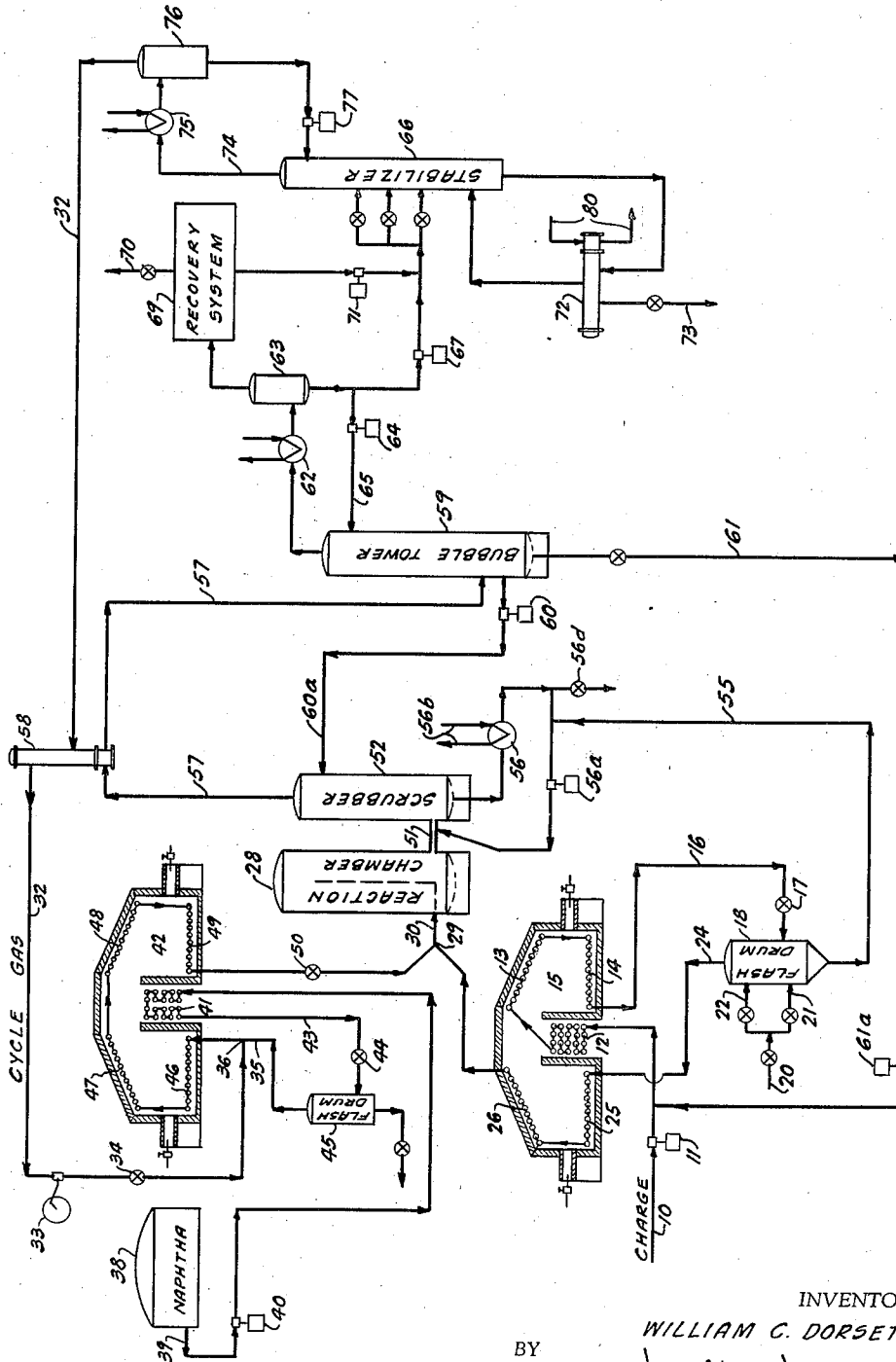


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INVENTOR.
WILLIAM C. DORSETT
Virgil E. Woodcock
ATTORNEY.

