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PROCESS OF AND APPARATUS FOR CONVERTING HEAVY MINERAL OILS INTO LOWER BOILING PRODUCTS

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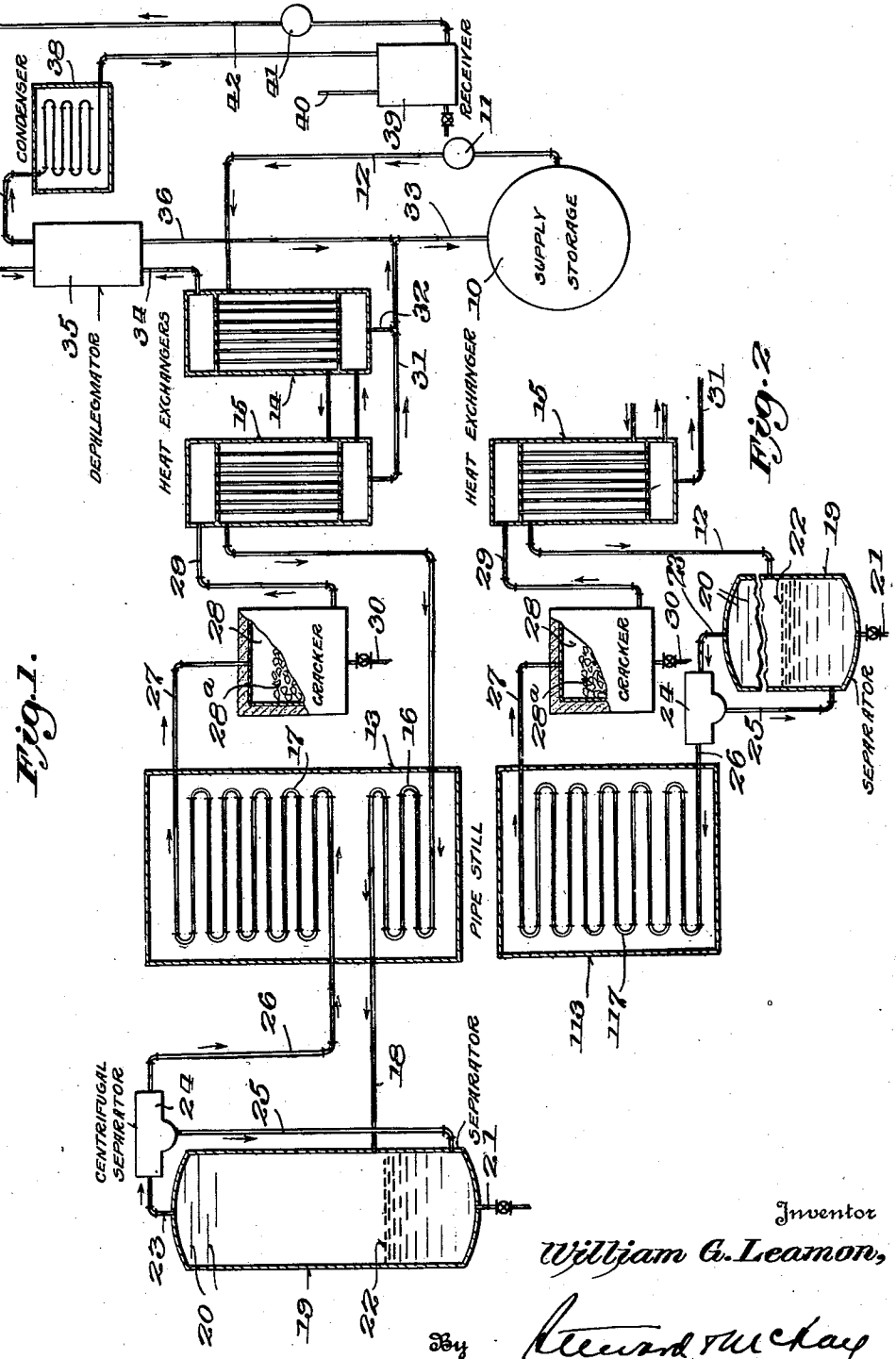


Fig. 1.

