

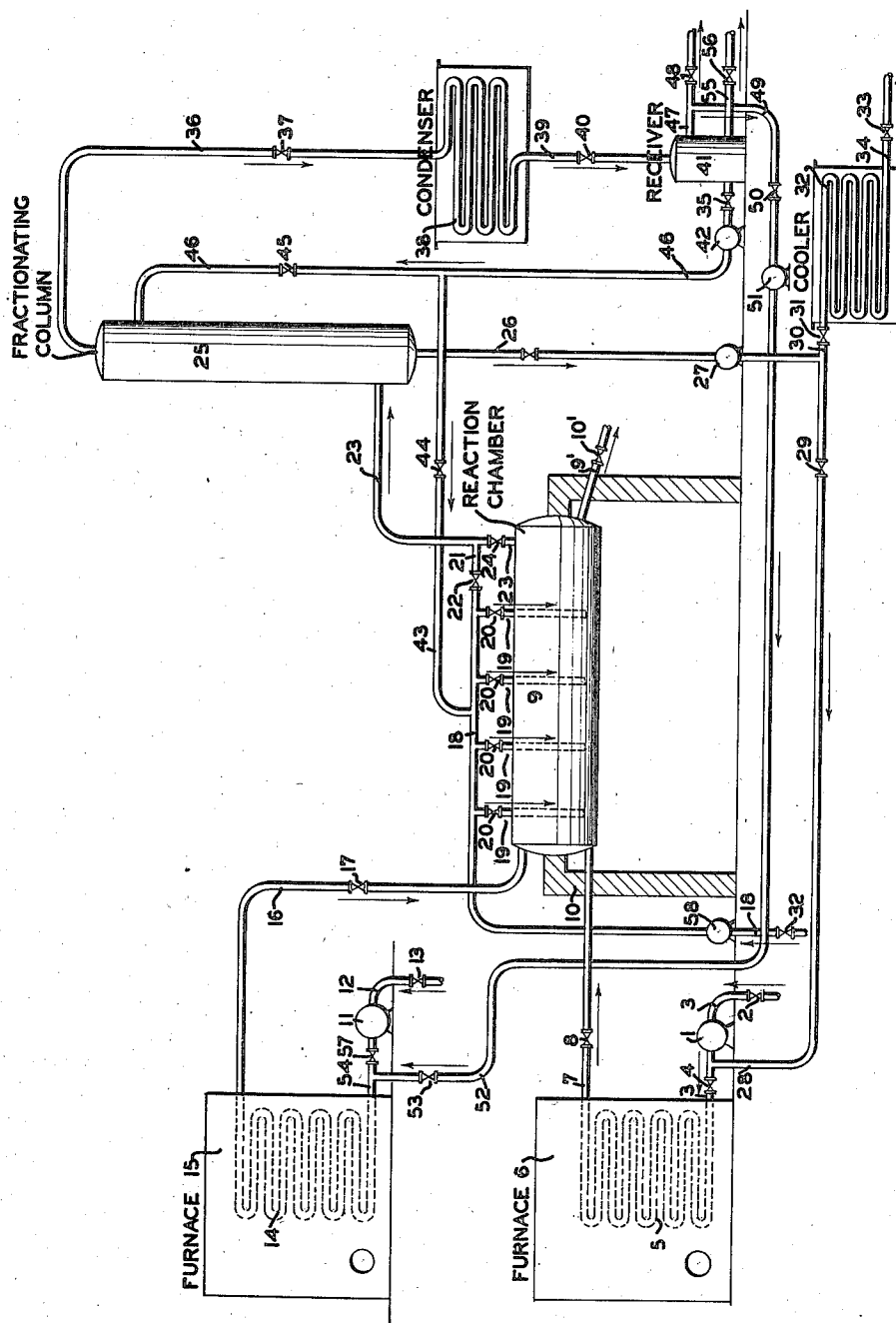
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TREATMENT OF HYDROCARBON OIL

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TREATMENT OF HYDROCARBON OIL

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The invention relates to the treatment of hydrocarbon oils pertaining more specifically to the conversion of higher boiling into lower boiling hydrocarbons.

One of the features of the invention resides in the hydrogenation of hydrocarbon oils.

A more specific feature comprises the hydrogenation of hydrocarbon oils under conditions of elevated temperature and pressure in a reaction zone, the reaction between the hydrogen and the oils being controlled by the introduction, into the reaction zone, of cooling hydrocarbons, preferably in the form of a plurality of streams.

Various other features of the invention will become evident from the following detailed description of a form of the invention which will be better understood by referring to the drawing. The drawing is diagrammatic, and is illustrative only, showing one form of apparatus suitable for carrying out the process.

