentage of the vapors are decomposed and any small amount of free carbon released may be allowed to settle and be withdrawn from the system. When the vapors are withdrawn from the heating zone or digesting operation and cooled a considerable deposit of carbon is formed during cooling while the vapors are passing through the lower range of temperature at which cracking takes place which deposit is frequently of a hard coke-like nature which adheres to and bakes on the walls of the passage and eventually fouls the apparatus. This condition necessitates stoppage of operation, cooling of the system, and removal of such deposits.

I have discovered that by suddenly cooling the vapors from, at or above the cracking temperature to a point below the cracking temperature by the injection of a cooling fluid, such as water, this objectionable deposition of carbon during the preliminary cooling operation, may be entirely prevented, thereby avoiding fouling of the apparatus and cessation of operation and the delays and losses incident thereto.

Accordingly in practicing or applying the present invention the oil may be heated according to any of the known methods in use, to or above the cracking temperature, and maintained at such temperature for a sufficient length of time to assure conversion of a substantial amount of the heavy constituents to lighter constituents. The oil may be subjected to this additional treatment while passing through a continuous coil to which heat is supplied in sufficient quantities to provide the heat required for the decomposition of the heavier constituents and compensate for heat lost by radiation, or the oil may be further subjected to a digesting treatment in an enlarged chamber from which loss of heat by radiation is prevented by insulation or by supplying an additional amount of heat thereto, either with or without the presence of a catalytic agent, during which time an additional amount of the heavier constituents are cracked. In some cases it may be advantageous to employ more than one digesting operation, for example, the oil may be maintained at or above the cracking temperature for a considerable time in the heating coils and subsequently heated or digested in an enlarged heat insulated chamber.

At the point of withdrawal of the vapors from the digesting operation and before the vapors have been permitted to cool materially I subject the vapors to a sudden chilling operation by injecting into the vapor line a cooling fluid, for example water, saturated steam or a portion of the condensed distillate. The quantity of cooling fluid injected may be sufficient to produce a complete condensation or may be merely sufficient to chill the vapors to a temperature below that at which further decomposition will take place. The remaining heat in the partially cooled vapors may be utilized in a heat exchanger to preheat fresh charging stock. The heat exchanger may be advantageously arranged to

function as a dephlegmator or fractionating tower the heavier vapors being fractionally condensed, the condensate withdrawn therefrom and the uncondensed vapors passed to a final condenser.

The pressure may be reduced at the point of withdrawal of the vapors from the digesting chamber to substantially atmospheric pressure or to a pressure intermediate that of the chamber and atmospheric, or pressure may be maintained to or beyond the dephlegmator, heat exchanger, or the final condenser.

According to another modification of the present invention the vapors may be subjected to the above chilling treatment by injecting the cooling fluid into the vapor line direct from the heating zone.

As an exemplification of the scope of the invention and its applicability to various methods of cracking hydrocarbon oils, I present the following description and the annexed drawings showing various forms of devices and apparatuses for practicing my invention including diagrams which illustrate in part the improved method of treating heavy hydrocarbon oils devised by C. B. Forward, and one other known method in which a catalytic chamber is employed. However it is to be understood that the reference to and showing of the diagram is merely illustrative and that the present invention is not limited thereto, as it is evident that various modifications of the invention may be employed without departing from the spirit of the invention as set forth in the appended claims.

In the accompanying drawings, Fig. 1 is a more or less diagrammatic representation of an apparatus similar to that described in the U. S. application of C. B. Forward, Serial No. 682,477, concerning which I am very familiar, and in connection with which I was led to devise the present invention. Fig. 2 is a diagram showing an adaptation of the present invention in connection with a known oil treating apparatus in which a catalytic chamber is employed. Figs. 3, 4, and 5, are sectional views of several different forms of devices which may be used to introduce the cooling fluid into the hot vapors. Fig. 6 is a diagrammatic representation partly in section of the apparatus described in the application of C. B. Forward, Serial No. 682,477, with the exception of the carbon settling chamber 35, which apparatus is modified to include the chilling means described in detail hereinafter.

Referring to Fig. 1, the apparatus shown therein is in part the same as devised and used by C. B. Forward, of Urbana, Ohio, for treating hydrocarbon oils by steam superheated to a high degree of superheat, wherein the highly-heated cracked product is discharged into a vertical drum A which I have termed a carbon settling column. This drum, in practice, is heavily insulated to prevent heat loss, and it is provided with a manhead 2 which may be removed to permit inspection of the interior. A sub carbon chamber 3 is connected to the bottom of drum A into which any finely divided free carbon which may settle in the column A may be blown through a pipe connection 4. The sub carbon chamber 3 may be cut off from the main column by means of a valve 5 and a bottom plate 6 may be removed without interrupting operation of the main system.

