June 20, 1933. E. W. GARD ET AL 1,914,914

METHOD FOR VAPOR PHASE CRACKING OF OIL

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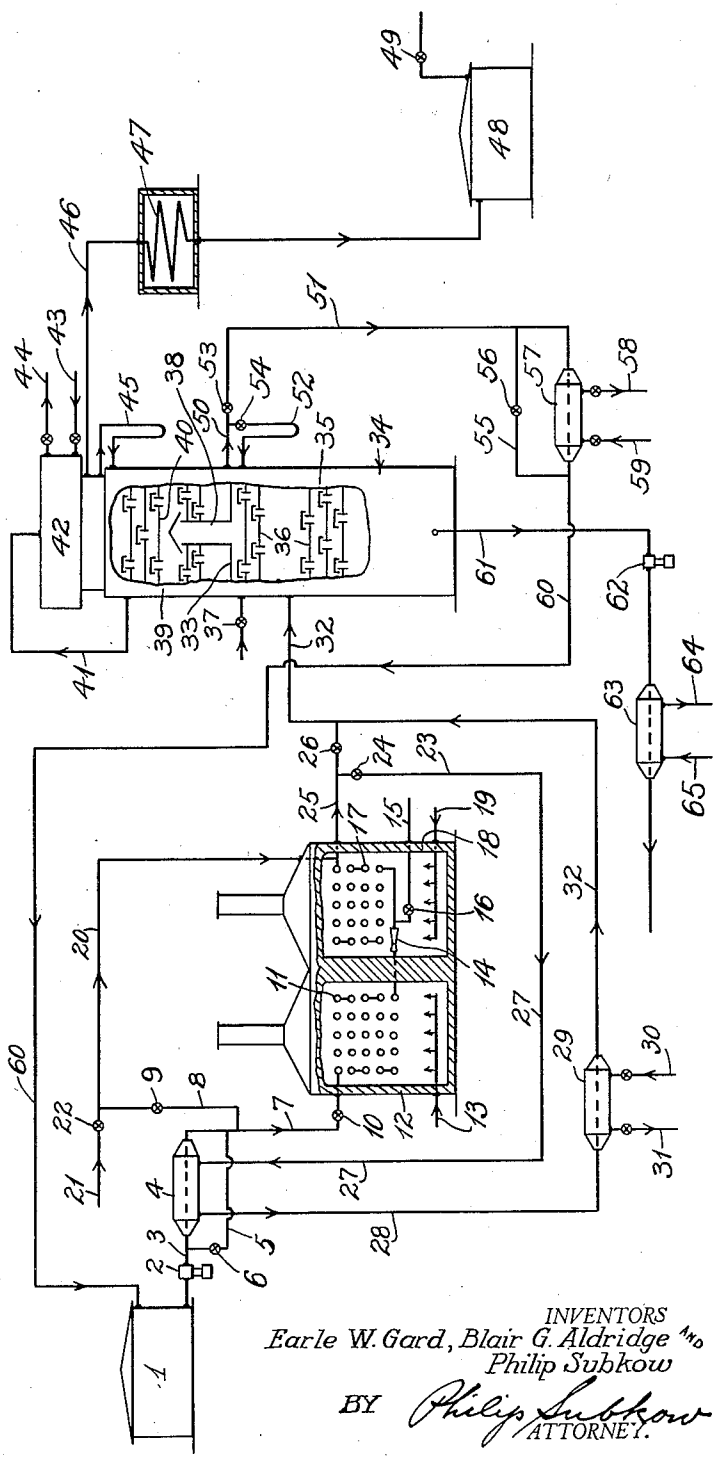


Fig. 1.

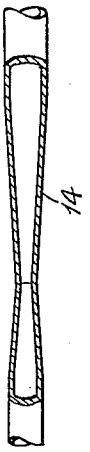


Fig. 2.

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Fig. 3.

