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METHOD FOR PRODUCING MOTOR FUELS

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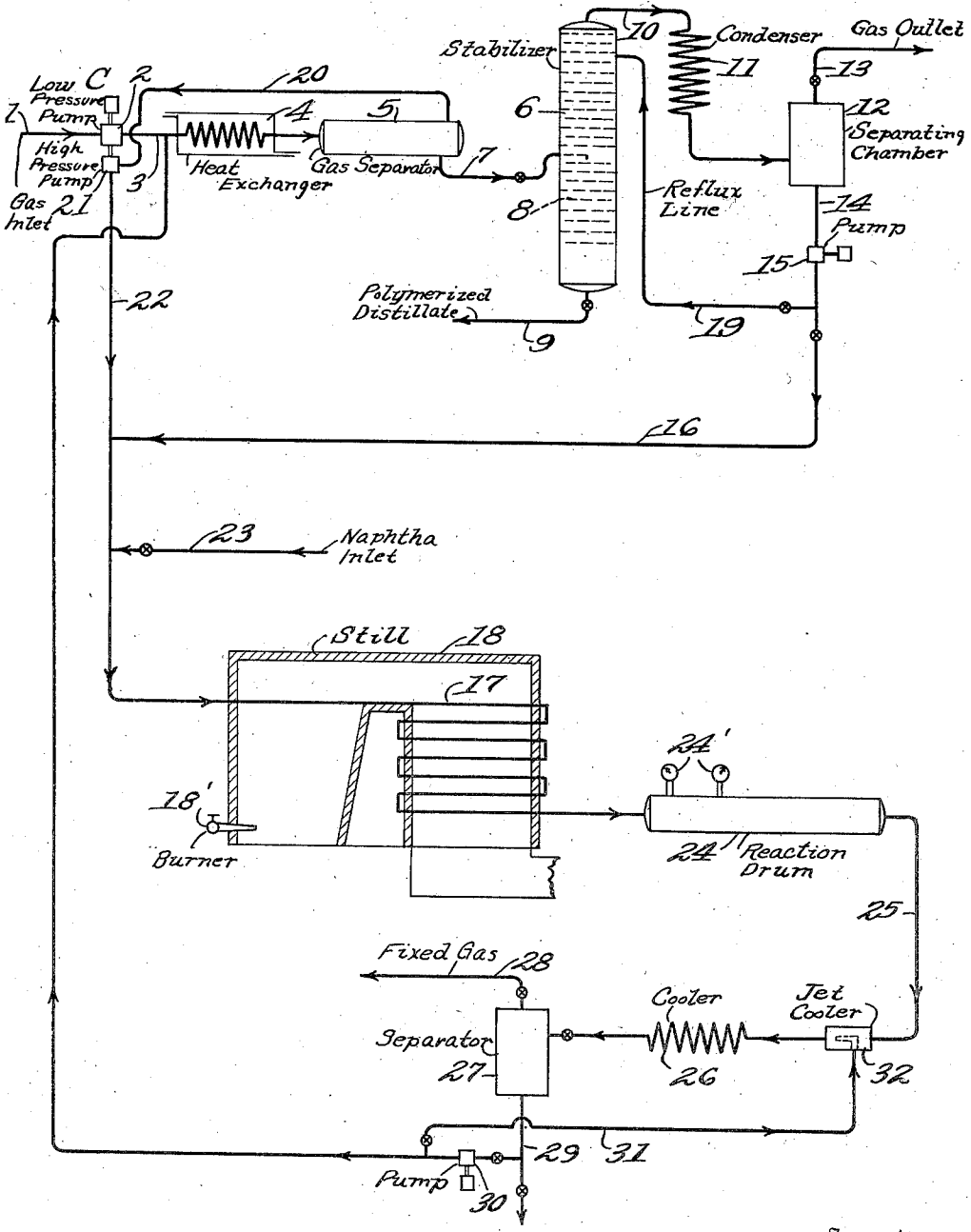

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METHOD FOR PRODUCING MOTOR FUELS

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8 Claims. (Cl. 196—9)

This invention relates to an improved system for producing hydrocarbon motor fuels of the type which contain high percentages of unsaturated hydrocarbons and, more particularly, the invention has to do with the treatment of unsaturated hydrocarbon gases, especially those obtained from vapor phase cracking systems, whereby a large proportion of such gases are, when subjected to controlled conditions of temperature and pressure, transformed into hydrocarbon compounds, liquid at normal temperatures and pressures, and which may be used as improved motor fuels.