Fig. 2.

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PROCESS OF AND APPARATUS FOR CONVERTING HEAVY MINERAL OILS INTO LOWER-BOILING PRODUCTS

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This invention relates to improvements in processes of and apparatus for converting heavy mineral oils into lower-boiling products; and it relates more particularly to the treatment of relatively heavy mineral oils of the petroleum type for the manufacture of lower-boiling products therefrom, such as motor fuel and the like.

In an advantageous practical embodiment, the process of the invention involves a procedure wherein the mineral oil to be converted or cracked is first heated to a temperature below that normally effective for cracking but sufficiently high to vaporize a substantial portion of the oil while leaving a higher-boiling portion, including tarry constituents, unvaporized and commingled with the vapors, the unvaporized liquid particles are then separated in any suitable manner from the vapors while avoiding extensive lowering of the temperature of the vapors, and the vapors alone are then brought to a temperature that is amply high to effect cracking, but so rapidly as to avoid such extensive cracking at this stage as would cause excessive deposition of carbon, whereupon the vapors thus rapidly superheated are directed into a cracking chamber maintained at temperatures somewhat lower but still effective for cracking, the vapors traveling through this cracking chamber slowly enough to give ample time for effective vapor-phase cracking, and the resultant cracked vapors being then appropriately treated to recover therefrom a lower-boiling condensate, such as a motor fuel condensate.

In said process, the initial heating of the oil, and the subsequent rapid superheating of the oil vapors free from liquid, are most desirably accomplished in the coils of one or more pipe-coil heaters or stills through which the oil and the oil vapors respectively pass in the form of a rapidly moving stream of relatively small thickness; and the vapor-phase cracking chamber or zone, which is most advantageously but not necessarily provided with a filling of adsorptive contact material, is maintained within the desired range of cracking temperatures by the superheat of the hot vapors supplied thereto rather than by external heating.

A further understanding of the principles of the invention can best be obtained through a concrete illustrative embodiment thereof which will now be described in connection with the accompanying drawings in which

Fig. 1 is a more or less diagrammatic or schematic representation, in side elevation, of one form of apparatus system that can be used to advantage in practicing the process of the invention; and

Fig. 2 is a similar view of a part of the aforesaid system showing a re-arrangement of certain of the units.

Referring to the drawings, and at first more particularly to Fig. 1, 10 represents a supply tank containing the heavy mineral oil to be cracked or converted. A topped crude petroleum is an example of a heavy mineral oil that can be successfully cracked or converted by the present process, but it is to be understood that many other kinds of mineral oil and residua may be used. From this tank the oil is drawn by pump 11 and pumped through line 12, either directly to pipe still 13, or, and more advantageously, through heat exchangers 14 and 15 where the oil is preheated by the hot vapors coming from the cracking zone to be referred to presently. In a typical instance, the pressure at the pump discharge may be in the neighborhood of 100 pounds, and ordinarily there is a drop of around 10 to 15 pounds in going through the heat exchanger system.

The preheated oil is next conducted into the first or lower coil 16 of the pipe still, the upper or superheater coil being indicated at 17. In this lower coil the oil is heated to a temperature ordinarily ranging from about 360° to 425° C., the exact temperature most desirable to employ being dependent somewhat upon the particular oil being treated. A temperature within this range, while insufficiently high to effect extensive cracking, is nevertheless high enough to vaporize practically all that portion of the oil which it is desired to permit to enter the cracking or converting zone. The mixture of vapors and liquid particles of unvaporized heavy con-

stituents commingled therewith leave the initial heating coil 16 and are subjected to suitable treatment for mechanical separation of liquid from the vapors with as little lowering of the vapor temperature as is practicable. Owing to the fact that the velocity of the oil and vapor stream is greatly reduced upon its discharge into the separating means, however, and that accordingly a substantial time factor is introduced, vaporization that was incipient in the heater coil 16 has an opportunity to go to completion in said separating means. Such further vaporization as may thus occur absorbs heat and hence there is some drop in temperature of the oil vapors in undergoing separation which may amount to from 10 to 30 degrees centigrade in typical instances, but this is not an "extensive lowering of temperature" within the intended meaning of this expression as herein employed. The pressure in the separating means is not substantially lower than that under which the mixture of liquid and vapor leaves coil 16.

