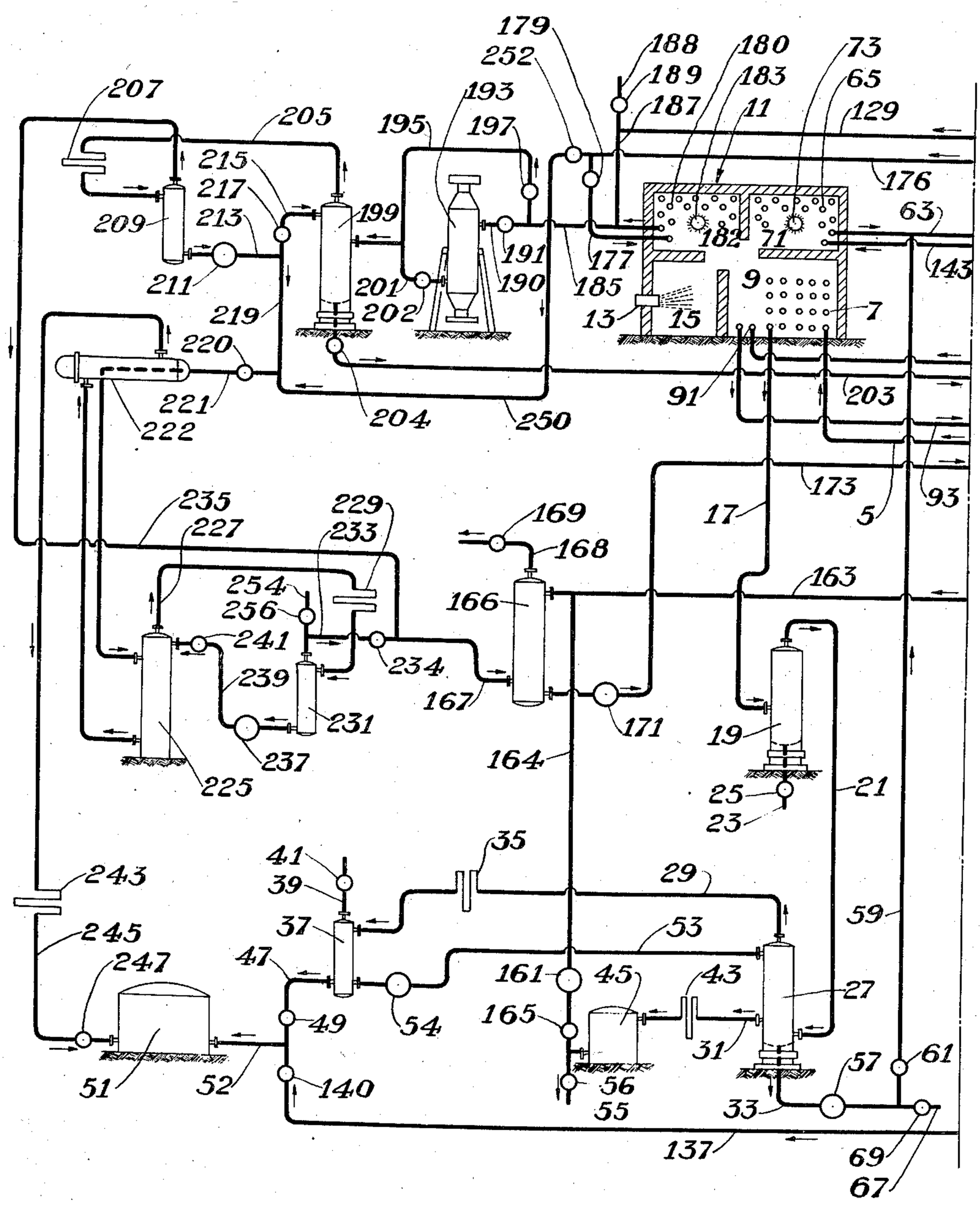
Aug. 2, 1938. P. A. MASCHWITZ 2,125,734

METHOD FOR PRODUCING HIGH OCTANE RATING MOTOR FUEL

Filed June 28, 1935 2 Sheets-Sheet 1

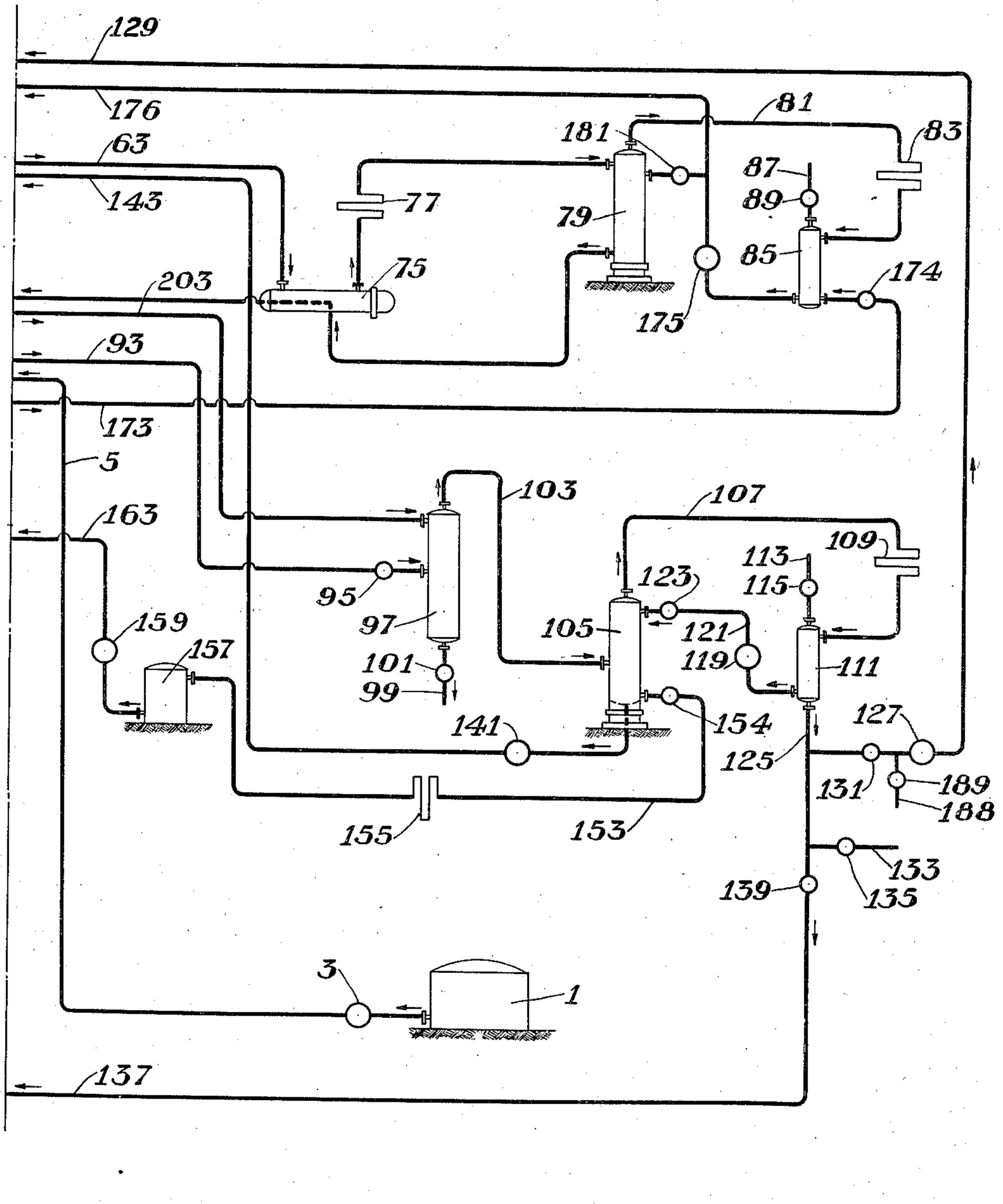


INVENTOR
Percy A. Maschwitz
BY Edward H. Lang
ATTORNEY

Aug. 2, 1938. P. A. MASCHWITZ 2,125,734

METHOD FOR PRODUCING HIGH OCTANE RATING MOTOR FUEL

Filed June 28, 1935 2 Sheets-Sheet 2



INVENTOR
Percy A. Maschwitz
BY
Edward H. Lang
ATTORNEY

Patented Aug. 2, 1938

2,125,734

UNITED STATES PATENT OFFICE

2,125,734

METHOD FOR PRODUCING HIGH OCTANE RATING MOTOR FUEL

Percy A. Maschwitz, Chicago, Ill., assignor to The Pure Oil Company, Chicago, Ill., a corporation of Ohio

Application June 28, 1935, Serial No. 28,866

11 Claims. (Cl. 196—9)

This invention relates to method for producing high octane rating gasoline and is more particularly concerned with method for converting hydrocarbon oils under high pressure into motor fuels and simultaneously polymerizing hydrocarbon gases, produced in the conversion, to motor fuel.

One of the objects of my invention is to provide a method for simultaneously distilling crude oil, cracking heavy oil, reforming naphtha, and polymerizing hydrocarbon gases in a single furnace structure.

Another object of my invention is the provision of a method for cracking oils and reforming naphtha under high pressures and for polymerizing the gases resulting from the cracking and reforming operations under high pressures without the necessity of compressing the gases.