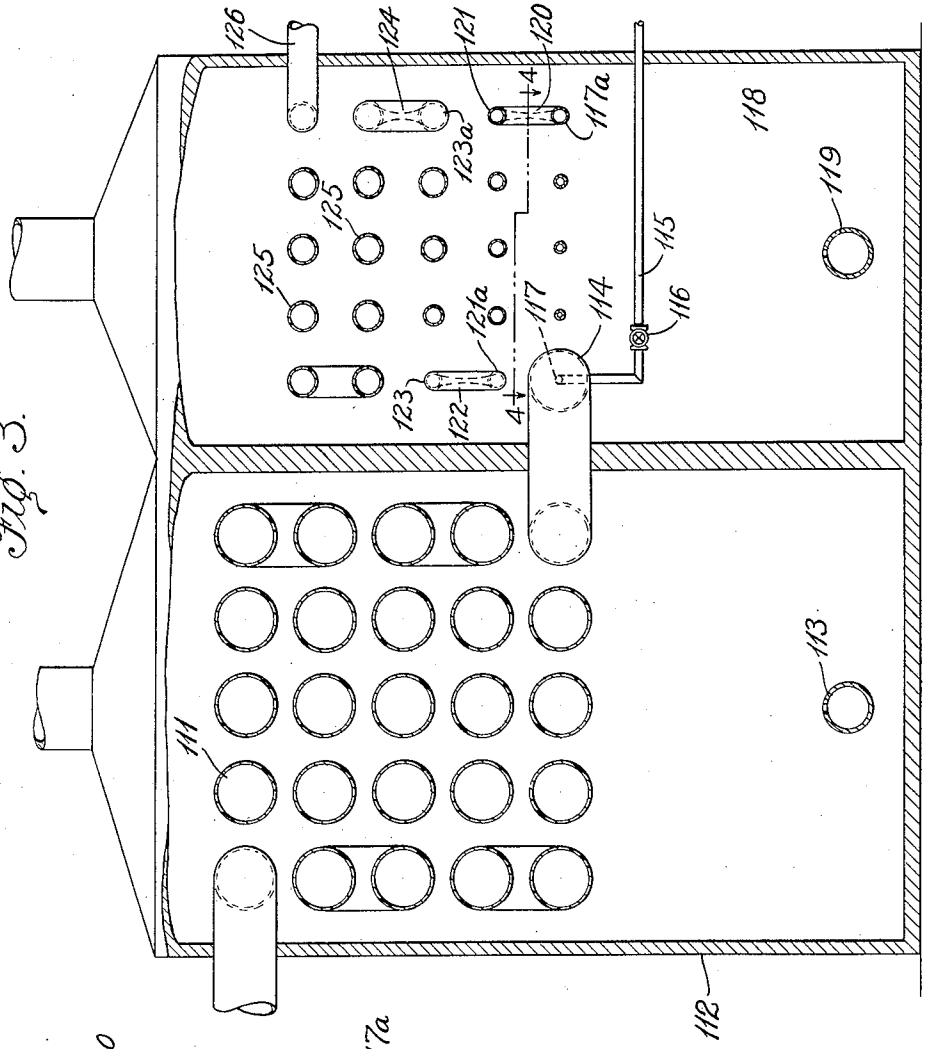
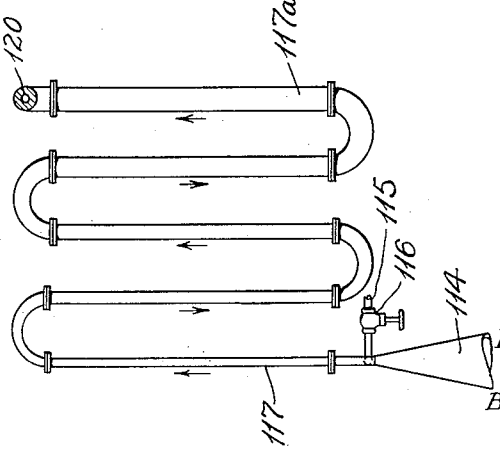


Fig. 4.