In the present example, the separating means comprise a plurality of serially arranged units, of which the first is an upright separator 19 of the vertical cylindrical type, optionally provided in its upper part with baffles 20. In this separator chamber the unvaporized constituents of the oil, including tarry matter, drop out in liquid form and collect in the lower part of the separator from which they may be withdrawn from time to time or continuously through valved discharge outlet 21. In practice, the liquid thus separated is usually allowed to collect in the separator until it reaches, say, the level indicated at 22, when it is then withdrawn.

The hot oil vapors, substantially free of liquid, leave the separator through exit pipe 23 and, in this particular instance, pass then through a second separator unit consisting of a centrifugal separator device of any known or suitable type, indicated at 24, where any slight residual traces of tarry or other liquid matter can be removed from the vapors, the liquid matter so separated passing through tar line 25 to the lower part of the separator 19, as indicated. Where the vapors leaving the lower coil of the pipe still through line 18 do not carry with them too large a proportion of liquid material, it is even feasible to dispense with the separator 19 and to rely entirely upon a centrifugal separator, such as that indicated at 24, for removal of unvaporized constituents from the oil vapors. From the separator 24, the mineral oil vapors pass through vapor line 26 into the upper heating coil 17 of the pipe still. This coil is subjected to more intense heat than coil 16, and the oil vapors in passing at high veloicty through coil 17 are very rapidly brought to a temperature in the neighborhood of 600° C. In practice, the pipe still is so operated that the vapors leaving the coil 17 through vapor line 27, are at a temperature as high as is attainable without causing coking in coil 17 or line 27. As a rule, it is found that this maximum temperature cannot ordinarily much exceed 600° C. without too much cracking and carbon deposition occurring in the heater coil. By the time the superheated oil vapors arrive at the discharge or outlet end of the superheater coil 17, they are under much less pressure than the oil entering the lower or preliminary heater coil 16. For example, the pressure on the oil vapors when they leave the superheater coil 17 may be only about 10 pounds, this reduction being due in large measure to frictional losses incurred in forcing the oil vapors through the pipe-coils of the heater.

The superheated vapors leaving the pipe still through line 27 enter the top of the vapor-phase cracking unit 28 and pass downwardly therethrough at very much reduced velocity. This cracker unit is here shown as of the vertical cylindrical type, providing in its interior a cracking zone. Most desirably this cracking zone contains a mass of porous adsorptive contact material 28[a] inert to sulfur, nitrogen and carbon under the conditions of opeartion, through which the oil vapors are obliged to pass. Pumice in lumps, ranging in size from 5 or 6 inches in diameter down, constitutes an admirable contact material for the purposes of the present process. While the use of such a contact material is to be recommended as giving best results, the invention in its broader phases is to be understood as not restricted to the use of such material. Where the cracking zone is not filled with contact material, the cracking reaction occurs much less rapidly and a larger proportion of fixed gases results.

The cracker unit should be provided with a heavy lagging of suitable heat insulation in order to cut down heat losses to a minimum. It is advisable also to similarly lag the heat exchangers 14, 15, the pipe still 13, and the separators 19 and 24, as well as all the piping connections between these parts. Within the cracking zone the temperature of the oil vapors decreases rapidly at first adjacent the point of their entry into said zone. The temperature then decreases more gradually to a minimum at the point where the vapors leave the cracking zone through vapor line 29. Under the operating conditions here assumed, the pressure of the vapors in the cracker may be very slightly above atmospheric, 4 or 5 pounds for example. The pressure drop between the superheater coil outlet and the cracking zone, is thus slight, say 5 or 6 pounds, and hence the temperature drop due to expansion of the superheated vapors upon entering the cracking zone is minimized. A large part of the decrease in temperature of the vapors as they progress through the

