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CONVERTING HEAVY MINERAL OILS INTO LIGHTER OILS

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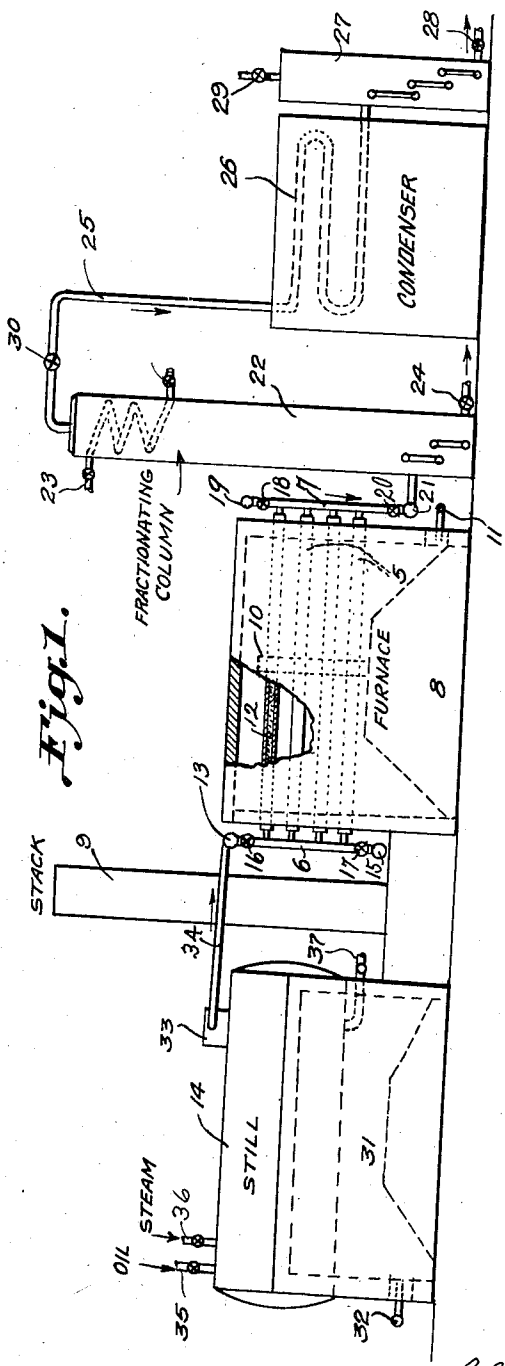


Fig. 1.

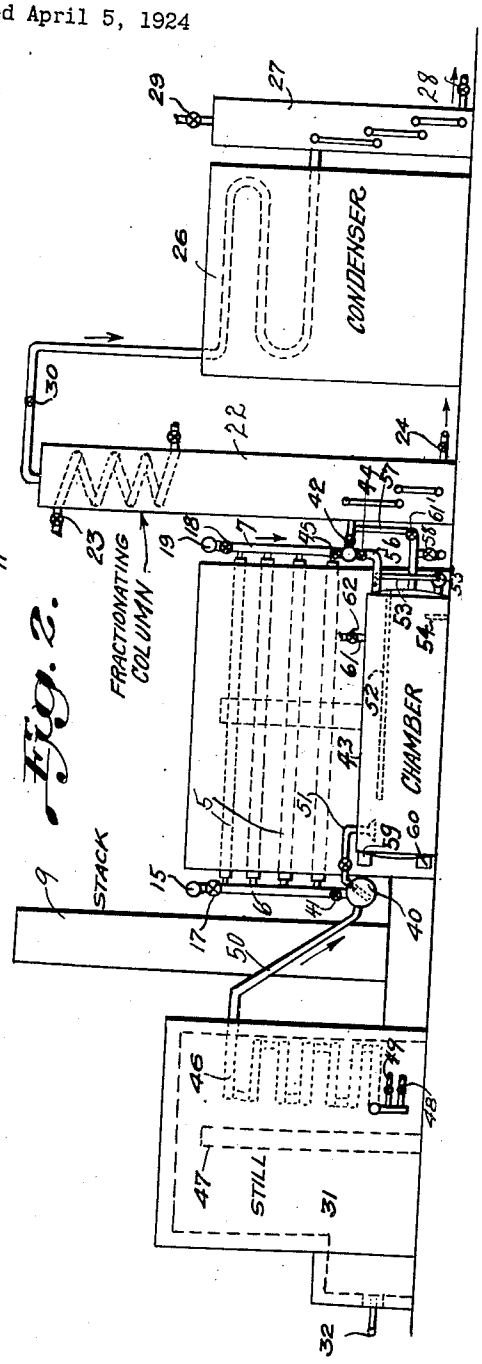


Fig. 2.