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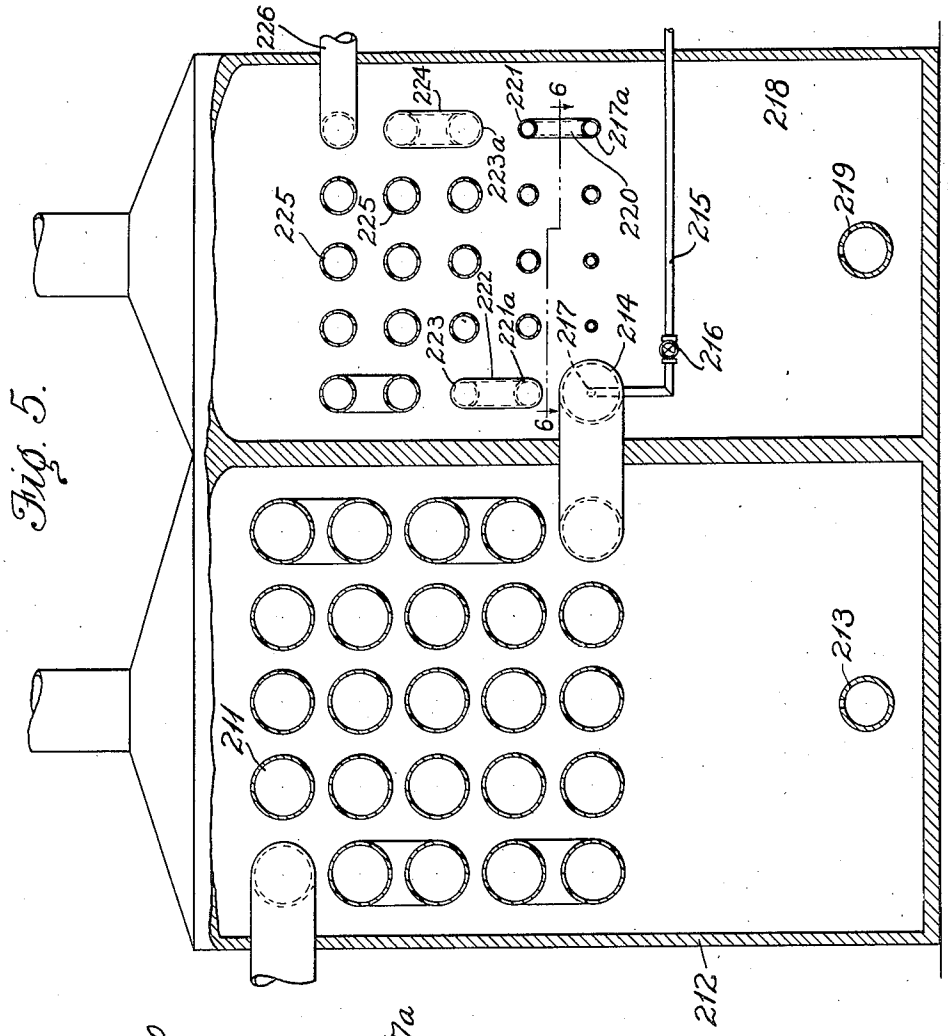


Fig. 5.

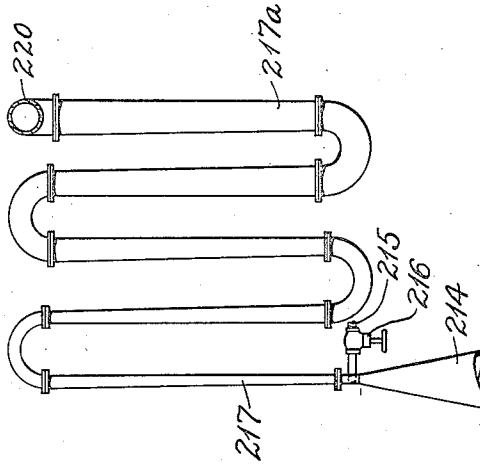


Fig. 6.

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UNITED STATES PATENT OFFICE

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METHOD FOR VAPOR PHASE CRACKING OF OIL

Application filed April 23, 1929. Serial No. 357,471.

This invention relates to a process of cracking oil and particularly to a process of cracking oil in the vapor phase.

It is an object of this invention to obtain extremely high velocity of vapors through tubular cracking coils and to insure that the vapors passing through the cracking coils are substantially free of entrained liquid, and to operate the process at maximum heat efficiency.