The oil to be cracked may be pumped through a pipe 7 to a coil 8 in a vapor heat exchanger 9, where the feed oil is heated by the hot vapors discharged from drum A through a connecting pipe 10. Reflux condensation of the heavy insufficiently cracked vapors is produced by the cooling effect of the feed oil and the condensate which collects in the bottom of heat exchanger 9 may be withdrawn through a pipe connection 11 fitted with a suitable control valve 12.

The hot oil passes from coil 8 in heat exchanger 9 to a series of heating and cracking coils in a series of steam heat exchangers (Fig. 6) where it is heated to the cracking temperature and conveyed by a pipe 14 into the drum or carbon settling column A in vapor form. The hot vapors which collect in drum A are maintained under a pressure of approximately 225 lbs. per square inch and temperature of 950 degrees Fahrenheit.

The hot oil vapors are discharged from the drum or carbon settling column A through pipe line 10, which contains a regulator R by means of which the pressure in the carbon settling column may be controlled, and the vapors thence pass to the shell of vapor heat exchanger 9. I have discovered that carbon deposits could be eliminated by pumping water or other cooling fluids under pressure into the line at the point at which the extremely hot vapors are withdrawn from drum A. The cooling fluid is introduced into the line in the form of a jet 15, and the quantity of cooling fluid to be introduced may be regulated by a valve 16 to reduce the temperature of the vapors to any desired temperature.

It is not essential that the cooling fluid shall be water, as other substances such as a portion of the distillate formed, may be used to produce the desired chilling effect, although I prefer water because of its high latent heat and because of the beneficial effect the steam formed therefrom has upon the quality of the distillate obtained. The pressures maintained on the various parts of the system are not an essential part of the present invention as these may vary considerably with different charging stocks, or when the system is operated to produce different grades or types of distillates therefrom. Any vapors not condensed in the vapor heat exchanger 9 pass to the final condenser 17.

Referring to Fig. 6 of the drawings, the apparatus of the Forward application Serial No. 682,477 is shown in detail with the chamber 35 omitted and a means inserted in the vapor line to illustrate the form of the invention involving the sudden chilling of the cracked vapors directly as they leave the heated digestion coils of the apparatus. The cracking apparatus shown diagrammatically in Fig. 6 comprises a series of heaters 1 to 10 supplied with a heating medium such as superheated steam. The superheated steam is produced by a flash boiler 18 which comprises a water heating and superheating coil 19 supplied with water from a source 20 and a conduit 21 in which is mounted a pump 22. Superheated steam of a temperature which may approximate 1200° F. or higher is conducted from the lower part of the boiler through a conduit 23, and supplied to a header 24 which is connected by means of valved supply pipes 25 with the cylindrical heaters 5 to 10. A second header 26 is also connected into cylindrical heaters 6 to 10 by means of separate valved steam discharge pipes 27. The superheated steam conducted through the separate pipes 25 to heaters 6 to 10 is passed at reduced temperatures through the connecting pipes 27 into the heater 26 from which

the steam is then conducted through a pipe 28 into cylindrical heater 4. Heaters 4 and 5 are provided with steam discharge pipes 29 which conduct steam at reduced temperature through a pipe 30 into the cylindrical heater 3. The exhaust steam from the heater 3 is then passed through a pipe 31 into the heater 2 and from the latter through a pipe 32 into the heater 1. The exhaust steam from heater 1 is conducted through a pipe 33 into a steam drum 34 from which steam may be conducted through a valved pipe 35 to the pumps or other power and heating apparatus used in the plant. The superheated steam supplied through the line 23 may be at a pressure of 250 pounds per square inch or higher, and the steam in drum 34 may be at approximately 200 pounds per square inch.

The oil to be treated in the apparatus shown in Fig. 6 may be withdrawn from storage through a line 36 and passed by means of a pump through a line 37, a coil 38 mounted in a vapor heat exchanger 39, and then through a line 40 to a relatively long coil 41 mounted in the heat exchange cylinder 1. The remaining heaters 2 to 10 inclusive contain similar long coils of pipe 41 connected in series with each other and with the first coil mounted in cylinder 1, so that the oil and vapors flow through the coils successively. The oil passing through the coils 41 is converted into vapor and heated to a high cracking temperature which is maintained throughout the latter coils in chambers 7 to 10 so that the oil constituents receive a digestion treatment.