A further object of my invention is the provision of a method whereby distillation and cracking of oil and polymerization of gases may be carried out as a unitary process or the distillation and/or cracking may be carried out independently of the polymerization step.

Still another object of my invention is to provide method for increasing the yield of gasoline obtainable from crude oil or other charging stock.

A still further object of my invention is to produce a larger amount of gasoline of high octane rating than has heretofore been produced from crude oil.

Other objects of my invention will be apparent from the following detailed description considered in connection with the accompanying drawings of which

The single figure is a diagrammatical, vertical view illustrating one form of the invention.

Referring to the drawings, the numeral 1 indicates a storage tank from which crude oil may be withdrawn by means of pump 3 through line 5 and charged to a heating coil 7 located in the convection zone 9 of a suitable furnace indicated generally by the numeral 11. The convection zone of the furnace may be heated by a suitable burner 13 located in the combustion section 15. During its passage through the heating coil 7 the oil may be heated to a temperature of approximately 700° to 800° F. After passing through the heating coil the oil is discharged therefrom through the line 17 into an intermediate point of the vaporizer and fractionator 19. The volatile portions including the gas oil pass overhead through the line 21 and the heavy residuum is withdrawn from the bottom of the vaporizer through the line 23 and valve 25. The vapors are discharged from the line 21 into an intermediate point of the fractionating tower 27 from which a light naphtha fraction may be taken overhead through the line 29. A heavy naphtha fraction may be taken off as a side stream through the line 31 and the gas oil may be discharged from the bottom of the tower through the line 33. The light naphtha taken overhead as vapor may be passed through the cooling coil 35 where it is condensed and then collected in separator 37. Any gas formed during the distillation may be withdrawn from the top of the separator 37 through line 39 and valve 41. The heavy naphtha withdrawn as a side stream through the line 31 may be passed through the cooling coil 43 and collected in a tank 45. From the separator 37 the light naphtha is withdrawn through the line 47 and valve 49 and sent to a collecting tank 51 through the line 52. A portion of the light naphtha from the separator 37 may be returned as reflux to the top of the tower 27 through line 53 by means of pump 54. A line 55 having a valve 56 is provided for withdrawing heavy naphtha from the system.