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By his Attorney

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CONVERTING HEAVY MINERAL OILS INTO LIGHTER OILS

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12 Claims. (Cl. 196—52)

This invention relates to a process of producing motor fuels. It relates more particularly to a method of converting heavy hydrocarbons or petroleum oils into lighter hydrocarbons or petroleum oils at elevated temperatures and pressures. A contact agent or catalyst may be utilized in the process.

By this invention vapors of heavy hydrocarbons are subjected to increased temperature and they may also be subjected to increased pressure whereupon lighter hydrocarbons are produced and carbon may be deposited upon a catalytic agent that will promote carbon oxidation. This catalyst may, for example, be a metallic carbonate. Steam may be mixed with the heavy hydrocarbon vapors and brought into contact with the catalyst or the steam may be brought into contact with the catalyst after the carbon has been deposited thereon for the purpose of removing carbon and cleansing the catalyst, the carbon being oxidized and removed in this manner with the formation of valuable gaseous products.

The decomposition of heavy petroleum hydrocarbons to lighter petroleum hydrocarbons commonly called "cracking" has become an essential part of petroleum refining. This cracking may be accomplished either in the liquid phase or the vapor phase or combinations of the two at high temperatures and usually with increased pressure. In some of the processes the decomposition is aided by the presence of a catalytic agent.

It is commonly known that in cracking the temperature and pressure conditions are somewhat dependent upon each other especially in liquid phase cracking. In either the vapor phase or liquid phase cracking, it is necessary to have a temperature at which decomposition of the heavy hydrocarbons is effected and if the process is to be carried out in the liquid phase, a pressure must be maintained sufficient to keep the hydrocarbons that are to be decomposed in the liquid phase. In vapor phase cracking the temperature and pressure may be varied over wide ranges and are not dependent upon each other as the results desired will determine the temperature and pressure that is to be used in any particular vapor phase process.

In processes in which heavy hydrocarbons are decomposed into lighter hydrocarbons, carbon is deposited and the amount of the carbon so deposited depends upon the conditions of operation. In some of the processes, the carbon is deposited within the container such as an ordinary still where the cracking takes place, or the carbon may be deposited in a separate chamber after the cracking conditions have been reached, as, for example, in processes where coils of pipes are used for heating the hydrocarbons and the products are then discharged into a reaction chamber. There are various mechanisms and procedures of operation in practice by which carbon is caused to deposit in a more accessible place and a more easily removable condition.

In all cracking processes it has been found that the removal of carbon is troublesome and involves considerable expense. One of the features of the present invention is to minimize the troubles which might be caused by carbon deposition during the cracking of heavy hydrocarbons and to provide for ready removal of the carbon which may be formed in the process.

One of the objects of my invention is to provide a process in which hydrocarbons are cracked in the vapor phase, the vapors being obtained from the distillation of a hydrocarbon oil. In order to increase the yield of light hydrocarbons such as those suitable for use as a motor fuel from the process, I propose to crack the residue obtained from the distillation chiefly by the heat contained in the cracked product resulting from the vapor phase cracking operation.

In general one modification of my process may be described as follows:

The process is one by which heavy hydrocarbons or petroleum oils are decomposed into lighter hydrocarbons and carbon, the carbon being set free in the presence of a contact agent and removed by oxidizing the carbon with steam.

In carrying out the process the hydrocarbons that are to be vaporized may be introduced into a vaporizing container which may be, for example, a coil of pipe in a furnace or an ordinary cylindrical still and the heavy hydrocarbons may be partly or entirely vaporized as desired. The vapors from the still may be passed through tubes which may contain a catalyst that is particularly suitable for causing carbon to be oxidized in the presence of steam. It has been found that metallic carbonates operate as suitable catalysts for this purpose and potassium carbonate has been found to be especially suitable therefor. The heavy hydrocarbon vapors that are to be cracked may be brought into contact with the catalyst at high temperature and high pressure either with or without the presence of steam. If steam is admixed with the hydrocarbon vapors when they are introduced into the reaction chamber where the cracking takes place and where the catalyst is located, it has

been found desirable to heat the chamber to a somewhat higher temperature than would be necessary where the steam is not admitted with the heavy hydrocarbon vapors, but is introduced into the chamber after carbon has deposited upon the catalyst.