The oil vapors at a temperature above 900° F. (975° to 980° F.) are discharged from the coil of the last heater 10 through a line 14 and directly brought into contact with a cooling fluid such as water discharged into a jet mechanism 15 so that the vapors are suddenly chilled to a temperature below 700° F. Water for effecting this chilling operation may be withdrawn from the water supply 20 through a valved line 42 and forced by means of pump 43 and a pipe 44 into the jet mechanism 15. The amount of water supplied through the line 44 may be controlled by valve 16 to effect the specified temperature reduction in the vapors. The fluids other than water referred to above may be used as cooling media and in such case they may be admitted to the pump 43 through the valve line 45 instead of water.

The mixture of oil vapors and chilling media is conducted through a line 46 into the lower part of heat exchanger 39 so that the vapors come in contact with the heat exchange coil 38. The vapors passing through the heat exchanger 39 may be cooled sufficiently to condense substantially all constituents of higher boiling point than the desired gasoline or pressure distillate, and such condensate may be withdrawn through a line 11 provided with a valve 12. The desired gasoline constituents as vapors are conducted from the heat exchanger 39 through a vapor line 47 to a final condenser 17 where the gasoline vapors are condensed. The vapor transfer lines 14 and 47 are provided with pressure-reducing valves R so that the pressure on the oil constituents may be reduced either in the line 14 or in the line 47 as stated above.

In cracking a gas oil the following temperature conditions were found to give good results such as would enable the process to be carried on continuously, but it is to be understood that these examples are merely illustrative of one particularly advantageous method of operation, and that the present process should not be limited thereto, as improved results have been obtained in operating over a wide range of temperatures and pressures with a number of different grades of charging stocks. Thus, in one instance the feed oil, a 38 degree Baumé gas oil with an initial boiling point of 450 degrees F., was heated to about 550 degrees F. in the vapor heat exchanger. In passing through the first steam preheaters the temperature of the oil was raised to about 900 degrees F. and maintained above this temperature throughout its passage through the remaining heaters and the carbon settling column A. A sufficient quantity of water was introduced at jet 15 to reduce the temperature of the vapors very quickly to below 700 degrees F. No carbon was deposited in the vapor line or other part of the system through which said vapors subsequently passed.

A subsequent fractional distillation of the condensate indicated a conversion of 60 per cent of the initial charging stock into a 450 degree F. end point gasoline. The carbon released during the operation amounted to about .05 per cent of the charging stock and was in the form of a dry finely divided powder which was readily removed from the carbon settling column through blow off connection 4.

Referring to Fig. 2, this diagram represents another embodiment of the present invention in a modified form of a vapor phase cracking apparatus. In the arrangement of apparatus shown therein, the oil to be treated is supplied by a pump (not shown) to heat exchanger 22 where it is preheated by heat exchange with the hot vapors. The preheated oil is then passed to the heater 19 and from an intermediate point therein the heavy unvaporized oil may be withdrawn. From the heater 19 the hot vapors pass through a pipe 18 to a catalytic chamber 20 and thence through a pipe 21 to a heat exchanger 22. A cooling fluid, for example, water, is introduced through a jet 15 into pipe line 21 between catalytic chamber 20 and heat exchanger 22, thereby suddenly reducing the temperature of the vapor in the required degree and preventing the deposit of carbon in that line and any subsequent part of the system.

Referring to Fig. 3, the device shown therein is the same as delineated in Fig. 1, except that it is made on a larger scale. The device comprises a flanged coupling member 23 affixed to the top of drum A having a vertical passage in which a rotatable and reciprocable clean out plunger 24 is confined. The plunger is provided with a hand wheel 25 and an operating screw 26 which is supported by a yoke 27 secured to the upper edge of coupling member 23. The jet or spray member 15 through which the cooling fluid is introduced into the horizontal passage 28 and pipe 10 may be connected, for example, with the water supply pipe 29 which extends through the closure plate 30 for one end of passage 28.

In Fig. 4, drum A is provided with a single T coupling 31 into which the cooling fluid is jetted by supply pipe 29 or pet 15 at right angles to the vapor discharge passage 32 at the top of the drum or carbon settling column A.

In Fig. 5, a globe fitting 33 having a vertical discharge connection 34 is affixed to drum A, and the water supply pipe 29 is provided with a depending extension 35 internally of this coupling member and a jet 36 at the lower end of this extension. Jet 36 has vertical discharge openings in its upper face to jet the cooling fluid

upwardly into the mouth of the discharge passage. The drum and vapor pipes are covered with asbestos or other suitable heat-insulating material, not shown in Figs. 4 and 5, but substantially as delineated by the outer layer or covering 37 in Fig. 3.

The subject-matter disclosed herein and relating to the use of the enlarged carbon settling and reaction chamber in connection with the process disclosed, is claimed in divisional application Serial No. 751,376, filed November 3, 1934, and the subject-matter relating to the use of the carbon screw as shown in Figs. 1 and 3, is claimed in divisional application Serial No. 155,867, filed July 27, 1937.