cracking zone is due to the consumption of heat by the endothermic reactions characterizing cracking. However, by thoroughly insulating the cracking zone as described, and by operating with small pressure drop between the outlet of the heater coil and the cracking zone, the cracking zone may be maintained at effective operating temperatures entirely by the superheat of the oil vapors entering the same and without the employment of external heating. This is especially advantageous because, where the mineral oil vapors are uniformly superheated as described to a temperature above that necessary to effect cracking, all the difficulties incident to external heating of a cracking zone, such as local overheating with attendant carbon deposition and coking, may be wholly avoided; while at the same time, by reason of the uniform heating conditions to which every portion of the vapor is subjected in the cracking zone according to the procedure herein set forth, the results are correspondingly much more dependable and uniform, especially where an adsorptive contact material of the character above mentioned is employed in the cracking chamber. Furthermore, the control of temperatures in the cracking zone is thus greatly simplified because of the fact that it becomes necessary only to regulate the rate at which the pipe still is fired and the rate at which oil is pumped through the heating coil or coils thereof.

In a typical instance, the pipe of the superheater coil 17 may be 2 to 4 inches in diameter and 1000 feet in length; while the furnace may be so fired as to give furnace temperatures around the coil near its outlet end high enough to ensure heating the oil vapors to the desired maximum temperature. Assuming that the vapors are discharged from the superheating coil 17 through the outlet of vapor line 27 at 600° C. or slightly above, and also assuming that the interior of the vertical cylindrical cracking unit 28 is 10 feet high and 10 feet in diameter, pyrometer observations at about the center of the cracking zone usually indicate temperatures ranging from 530 to 550° C., or somewhat higher, under normal operating conditions; while the temperature of the vapors just before they leave the cracker unit through vapor line 29 may be 20 to 30 degrees lower. These figures, as well as those given for the dimensions of the superheating coil of the pipe still are to be understood as merely illustrative of good practice and not as restrictive. Assuming an installation having the dimensions heretofore given, the time of passage of the vapors through the cracker unit, where it is largely filled with lumps of porous adsorptive contact material is normally of the order of 10 to 12 seconds. When the contact material is omitted, and the cracking zone is substantially free of any obstruction, the time of passage of vapors therethrough should ordinarily be two or three times as long. These times are to be understood as merely approximate and only generally illustrative of one mode of successful operation.

In general it may be said that around 490° C. is usually about the minimum temperature at which cracking reactions proceed with sufficient rapidity to be practically useful in carrying on the present process, and hence it is desirable to so proportion and arrange the apparatus, and to so operate it, that the temperature of the vapors leaving the cracking zone is not materially below that point.

In the cracking or converting chamber 28, the oil undergoes a vapor-phase cracking or splitting operation with production of a large proportion of lower-boiling constituents on the one hand, and formation of a small amount of heavy liquid products on the other due to re-combination of certain of cracked products. Such liquid products may be withdrawn continuously or intermittently through valved tar outlet pipe 30. While it is in this chamber that the main cracking or conversion of the vapors occurs, and while reference has been made to the fact that no extensive cracking of the oil occurs during the brief period of its passage through the pipe still in the preliminary superheating operation, it is to be understood that this statement is relative and is not intended to imply that absolutely no cracking whatever may occur in the superheating coil of the pipe still, but such cracking as may occur should not be so extensive as to cause substantial deposition of carbon in said coil.

Where the cracking chamber 28 contains porous adsorptive contact material of the character hereinabove mentioned, substantially no separation of carbon occurs in the cracking zone and, in particular, none that produces coky deposits and chokes up the converting or cracking zone. In starting up the plant for the first time, it is found that a very thin film-like deposit of carbon is soon formed on the lumps of pumice or other contact material; in fact the existence of this film-like deposit on said contact material is apparently highly advantageous in the way of assisting and accelerating the converting action, and it is even possible that it is an essential factor in attaining thoroughly satisfactory and efficient action of the contact material. But, once this film-like deposit is formed, it does not grow thicker as time goes on but seems to remain unchanged. At all events, it is entirely feasible in practice to run the plant continuously for weeks or even months at a time without shutting down to clean out the cracking chamber.