We have found that among the elements conducive to efficient vapor phase cracking are that the vapors passing through the vapor cracking coils must be uniformly heated. In order to obtain this, high vapor velocities are necessary. In order to get good heat conduction to the interior of the moving core of vapor, high turbulency is desirable. In order to obtain conditions wherein no carbon deposit occurs it is essential that no liquid enters into the highly heated vapor phase cracking coils. If liquid does so enter, high temperature distillation of the liquid occurs with consequent coking. An additional advantage of high vapor velocity is that it acts to scour the tubes to remove from the tubes any deposited carbon and to carry it out with the vapor stream.

It is well known that heating efficiency is greater when the oil is heated in the liquid phase. We, therefore, propose to heat the oil to its cracking temperature in the liquid phase and then to expand the heated oil into the vapor phase cracking tubes operated without any back pressure except the frictional resistance to the flow of the vapors to the tubes.

In order to insure that no liquid enters into the vapor phase cracking coils, it is proposed to heat the oil under high pressure to a temperature such that complete vaporization occurs. Thus the oil is heated above its maximum boiling point at the pressures employed and then expanded into the vapor phase cracking coil. In the preferred form the oil is heated to a temperature at least as high as the critical temperature of the oil at the point of expansion of the oil into the vapor phase cracking coils.

It is well known that there is a critical temperature above which, no matter how large the pressure, liquids or mixtures of liquids such as petroleum oils cannot remain in the liquid state. This temperature is known as the "critical temperature". This temperature is determined by the well known meniscus method in which the liquid is heated in a sealed tube, which is partially filled with the liquid. The temperature at which the meniscus which constitutes the level of the liquid disappears, is the critical temperature of the liquid. Certain investigators have shown that there is a relationship between the average boiling point of petroleum oil and the critical temperature, and have evolved the following formula. The average boiling point, T_o, is defined as the average obtained by averaging the temperature at which the first drop comes over with that recorded for each 10 cc cut in the standard A.S.T.M. distillation. The critical temperature T_c is then expressed by the following:

$$T_c = 1.05T_o + 160$$

While this formula has been shown to represent the critical temperature as observed by the meniscus method with great accuracy, the experimental determination of this critical temperature is the most desirable one. This is because many oils contain other than straight chain hydrocarbons, for which the above formula is designed. Thus, for instance, the equation for pure aromatic hydrocarbon is:

$$T_c = T_b + 208$$

where T_b is the boiling point of the pure aromatic hydrocarbon. Many petroleum oils fall between the two formulas, indicating the existence of aromatics in the oil. It will, therefore, be desirable to determine the critical temperature of the oil experimentally.

The critical temperature of the oil is changed by heating, for, in bringing oil to the critical temperature some incidental cracking may occur, generating lighter hydrocarbons which lower the critical temperature. However, if the oil is heated under very high pressure to at least the critical temperature of the initial oil, it will be safe

to assume that the oil when it reaches the temperature found to be the critical temperature of the original oil, it will be entirely in the vapor phase.

It is, therefore, an object of this invention to heat oil to its critical temperature and under high pressure and to flash the vapors into a vapor phase cracking coil to permit the expansion of the vapors and high velocity travel during cracking.

It is, therefore, another object of this invention to heat oil under high pressure substantially such to keep the oil in a liquid phase until the oil reaches a condition such that it is substantially entirely converted into vapor, that is, heating the oil under high pressure in liquid phase to the critical temperature of the heated oil and then flashing the vapors from this region of high pressure through a coil on which the only back pressure is the frictional resistance to the flow of the vapors through the coil and heating the vapor passing through the coil to crack them in the vapor phase, to produce an unsaturated, anti-knock gasoline.

The invention will be better understood by reference to the drawings which show a schematic form of an apparatus for carrying out this invention.

Fig. 1 is a schematic form of the complete apparatus.

Fig. 2 is a detail view of the venturi shown in Fig. 1.

Fig. 3 is a more detailed view of one form of furnace and tube construction shown in Fig. 1.

Fig. 4 is a detail of tubes shown as taken on line 4—4 of Fig. 3.

Fig. 5 is another form of furnace and tube construction as used in apparatus illustrated in Fig. 1.

Fig. 6 is a detailed view of the tube structure shown as taken on line 6—6 of Fig. 5.