What I claim is:

1. The improvement in the cracking of hydrocarbon oils comprising passing the oil at high velocity through a heating coil, heating the oil therein to a temperature in excess of 900° F. and maintaining the oil above this temperature for a period of time sufficient to effect substantial conversion of the oil in the vapor phase and suddenly cooling the vapors without substantial prior cooling to a temperature below 700° F. by introducing a cooling liquid into direct contact with the vapors, and further treating the vapors.

2. The method of treating heavy hydrocarbon oil to produce light hydrocarbons suitable for use as motor fuel, which comprises subjecting the oil to cracking in the vapor phase by causing the same to flow rapidly through an elongated heating conduit and heating the same therein to a vapor phase cracking temperature until a substantial portion of the oil is converted into light constituents suitable for use as motor fuel, avoiding overheating of the cracked product and any substantial carbon deposit in the heating conduit, and prior to substantial cooling of the hot cracked product discharged from said heating conduit, immediately chilling said hot cracked product to a temperature below about 700° F. by injecting a cooling liquid into direct and intimate contact with said hot cracked product.

3. The improvement in the art of cracking mineral oils for the production of cracked gasoline therefrom, which comprises passing the oil to be cracked in a rapidly flowing stream of restricted cross-section through a heating and cracking zone in which the stream of oil is heated to a high vapor phase cracking temperature for a period of time sufficient to convert a substantial proportion of the oil to constituents boiling in the gasoline range, and then before the resulting highly heated cracked vapor products have been permitted to cool materially, reducing their temperature substantially instantaneously to a temperature below approximately 700° F. by bringing a sufficient quantity of a liquid cooling medium into intimate contact with the said highly heated cracked vapor products resulting from the cracking operation, whereby coke formation and deposition from the said cracked vapor products is prevented.

4. The process of cracking mineral oils as defined by claim 3 in which a superatmospheric pressure of at least about 225 pounds per square inch is maintained on the stream of vapors being cracked in said zone.

5. The process of cracking mineral oils as defined by claim 3 in which the oil products are subjected to the cracking conditions of said heating and cracking zone for a period of time sufficient to convert approximately 60% of the charging stock into condensable constituents boiling below approximately 450° F.

6. The process of preventing coke formation and deposition due to the gradual cooling of highly heated cracked hydrocarbon vapor products in a cracking apparatus having a high temperature cracking zone and a cooling zone, the process being characterized by abruptly cooling the highly heated cracked vapor products from a temperature above the coke formation range to a temperature below said range by introducing directly into and intimately mixing a cooling fluid with the highly heated cracked vapor products in such proximity to the cracking zone that the abrupt cooling takes place prior to any gradual cooling of the highly heated cracked vapor products to a temperature within the coke formation range, said abrupt cooling being effected from a cracking temperature above the coke formation range.

7. The process of preventing coke formation and deposition in a cracking apparatus due to the gradual cooling of highly heated cracked hydrocarbon vapor products formed by the cracking of a stream of oil while passing through a heating zone in which the oil is heated in a stream of restricted cross section to a temperature of approximately 900° F., and then further heated to a temperature upwards of 900° F. but not substantially exceeding approximately 980° F. while passing in a stream of restricted cross section through a digesting zone at a pressure upwards of about 225 pounds per square inch, the process of preventing said coke formation and deposition being characterized by abruptly cooling the highly heated cracked vapor products from a temperature above the coke formation range to a temperature below said range by introducing directly into and intimately mixing a cooling fluid with the highly heated cracked vapor products in such proximity to the digesting zone that the abrupt cooling takes place prior to any gradual cooling of the highly heated cracked vapor products to a temperature within the coke formation range, said abrupt cooling being effected from a cracking temperature above the coke formation range.

8. The improvement in the art of cracking mineral oils for the production of cracked gasoline therefrom, which comprises passing the oil to be cracked in a rapidly flowing stream of restricted cross-section through a heating and cracking zone in which the stream of oil is heated to a high vapor phase cracking temperature for a period of time sufficient to convert a substantial proportion of the oil to constituents boiling in the gasoline range, and then before the resulting highly heated cracked vapor products have been permitted to cool materially, and directly upon their discharge from said heating and cracking zone, reducing their temperature substantially instantaneously to a temperature below approximately 700° F. by bringing a sufficient quantity of a liquid cooling medium into intimate contact with the said highly heated cracked vapor products resulting from the cracking operation directly upon their discharge from said heating and cracking zone, whereby coke formation and deposition from the said cracked vapor products is prevented.

LOUIS D. FORWARD.