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2,296,601

CRACKING AND REFORMING SYSTEM

William C. Dorsett, Elizabeth, N. J., assignor to
Petroleum Conversion Corporation, Elizabeth,
N. J., a corporation of Delaware

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7 Claims. (Cl. 196—66)

My invention relates to improvements in processes of cracking hydrocarbon oils into compounds or products suitable as motor fuels and to reforming naphtha or straight run gasoline, and has for an object the provision of a process in which both the cracking and reforming may be accomplished without imposing a materially greater heat load than has heretofore been required for the cracking operation alone.

It has been previously proposed, Sachs Patents #2,016,297 and #2,073,456, to mix a light hydrocarbon such as naphtha with a heavier hydrocarbon such as gas oil, and after separating and heating a vapor stream derived therefrom, to crack it by adding a heat-carrier gas thereto, the reaction time being provided by a reaction chamber. While such systems are operative, they leave something to be desired, since there is a compromise between the conditions for optimum reformation of the lighter hydrocarbons and the conditions for optimum simultaneous cracking of the heavier hydrocarbons.

In accord with the disclosure of Colony Patent #2,107,235, a substantial part of the gas made during the cracking operation is returned to a flash drum and a mixture of vapors and gas therefrom subjected to a cracking temperature in a heating coil disposed in a furnace. A process of this kind does not take advantage of the unusual and phenomenal cracking operation which results from the use of a hydrocarbon heat-carrier gas suddenly to elevate the hydrocarbon vapors to cracking temperature.

In accordance with my invention in one form thereof, I have found that a very high yield and a greater over-all efficiency of the system may be obtained by reforming naphtha or straight run gasoline in admixture with the heat-carrier gas; the mixture then serving as the heat-carrier for the cracking of a stream of heavier hydrocarbons. Important to the foregoing is the relatively accurate control of the time of reaction for the reformation of the naphtha or straight run gasoline, which is relatively short, since the mixture of carrier gas and naphtha is heated to a temperature of between 1060° F. and 1200° F., and due to the further fact that the reforming is accomplished by the actual cracking of only about 20% of the naphtha or straight run gasoline to impart to it greatly increased and high anti-knock characteristics, for example by increasing from about 40 the octane number to 70 to 80, or higher, 1939 research method.

Further in accord with my invention, I prefer to utilize the foregoing heat-carrier and reformed

naphtha to effect the rapid vapor phase cracking of a stream of heavier hydrocarbons whose optimum cracking temperature is short of or below the active reforming temperature of the naphtha or straight run gasoline; wherefore, the concurrent heating of the heavier hydrocarbons and the cooling of the naphtha serves substantially to terminate the active reforming reaction, and from practical considerations it is terminated.

In addition to the foregoing, the commingling of the reformed naphtha with the heavier hydrocarbons is advantageous since constituents of both the cycle gas and of the naphtha vapors are in a nascent state, and in a condition readily to combine with certain of the heated heavier vapors to form compounds valuable to, and within the boiling range of those forming the end product of gasoline. Thus in accord with my invention, advantages are achieved which are not obtained by separate treatment of the two charging stocks.

For a more complete understanding of my invention reference should now be had to the drawing in which I have diagrammatically illustrated a system embodying a preferred form of my invention, single lines for the most part indicating the connecting pipe lines.

Referring to the drawing, I have shown my invention in one form as applied to a cracking process in which a charge, such for example as gas oil, enters through supply line 10 and by pump 11 is forced through a convection bank 12 and roof and floor tubes 13 and 14 of a double-end fired heater 15, and by transfer line 16, under the control of pressure regulating valve 17, is discharged into a flash drum 18. To assist in vaporizing the hydrocarbons, a heated flash gas, preferably comprising hydrocarbon compounds, chiefly consisting of those having less than three carbon atoms per molecule, is introduced through supply line 20 and line 21 into the lower part of the flash drum and by line 22 to the upper part of the flash drum, the gas entering through the line 22 serving to dry the vapors withdrawn through an overhead outlet line 24. The derived stream of vapors then passes through a bank of floor tubes 25 and a bank of roof tubes 26, located in the double-end fired heater 15, and in which the vapors are superheated to within or just below the range of their cracking temperature, but during a time interval insufficient for material cracking to occur. Material cracking of these superheated vapors occurs within a reaction chamber 28 due to admixture with a highly heated heat-

carrier introduced at the mix point 29 of transfer line 30.