Oil, such as gas oil, contained in tank 1, is passed by pump 2, through line 3, and heat exchanger 4, regulated by a by-pass 5, controlled by valve 6, into line 7. Oil may be by-passed through line 8, controlled by valve 9, as will be further described. The oil passed through line 7, controlled by valve 10, is passed through coils 11, situated in furnace 12, heated by burners 13. Oil is then passed through a Venturi throat 14, shown in Fig. 2, wherein it may meet a jet of high temperature steam or gas admitted through line 15, controlled by valve 16. The oil is then introduced into coil 17, positioned in furnace 18, heated by burners 19. On exiting from the coils 17, the heated oil meets oil injected through line 20. Additional media to function in an analogous manner may be injected. Additionally, gas may be introduced as will be understood by those skilled in the art. This oil from line 20 may be the oil by-passed through line 8, and/or additional oil introduced through line 21, controlled by valve 22. The oil passing through line 25, is passed through valve 24, in line 27. The passage may be controlled by by-pass valves 26. The vapor from line 27, passes through heat exchanger 4, and through line 28, into cooler 29, cooled by cooling fluid introduced at 30, and exiting at 31.

The partially cooled vapors are then introduced, through line 32, into fractionating column 34. Fractionating column 34, is divided into a stripping section 35, and a fractionating section 39. Vapors from 35, are partially condensed and collected on 33, by passage through bubble cap plates 36, where they meet, counter-currently, condensate introduced through 52, as will be further described, and the additional cooling fluid introduced when desired through 37. Steam may be introduced in 35, to aid stripping and reboiling. The uncondensed vapors pass through throat 38, into the fractionating column 39, where they pass through bubble plates 40. The condensate formed on those plates is collected in deck 33, to be withdrawn through 50, as will be later described. The uncondensed vapors pass through 41, downwardly through dephlegmator 42, cooled by the cooling fluid entering at 43, and exiting at 44. The uncondensed vapors exit through 46, and are condensed in condenser 47, collected in run-down tank 48 and the fixed gases are vented through 49. The condensate formed in 42, is withdrawn through trap 45, and introduced on the top plate in the fractionating section 49. The condensate collecting on deck 40, is withdrawn through 50, part is by-passed through valve 54 and trap 52, into the stripping section and part is sent through valve 53, and line 51, to cooler 57, cooled by a cooling fluid introduced at 59, and exiting at 58, and controlled by by-pass 55, in which there is a valve 56. The cooled condensate is passed through line 60, back into the tank 1. The unvaporized fraction is withdrawn through line 61, by pump 62, passed through a cooler 63, into which a cooling fluid circulates via 65, and 64, and sent to storage.

Figs. 3, and 4, show in more detailed form one construction of the heating units.

The function of this type of heater is to permit the gradual expansion of the high pressure vapors in order that heat may be imparted as the vapors expand so that the excessive cooling resulting from expansion is prevented. It will be observed that the coils in the vapor phase furnace 118, are smaller than the high pressure coils in furnace 112. In furnace 112, heated by burners 113, the coils are composed of straight tubes with return bends to form a continuous coil.

It will be observed that in furnace 118, heated by burners 119, the coils are composed

of banks increasing in size in direction of flow of the vapors. The oil passes from 111, into a constriction 114, which joins with a narrow tube 117. Each tube is of constant diameter, but on the lowest row the tubes from 117, to 117*a*, are increasing in diameter. Vapors passing from tube 117*a*, cross over to 120, into tubes 121 to 121*a*. These tubes are of constant diameter, that is, all the tubes in the row are of the same diameter. The vapors then pass into a cross-over 122, into tubes 123, to 123*a*. Each tube is of the same diameter, but the tubes increase in diameter across the bank in the direction of flow of the vapors. Vapors then pass into cross-over 124, and into tubes 125. All of the tubes 125, are of constant diameter, and the oil finally exits in 126. This drawing is entirely schematic to illustrate the invention. The tube banks may be increased in number and the tubes in the banks increased in number and size and the variations of size are a matter of design depending on the amount, character of the oil processed and the temperatures and pressures. The essential idea is to permit gradual expansion of the vapors. Means for introducing heated gas is shown at 115, controlled by 116, to aid in heating the gases and increasing their velocity.

