

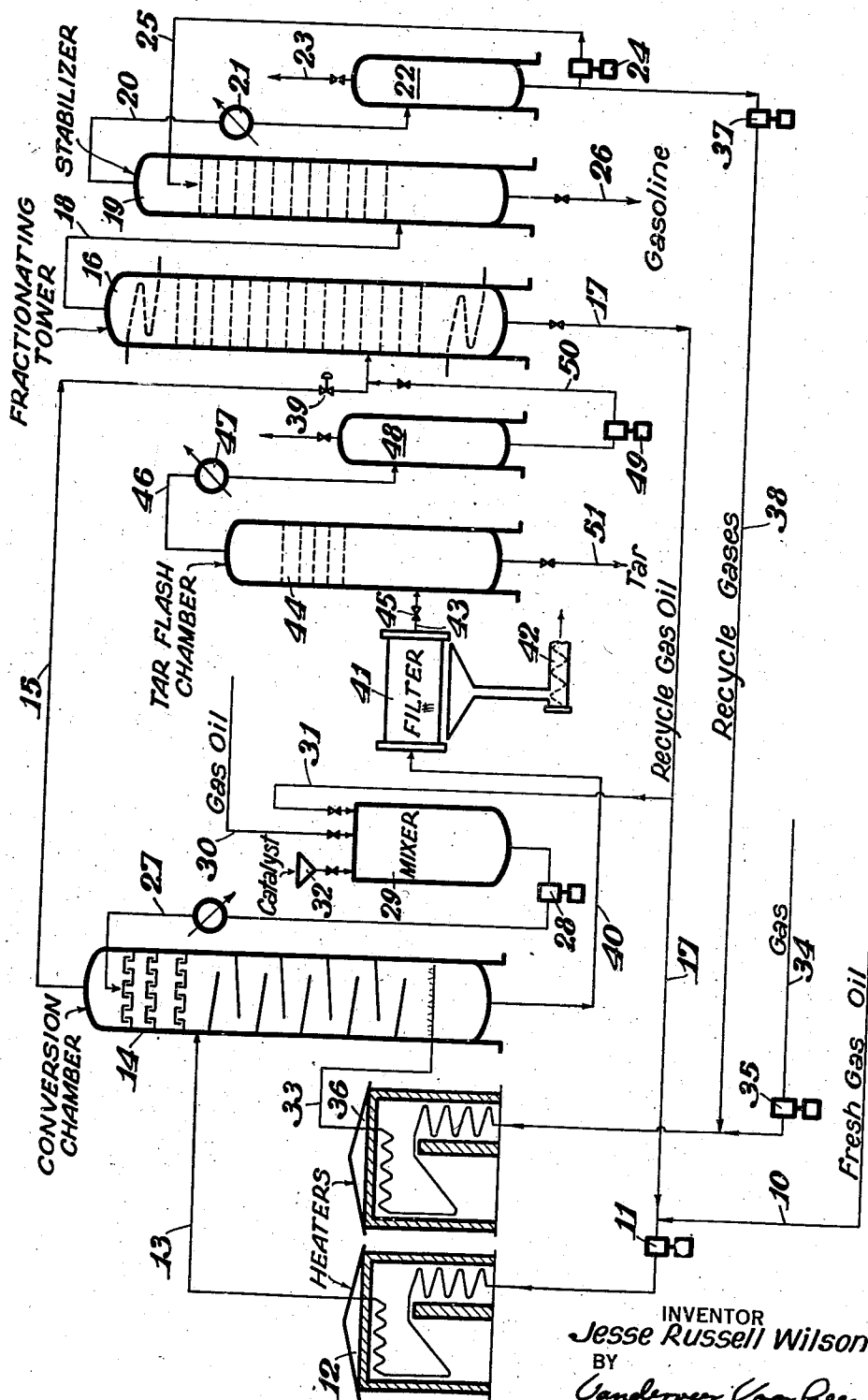
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CATALYTIC CONVERSION OF HYDROCARBONS

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CATALYTIC CONVERSION OF HYDROCARBONS

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10 Claims. (Cl. 196—9)

This invention relates to a process of converting hydrocarbons into motor fuels wherein hydrocarbons heavier than gasoline are simultaneously converted with hydrocarbons lighter than gasoline to produce hydrocarbons boiling within the gasoline boiling range, which may be defined as an initial boiling point of about 80 to 120° F. and a final boiling point of about 350 to 450° F. One object of the invention is to facilitate the interaction of normally gaseous hydrocarbons such as ethane, propane and butane, ethylene, propylene and butylene with gas oil and its decomposition products.