The heat-carrier or cycle gas is preferably derived from the gas made in the cracking system, and in the illustrated embodiment of my invention, a gas consisting chiefly of hydrocarbon compounds having between three to five carbon atoms per molecule is supplied by line 32 to a compressor 33 which, under the control of valve 34, discharges the gas into a line 35 at a mix point 36.

In accord with my invention, naphtha, or straight run gasoline, whose anti-knock characteristics are to be increased by reforming, is supplied from any suitable source, as for example storage tank 38 by line 39, pump 40 to the convection bank 41 of a double-end fired heater 42, the stream passing by way of line 43, under the control of valve 44, to a flash drum 45. The overhead stream of vapors from the flash drum mixes with the cycle gas at the point 36, and the mixture then passes through floor tubes 46, roof tubes 47, roof tubes 48, and floor tubes 49 of the heater 42. During its passage through the tubes of the heater 42, the stream is elevated in temperature to between 1060° and 1200°, the exact temperature depending upon the characteristics of the particular naphtha or straight run gasoline to be reformed, and upon the optimum temperature requirements for the cracking of the heavier hydrocarbon vapor stream which is superheated in the heater 15.

For a given temperature, it is highly desirable, if not necessary for good results, reasonably accurately to control the time of active reforming of the naphtha or straight run gasoline. In accord with my invention, this time may be precisely controlled by quantitatively regulating the ratio of naphtha to the cycle or heat-carrier gas. For example, by increasing the ratio of naphtha to gas during its passage through the heating coils 46-49, while maintaining constant the total quantity (by weight) of the gas-naphtha mixture, it is possible to increase the effective time of reformation for the naphtha while at the same time maintaining substantially unchanged the heat delivery from the cycle gas and naphtha to the heavier vapors to be cracked, such as those withdrawn from the flash drum 18 by way of line 24. Conversely by decreasing the ratio of naphtha to gas, the time of reformation for the naphtha may be decreased. The ratio is readily controlled by adjustment of valves 17 and 44 and/or the speeds of pumps 11, 40 and 61a.

Preferably, the mixture of naphtha and cycle gas during its passage through floor and roof tube banks 46 and 47 is elevated to approximately the optimum reforming temperature for the naphtha. During its subsequent passage through the roof and floor tube banks 48 and 49, this active reforming temperature is maintained, and preferably not materially increased, to provide both a "soaking" time and to supply the heat of reaction, which reaction is decidedly endothermic. In consequence, the reformed naphtha or straight run gasoline, herein generically designated as light hydrocarbons, may be delivered to the mix point 29, under the control of valve 50, at a temperature not greatly below, and preferably the same as, the active reforming temperature, in contrast with prior suggested schemes in which the endothermic characteristic of the cracking reaction produces a material drop in temperature.

At the mix point 29, the superheated stream of heavier hydrocarbons is commingled with the high temperature stream of heat-carrier gas and the reformed lighter hydrocarbons, the effect of which is to elevate suddenly and substantially instantaneously the temperature of the superheated heavier vapors to within the range of their active cracking temperature, and quite as suddenly and effectively to decrease the temperature of the lighter hydrocarbons to below their active reforming temperature. The mixture then passes by way of the transfer line 30 into the reaction chamber 28, where a sufficient time interval is provided for the substantial completion of the cracking reaction for the heavier hydrocarbons.

It is to be understood that the character of the gas may be varied and while I prefer to use gas which is rich in or contains a substantial percentage of C₃ and C₄ compounds, a gas composed chiefly of lighter compounds may be utilized. In the following example I have selected by way of example and not by way of limitation, a gas consisting of hydrogen, methane, ethane, propane, and butane along with the corresponding unsaturates, and having a molecular weight of about 30, and a naphtha consisting of a fraction boiling between 200 and 300° F., and having a molecular weight of about 120.