The raw hydrocarbon oils to be treated are supplied to pump 1 through line 3, controlled by valve 2, and are fed through valve 4 in line 3, into the heating element 5 located in furnace setting 6, and are discharged through line 7, controlled by valve 8, into the catalytic reaction chamber 9. This catalytic reaction chamber is located in a suitable setting 10, either directly fired or receiving its heat from the flue gases from any one of the heaters used in the process. Chamber 9 is provided with draw-off line 9' controlled by valve 10'. Simultaneous with the introduction of the hydrocarbon oils undergoing treatment into the catalytic reaction chamber 9, hydrogen supplied through line 12 and valve 13 is introduced by means of a suitable pump 11 through line 54, controlled by valve 57, into the heating element 14 located in furnace setting 15. The heated hydrogen passes through line 16, controlled by valve 17, and is introduced into the catalytic chamber 9. This catalytic chamber contains suitable catalytic material or mixtures thereof, examples of which are metals such as tin, zinc, copper, aluminum, iron, nickel, silver, cobalt and chromium, or the noble metals including gold, platinum, palladium, iridium, indium, and osmium, or metallic oxides such as the oxides of cobalt, nickel, manganese and those of the above metals which form oxides, or mixtures thereof. In some cases, the catalyst is substantially composed of one metal with a small percentage of another metal or another substance, the latter functioning as a promoter catalyst, or one metal coated with another may be used such as iron

coated with tin. Mixtures of oxides have also given good results, for example, a mixture of molybdenum oxide and iron oxide. In some cases two step catalysts may be used, such as iron in the liquid phase and a mixture of oxides, such as those of iron and molybdenum, in the vapor phase.

Suitable cooler hydrocarbons from an external source, such as crude petroleum and products from the straight distillation of petroleum, or cracked products, or hydrocarbon gases, or products of the process itself, which are preferably not of a distinctly coke-forming character, may be supplied to pump 58 through valve 32 in line 18 and introduced into the catalytic chamber 15 through line 18 and any or all of a multiplicity of lines shown as 19, controlled by valves 20 for the purpose of controlling the rate and character of the catalytic reaction. A portion of the cooling material may be likewise introduced into the vapor discharge 23 from chamber 9 through line 21, controlled by valve 22. The vapors leaving the catalytic reaction chamber 9 pass through line 23, controlled by valve 24, into a suitable fractionating means 25 where they are separated by fractionation into lower and higher boiling products, the fractionation being assisted by the introduction into the fractionating zone of a portion of the product of the process which serves to cool the vapors and regulate the fractionation thereof. The reflux leaving the fractionator 25 passes through line 26 and is pumped by means of pump 27 through line 28, controlled by valve 29, into line 3, and subsequently into the heating element 5 where it is subjected to further heating and where it combines with the charging oil; or the reflux may be withdrawn from the process for other purposes through line 30, controlled by valve 31, passing through cooler 32 and from there to storage through line 33, controlled by valve 34. The vapors leaving the fractionator 25 pass through line 36, controlled by valve 37, into the cooler and condenser 38, and through line 39, controlled by valve 40, into the receiver 41. A portion of the distillate accumulating in the receiver may be recirculated into the fractionator 25 for cooling purposes, being supplied to pump 42 through valve 35 in line 46 and pumped by means of pump 42 through line 46, controlled by valve 45, into the fractionator 25. A portion of this distillate may be diverted from line 46 through line 43 controlled by valve 44 into line 18, thence passing through lines 19 and valves 20 into chamber 9 to assist cooling in this zone. The

gaseous products of the process may be withdrawn through line 47, controlled by valve 48, or a portion thereof may be passed through line 49, controlled by valve 50, and pumped by means of pump 51 through line 52, and valve 53 into heating element 14 combining with the hydrogen and passing therewith to chamber 9 where it may serve to assist in the hydrogenation. The distilled liquid products of the process are withdrawn through line 55, controlled by valve 56.

As a specific example of the results obtained by the operation of the process of my invention, a petroleum residue of approximately 18 A. P. I. gravity, when treated with hydrogen, introducing the heated petroleum residue together with the hydrogen into the catalytic chamber so that the mixture is at a temperature of approximately 900° F. at a pressure of approximately 2,000 lbs. per sq. in., should produce a yield of approximately 45% of low boiling hydrocarbons within the range of materials suitable for motor fuel and a residual product suitable for fuel oil with very little production of coke and gas. In this example, approximately 10% of hydrogen by weight of the oil would be required and a catalyst consisting of tinned iron or a mixture of molybdenum oxide and iron oxide, has been found to give good results.

In another example, increasing the amount of hydrogen to 20% by weight and raising the temperature to approximately 925° F. with a pressure of 2,000 lbs. per sq. in. in the catalytic reaction chamber using an 18 A. P. I. gravity residual oil as charging stock with a mixed catalyst of tinned iron in the liquid phase and a mixture of iron oxide and molybdenum oxide in the vapor phase, a yield of 60% gasoline may be obtained with a heavy residual oil which by blending could be utilized as a fuel oil. Excess hydrogen in both cases may be recycled along with the uncondensable gases.

Oils containing a higher proportion of hydrogen relative to the carbon content such as a 24 A. P. I. gravity Mid Continent gas oil would give correspondingly better results under the conditions cited.