Another object of the invention is to simultaneously convert hydrocarbon gases having a relatively high hydrogen to carbon ratio and heavy oils, thereby producing a larger yield of gasoline with a smaller production of carbonaceous matter, coke, asphalt, etc. By carrying out the reaction in the presence of a catalyst I am also enabled to produce a gasoline having a high knock rating. For example, instead of obtaining a gasoline having a knock rating of 65 to 70 octane number from Mid-Continent gas oil, I am enabled to produce a gasoline having an octane number of between 75 and 90 as a result of the specific effect of the catalyst in rearranging the structure of the heavy hydrocarbons by interaction with the normally gaseous hydrocarbons which I employ.

In all catalytic conversion processes employed heretofore great difficulty has been encountered with the deposition of carbonaceous matter, coke, etc. on the catalyst, rapidly rendering it inactive. Various devices have been employed to overcome this difficulty, such as burning off the carbonaceous matter at intervals without removing it from the catalyst chamber. An object of my invention is to employ the catalyst in a fine state of subdivision and maintain it continuously in a liquid slurry throughout the process, in which form the catalyst is pumpable and may be continuously introduced into the conversion zone and withdrawn therefrom after it has lost its activity. Another object of my invention is to conduct the conversion reaction under such conditions that substantially only the high boiling asphaltic oils produced in the process are discharged with the catalyst from the conversion chamber and this object is accomplished by regulating the temperature and introduction of the hydrocarbon gas stream entering the conversion chamber. Still another object of my invention is to control the temperature of the conversion chamber by introducing at the upper

end thereof gas oil preheated to cracking temperature and partially cracked before its admission to the conversion chamber where the heat thus provided serves to heat a slurry of catalyst and cooler gas oil separately introduced near the same point in the conversion chamber, thus avoiding the necessity of directly heating the catalyst to the desired conversion temperature, an operation which is beset with many difficulties. Other objects of the invention will be apparent from the following description.

The drawing which forms a part of this specification illustrates diagrammatically apparatus for carrying out the process wherein gas oil and gases are separately heated and discharged into a conversion chamber in contact with a continuous stream of dispersed catalyst, after which the products are separated and partly recycled. Referring to the drawing, gas oil, for example straight-run Pennsylvania or Mid-Continent gas oil, is introduced by line 10 and pump 11 to pipe heater 12 wherein it is heated to a temperature above the cracking temperature, for example 850–900° F., or 950° F. Under these conditions about 10 to 25% of the gas oil may be converted to gasoline. The stream of hot gas oil and gas oil vapors is conducted under high pressure by line 13 to conversion chamber 14, the stream entering the tower near the upper end thereof. Tower 14 is provided with suitable baffle plates or other contact means such as bubble plates which provide an extended surface for contact between liquid and vapor, permitting the liquid to flow without obstruction to the bottom of the tower and permitting the vapor and gases in the tower to flow to the top thereof and escape by vapor line 15 leading to fractionating tower 16 where the vapors and gases are fractionated to separate therefrom constituents heavier than gasoline which are withdrawn as a reflux by line 17 and gasoline vapors and gases which are withdrawn by line 18, leading to stabilizer tower 19. In stabilizer tower 19 the normally gaseous hydrocarbons undesired in the gasoline are fractionated therefrom and withdrawn by line 20 leading to condenser 21 and receiver 22 wherein the 3 and 4 carbon hydrocarbons are condensed with some ethane and ethylene. Uncondensed gases are discharged by line 23. A portion of the condensate is withdrawn by pump 24 and recycled by line 25 to the upper part of stabilizer 19 as a reflux. The remainder is recycled to the process as hereinafter described. The gasoline produced in the process, now having the desired

initial and final boiling points, is withdrawn by line 26.

Now returning to the conversion chamber 14, a slurry of catalyst is introduced at the upper part thereof by line 27 through which the slurry is forced by pump 28, taking suction on mixer 29. Mixer 29 is supplied by a stream of gas oil through valved line 30 or by a stream of cycle oil to valve line 31 as desired. When employing cycle oil for mixing the slurry I prefer to withdraw it directly from line 17 without cooling, thus providing a slurry which is relatively hot and which therefore produces a minimum amount of cooling in the top of the conversion chamber 14. Catalyst for making slurry is introduced in the form of a powder through hopper 32. The catalyst may be finely divided fuller's earth, bentonite, Attapulgius clay fines, Death Valley clay, etc. and I find that the catalytic activity of some of these clays, for example the bentonite may be considerably increased by initially acid treating them in a manner known to the art. Said treatment may be carried out with phosphoric acid and a small amount of acid may be allowed to remain on the clay which is then dried before mixing with the oil in mixer 29. I may also employ finely divided bauxite, aluminum silicate, boron silicate, etc.