With the foregoing materials a given quantity, by weight, of the naphtha vapor will occupy approximately 25% of the volume of an equal quantity, by weight, of gas displaced by it. It will now be assumed that the normal quantity of cycle gas required for the heating of 27,000 lbs. per hour of the heavy vapor to its active cracking temperature is 4,200 lbs. per hour. Therefore, on the basis of the gas alone, this would mean 53,200 cubic feet per hour for the total volume of the gas at the assumed standard conditions of 60° F. and atmospheric pressure. In accordance with my invention instead of relying entirely upon the gas for the supply of heat for the heavy vapors, it will be assumed that 25% by weight of naphtha vapor is commingled with 75% by weight of the cycle gas to supply the aforesaid needed 4,200 pounds per hour of heat-carrier medium. In consequence, there would be supplied to the heating coils 46-49 40,000 cubic feet per hour of gas and 3,300 cubic feet per hour of naphtha vapors, or a total of 43,300 cubic feet per hour of the mixture. This total corresponds to approximately 81 per cent of the original volume of 53,200 cubic feet per hour of needed cycle gas. Stated differently, with the quantity or weight per hour of the total heat carrier remaining the same, the naphtha would remain within the heating coils 46-49 during a time interval approximately 12.3 per cent longer than the time interval required for the passage of the same total weight of cycle gas through the coils. Obviously by further decreasing the proportion of naphtha to gas the time interval of reformation is decreased. By further increasing the ratio of the naphtha to the gas the time interval may be further increased.

It is therefore seen that my system provides great flexibility in operation, and that the reformation time may be readily and accurately controlled within fairly wide limits while at the same time there is maintained constant the desired total quantity of heat-carrier delivered from the coil 49 for mixture with the heavy vapors in transfer line 30. Obviously, further adjustments may be readily made to compensate for the dif-

ferences in the specific heats of the naphtha and the gas, as by increasing or decreasing the generation of heat within heater 42; and added heat may be supplied in this manner to compensate for the endothermic character of the reaction.

It is well known that temperature and time are important factors in considering the thermally induced cracking of the hydrocarbons. In the event it is necessary or desirable to crack the heavier vapors at a higher temperature to change the degree or depth of cracking, it is only necessary to fire the heater 42 at a higher rate to increase the outlet or discharge temperature of the heat-carrier and concurrently to decrease the ratio of naphtha to the cycle gas, correspondingly to decrease the time of reformation and thereby compensate for the increased temperature. Thus, I provide for such a nicety of operation that the time and temperature for both the light and heavy hydrocarbons may be maintained at an optimum without departure of either from their optimum conditions.

It is to be further observed that the quantity of heat supplied by the heat-carrier may be maintained constant even if the quantity, in pounds, of either should be changed. If the quantity is decreased, the outlet temperature may be increased, with the foregoing compensation made for the reforming operation, and vice versa. Stated differently, my invention is not alone concerned with concurrent cracking of heavier vapors and the reforming of light vapors, but it is directed towards the achievement of optimum conditions of time and temperature for both the light and heavy streams of hydrocarbons and controllable for widely varying conditions and a relatively wide range of charging stocks.

From the reaction chamber 28, preferably operated at around 110 pounds per square inch gauge, the reaction products and heat-carrier gas are discharged through transfer line 51 into the lower part of a scrubber 52, which is preferably provided with a number of bubble caps and trays (not shown) in its upper portion and several baffles (not shown) in the lower part thereof. The reaction products are scrubbed by a relatively large volume of scrubbing medium comprising the residual oil from the flash drum 18, which through line 55 mixes with the residuum from the bottom of the scrubber 52 which may be cooled at 56, and by pump 56a forced into the transfer line 51 for intimate mixture with the reaction products. For example I have shown the cooler 56 as provided with lines or pipes 56b for the circulation of a cooling medium, for simplicity shown as water, although a heat exchanger would ordinarily be provided to elevate the temperature of the charge 10, or of the naphtha, or for other useful heating purposes in the system. Residuum may also be withdrawn from the system under the control of valve 56d.