The gas oil, withdrawn through the line 33, may be pumped by means of pump 57 and charged through line 59 and valve 61 to the line 63 where it acts as a cooling medium to shock chill the reaction products discharged from the cracking coil 65. If necessary, suitable heat interchangers may be placed in the line 59 to cool the gas oil. A line 67 having valve 69 therein is provided for withdrawing gas oil from the line 33 when it is desired to shut down the cracking still 65 for cleaning or repairing.

The cracking coil 65 is located in a separate section 71 of the furnace 11 and is heated chiefly by means of radiant heat supplied by the burner 73. The oil undergoing cracking is preferably charged to the coil 65 at a pressure of from 500 to 1500 pounds per square inch and heated therein to a temperature of from 800° to 1000° F. The reaction products which have been cracked in the heating and conversion coil 65 are discharged through the line 63 and are shock chilled to a temperature below conversion temperature by the gas oil supplied through the line 59. If desired a suitable reaction chamber may be connected to the outlet of the coil 65 to provide additional time for the cracking reaction to take place. The chilled products may then pass through a suitable heat exchanger 75 and cooling coil 77 where they are cooled sufficiently to lower their temperature to approximately 450° to 600° F. and then passed into the upper section of the frac-

tionating tower 79. The fractionating tower 79 is preferably maintained under the high pressure of the cracking system and is operated under such conditions that substantially nothing heavier than butane passes over as vapors. For this purpose the top temperature of the tower may be maintained at from 200° to 300° F. The gases are taken off the top of the tower through the line 81 and partially condensed by passing through cooling coil 83. The resulting liquid and gases are passed to the separator 85 from which uncondensed gases consisting chiefly of methane, ethane, and hydrogen and some ethylene are bled off through the line 87 and valve 89.

The liquids collected in the bottom of the fractionating tower 79 may be passed through heat interchanger 75 and then through a heating coil 91 located in the convection section 9 where the oil is heated to a temperature of approximately 700° to 800° F. and discharged into the line 93, then through pressure release valve 95 into a vaporizer 97. The heavy tar may be withdrawn from the vaporizer 97 through line 99 and valve 101 and the vapors including the gas oil are taken off overhead through the line 103 and discharged into an intermediate point of the fractionating tower 105. The fractionating tower 105 is maintained under pressure approaching atmospheric and under such temperatures that only the fractions within the gasoline boiling range are taken overhead as vapors. The vapors are taken from the top of the fractionating tower 105 through the line 107 and are condensed by passing through condenser 109. The condensate passes into the separator 111 from which gases, if any, are bled from the system through the line 113 and valve 115. The condensate is in part withdrawn from the bottom of the separator 111 by means of the pump 119 and charged through line 121 and valve 123 into the top of fractionating tower 105 to act as reflux liquid. The remainder of the condensate from separator 111 may be withdrawn from the bottom thereof through line 125 from which all or a portion thereof may be withdrawn by pump 127 through line 129 and valve 131; or the remainder may in whole or in part be withdrawn from the system through line 133 controlled by valve 135, or may be sent through line 137 controlled by valve 139 into the collecting tank 51 through valve 140 and line 52.

The liquid fraction collecting in the bottom of fractionating tower 105 is withdrawn therefrom by means of pump 141 through line 143 and charged to the inlet of cracking coil 65 under pressure between 500 and 1500 pounds per square inch.