The catalyst slurry which may contain about 25 to 50% of catalyst carried in the oil with which it is mixed is preferably introduced at a higher point in the tower than the point of introduction of the hot gas oil stream from line 13, thus providing a refluxing action and preventing undesirable entrainment of partially cracked products in the vapors discharged through line 15. For this purpose I prefer to employ several bubble plates above the point of admission of the hot gas oil vapors. The slurry of catalyst descends through the tower 14 over the baffle plates therein provided and is intimately contacted with the gas oil, the unvaporized portions of which also flow downward through the tower with the catalyst. The amount of catalyst slurry introduced may be regulated to give the desired ratio of catalyst to hydrocarbons in the conversion zone. Thus I may employ about 5 to 20% by weight of catalyst in most cases.

In the downward passage through the tower the catalyst and oil come in contact with a stream of gas passing upward through the tower from gas inlet line 33. Gas required for the process is obtained partly from external sources and partly by recycling within the system as hereinafter described. Externally provided gas which may suitably consist of the 2, 3, and 4 carbon hydrocarbons is introduced by line 34 and compressor 35 to heater 36 where the temperature is raised to a high temperature, for example to 900, 950, or 1000° F. and even to 1100° F. in some cases. At these temperatures the gas may be partially desaturated in passing through the heater with the result that the gas supplied to the conversion chamber by line 33 contains a considerable proportion of olefins, e. g., about 30 to 50%, and as high as 60% in some cases. Olefins are particularly desired for the process because of the greater facility with which they react with the oil and because of the exothermic nature of this reaction which assists in maintaining the temperature of the conversion chamber within the desired reaction range. The temperature of the gas, however, may be varied to control the degree of evaporation of oil in

the lower part of tower 14, thus making it possible to control the process with a substantially saturated gas if desired.

In addition to external gas from line 34 or, as a substitute therefor, I may also recycle normally gaseous hydrocarbons from receiver 22, employing recycle pump 37 and line 38 for this purpose. As previously indicated, these gases thus recycled comprise mainly the propane, propylene, butanes and butylene constituents of the reaction products which are separated from the gasoline in stabilizer 19.

In order to maintain a maximum temperature in conversion chamber 14 and maintain a liquid phase throughout the chamber as a medium for supporting and transferring the dispersed catalyst I prefer to employ a high pressure in the system. The high pressure is also advantageous in operating the fractionating tower 16 and stabilizer 19, although the pressure maintained in towers 16 and 19 may suitably be reduced below the pressure of the conversion chamber by pressure reducing valve 39 in line 15. I prefer to maintain a pressure in chamber 14 of only slightly below the critical pressure of the heavy oil withdrawn at the base thereof. Thus I may suitably employ pressures of 500 to 1000 lbs. per sq. in. in the chamber 14, although somewhat lower pressures may be employed, for example 200 to 400 lbs. per sq. inch. When lower pressures are employed it is necessary to operate at a correspondingly lower temperature, thus decreasing the conversion rate and reducing the capacity of the unit. I prefer to employ pressures of the order of 200 to 400 lbs. per sq. in. in fractionator tower 16 and stabilizer 19. The oil withdrawn from the base of the tower is comprised principally of high boiling asphaltic reaction products of the process, together with some gas oil dissolved therein. It is withdrawn by line 40 and forced through filter 41 wherein the oil is removed from the catalyst, the catalyst being discharged by conveyor 42 and the oil by line 43 leading to tar flash chamber 44. The pressure having been reduced in filter 41 and valve 45, distillate is removed from the tar in 44 by line 46 leading to condenser 47 and receiver 48. I may also employ subatmospheric pressures on tar chamber 44 to increase the recovery of hydrocarbons from the tar and reduce the tar gravity. The products thus separated may be conducted by pump 49 and line 50 to fractionating tower 16, previously described. Tar is withdrawn from the base of tower 44 by line 51. The catalyst which is withdrawn from the filter 41 by conveyor 42 is preferably conducted to a reburning furnace (not shown) wherein the carbonaceous matter with which it is impregnated is destroyed, leaving the catalyst in an active condition for reuse in the process.

One of the unique advantages of my process arising from the countercurrent treatment of the gas oil and gas is the greater conversion of gases, especially the saturated gases. Fresh catalyst contacts the gases as they are leaving the conversion zone, thus exerting the maximum action thereon. Later, when the catalyst is becoming exhausted, it contacts the more unsaturated and hotter gases, all in the presence of heavy oil, thereby obtaining maximum catalyst utilization.

Although I have described my process with respect to a specific example thereof, I intend that it be limited only by the following claims.

I claim:

1. The process of simultaneously converting heavy hydrocarbon oils and normally gaseous hydrocarbons into gasoline, which comprises heating the heavy hydrocarbon oil to a cracking temperature, introducing the heated oil into the upper part of an elongated, vertically disposed conversion zone, introducing a dispersed contact catalyst solid at the temperature employed into the heated oil near the point of introduction into said zone, allowing the catalyst and heated oil to mingle and descend through said conversion zone, heating said hydrocarbon gas above said cracking temperature and introducing it into the lower part of said conversion zone, regulating temperature and pressure to maintain said oil in the liquid phase and effecting a conversion reaction between said heated hydrocarbon gas and said oil counterflowing in said conversion zone in contact with said catalyst whereby a high knock rating gasoline is produced.