In general, the higher the ratio of hydrogen to carbon in the charging stock, the greater will be the yield of lower boiling hydrocarbons for the same condition.

I have found that the character of products resulting from catalytic hydrogenation varies greatly depending upon very small differences in the conditions of operation, particularly the temperatures maintained during the reaction. The variations to which large changes in the character of the product may correspond are at times so small that it is required to control the conditions to a nicety and closer than permitted by the use of the usual heating means. The injection into the catalytic zone of a separate temperature controlling medium as herein set forth has been found to be of considerable advantage in the control of the character of the product desired.

It further permits varying the character of the products during an operation at any time and to any extent desirable without changing the heating conditions of the process in the heating zones.

For example, when treating an 18 A. P. I. gravity residual oil charging stock, raising the temperature initially to approximately 975° F. with a pressure of 2000 pounds per square inch in the catalytic chamber and subsequently cooling the

charge in the catalytic chamber to approximately 940° F., introducing excess hydrogen into the catalytic chamber along with the heated uncondensable gases, approximately 65% of hydrocarbon for motor fuel may be obtained in addition to approximately 30% of heavy residual fuel oil which may be utilized as a fuel oil or which may be recycled as charging stock for further treatment. The catalyst described in the previous examples may be used. Cooling is effected by introducing a light distillate directly in the catalytic zone.

By maintaining the same conditions as in the preceding example, with the exception that more cooling agent is used to lower the temperature of the mixture in the catalytic chamber to approximately 900° F., a yield of 50% hydrocarbons suitable for motor fuel may be obtained and an increased yield of residual oil suitable for recycling over that shown in the previous example. The cooling agent in both cases undergoes conversion in the same manner as the charging stock and the yields herein given are based on the combined feeds. Ultimate yields of hydrocarbons suitable for motor fuel may be made by recycling the residual oil.

The examples given are illustrative of a wide range of conditions which may be employed in the operation of the process of the invention and they are not to be interpreted as limitations upon the scope of the invention.

Having thus described my invention, what I claim is:

1. A hydrocarbon oil conversion process which comprises heating the charging oil to a hydrogenating temperature under pressure in a heating zone, thence introducing the heated oil into a reaction zone and reacting the same therein with hydrogen under hydrogenating conditions of temperature and pressure, removing and dephlegmating hydrogenated vapors and then subjecting the same to final condensation thereby forming gasoline-containing distillate, and introducing a portion of the gasoline-containing distillate into the reaction zone to control the reaction temperature therein.

2. A hydrocarbon oil conversion process which comprises heating the charging oil to a hydrogenating temperature under pressure in a heating zone, thence introducing the heated oil into a reaction zone and reacting the same therein with hydrogen under hydrogenating conditions of temperature and pressure, removing hydrogenated vapors and dephlegmating the same to condense fractions thereof heavier than gasoline, finally condensing the dephlegmated gasoline vapors thereby forming gasoline-containing condensate, and introducing a portion of said condensate, while substantially below hydrogenating temperature, to the reaction zone to control the reaction temperature therein.

3. In the conversion of heavy hydrocarbon material into lower boiling oils by catalytic hydrogenation and wherein the hydrocarbon material is subjected to the hydrogenating conditions of temperature and pressure while passing with hydrogen through an enlarged reaction zone containing the hydrogenating catalyst, the improvement which comprises introducing separate streams of cooling oil into said enlarged zone at spaced points in the path of travel of the hydrocarbon material and hydrogen through said zone, removing the vapors and fractionating and condensing the same, and returning condensed por-

tions of the vapors in separate streams to the reaction zone to constitute said cooling oil.

4. In the conversion of heavy hydrocarbon material into lower boiling products by catalytic hydrogenation, the method which comprises introducing the hydrocarbon material at hydrogenating temperature and hydrogen at one end of an elongated reaction chamber containing the hydrogenating catalyst and maintained under hydrogenating pressure, passing the mixture of heated hydrocarbon material and hydrogen through the catalyst chamber to the opposite end thereof and hydrogenating the hydrocarbon material during such travel of the mixture through the chamber, removing the products of hydrogenation from said opposite end of the chamber, and controlling the catalytic reaction of the hydrocarbon material and hydrogen during the passage of the mixture through the reaction chamber by introducing separate streams of cooling oil, consisting of hydrogenated products, to

the chamber at spaced points in the path of travel of the mixture through the chamber, fractionating and condensing the vaporous hydrogenation products, and supplying condensed portions of the vapors in separate streams to the chamber to constitute said hydrogenated cooling oil.

5. The improvement as defined in claim 3 further characterized in that the hydrocarbon material is introduced to the reaction zone at hydrogenating temperature and in that the quantity and temperature of said cooling oil are such as to prevent a temperature rise in the reaction zone above that at which the hydrocarbon material is introduced to said zone.

6. The method as defined in claim 4 further characterized in that said cooling oil is sufficient to prevent a temperature rise in the chamber above that at which the hydrocarbon material is introduced to the chamber.

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