It has been found that operating at the lower temperature for decomposition without the presence of steam, a product well adapted for use as a motor fuel is obtained. When operating the process in this manner the carbon formed by the decomposition or cracking in the reaction chamber is deposited on the catalyst or metallic carbonate and after a certain period of time, the flow of oil vapors is stopped. The carbon deposit is advantageously removed by passing steam therethrough under high temperature and high pressure conditions similar to those used in the hydrocarbon decomposition period. Steam at lower pressures and somewhat lower temperatures may be employed. In this manner the carbon is oxidized by the steam in the presence of the catalyst and gases of high heat value containing hydrogen and carbon monoxide together with some carbon dioxide are obtained. The temperatures may be from about 700° F. to 1200° F. and the pressures may range from atmospheric to 200 pounds per square inch.

The carbon that is deposited upon the catalyst during the cracking operation is removed by chemical action and valuable products are thereby formed. This is particularly advantageous both because the operation of the process is facilitated and valuable by-products are formed. The calorific value and the sensible heat of the gases thereby developed may be utilized for further cracking of the heavy oils or for other purposes.

A suitable catalyst or contact agent to be used in this process may be prepared as follows:

Dried lumps of calcium carbonate or porous solids of various compositions may be impregnated with potassium carbonate and dried. For example, the contact lumps may be formed by breaking up limestone or other minerals. This may be dried and then saturated with a saturated solution of potassium carbonate followed by again drying the lumps. This is given merely as an example of the catalyst that may be used since other alkali and alkaline earth carbonates are suitable for this purpose.

In a modification of my process I may pass the high temperature hydrocarbons and other gaseous products that come from the primary reaction chamber into another reaction chamber of large volume in which a slow velocity may be maintained. Further decomposition of the hydrocarbons may be made to take place in this chamber with a further deposition of carbon. For example, if heavy oils such as fuel oils and reduced crude oils are used which do not appreciably vaporize at atmospheric pressure, or above, without molecular decomposition, as commonly known, they are not completely vaporized in the still and therefore the entire charge to the vaporizing still does not go through the primary reaction chamber in the form of vapors. In order to subject the heavier or unvaporized portion to cracking conditions it may be discharged into the secondary reaction chamber with a small drop in pressure and therein energetically circulated as a liquid to give thorough contact with the high temperature hydrocarbons and other gaseous products coming from the primary reaction chamber. The contacting of this liquid heavy oil with the high temperature hydrocarbons and its energetic circulation in this chamber results in decomposition with deposition of carbon and the formation of lighter hydrocarbons, the carbon being deposited in a disintegrated condition so that it may be readily removed from this chamber. No substantial condensation of low boiling products takes place in the secondary reaction chamber. After the hydrocarbons leave the secondary reaction chamber they may pass through a series of fractionating towers and condensing equipment in order to obtain the desired fractional products.

The amount of carbon formed by cracking the unvaporized heavy oil with the high temperature hydrocarbons is not excessive and it is formed and deposited in such a condition that it is not difficult to remove the same from the chamber. By operating in this manner no excessive overheating occurs and the decomposition is effected under readily controlled conditions by circulating the heavy oil and causing it to contact with the high temperature hydrocarbons and other gaseous products in the secondary reaction chamber.

Although the metallic carbonates which may be used in this process operate as a catalyst to cause the carbon deposition to be readily oxidized by the steam, these carbonates may or may not operate as catalysts to cause the heavy hydrocarbon vapors to be decomposed into the lighter hydrocarbons as the high temperature and the pressure used is sufficient to cause this reaction to take place. It will be readily understood therefore that the carbonates need not be used. The metallic carbonates operate as catalysts whether the steam is introduced together with the heavy hydrocarbons to be cracked or whether the steam is introduced after the carbon is deposited.

