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SUPPRESSING GAS PRODUCTION IN THE VAPOR PHASE CONVERSION OF HYDROCARBONS

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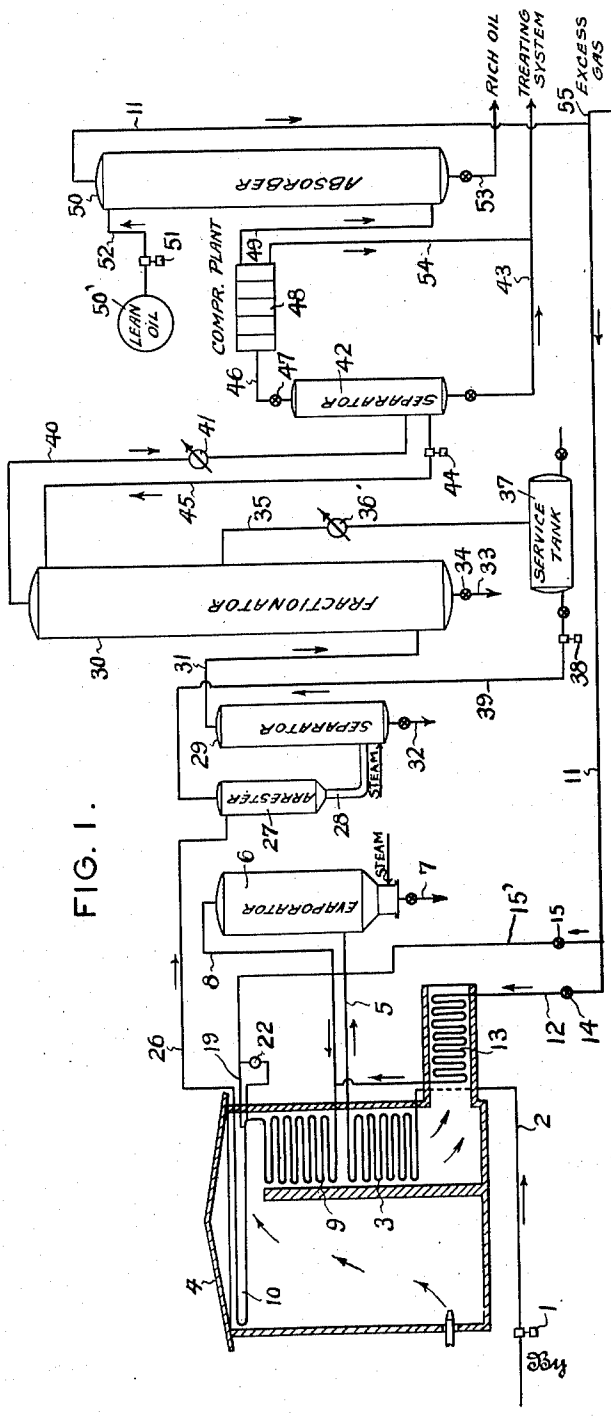


FIG. 1.

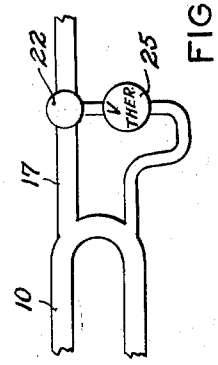


FIG. 3.

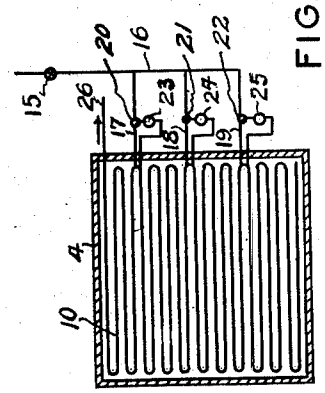


FIG. 2.

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SUPPRESSING GAS PRODUCTION IN THE VAPOR PHASE CONVERSION OF HYDROCARBONS

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2 Claims. (Cl. 196—61)

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This invention relates to the conversion of hydrocarbons in the vapor phase, and more particularly to the conversion of heavier hydrocarbons into lighter products within the motor fuel boiling range. It also relates to the conversion or reforming of light virgin hydrocarbons of low octane rating into other hydrocarbons of high octane rating, without materially changing the boiling points of the material under treatment.