An absorption liquid, which may be an intermediate cut withdrawn from the fractionating tower 105 through the line 153, valve 154, cooling coil 155, vessel 157, and pump 159, or the heavy naphtha collected in the vessel 45, may be charged by pumps 159 and 161 through the lines 163 and 164 and valve 165 respectively into the top of the absorption tower 166 wherein it flows downward in counter-current relation with the rising stream of gases. The absorption tower is preferably operated under pressures of approximately 160 to 210 pounds per square inch and approximately atmospheric temperature. Gases containing olefinic hydrocarbons are fed into the bottom of the absorber through line 167. The fixed dry gases which may be chiefly methane, ethane, ethylene, and hydrogen, are bled from the top of the absorber through the line 168 and valve 169 to any suitable point, for use as fuel or for other purposes. The absorber oil charged with dissolved gases may be withdrawn from the bottom of the absorber 166 by means of the pump 171 through line 173 and valve 174 and charged into the separator 85 where it commingles with the liquefied gases coming from the fractionating tower 79. The combined products may be withdrawn from the lower portion of the separator 85 by means of pump 175 through the lines 176 and 177 and valve 179 and charged into the inlet end of the polymerizing and reforming coils 180. A portion of the products from the bottom of the separator 85 may be passed into the top of the tower 79 through valve controlled line 181 to act as reflux. The coils 180 are located in a separate section 182 of the furnace 11, and are heated chiefly by radiant heat from the burner 183. The combined charge of heavy naphtha and liquefied gases is heated to a temperature of approximately 900° to 1100° F. under pressures of approximately 500 to 1500 pounds per square inch in the coils 180. Upon leaving the coils 180 through the line 185, the reaction products are shock chilled by injecting therein through the line 187 a portion of the pressure distillate withdrawn from the separator 111, through line 129. If desired, a reaction chamber may be connected to the outlet of the coils 180 to provide additional reaction time for the products undergoing conversion. Distillate from an extraneous source may be fed through line 188 and valve 189 and used as chilling fluid in place of or together with condensate from separator 111. The reaction products which have been chilled to a temperature below conversion temperature, preferably 550° to 700° F., may then be passed through either line 190 and valve 191 into a clay treating chamber 193, or may be by-passed around the chamber 193 through line 195 and valve 197 into fractionating tower 199.

The chamber 193 may be filled with a suitable solid adsorptive catalyst such as fuller's earth or similar clay, and is preferably maintained under the pressure existing in the coil 180. During the passage through the clay tower the conversion products are decolorized and degummed. After treatment with the adsorptive catalyst all the products undergoing treatment may be withdrawn from the tower 193 through the line 201 and valve 202 and charged into an intermediate point of the fractionating tower 199. The fractionating tower 199 is preferably operated under super-atmospheric pressure of approximately 175 to 225 pounds per square inch. The liquid collecting in the bottom of the tower 199 may be withdrawn through line 203 and valve 204 and charged into vaporizer 97. The uncondensed vapors which may include the major portion of the gasoline fractions, and the uncondensable gases, may be withdrawn from the top of the fractionating tower 199 through the line 205 and condenser 207 and pass into the gas separator 209. The condensate may be withdrawn from the separator 209 by means of the pump 211 through the line 213 and a portion thereof returned to the top of the fractionating tower 199 through the line 215 and valve 217 to act as reflux. The remainder of the condensate may be discharged through line 219 and valve 220 into line 221, heat interchanger 222 into an intermediate point of the stabilizer 225. The stabilizer is preferably operated under super-atmospheric pressure of 175 to 250 pounds per square inch and under temperature conditions suitable to separate the light ends unsuitable for gasoline, as an overhead

which is withdrawn from the tower through the line 227. For this purpose a temperature of approximately 120° to 150° F. is maintained at the top of the stabilizer. The overhead products are then cooled by passing through cooling coil 229 and discharged into separator 231. The gases from the top of the separator 231 are withdrawn through the line 233 and valve 234 and may be charged to the bottom of the absorption tower 166 where the heavy fractions such as propane, propylene, butane and butylene, are absorbed. Gases which come off the top of the separator 209 areb led into the line 233 by means of the line 235 and also charged to the absorber. Any liquids collected in the separator 231 may be discharged therefrom by means of pump 237 through line 239 and valve 241 into the top of the stabilizer 225 to act as reflux. The stabilized gasoline may be withdrawn from the bottom of the stabilizer 225 through the heat interchanger 222 and cooling coil 243 through line 245 and valve 247 into the collecting tank 51.