When the heavy hydrocarbon decomposition is effected at the high temperature and pressure in the presence of the metallic carbonate without steam being present, a somewhat lower temperature may be used than when the steam is present. In this case the removal of the carbon or the carbon oxidation reaction is carried on after the cracking period. These two periods may be termed "make" and "blow." And under such conditions where the hydrocarbon decomposition and the carbon oxidation in the reaction chamber are intermittent, a more gasoline-like and lighter hydrocarbon product is obtained than is the case when the higher temperature conditions are used which are necessary when the steam is mixed with the hydrocarbon vapors and simultaneous contacting with the contact agent or catalyst is effected in the primary reaction chamber. In the latter case with the steam and heavy hydrocarbons admixed during the reaction, the light hydrocarbons which are produced are more apt to be of the aromatic and cyclic type.

The process may be practiced by using an arrangement of apparatus as illustrated in the accompanying drawing in which,

Fig. 1 shows somewhat diagrammatically and partly in section an arrangement of apparatus whereby the process can be carried out; and

Fig. 2 shows a similar arrangement of apparatus modified in some respects whereby the process or a modification thereof may be practiced.

In the drawing, reference character 5 indicates tubes which constitute a primary reaction chamber. These tubes terminate at one end in the header 6 and at the other end in the header 7 and are located in the furnace 8 which is provided with a stack 9 for products of combustion

and with the baffle wall 10. Fuel for the furnace 8 may be injected through the pipe 11 into the combustion space of the furnace. The tubes 5 contain catalyst 12 for the purpose to be described more in detail below. The header 6 terminates at one end in a manifold 13, a valve 16 being interposed, and the header 6 terminates at the other end in the manifold or inlet 15, a valve 17 being interposed. The header 7 terminates at one end in the manifold 19, the valve 18 being interposed, and the header 7 terminates at the other end in a manifold 21, a valve 20 being interposed. A pipe leads from the manifold 21 to a fractionating column 22 which is provided near its lower end with gauges for indicating the level of the liquid therein and an outlet pipe 24 for drawing off the liquid, while its upper end is provided with a cooling coil 23. A pipe 25 having a valve 30 therein leads from the upper portion of the fractionating column 22 to the condenser 26 and a pipe leads from this condenser to the separator 27 for gas and liquid which is provided with a draw-off pipe 28 for the liquid and an outlet pipe 29 for the gas.

An ordinary cylindrical still 14 is mounted in the furnace 31 which is provided with a fuel inlet 32, the products of combustion from this furnace 31 being permitted to pass out thru the stack 9. The still 14 is provided with an inlet pipe 35 for heavy hydrocarbons or petroleum oils and an inlet pipe 36 for steam. This still also has a dome 33 from which a pipe 34 leads to the manifold 13 and an outlet pipe 37 is provided at the bottom of the still 14 for drawing off residues or unvaporized heavy oils. The manifolds 13, 15, 19 and 21 may be divided into sections so that some of the tubes 5 may be used for cracking while carbon is being removed from the others.

In the modification shown in Fig. 2, a coil still 46 is substituted for a cylindrical still and is placed in the furnace 31 which is provided with a baffle 47. An inlet pipe 48 for the heavy hydrocarbons or petroleum oils and an inlet pipe 49 for steam is connected to the pipe still 46 and an outlet pipe 50 leads from this still to the vapor and oil separator 40. The upper side of this separator 40 is connected to the header 6 through the valve 41 and an outlet pipe 51 leads from the lower or liquid containing portion of the separator 40 to the chamber 43. A number of valves 42, 44 and 45 are located in communication with the header 7 as indicated, the valve 45 closing the lower end of the header 7, the valve 42 closing the pipe between the header 7 and the fractionating column 22, and the valve 44 being located in the pipe 56 which leads from the manifold 21 to the chamber 43. The pipe 56 enters the chamber 43 above plate 52. The chamber 43 is provided with a baffle 54 at the bottom near one end and a pipe leads from this end of the chamber 43 to a pump 55 from whence a pipe 53 leads into the pipe 56 and terminates therein. A pipe 57 provided with a valve 61' leads from the chamber 43 to the fractionating column 22 and a valved blast exit 58 is provided for cleaning out chamber 43 while other portions of the apparatus are still in use. A steam inlet 61 controlled by the valve 62 leads to the chamber 43. The chamber 43 is provided with clean-out heads 59 and 60, the remainder of the apparatus shown in Fig. 2 being the same as that shown in Fig. 1 except that the steam inlet 15 and valve 17 are shown at the upper end of the header 6 instead of the lower end.