This invention is directed particularly to the pyrolytic decomposition of hydrocarbons under mass reaction conditions, the decomposition being effected in a manner retarding or inhibiting the excessive production of fixed gases which usually accompanies high temperature operations of this character. It also is directed to the maintenance of substantially constant temperature conditions in the decomposition zone during the reaction period, and the avoidance of high peak temperatures which contribute materially to excessive gas production.

Vapor phase cracking has always been associated with high gas production because of the absence of effective means of controlling the conditions which promote the formation of gaseous hydrocarbons; such, for example, as progressively rising temperatures throughout the conversion zone, culminating in high peak temperatures which promote the formation of gaseous fractions rather than low-boiling liquid hydrocarbons; or the current removal of gaseous fractions from the reaction zone without their replacement by products of a similar character which, according to the principles of mass reaction, suppress the further formation of such gaseous fractions.

There is always a tendency in the reaction zone toward the establishment of an equilibrium between the gaseous and the heavier vaporous hydrocarbons present, which is maintained at a substantially constant level as a result of the decomposition and polymerization reactions which proceed concurrently throughout the reaction period. If this equilibrium becomes unbalanced by the removal of either the gaseous or vaporous fractions beyond their normal production under established operating conditions, the further tendency is toward an increased production of the removed fraction in order to reestablish the equilibrium. And conversely, if either of such fractions is introduced into the reaction zone from an extraneous source, the equilibrium is maintained only through the suppressed production of the compounds corresponding to the added fraction. This principle is applicable to all thermal cracking operations, and it is particularly adaptable to vapor phase cracking because of the normally high operating temperatures which are conducive to the formation of gaseous hydrocarbons. If the added fraction is of the gaseous variety, the yield of motor fuel fractions is increased since the overall degree of conversion remains substantially unchanged.

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In order to suppress the production of fixed gas, an excess of such gas should be present in the reaction zone. Thus, the production of hydrogen, methane and the C_2 and C_3 compounds may be retarded by introducing an excess of these gases into the reaction zone from an extraneous source. The products of the process itself provides the most suitable source, since the gases may be returned to the reaction zone in the same relative proportions in which they are produced. The C_4 compounds or any portion or fraction thereof may also be handled in a similar manner, if desired, along with the lighter fractions.

It is therefore an object of this invention to provide a method and means whereby all or any part of the fixed gases produced in the process, or gases of a similar nature from any other source, may be admitted to the reaction zone currently for the purpose of suppressing the formation of such gaseous fractions during the decomposition reaction.

It is another object of this invention to provide method and means employing gases of this character for the purpose of checking the progressive rise in temperature in the reaction zone after it has reached the predetermined degree required to effect the desired molecular decomposition of the hydrocarbons under treatment. The gases used in this manner also contribute to suppressing the formation of similar gaseous fractions, but to a lesser degree than the gas specifically used for this purpose because of the shorter time of contact with the decomposition products.

Thus the fixed gas fractions produced in the process, or otherwise obtained, are circulated continuously through the reaction zone, supersaturating the hydrocarbon vapors therewith and inhibiting the production of like gaseous products.

Other objects and advantages of this invention will become apparent to those skilled in the art by reference to the following description of the process and the apparatus or equipment in which

it may be practiced, the same being shown in the accompanying drawing forming a part of this specification, and wherein:

Fig. 1 represents diagrammatically a side elevational view, partly in vertical section, of apparatus and equipment adapted to carrying out this invention;

Fig. 2 is a horizontal sectional view taken through the converter unit and showing the continuous heating element wherein the decomposition of the hydrocarbon charge is effected.

Fig. 3 is a fragmentary view of an automatic valve-control for the conversion zone of the apparatus.

Referring to the drawing, the numeral 1 represents a pump which delivers the raw charging stock through line 2 to a vaporizing coil 3, located preferably in the lower convection section of the furnace 4, wherein the liquid hydrocarbon charge is heated to its vaporization temperature. The vaporized oil then passes through line 5 into an evaporator 6 wherein the vapors are separated from any heavy unvaporized fractions, preferably by the aid of steam introduced into the lower section of the evaporator, the unvaporized fractions being withdrawn from the bottom of the evaporator through the valved line 7 and diverted from the system.

The vapors leaving the top of the evaporator through line 8 then pass to a bank of drying and preheating tubes 9 located in the upper portion of the convection section wherein the vapors are preheated to a temperature at about which incipient cracking begins. The dried and preheated vapors then pass into the cracking or conversion coil 10 where decomposition is effected under the influence of heat, in an atmosphere composed primarily of the so-called "fixed" or "permanent" gases, that is, hydrogen, methane, and the C_2 and C_3 hydrocarbon compounds, either or both the saturated and unsaturated types.