A vaporous overhead stream is taken from the scrubber 52 by way of line 57, heat exchanger 58 included in the line 32 for the cycle gas, and discharged into the lower portion of a bubble tower or fractionator 59. A relatively heavy fraction, such as gas oil, may be taken from the lower part of the bubble tower and by pump 60 and line 60a introduced into the upper part of the scrubber 52 as reflux therefor. The bottoms from the bubble tower pass by way of line 61 and pump 61a into the charging line 10 and comprise the recycle stock for the system. The overhead stream of vapors from the bubble tower 59 is reduced in temperature by a suitable heat ex-

changer or a cooler 62, and resulting condensate is collected in an accumulator or storage vessel 63. Part of the condensate is returned by pump 64 and line 65 to the bubble tower as reflux therefor, the remaining part of the condensate being introduced into a stabilizer 66 by means of a pump 67.

Because the gases and vapors which are not condensed in the accumulator 63 contain constituents desirable in the final product of motor fuel, such lighter constituents are removed from the top of the accumulator 63 and sent to a recovery system designated at 69. The system 69 may be of any conventional type, such as an absorption system, in which the gases are contacted with an absorbing menstruum to remove desirable constituents; or it may comprise a compressor system in which the gases are compressed and cooled and the desirable constituents recovered as a condensate. In either case light gases, including hydrocarbon compounds of less than about three carbon atoms per molecule are discharged from the recover system by a line 70. These gases are known in the art as the make gas, and may form the chief supply for the flash gas which is heated and introduced by the line 20 into the flash drum 18. The desirable constituents recovered from the system 69 are introduced by pump 71 into the stabilizer 66.

In the stabilizer, as is well understood in the art, heat is supplied to the lower part thereof as by a reboiler 72, stabilized gasoline and stabilized reformed naphtha being withdrawn by line 73 to storage. The lighter constituents are withdrawn from the top of the stabilizer through line 74, and by heat exchanger or cooler 75 reduced in temperature and resulting condensate collected in accumulator 76 from the bottom of which a liquid stream is returned to the top of the stabilizer by pump 77 as reflux therefor. The constituents which are not condensed in the accumulator 76 are chiefly hydrocarbon compounds having from three to four carbon atoms per molecule, and these rich gases pass by way of transfer line 32, through heat exchanger 58 where they are elevated in temperature. These gases form the supply of cycle gas for the operations described above.

Where a compressor type recover system is utilized at 69, it is to be understood the compressor 33 may not be necessary. Also, the heating medium supplied to the reboiler 72, as by lines 80, may be derived as a side stream from the scrubber 52, or any available heating medium used in place thereof. Further within the scope of my invention, is the control of the reaction time within the reaction chamber 28, by varying the sum of the naphtha and heat-carrier gas with respect to the heavier vapor stream. For example, by increasing the ratio of the heavier hydrocarbons to the lighter hydrocarbons and the heat-carrier, the reaction time is increased while the ratio of the light hydrocarbons to the heat-carrier or cycle gas remains the same, for the optimum reforming of the light hydrocarbons, although the sum of the two may be readily varied to provide the optimum time within the reaction chamber 28 for the heavier vapors.

The foregoing may be more specifically illustrated by assuming that a charge of gas oil is supplied by way of line 10, the gas oil having a gravity of 30° A. P. I. and the stream of vapors derived therefrom having an optimum cracking temperature of about 1010° F. Such a stream of vapors is preferably superheated to about 990°

F. and a ratio of such vapors to the heat-carrier of about 6.4 to 1 is preferred, to provide a reaction time in chamber 28 of about one minute. At the same time a stream of light hydrocarbons having a gravity of about 55° A. P. I. is supplied to the flash drum 45, and the overhead vapor stream preferably forms a ratio of about 0.33 to 1 with the heat-carrier gas. The mixture is heated to about 1150° F., and maintained at that temperature for a time interval of about one minute and during passage through the soakage section 48-49, and admixed at about that temperature with the superheated heavy vapors. Upon commingling of the two streams, the temperature of the heavy vapors is quickly elevated to about 1010° F., and the light hydrocarbons are quickly cooled to that temperature, which is below their active reforming temperature; wherefore, the subsequent cracking of the heavier hydrocarbons in the reaction chamber 28 is not accompanied by further reforming of the lighter hydrocarbons, and any further reforming or parasitic reaction that may occur is of such an inconsequential character as to be negligible in percentage of lighter products further changed by parasitic reaction.