This invention is a continuation in part of the disclosures contained in my prior application, Serial No. 573,233 filed Nov. 5, 1931, which has matured into Patent No. 2,088,886, granted August 3, 1937.

It is a primary object of the present invention to subject cracked hydrocarbon gases containing ethylene and its homologues to conditions of elevated temperature and pressure to polymerize such gases, in part, into hydrocarbons of higher molecular weights and to accomplish this result in such manner as to provide for an increased yield of the more valuable liquid products with an accompanying decrease in the unusable permanent gas production.

For a further understanding of the invention, reference is to be had to the following description and the accompanying drawing, wherein:

The figure is a diagrammatic view illustrating the apparatus which may be employed in carrying the present invention into effect.

It will be understood that the apparatus has been but diagrammatically illustrated in order to serve as a flow chart and that the positional order and elevations of the apparatus illustrated is not necessarily that which may be used in commercial operations.

Referring more particularly to the drawing, the charging hydrocarbon gas which may be of an olefinic character and obtained, for example, from the gas separator (not shown) of a vapor phase oil cracking system, is passed under ordinary flowing pressures of the order of 15 pounds through a pipe line 1 for delivery to the low pressure cylinder 2 of a two-stage compressor C. After being compressed in the cylinder 2 to a pressure of the order of 250 pounds per square inch, the gas is forced through a pipe line 3, and a heat exchanger 4 to a gas separator 5. In this separator there takes place the separation of the more readily liquefiable constituents of the charging gas from the remaining compounds which do not form liquids under the pressures specified.

The substantially liquefied compounds are removed from the bottom of the separator 5 and, without any substantial release of pressure thereon, are passed to a stabilizing or fractionating column 6 through the connecting pipe line 7, the latter leading from the bottom of the separator 5 to a point substantially intermediate of the height of the column 6. This column may be provided with the usual internally situated baffles or trays 8, or other standard liquid and vapor contact means, whereby low boiling compounds entrained in the oils delivered to the column 6, and present as vapors, may be brought into intimate counter-current contact with the higher boiling liquid compounds. Those compounds which accumulate in the bottom of the column 6 as stabilized liquids are withdrawn either continuously or intermittently through the valved draw-off line 9 and possess the boiling range of gasoline. These oils may be referred to as the polymerized distillate and due to the high percentage of unsaturated hydrocarbons which they contain, may be used directly as an anti-knock motor fuel, or as a blending oil for increasing the anti-detonating value of a lower grade motor fuel oil.

The remaining vapors or gases are withdrawn from adjacent the top of the column 6 and are passed through a pipe line 10 to a suitable condenser 11, and thence to a separating chamber 12 in which a variable pressure usually not in excess of 250 pounds is maintained. Permanent gas is removed from the top of the chamber 12 through the valved gas outlet line 13, while the condenser cooled liquid fraction is withdrawn from the bottom of said chamber through the pipe line 14 and delivered to the suction side of a pump 15. A pipe line 16 leads from the outlet side of said pump to a heating coil 17 located in a pipe still 18, the latter being provided with the customary burners 18'. Also leading from the pipe line 16 is a branch 19, which extends to the top of the column 6 to provide for the passage of a reflux oil downwardly through said column to control the fractionation taking place therein.

The gases removed from the primary separator 5 by way of the top line 20 are passed to the high pressure cylinder 21 of the compressor C, wherein the pressure of the gas is increased from approximately 250 pounds to a considerably higher pressure of the order of 500 to 2000 pounds per square inch, and under this latter pressure, the gases are delivered to the line 16 leading to the

heating coil 17, a connecting pipe line 22 being employed for this purpose.