While the fixed gases used for this purpose are produced initially within the system, they are not formed in appreciable amounts as the decomposition reaction proceeds. On the contrary, being introduced into the reaction zone from an extraneous source by mechanical means, they establish a reaction equilibrium with the higher molecular weight decomposition products, which condition inhibits the production of similar light gaseous fractions.

The fixed or permanent gases may be defined as those hydrocarbon fractions which remain in the gaseous phase under standard conditions of temperature and pressure, that is, at 0° C. and 760 mm. of mercury pressure. Such gases are separated advantageously from the heavier decomposition products by well known and generally practiced means, such as compression, cooling, absorption, etc., and are returned under pressure to the zone of decomposition in a continuous cycle through the lines 11 and 12 and the flue gas heat exchanger 13, to the reaction zone, entering the preheating coil 9 along with the vaporized hydrocarbons from the evaporator 6.

It is not to be concluded that the continuous circulation of these extraneous gases throughout the system reduces the motor fuel producing capacity of the equipment, since they occupy only the volumetric space which would otherwise be required in the continuous production of similar gaseous fractions. The gas is circulated through the system virtually in an unchanged condition because of the higher temperatures necessary for its decomposition than those required for the heavier charging stocks. There is, however, a limited production of fixed gases in the decomposition reaction which is evidenced by the necessity of venting a small amount of excess gas from the absorber through the line 55, but it is only a negligible quantity, not to be compared with the total gas production when fixed gas is not recycled through the system. It is difficult, if not impossible, to suppress completely the formation of such gaseous fractions, but the amount is so small that it may be neglected for all intents and purposes.

The gas returning to the system through line 11 is divided into two streams, controlled by valves 14 and 15, respectively, the portion passing through valve 14 being conducted to the heat exchanger 13; while the portion passing through valve 15 is introduced into the cracking coil 10 as a temperature control medium, preferably at a plurality of points as indicated in Fig. 2.

Heretofore vapor phase cracking operations have been conducted under progressively rising temperature conditions throughout the decomposition zone, reaching the maximum temperature only at the end of the reaction period. Such conditions are known to cause overcracking and high gas production in the final stages of the reaction. It is therefore another object of this invention to provide means whereby relatively constant temperatures are maintained in the cracking zone throughout the reaction interval. To this end a portion of the recycle gas is directed through the line 15', controlled by valve 15, to a manifold header 16 which is connected at one or more points with the conversion coil 10. Such connections are shown by the lines 17, 18 and 19, provided with the valves 20, 21 and 22 respectively. These valves may be manually operated or automatically controlled, the controllers 23, 24 and 25 being actuated by temperature sensitive devices inserted into the respective sections of the conversion coil. As the temperatures in the coil exceed the predetermined reaction temperature, the controllers actuate the valves 20, 21 and 22, admitting small quantities of relatively cool recycle gas into the coil as a tempering agent, thereby maintaining a substantially constant temperature throughout the conversion coil.

It is a further object of this invention to combine the aforesaid features of inhibiting the production of fixed gases by continuously circulating gases of a similar character through the reaction zone in sufficient quantities to maintain a reaction equilibrium between the light and heavy decomposition products; and of injecting relatively cool recycle gas into the hydrocarbon vapor stream undergoing decomposition at suitable points and in small but sufficient amounts to arrest the progressively rising temperature, and to maintain a substantially constant temperature level throughout the reaction zone.

Leaving the reaction zone through line 26, the mixture of decomposed hydrocarbon vapors and recycle gas enters a conventional temperature arrester 27 wherein the temperature of the mixture is substantially instantaneously reduced to a degree below that at which further cracking can take place, that is, about 600° F., by direct and intimate contact with a clean, carbon-free cooling agent, preferably produced within the system, which is delivered to the top of the arrester. The mixture of cooled vapors, gas and unvaporized liquid fractions leaving the bottom of the arrester through line 28 then passes into a separator 29 where separation is effected by the aid of steam, the volatile overhead fractions

being conducted to a fractionating column **30** through the line **31**, while the heavy tarry materials, consisting largely of polymers produced in the cracking operation, are withdrawn from the bottom of the separator through the valved line **32** and diverted from the system.