Further in accord with my invention there is achieved a great economy in the heat requirements of my cracking systems. Where, in the past, the reforming and cracking operations were separately carried out, practically twice as much heat was required as in the combined process of my invention. All of the heat required to elevate the lighter hydrocarbons to their reforming temperature in accord with my invention is usefully employed in conjunction with the heat-carrier gas to supply the thermal units necessary for the cracking of the heavier hydrocarbons. Thus, though a dual cracking process is provided, the heat requirements of it are only slightly above those necessary to but one of such processes, and only above the requirements of such a one by that amount of heat necessary to compensate for additional losses due to radiation, and to supply the heat of reaction for the reforming operations. At the same time, none of the advantages of "true vapor phase" cracking are lost since the heavier hydrocarbons are effectively cracked by mixture with a heat-carrier gas. In both the reforming of the naphtha or lighter hydrocarbons and the cracking of the heavier hydrocarbons greater yields may be expected of a superior high anti-knock motor fuel, one having an octane rating, 1939 research, of from 70 to 90; such greater yields may in part be due to the combination of constituents of the cycle gas with constituents of both the naphtha and heavier vapors to form compounds within the boiling range of, and highly desirable for inclusion in, the motor fuel or gasoline.

While I have shown a particular embodiment of my invention, it will be understood that I do not limit myself thereto since many modifications may be made, and I therefore contemplate by the appended claims to cover any such modifications as fall within the spirit and scope of my invention.

What I claim is:

1. The method of thermally cracking heavy hydrocarbons to produce motor fuel and reforming light hydrocarbons, which comprises heating and separating from the heavy hydrocarbons a stream of vapors, generating heat in a heating zone, heating a mixture of cycle gas and the light hydrocarbons during passage through tubes

in said heating zone to an active reforming temperature of said light hydrocarbons, controlling the ratio in said mixture of said light hydrocarbons to said cycle gas to procure for said mixture a time-interval at said reforming temperature for the desired extent of completion of the reforming action, thereafter commingling said mixture with said stream of heavy vapors in ratio thereto for the supply of adequate heat to crack said heavy vapors, and recovering products suitable as motor fuel from the reformed lighter hydrocarbons and the cracked heavy vapors.

2. The method of thermally cracking heavy hydrocarbons to produce motor fuel and reforming light hydrocarbons, which comprises heating and separating from the heavy hydrocarbons a stream of vapors of a character which may be cracked within a temperature range below the active reforming temperature of said light hydrocarbons, generating heat in a heating zone, heating a mixture of cycle gas and the light hydrocarbons during flow through tubes within said heating zone to a temperature within the active reforming temperature of said light hydrocarbons, controlling the flow of said cycle gas and of said light hydrocarbons to predetermine the time of passage of said light hydrocarbons through said tubes, thereby to produce the desired extent of completion of the reforming reaction, while maintaining relatively unchanged the weight of said mixture per unit of time, thereafter commingling said mixture with said stream of heavy vapors in ratio thereto for the supply of adequate heat to crack said heavy vapors within their active cracking temperature range, and below said active reforming temperature range, and recovering products suitable as motor fuel.

3. The method of thermally cracking heavy hydrocarbons to produce motor fuel and reforming light hydrocarbons, which comprises heating and separating from said heavy hydrocarbons a stream of vapors, generating heat in separately-fired heating zones, heating a mixture of cycle gas and said light hydrocarbons in a first of said heating zones to a temperature within the active reforming temperature of said light hydrocarbons, in said other of said heating zones supplying heat to the mixture in amount adequate to supply the heat for the endothermic reforming reaction, retaining the mixture in said second zone for a time interval adequate for the substantial completion of the desired reforming reaction, thereafter commingling said mixture with said stream of heavy vapors in ratio thereto for the supply of adequate heat to crack said heavy vapors at a temperature below the active reforming temperature of said light hydrocarbons, and recovering products suitable as motor fuel from said reformed light hydrocarbons and said stream of vapors.