A line 250 having a valve 252 therein is provided for passing liquefied gases from the separator 85 directly to the line 221 and stabilizer 225 when it is desired to operate the cracking portion of the system without operating the reforming and polymerizing portion. A line 254 having valve 256 is connected to the top of gas separator 231 for the purpose of withdrawing gases from the system when the reforming and polymerization unit is not in operation.

The furnace 11 is preferably built in sections with heating means for each section so that any one section may be shut down and the other sections be operated independently thereof. As shown in the drawing, the furnace has bridge walls separating the furnace into three separate heating sections and the products of combustion are withdrawn from the bottom of the furnace. Any suitably designed furnace may be used instead.

As a specific example of one method of carrying out my invention, crude oil may be rapidly heated in the coil 7 to a temperature of approximately 750° F. and discharged into the vaporizer and fractionator 19 from which heavy residuum may be withdrawn. The vapors coming off the top of the vaporizer or fractionator are further fractionated in tower 27 into a heavy portion constituting the gas oil fraction, an intermediate condensate constituting the heavy naphtha boiling between 200° and 600° F., and vapors constituting the light naphtha. The light naphtha may be withdrawn through the line 29 and after cooling and separation of gas, collected in the tank 51. The top of the fractionating tower may be maintained at a temperature of from 250° to 300° F. The heavy naphtha, after having been cooled to approximately atmospheric temperature, is charged to the top of the absorption tower 166 where it is contacted with the gases entering the bottom of the absorption tower through line 167. The absorption tower may be maintained at a pressure of approximately 200 pounds per square inch and at a temperature approximately atmospheric. Under these conditions the major portion of the propane, propylene, butane and butylene is absorbed together with a portion of the ethylene, and the dry gases consisting chiefly of methane, ethane, ethylene, and hydrogen escape from the top of the tower through the line 168. These gases are used for fuel or any other suitable purpose.

The gas oil fraction collected in the fractionating tower 105 may be charged to cracking coil 65 at a pressure of approximately 1000 pounds per square inch and heated therein to a temperature of approximately 925° F. The products leaving the cracking coil may be immediately chilled to a temperature of 700° F. by injecting therein the gas oil from the bottom of the tower 27. The chilled products may then be cooled sufficiently to lower their temperature to approximately 600° F. and charged at this temperature into the fractionating tower 79 which may be maintained under a pressure of approximately 600 pounds per square inch. The top of the tower may be maintained at a temperature of approximately 250° F. Under these conditions of temperature and pressure, nothing heavier than butane will escape as an overhead product. The vapors may then be cooled to approximately atmospheric temperature under existing pressure and the heavier portions of the gas such as the propane, propylene, butane, and butylene, will liquefy. The liquid products from the fractionator 79 may then be heated to a temperature of approximately 750° F. and charged into the vaporizer 97 where the pressure is reduced to approximately 15 pounds per square inch. Substantially everything except the tar will pass overhead as vapors and the vapors are fractionated in the tower 105 into gasoline distillate, heavy naphtha, and gas oil. The fractionating tower 105 may be maintained under a pressure of approximately atmospheric to 15 pounds per square inch, and the top of the tower may be maintained at a temperature of approximately 350° F. Additional oil for absorption may be withdrawn as a side cut from the fractionating tower 105 when necessary.