The fractionating column, which is preferably of the bubble tower type, is provided with a suitable number of trays to effect the desired separation between the motor fuel fractions and the heavier products, the latter being withdrawn from the bottom of the tower through the line **33**, controlled by the valve **34**, and further refined for fuel oil or other desired products. This fraction also may be returned to the system for recracking along with the fresh charge, if desired, in order to increase the gasoline yield. Because of its refractory nature, however, this practice is not generally followed, its disposition being subject to market demands.

The fractionating column furnishes a convenient and altogether satisfactory source of supply for the quenching oil used in the temperature arrester. For this purpose a side stream is withdrawn from the mid-section of the tower through the line **35** and cooler **36**, into a service tank **37**, from which it is delivered by pump **38** through the line **39** to the top of the arrester where it contacts the highly heated decomposition products leaving the conversion coil, abruptly checking the decomposition reaction. This oil fraction is admirably suited for the purpose, having a rather narrow range of boiling points and not readily given to vaporization or coking.

The overhead vapors leaving the top of the fractionating column through line **40** pass through the condenser **41** and the products are collected in a gas-liquid separator **42** from the bottom of which the raw motor fuel is withdrawn through the valved line **43** and sent to the treating and finishing system (not shown). A portion of the condensate is returned to the top of the fractionator by pump **44** through the line **45** as a temperature-control refluxing medium.

The relatively wet gaseous fractions leaving the top of the separator through line **46**, controlled by valve **47**, are sent to a compression plant **48**, operated preferably in a plurality of successively higher compression states, with intermediate cooling between the individual stages, for the recovery of the higher molecular weight liquefiable fractions, the uncondensed gas leaving the compressors through the line **49**. This gas is then sent to an absorption tower **50**, also preferably of the bubble tower type, which is maintained at approximately the same pressure as that employed in the last and highest compression stage, usually between 250 and 450 pounds per square inch gage. The gas entering the bottom of the absorber still contains some C_4 and higher fractions which are largely removed as it flows upwardly through the tower in counter-current direction to a descending absorption medium, such as heavy naphtha or a light gas oil, which is delivered to the top of the absorber from the lean oil tank **50'** by the pump **51** through the line **52**. The rich oil leaving the bottom of the absorber through the valved line **53** is then processed for the recovery of the motor fuel fractions, the lean oil being returned to the tank **50'** for reuse.

The now comparatively dry gas leaving the top of the absorber through the line **11** is returned to the system under its own pressure for the above recited purposes, while the condensed liquid hydrocarbons leaving the compression plant through the line **54** are sent to the motor fuel treating and finishing system along with the condensate from the separator **42**. The small amount of excess gas formed in the operation is released through the line **55**, usually going to the plant fuel system.

I claim:

1. A process for the vapor phase conversion of relatively high-boiling hydrocarbons into low-boiling hydrocarbons, the steps which comprise: continuously advancing a stream of vaporized hydrocarbons through an elongated conversion zone of restricted cross section disposed in a heat-confining structure, heating the vapors during their passage through said zone by the passage of hot furnace gases thereover to conversion-producing temperatures, fractionating and condensing the products of such conversion to obtain in a separate state gaseous and liquid hydrocarbon fractions, returning a portion at least of said gaseous fraction to said conversion zone for direct admixture with the hydrocarbon vapors passing therethrough, regulating volumetrically the introduction of the gaseous hydrocarbons into admixture with the hydrocarbon vapors in limited amounts sufficient to maintain the hydrocarbon vapors at substantially uniform conversion temperatures during the travel of the vapors throughout the length of said zone in which conversion temperatures are produced.

2. A process for the vapor phase conversion of relatively high-boiling hydrocarbons into low-boiling hydrocarbons, the steps which comprise: passing continuously a stream of vaporized hydrocarbons through an elongated externally heated conversion zone of restricted cross section to bring said vapors to conversion temperatures, fractionating and condensing the products of such conversion following their discharge from said zone to obtain in a separated state low-boiling liquid hydrocarbons suitable for use as motor fuel and a fraction composed of normally gaseous hydrocarbons, returning a portion at least of said gaseous hydrocarbons to said conversion zone, directly introducing said gaseous hydrocarbons into said conversion zone at a plurality of spaced positions in the length of said zone, maintaining the gaseous hydrocarbons at a temperature sufficiently low so that when the same enter into direct admixture with the vapors undergoing conversion in said zone, the said hydrocarbon gases exercise a cooling effect on the vapors to maintain the same at substantially uniform temperatures in which the process produces a maximum yield of low-boiling hydrocarbons of motor fuel boiling range and a minimum of gaseous hydrocarbons.

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