It will be advisable also, to provide a plurality of Venturi throats between each section of tube so that the expansion shall be insured to occur in stages. Thus a Venturi throat may be introduced in the cross-over valves 120, 122, 124, as see Fig. 3. The several venturi are so designed to maintain a regulated pressure which is reduced in the directon of flow of the vapors. This is a matter of design as will be understood by those skilled in the art.

Fig. 5 shows another variation of the heating furnace.

As before, 212, is the high pressure furnace in which are positioned high pressure coils 211, heated by burners 213. The vapor phase cracking furnace 218, is heated by burners 219. The oil passing from coils 211, is passed through the constriction 214, and into the tubes 217, to 217*a*. The tubes in this bank increase in size uniformly in the direction of the flow; that is, each tube increases in size, and each tube is of greater diameter than the preceding tube. The oil passing from 217*a*, passes to cross-over 220, into the tubes 221, to 221*a*. As previously described, each tube increases in size uniformly in the direction of the flow and each succeeding tube is greater than the preceding one, tube 221, is greater than tube 217*a*; that is, the tubes are of cone shape; that is, the exit of the tube 217*a*, is smaller than the entrance of tube 221. The oil passes through cross-over 222, into the tube 223, to 223*a*. These tubes increase in size in the same manner as previously described. The oil is passed through cross-over 224. It enters tubes 225, which are all of the same diameter in the direction of flow of the vapors and exiting at 226. It will be seen that tubes 217, to 223*a*, constitute an elongated Venturi tube, permitting gradual expansion of the vapors during which expansion heat is imparted to make up for the cooling incidental to expansion. Means are provided for the introduction of hot gases by means of line 215, controlled by valve 216, to aid in heating the gases and increasing their velocity.

The forms of furnaces here shown permit for the expansion of the gases gradually so that heat may be imparted to them as they expand, to compensate for the temperature drop. This also permits a rapid heating of the oil to its cracking temperature. This is desirable for a greater proportion of the gasoline formed is true vapor phase cracked gasoline. It is obvious, however, that since the vapors were at or above their critical temperature before expansion, there will be no condensation in any form of design here shown. The vapors will always be superheated at their lower pressure, that is, they will be above the temperature at which the vapors are saturated at the lower pressures. However, since a drop in temperature will inhibit the vapor phase cracking reaction, the imparting of the heat will maintain them at the high cracking temperatures desired for vapor phase cracking and prevent the necessity of imparting a very intense heating at the exit to the Venturi throat. It will be observed that the neck of the constriction of 14, 114, and 214, respectively, are the throats of the venturi or modified venturi, respectively.

The operation of the process will be explained below, with reference to a specific example, given by way of illustration.

Assuming that we are operating on a California gas oil having a gravity of 27.8° A. P. I., and an average boiling point of 547° F. the oil is pumped from tank 1, (Fig. 1) through the pre-heater 4, and introduced into coil 11, under a pressure of about 1,000 to 2,000 pounds. The oil is heated in coil 11, to a temperature above 862° F., which is the critical temperature of the oil in tank 1. It will be sufficient to heat the oil to about 875° F. At this temperature the oil is entirely in vapor phase before it reaches the expansion point 14. The oil is expanded into coil 17, valve 24, being wide open, valve 26, is closed. The coil 17, is heated to a temperature sufficient to raise the vapor passing through the coil to a temperature above 1,000° F., and is heated in coil 17, for a period of time sufficient to give the proper conversion, about 50%. The cracking temperature may be between 900 to 1,500° F., depending on the rate and amount of conversion desired, as will be

understood by those skilled in the art. At the point of exit from coil 17, these vapors meet oil introduced through 21, or 8, via line 20, in amount and temperature sufficient to considerably cool the vapors and coalesce carbons or tars formed in the cracking. Approximately 20 to 30% of injection oil is thus introduced.

The co-mingled oil and vapor pass through heat exchanger 4, and cooler 29, and there introduced into a fractionating equipment at a temperature of about 650° F. By-pass 26, may be operated to regulate the heat exchanger 4, and cooler 29. The vapors introduced into 34, via 32, are stripped of the heavy fractions in 35, and the vapors passed into fractionator 39, where they are fractionated by means of the reflux introduced through 45, as explained, to produce a gas oil fraction, part of which is introduced into 35, via 52, and the remaining portion passed through cooler 57, into stock tank 1, to be recracked. The uncondensed fraction issuing through 46, is condensed from 47, and collected in 48. Uncondensable gas is being withdrawn from 49.