The operation may be carried out with the apparatus shown in Fig. 1 as follows:

The heavy hydrocarbons or petroleum oils to be cracked are introduced through the inlet 35 into the still 14 where distillation takes place, the vapors passing through the pipe 34 and header 6 into the tubes 5 which may or may not contain the catalyst 12 such as metallic carbonates of which potassium carbonate has been found to be the most satisfactory. The vapors are subjected to high temperatures in the tubes 5, say about 700° F. to 1200° F. and the pressure thereon is maintained at atmospheric to 200 pounds by controlling the valves. The heavy hydrocarbon vapors are decomposed or cracked in the tubes 5 with the formation of lighter hydrocarbons and the deposition of carbon upon the catalyst 12 in the tubes 5, the hydrocarbon vapors passing through header 7 to the fractionating column 22 where a portion of the same is condensed and the liquid is withdrawn through the outlet 24, the remainder passing through the pipe 25 into the condenser 26 where more of the vapors are condensed and pass into the separator 27 from whence the liquids are withdrawn through the outlet pipe 28 and the uncondensed gases pass out through the pipe 29.

If steam is admitted through the inlet 36 into the tank 14 it becomes admixed with the vapors from the heavy hydrocarbons and its presence therewith in contact with the metallic carbonate catalyst in tubes 5 will cause a large portion of the carbon that is formed to become oxidized, this reaction forming hydrogen, carbon monoxide and carbon dioxide and greatly decreasing the accumulation of carbon in the tubes 5. The admixing of steam aids distillation and results in more complete vaporization of the heavy oil and also makes practical the use of higher pressures.

If steam is not introduced into the still 14 the reaction which decomposes the hydrocarbons and deposits carbon upon the catalyst 12 in the tubes 5 is permitted to continue for a period of time until the deposit of carbon begins to be excessive whereupon the valves 16 and 20 are closed and steam is admitted through the inlet 15 and valve 17 and passes through the several tubes under high pressure and temperature thus oxidizing the carbon and cleaning the catalyst, the products from this reaction passing out through the valve 18 and outlet 19 without passing through the fractionating column 22. By operating in this manner, the process is made intermittent first having a cracking period and then having a carbon oxidizing period which enables the process to be carried out at somewhat lower temperatures than would be the case if steam were present with the hydrocarbons that are being cracked. The introduction of steam into the still 14 may, however, prevent objectionable cracking from taking place in this still.

In the modification shown in Fig. 2, the hydrocarbons are heated in the pipe still 46 so as to vaporize a portion thereof and a mixture of vapor and oil passes into the separator 40 from whence the vapors and gases pass to the tubes 5 and are cracked while the unvaporized or liquid portion passes through the pipe 51 at a slightly reduced pressure into the chamber 43 where it meets the high temperature vapors and gases entering the chamber 43 from the pipe 56, the circulation of the liquid being maintained by the pump 55 through the pipe 53 over the plate 52 in the chamber 43 valves 44, 45 and 61 prime being open and the valves 42 and 58 being closed. In this way the heavy liquids from pipe 51 and the high tem-

perature light hydrocarbons and other gases from pipe **56** are intimately contacted and decomposition or cracking of the heavy hydrocarbons is caused to take place also in chamber **43**, the light hydrocarbons and other gases passing through pipe **57** into the fractionating column **22**. Carbon can be removed from the reaction chamber **43** when necessary through the clean-out heads **59** and **60**. It is obvious that instead of contacting the cracked high temperature hydrocarbons from tubes **5** with the heavy liquids from separator **40**, these vapors may be passed through the valve **42**, the valve **44** being closed, into the fractionating column **22** as above described in connection with Fig. 1 so that the arrangement of apparatus shown in Fig. 2 may either be operated substantially the same as that shown in Fig. 1 or the secondary decomposition or cracking effect can be caused to take place in the chamber **43** as described. Steam may be admitted through inlet **49** and be mixed with the vapors or the process can be operated intermittently by admitting steam through the inlet **15** and valve **17** after the carbon has accumulated in the tubes **5**.

When the secondary reaction chamber **43** is used it is often desirable to blast through this chamber and allow the products from the oxidation reaction from the primary reaction chamber **5** to cause through their sensible heat, further cracking of the heavy oil being circulated in chamber **43** and also to become carbureted producing thereby a higher calorific gas. In such cases the gases may be permitted to escape from chamber **43** through pipe **58** after which they may be further treated to recover valuable products, as for example, by scrubbing and condensing.