Naphtha obtained from topping plants or the like may be introduced into the system by way of the lines 16 or 23 for reforming purposes. I have found that the conditions of temperature and pressure which obtain in the coil 17 for gas polymerization purposes are well suited for the reforming of naphtha into a low boiling motor fuel oil containing high percentages of unsaturates. Thus the general utility of the present system is materially increased by its ability to reform naphtha without requiring additional refinery equipment for effecting this increasingly important operation. In the coil 17, the gases alone, or a mixture of the gases and liquids, are heated to temperatures of the order of 850° F. to 1100° F. while maintained under superatmospheric pressures varying between 500 to 2000 pounds per square inch. The system operates quite satisfactorily, however, when the products discharged from the coil 17 possess a temperature of the order of 950° F. to 1000° F. and a pressure of about 700 pounds.

These products are then transferred to an externally disposed reaction drum 24, which is preferably unheated from external sources, although the metallic drum may be covered by a suitable heat insulating material if desired. The drum 24 may be lined with silica or ganister, if desired, to avoid catalytic dehydrogenation in some cases. Since the polymerizing reactions which are effected in the zone 24 are highly exothermic in character, care must be exercised to prevent the reaction compounds from attaining undesirably high temperatures, such as 1100° F. to 1200° F., since such high temperatures tend to crack or decompose the compounds, thereby causing excessive fixed gas formation and marked reduction in the recovery of the desired liquid products and also undesirable coke formation. Suitable pressure and temperature recording instruments 24' may be employed in connection with the reaction drum, as in other parts of the system, to enable an operator to exercise accurate control over the functioning thereof. The temperature of the products within said drum is preferably maintained at substantially 950° F. to 1025° F., together with pressures of the order of 600 pounds per square inch.

Further, regulation of the temperature in the polymerization zone, which includes the reaction drum 24 may be effected by regulating the introduction of naphtha into the polymerizing zone. Thus naphtha may be added in such quantities so that the endothermic heat of the reactions involved in cracking or reforming naphtha approximately balances the exothermic heat produced by the polymerizing of olefins. In this manner effective control of reaction-producing temperatures in the polymerizing zone is obtained.

Following the completion of the desired reactions in the drum 24, the heated products are then passed through a pipe line 25 to a cooler or heat exchanger 26 and thence to a final separator 27. This separator is maintained under a variable pressure, but usually one of the order of 450 pounds. The fixed gas may be withdrawn from the separator 27 by way of the overhead valved line 28 and removed from the system for storage or other suitable use, while the liquid fraction is withdrawn from the bottom of the separator and transferred by way of the pipe line 29, containing the pump 30, and delivered to the pipe line 3 for passage through the heat exchanger 4, the gas separator 5 and the stabilizing column 6. A branch pipe line 31 may be employed to divert a part of the liquid passing through the line 29 to a jet cooler 32 disposed in the pipe line 25 at the outlet of the reaction drum 24, whereby accurate control is obtained of the temperature of the products delivered to the separator 27, insuring condensation of all normal liquid-like products together with minimum formation of carbon deposit, the products discharged from the drum 24 being shock chilled to non-reacting temperatures in a very short interval of time.

The present system provides for a very high recovery of liquid oils of motor fuel boiling range from cracked refinery gases or other olefine-containing gases. It will be noted that waste or fixed gas may be withdrawn optionally through the lines 13 and 28, insuring a complete elimination of those gaseous compounds which do not polymerize and, conversely, the system provides for the subjection in a sustained manner of all hydrocarbons which under the conditions of temperature and pressure specified tend to polymerize into higher boiling hydrocarbons, thus effecting the formation and recovery of a maximum quantity of liquid oils or motor fuels from a given amount of charging gas.

What is claimed is:

1. In a process of producing motor fuel of high anti-knock rating which comprises mixing gas having an olefin content sufficiently high to react exothermically with rise in temperature and a hydrocarbon oil which reacts endothermically under the conditions to which the mixture is subjected, heating the mixture to a temperature of the order of 850° to 1100° F. under pressures of from 500 to 2000 pounds per square inch, and maintaining the mixture within the reacting temperature range for a period of time sufficient to bring about the desired conversion, the step which consists in proportioning the gas and oil in such quantities that the heat liberated by the reaction of the gas is substantially balanced by the heat absorbed by the reaction of the oil.