4. The method of thermally cracking heavy hydrocarbons to produce motor fuel and reforming light hydrocarbons which comprises heating and separating from the heavy hydrocarbons a stream of vapors, generating heat in a heating zone, within an elongated passageway disposed in said heating zone, heating a mixture of cycle gas and said light hydrocarbons to a temperature within the active reforming temperature for said light hydrocarbons, controlling the time the light hydrocarbons are subjected to a reforming temperature by varying the ratio of the light hydrocarbons to the cycle gas so as to provide an optimum time interval for the desired reformation

of said light hydrocarbons while maintaining approximately the same weight of said mixture per unit of time, thereafter commingling said mixture with said stream of heavy vapors in ratio thereto for the supply of adequate heat materially to crack said heavy vapors, and recovering from said reformed and cracked hydrocarbons products suitable for motor fuel.

5. The method of thermally cracking heavy hydrocarbons to produce motor fuel and reforming light hydrocarbons, which comprises heating and separating from the heavy hydrocarbons a stream of vapors, generating heat in a heating zone, in an elongated passageway disposed within said heating zone, heating a mixture of cycle gas and said light hydrocarbons to a temperature within the active reforming temperature of said light hydrocarbons, regulating the ratio of light hydrocarbons to cycle gas to provide a time interval for the substantial completion of the reforming reaction to take place before discharge of said light hydrocarbons from said elongated passageway, commingling said mixture with said stream of heavy vapors in ratio thereto for the supply of adequate heat to crack said heavy vapors, retaining said heavy vapors within a zone for a time interval sufficient for the substantial completion of the cracking reaction of said heavy vapors, and for a given cracking temperature of said heavy vapors controlling the time the heavy vapors are retained within said last-named zone by regulating the quantitative ratio of said mixture and the heavy vapors, and recovering products suitable as motor fuel therefrom.

6. The method of thermally cracking heavy hydrocarbons to produce motor fuel, which comprises heating and separating from the heavy hydrocarbons a stream of vapors, superheating them, generating heat in a heating zone, in an elongated passageway disposed within said zone heating a mixture of cycle gas and of light hydrocarbons to be reformed to a temperature of

around 1200° F., retaining said light hydrocarbons within said passageway for an interval sufficient for the optimum reformation thereof by regulating the ratio of said light hydrocarbons to said cycle gas while maintaining approximately the same weight of said mixture per unit of time, thereafter commingling said mixture with said stream of heavy, superheated, vapors in ratio thereto for the supply of adequate heat to crack said vapors, and recovering therefrom cracked and reformed products suitable as motor fuel.

7. The method of thermally cracking heavy hydrocarbons to produce motor fuels, which comprises heating and separating from the heavy hydrocarbons a stream of vapors, preheating a stream of light hydrocarbons and a stream of vapors, preheating a stream of light hydrocarbons and a stream of cycle gas, in an elongated passageway disposed within a heating zone heating a mixture of said cycle gas and said light hydrocarbons to a temperature within the active reforming temperature of said light hydrocarbons, regulating the time interval required for the light hydrocarbons to pass through said passageway to an interval for optimum reforming thereof by varying the ratio of said light hydrocarbons to said cycle gas while maintaining the weight of said mixture per unit of time relatively unchanged, thereafter commingling said stream of heavy vapors with said mixture in ratio thereto for the supply of adequate heat for the cracking of said heavy vapors into products suitable for inclusion in motor fuel, fractionating the products of both the reforming and cracking reactions for withdrawal of recycle stock of character similar to said heavier hydrocarbons, returning said recycle stock for mixture with said heavy hydrocarbons, and recovering as an end product constituents suitable for inclusion in motor fuel.

WILLIAM C. DORSETT,