The liquefied gases plus the absorbent oil charged with dissolved gases may be charged from separator 85 to the heating and reaction coils 180 at a pressure approximately 1000 pounds per quare inch and heated therein to a temperature of approximately 1000° F. In the coils 180 the heavy naphtha is reformed into high octane rating naphtha and part of the dissolved gases are polymerized to heavier hydrocarbons boiling chiefly within the gasoline range. The products leaving coils 180 are immediately chilled to a temperature of approximately 550° F. and may be passed at this temperature through the clay tower 193 wherein the color-imparting and gum-forming constituents are polymerized to heavy hydrocarbons which may be subsequently removed by fractionation. The pressure in the clay tower is maintained at approximately the pressure of the heating and reaction coils 180. Pressure on the products leaving the clay tower may be partially reduced and the products then charged into vaporizing and fractionating tower 199 at a pressure of approximately 200 pounds per square inch where separation into gasoline vapors and heavier liquids takes place. The temperature at the top of the tower may be maintained at approximately 450° F. The gasoline vapors leaving the top of the fractionating tower 199 are condensed and the condensate passed to the stabilizer tower 225 which may be maintained under a pressure of approximately 225 pounds per square inch. The temperature of the top of the stabilizer is maintained at approximately 120° F. and the bottom of the tower is maintained at approximately 300° F. Under these conditions the gasoline is freed of fractions lighter than butane. The gases from the stabilizer together with gases from the tower 199 are charged to the bottom of the absorber. The oil charged with dissolved gases

may be commingled with liquefied gas in separator 85.

When it is desired to shut down the cracking and polymerizing units for cleaning, repairing or other reason, the running of the crude oil through the coils 7 may be continued without interruption by closing valve 61 in line 59 and valve 165 in line 164. The gas oil will then be withdrawn from the tower 27 through line 33, line 67 and valve 69. The heavy naphtha will be withdrawn from the vessel 45 through line 55 and valve 56. Burners 73 and 183 in sections 71 and 182 respectively of furnace 11 will be shut off.

When it is desired to run the cracking unit and shut down only the reforming and polymerizing unit, the coil 180, the clay chamber 193, the fractionating tower 199 and the absorber 166 will remain idle. To isolate the coil 180, valve 179 in line 177 will be closed. To isolate the chamber 193, the valve 131 in line 129 will be closed. To isolate the fractionating tower 199, valve 204 in line 203 and valve 220 in line 219 will be closed. To isolate the absorber 166, valve 154 in line 153, valve 165 in line 164, valve 174 in line 173, and valve 234 in line 233 will be closed. The burner 183 in section 182 of furnace 11 will be shut off. The heavy naphtha from tank 45 may be withdrawn from the system through line 55, the gasoline collected in separator 111 may be sent to collecting tank 51 or withdrawn from the system through line 133 for chemical treatment, and the liquefied gases in separator 85 may be sent directly to the stabilizer through lines 250 and 221. The gases from separator 231 may be bled from the system through line 254 and valve 256.

It will be observed that by means of my invention I have completely eliminated the necessity for compressing gases and the expense attendant therewith. All the products are pumped through the process in the liquid phase thereby enabling the system to handle much larger thruputs than is possible where the products are processed in the vaporous or gaseous phase.

Although I have set forth certain conditions of temperature and pressure in various parts of the system, it is to be understood the invention is not limited to the conditions stated but that the invention is intended to broadly cover a system of cracking, reforming, and polymerizing in which products are handled in the liquid state without the necessity of compressing the gases.

What I claim is:

1. A continuous method for simultaneously cracking oil and polymerizing hydrocarbon gases which comprises subjecting oil to elevated conditions of temperature and pressure suitable for cracking the oil, fractionating the reaction products without release of pressure under temperature conditions suitable for separating the normally gaseous fraction from the normally liquid fraction, cooling the gaseous fraction while under elevated pressure sufficiently to liquefy the heavier portion thereof without compression of said gaseous fraction, absorbing olefinic gases from a separate source in lean heavy naphtha, commingling the rich naphtha with said liquefied gases, subjecting the commingled naphtha and liquefied gases to elevated conditions of temperature and pressure suitable for reforming the naphtha and polymerizing the gases, separating the normally gaseous hydrocarbons from the normally liquid reaction products, and absorbing the heavier fractions of the last mentioned gases in said lean heavy naphtha, said last mentioned gases being those of said separate source.