2. In a process of simultaneously reforming naphtha and polymerizing olefin containing gases to liquid hydrocarbons which comprises heating a mixture of said gases and naphtha in a restricted stream sufficient to enable the mixture to attain a temperature of from 850° to 1100° F. under a pressure above 500 pounds per square inch but not substantially in excess of 2000 pounds per square inch, passing the heated mixture into an enlarged reaction zone without substantial reduction in pressure, and maintaining said mixture in said zone for a period of time sufficient to convert a substantial portion of olefinic gases to liquid hydrocarbons of gasoline boiling range, the step which consists in proportioning the gases and naphtha in the mixed stream subjected to heating and polymerization in such quantities that the heat evolved by the exothermic polymerization of the gases substantially balances the heat absorbed by the endothermic reforming of the naphtha.

3. In a process for simultaneously reforming naphtha and polymerizing olefin containing gases to liquid hydrocarbons which comprises heating a mixture of said gases and naphtha in a restricted stream, and passing the heated mixture into an enlarged reaction zone wherein the mixture is maintained under pressures of from 500 to 2000 pounds per square inch and at temperatures of 850° to 1100° F. for a period of time

sufficient to convert a substantial portion of olefinic gases to liquid hydrocarbons of gasoline boiling range, the step which consists in adding additional quantities of naphtha to the reaction zone in such amounts that the heat absorbed by the endothermic reaction of the naphtha will substantially balance the heat liberated by the exothermic reaction of the gases.

4. The process for converting olefinic gaseous hydrocarbons to normally liquid hydrocarbons which comprises heating said gases to a temperature sufficient to initiate exothermic polymerization of the gases while maintained under super-atmospheric pressure, maintaining the heated gases in a polymerization zone under temperatures and pressures sufficient to convert a substantial portion of the gases to normally liquid hydrocarbons, and regulating the temperature in the polymerization zone by introducing naphtha therein in such quantities that the heat absorbed by the reaction of the naphtha substantially balances the heat liberated by the reaction of the gases.

5. Process in accordance with claim 4 in which a temperature of 850° to 1100° F. and a pressure of 500 to 2000 pounds per square inch are maintained in the polymerization zone.

6. In a process of simultaneously polymerizing hydrocarbon gases rich in olefines and reforming naphtha which comprises heating and compressing a mixture of said gases and naphtha to temperatures and pressures respectively, suitable for polymerization of said gases and maintaining the mixture at such temperatures and pressures for a period of time sufficient to convert a substantial portion of said gases to liquid hydrocarbons, the step which consists in proportioning the gases and naphtha in the mixed stream subjected to heating and polymerization in such quantities that the heat evolved by the exothermic polymerization of the gases substantially balances the heat absorbed by the endothermic reforming of the naphtha.

7. The process of simultaneously polymerizing hydrocarbon gases rich in olefins and reforming hydrocarbon oil which comprises heating a mixture of said gases and hydrocarbon oil under high superatmospheric pressure to a temperature suitable for polymerization of said gases, maintaining the mixture in an unheated polymerization zone at such temperature and pressure for a period of time sufficient to convert a substantial portion of said gases to liquid hydrocarbons, and adding further quantities of hydrocarbon oil to the reaction products in the reaction zone in amounts sufficient to prevent excessive temperature rise but in insufficient amounts to effect material lowering of the temperature.

8. The process of simultaneously polymerizing hydrocarbon gases rich in olefins and reforming naphtha which comprises heating a mixture of said gases and naphtha under high super-atmospheric pressure to a temperature suitable for polymerization of said gases, maintaining the mixture in an unheated polymerization zone at such temperature and pressure for a period of time sufficient to convert a substantial portion of said gases to liquid hydrocarbons, and adding further quantities of naphtha to the reaction products in the reaction zone in amounts sufficient to prevent excessive temperature rise but in insufficient amounts to effect material lowering of the temperature.

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