It is to be understood that any residual oil which is unstable in its vapor state may be mildly cracked in the secondary reaction chamber, preferably this residual oil contains no compounds boiling below 650° F. and this oil will be commingled with the hot cracked vapors while it possesses a temperature of at least 500° F. Such oils herein referred to as "residual oils" are those commonly known to have viscosities up to 300 seconds Saybolt Furol at 122° F.

I claim:

1. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises subjecting vapors from the latter and steam to elevated temperature and pressure in the presence of potassium carbonate, and condensing the vapors.

2. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises subjecting vapors from the latter to elevated temperature and pressure in the presence of potassium carbonate and removing carbon so formed by admitting steam to come into contact with the catalyst, and condensing hydrocarbon vapors.

3. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises removing vapors from the latter and subjecting them to elevated temperature and pressure in the presence of a catalyst that will promote reaction between carbon and steam and passing the light hydrocarbons so formed without further heating of the same into contact with the unvaporized portions of the higher boiling hydrocarbons that have been withdrawn from the place where said vapors were removed.

4. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises removing vapors from the latter and subjecting them to elevated temperature and pressure in the presence of a catalyst that will promote reaction between carbon and steam and passing the light hydrocarbons so formed without further heating of the same into contact with the unvaporized portions of the higher boiling hydrocarbons while circulating the latter in vertically disposed planes.

5. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises removing vapors from the latter and subjecting them to elevated temperature and pressure in the presence of a catalyst that will promote reaction between carbon and steam and passing the light hydrocarbons so formed without further heating of the same into contact with the unvaporized portions of the higher boiling hydrocarbons at a slightly lowered pressure.

6. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises removing vapors from the latter and subjecting them to elevated temperature and pressure in the presence of potassium carbonate and passing the light hydrocarbons so formed without further heating of the same into contact with hot unvaporized portions of the higher boiling hydrocarbons.

7. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises removing vapors from the latter and subjecting them and steam to elevated temperature and pressure in the presence of a catalyst that will promote reaction between carbon and steam and passing the light hydrocarbons and gases so formed without further heating of the same into contact with the unvaporized portions of the higher boiling hydrocarbons.

8. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises removing vapors from the latter and subjecting them to elevated temperature and pressure in the presence of a catalyst that will promote reaction between carbon and steam and passing the light hydrocarbons so formed without further heating of the same into contact with the unvaporized portions of the higher boiling hydrocarbons, and passing steam over said catalyst at an elevated temperature and pressure.

9. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises removing vapors from the latter and subjecting them to temperatures between about 700° F. and 1200° F. in the presence of a catalyst that will promote reaction between carbon and steam and passing the light hydrocarbons so formed without further heating of the same into contact with the unvaporized portions of the higher boiling hydrocarbons.

10. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises removing vapors from the latter and subjecting them to temperatures between about 700° F. and 1200° F., at a pressure between atmospheric and 200 pounds, in the presence of a catalyst that will promote reaction between carbon and steam and passing the light hydrocarbons so formed without further heating of the same into contact with the unvaporized portions of the higher boiling hydrocarbons.

11. The process of producing lower boiling hydrocarbons from higher boiling hydrocarbons which comprises removing vapors from the latter and subjecting them to elevated temperatures and pressures in the presence of a metal-

lic carbonate that will not completely decompose at said elevated temperature, chemically removing the carbon deposited by the hydrocarbon decomposition through contacting with steam at elevated temperatures and pressures in the presence of the catalyst, and passing the gaseous products therefrom into contact with unvaporized portions of the higher boiling hydrocarbons.

12. The method of converting high boiling hydrocarbons into low boiling hydrocarbons suitable for use as a motor fuel, including the steps of heating a hydrocarbon oil in an elongated confined stream to vaporizing temperature in a heating zone, flashing the oil so heated into vapors and unvaporized oil in an evaporating zone, separately withdrawing the vapors and the unvaporized oil from said evaporating zone, passing said vapors without substantial condensation to a conversion zone and there cracking the vapors, contacting the cracked vapors with a stream of the unvaporized oil withdrawn from said evaporating zone, to reduce said unvaporized oil to a heavy residue chiefly by the sensible heat of said vapors, dephlegmating said vapors and condensing the vapors to recover low boiling hydrocarbons.

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