2. Method in accordance with claim 1 in which the oil is cracked under pressures of 500 to 1000 pounds per square inch, and the gases produced in the oil cracking step are separated and partially liquefied without materially reducing the pressure.

3. Method in accordance with claim 1 in which the gases produced in the reforming and polymerizing step are separated from the normally liquid hydrocarbons under sufficiently high pressure to avoid the necessity of compressing the gases for the purpose of absorption in the heavy naphtha.

4. Method in accordance with claim 1 in which the heavy naphtha is obtained as an intermediate cut from the reaction products of the cracking step.

5. A method for producing high octane rating gasoline from crude oil which comprises separating the crude into light naphtha, heavy naphtha, and a heavier cracking stock, subjecting hydrocarbon oil to elevated conditions of temperature and pressure suitable for cracking the oil, immediately chilling to below cracking temperature, the reaction products leaving the cracking stage, by direct contact with said cracking stock, fractionating the combined products under elevated pressures and at temperatures suitable for separating the normally liquid products from the normally gaseous products, cooling the gaseous products while under elevated pressure sufficiently to liquefy the heavy fractions thereof without compression of said gaseous product, separating the normally liquid products into a fraction boiling within the gasoline range and a condensate heavier than gasoline, charging said heavier condensate to the cracking stage, contacting said heavy naphtha with olefine-containing hydrocarbon gases under conditions of temperature and pressure suitable for dissolving a substantial portion of the olefines contained therein, commingling the rich naphtha with said liquefied hydrocarbon gases, subjecting the commingled naphtha and gases to elevated conditions of temperature and pressure suitable for reforming said naphtha and polymerizing said gases, separating the resulting products into normally liquid and normally gaseous products, and contacting the last mentioned normally gaseous products with said heavy naphtha to dissolve the olefinic hydrocarbons contained in said gases.

6. Method according to claim 5 in which the oil is cracked under a pressure of from 500 to 1500 pounds per square inch, and the reaction products resulting from the cracking stage are separated into normally liquid and normally gaseous hydrocarbons without material drop in pressure.

7. Method according to claim 5 in which the naphtha is reformed and the gases polymerized at pressures ranging from 500 to 1500 pounds per square inch.

8. Method according to claim 5 in which the naphtha is reformed and the gases polymerized at pressures of from 500 to 1500 pounds per square inch and at temperatures of 900° to 1100° F.

9. The method of simultaneously converting naphtha into high octane gasoline and polymerizing hydrocarbon gases which comprises absorbing said gases in the naphtha, charging the enriched naphtha to a heating and reaction zone wherein the said naphtha is heated to a tempera-

ture between 900 and 1100° F. under pressures of 500 to 1500 pounds per square inch, chilling the products leaving said zone, by means of direct contact with cool oil, to a temperature sufficient to arrest conversion but above the normal vaporizing temperature of gasoline and before releasing the pressure on the reaction products and without prior fractionation thereof, contacting them with a solid adsorbent catalyst.

10. Method in accordance with claim 9 in which the cooling oil is raw gasoline from a cracking operation.

11. The method of converting heavy oils into gasoline which comprises subjecting said oil to conditions of temperature and pressure in a cracking zone suitable for converting a substantial portion of said oil to gasoline boiling hydrocarbons, separating the conversion products into gas, gasoline distillate, and products heavier than gasoline distillate, subjecting gases from the oil cracking step to polymerization conditions of elevated temperature and superatmospheric pressure in a separate zone, quenching the products issuing from the polymerization zone by means of said gasoline distillate to a temperature below polymerization temperature, and contacting the total quenched products with adsorptive catalytic clay without release of pressure at a temperature sufficient to induce polymerization of the gum-forming and color-imparting bodies in said products.

PERCY A. MASCHWITZ.