If desired, valve 24, and/or 26, may be partially closed to control the rate of passage of the vapors through 17, if an increased time is desired in the coils. Ordinarily it would be preferable to design the length of coil sufficient to give the necessary time to operate with no back-pressure on the coil, except that of resistance to flow. In the forms illustrated in Figs. 3 and 5, the coils are designed to permit the gradual expansion of the vapors so that heat may be imparted to them as they expand and the drop in temperature necessarily resulting on expansion, is mitigated and the rate at which the oil is raised to its cracking temperature, 1,000° F. and over, is increased. It is desirable to raise the vapors to that temperature as quickly as possible. The operation of the modification shown in 3 and 5 will appear from what has been previously said.

The above description is not to be taken as limiting our invention but merely as illustrative of the invention and the best mode of carrying it out. Many changes can be made within the scope of this invention, which we claim to be:

1. A method of cracking oil which comprises heating oil in a flowing stream under high back pressure sufficient to maintain the liquid phase up to its critical temperature, completely vaporizing said oil under said high pressure then substantially releasing the back pressure on the flowing stream and expanding said oil vapors through a heated zone to crack said oil in the vapor phase.

2. A method of cracking oil which comprises heating oil while flowing through a coil to completely vaporize said oil under high pressure sufficient to maintain the liquid phase up to its critical temperature and then substantially releasing said pressure and expanding said oil through a coil under reduced pressure and heating said expanded oil to crack said oil in the vapor phase.

3. A method of cracking oil which comprises passing oil through a heated coil under high pressure sufficient to maintain the liquid phase up to its critical temperature, completely vaporizing said oil in said coil under said high pressure, then substantially releasing said pressure and expanding the vapors through a heated zone to crack said vapors under reduced pressure.

4. A method of cracking oil which comprises passing oil through a coil under high pressure sufficient to maintain the liquid phase up to its critical temperature, heating the oil in said coil to at least its critical temperature, then substantially releasing said pressure and expanding the vapors thus formed through a second coil, heating said second coil to a high temperature sufficient to crack the oil in the vapor phase.

5. A method of cracking oil which comprises heating the oil in a flowing stream in a coil under high pressure sufficient to maintain the liquid phase up to its critical temperature, raising the temperature of the oil to at least its critical temperature and then substantially releasing said pressure and expanding the vapors through a heated zone to crack said vapors under a reduced pressure.

6. A method of cracking oil which comprises heating oil in a flowing stream, completely vaporizing said oil under high pressure sufficient to maintain the liquid phase up to its critical temperature and then substantially releasing said pressure and gradually expanding said vapors through a heated zone to crack said vapors in the vapor phase.

7. A method of cracking oil which comprises heating oil while flowing through a coil to completely vaporize the oil under pressure sufficient to maintain the liquid phase up to its critical temperature and then substantially releasing said pressure and gradually expanding the oil through a heated zone to quickly raise the oil to a sufficiently high temperature to crack said oil in the vapor phase.

8. A process for cracking oil to produce unsaturated and anti-knock gasoline which comprises rapidly heating oil in a flowing stream under a super-atmospheric pressure to the critical temperature of said oil, said pressure being sufficient to maintain the oil in substantially liquid state up to its critical temperature, vaporizing the oil while under said pressure to form a vapor free of liquid particles and then substantially releasing said pressure and introducing said vapors free of liquid particles into a vapor-phase cracking coil and expanding the vapors through said vapor-phase cracking coil at

high velocity and under a condition of high turbulence, heating said vapors in said vapor-phase cracking coil to a high cracking temperature of 900° F. and above and sufficient to form said unsaturated and anti-knock gasoline and controlling the temperature and rate of heat in the vapor-phase cracking stage to produce the greater part of all of said gasoline produced during said process during said cracking stage.

Signed at Los Angeles, in the county of Los Angeles, and State of California, this 13th day of April, A. D. 1929.

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