2. In the process of claim 1 withdrawing the reaction products formed within said conversion zone and fractionating them to separate therefrom gas, gasoline and heavier cycle oil, heating said cycle oil and returning it to the upper portion of said conversion zone, condensing a portion of the gas under pressure, heating said condensed portion above said cracking temperature and returning it to the lower part of said conversion zone and withdrawing gasoline from the process.

3. The process of claim 1 wherein the oil descending in the conversion zone with the catalyst is largely but not entirely evaporated by the hot gas introduced therein and the catalyst suspended in unevaporated asphalt is withdrawn from the conversion zone, is filtered to remove the catalyst from the asphalt and the resulting catalyst-free asphalt is evaporated to recover a distillate and said distillate is returned to the conversion system.

4. The process of continuously converting heavy hydrocarbon oils and gases to gasoline without the necessity of periodically stopping the process to remove coke from the reaction vessels, which comprises countercurrently flowing in a vertical elongated reaction zone, streams of said oil and said gas heated to a conversion temperature and simultaneously introducing a dispersed contact catalyst solid at the temperature employed into said oil stream in said reaction zone to accelerate the rate of reaction between said gas and said oil and to adsorb carbonaceous products formed in said reaction, regulating the temperature and pressure to maintain a liquid phase in said reaction zone, and continuously removing said catalyst and adsorbed products from the reaction zone.

5. The process of converting hydrocarbon gases and heavy oils to gasoline which comprises subjecting the said hydrocarbon gases to a high temperature sufficient to convert saturated constituents thereof into olefins, subjecting a heavy oil to a cracking temperature and partly converting

it into gasoline, unsaturated gases and high boiling asphaltic products, introducing said heated oil and a dispersed contact catalyst solid at the temperature employed into the upper section of a contact conversion zone, introducing said heated gas into the lower section of said contact conversion zone, passing said gas upward through said contact conversion zone in countercurrent contact with said oil and catalyst whereby said gas is caused to react with said oil to produce gasoline, withdrawing the vapors of gasoline and said gas from the upper section of said contact conversion zone, subjecting said vapors to fractionation to produce gas, gasoline and heavy recycle oil, recycling said heavy recycle oil and said gas to said contact conversion zone, and withdrawing a slurry of said asphaltic products and spent catalyst from the lower section of said contact conversion zone.

6. The process of claim 5 wherein the spent catalyst is separated from the asphaltic products and thereafter revived and recycled to the process.

7. In the process of converting a heavy hydrocarbon oil to gasoline by contacting it at a high conversion temperature with a finely divided contact catalyst solid at the temperature employed wherein the heat required for the reaction is introduced into the oil prior to contact with the catalyst and the reaction mixture suffers an undesirable loss in temperature because of the endothermic nature of the cracking reaction, the improvement comprising heating said heavy hydrocarbon oil and introducing it into a conversion zone, introducing a stream of finely divided catalyst into said zone at a point near the point of introduction of said oil, and maintaining the desired conversion temperature by introducing a stream of heated unsaturated hydrocarbon gas to flow countercurrent to said reaction mixture at a high pressure whereby the hydrocarbon gas is caused to react exothermically with the oil in the presence of said catalyst.

8. The process of converting a heavy hydrocarbon oil into high knock rating gasoline by heating at elevated temperatures and in the presence of catalysts, comprising heating said oil to cracking temperature and passing it downward through an elongated reaction zone concurrently and in intimate contact with a finely divided catalyst which is solid at the reaction temperature employed, passing an unsaturated hydrocarbon gas upward through said reaction zone regulating temperature and pressure to maintain a liquid phase in said reaction zone and supplying sufficient heat to said gas prior to its introduction to said reaction zone to maintain the desired cracking temperature therein.

9. The process of claim 8 wherein the temperature and amount of said gas introduced into said reaction zone are controlled to prevent complete vaporization of said oil in said reaction zone.

10. The process of claim 9 wherein said reaction zone is maintained under a pressure of about 200 to about 1000 lbs. per square inch.

JESSE RUSSELL WILSON.

CERTIFICATE OF CORRECTION.

Patent No. 2,249,924.

July 22, 1941.

JESSE RUSSELL WILSON.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 3, second column, line 63, claim 10, for the claim reference numeral "9" read --8--; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office..

Signed and sealed this 2nd day of September, A. D. 1941.

(Seal)

Henry Van Arsdale,
Acting Commissioner of Patents.