Where the process is carried out without the use of contact material in the cracking zone, some perceptible deposition of carbon oc-

curs therein, and a somewhat greater amount of tarry and other heavy products is deposited. However, even where contact material is not employed in the cracking zone, the fact that cracking by contact of the oil vapors with directly heated or superheated surfaces is eliminated greatly reduces the tendency for carbon to be deposited either from further cracking of the aforesaid tarry or other heavy products or from excessive cracking of the feed oil vapors. Hence, in this embodiment of the invention also, much longer operation can be had without the necessity of shutting down to clean out than is possible with the externally fired chambers heretofore used in vapor-phase cracking.

Hot cracked vapors leaving the cracking chamber through exit line 29 are conducted through heat exchangers 15 and 14 in succession where they give up a part of their heat units to the liquid oil that is being supplied to the pipe still 13, thus serving to preheat such oil as already explained. At the same time, the cracked vapors lose their superheat and some undesirable heavy constituents are liquefied and separated. The liquid separated in the heat exchangers may be disposed of in any desired manner, but in the present instance it is conducted by lines 31, 32 and 33 to the storage tank 10 for re-running.

The vapors leaving the last of the series of heat exchangers (which may of course be more than two in number) pass through vapor line 34 into a dephlegmator 35 of any suitable type. Here further relatively high-boiling constituents that it is desirable to exclude from the motor fuel condensate sought are separated and are most desirably sent by way of lines 36 and 33 to the supply storage tank 10.

The vapors leaving the dephlegmator pass through line 37 to condenser 38, and a crude motor fuel condensate collects in receiver 39, fixed gases passing off through vent pipe 40. A pump 41 may be arranged to withdraw a part of the crude condensate from receiver 39 and return the same through line 42 to the top of the dephlegmator 35 in order to aid effective functioning of the latter.

The crude motor fuel condensate obtained in receiver 39 as hereinabove described may be further refined by redistillation or other suitable refining method to produce a refined gasoline or other motor fuel of desired specifications. Any residue from redistillation may be sent to storage tank 10 and worked through the process again.

Fig. 2 illustrates how the process of the invention may be advantageously carried out in a manner somewhat different specifically from that described in connection with Fig. 1. In this modified form of procedure, the heat exchangers 15 and 14, supplemented by such others in series therewith as it may be found desirable to employ in practice, are relied upon to bring the topped crude or other starting material up to a temperature corresponding to that which it attains by passage through the lower coil 16 of the pipe still 13 shown in Fig. 1. Accordingly, the hot oil coming from heat exchanger 15 through line 12, and consisting of a mixture of oil vapors and unvaporized heavy liquid oil, is passed directly into separator unit 19 where the unvaporized heavy material drops out as liquid, the vapors leaving the top of the separator and passing by way of vapor line 23, centrifugal separator unit 24, and line 26, into the pipe still 113 which in this instance may contain a single continuous coil 117 corresponding in function to the superheater coil 17 of Fig. 1. The course of the superheated vapors leaving the pipe still 113 through vapor line 27 is the same as before described in connection with Fig. 1.

By vaporizing the desired proportion of the oil and dropping out the liquid or unvaporized portion of the vapor-liquid mixture before the oil vapors enter the pipe still, the advantage is gained that only oil vapors, substantially free of liquid oil, are treated in the coil of the pipe still, and hence the danger of carbon deposition in the heater coil is rendered still more remote and the operation of the system as a whole is rendered correspondingly simpler and more easily controllable.

Although in the description given hereinabove in explaining the principles of the invention the cracking zone is refered to as being maintained substantially at or only very slightly above atmospheric pressure, it is to be understood that substantial superatmospheric pressures may be employed in the cracking zone and other parts of the system within the scope of the invention.

The terms "converting" and "cracking" are used herein interchangeably and each generic to the other, to designate broadly the molecular changes undergone by mineral oils generally when subjected to heat at a sufficiently high temperature and for a sufficient length of time to cause breaking down, splitting, or cleaving of the molecules, with or without deposition of carbon and with formation of at least some lighter or lower-boiling products.

What I claim is:

1. The process of converting mineral oil into lower-boiling products which comprises heating relatively heavy mineral oil and vaporizing a substantial portion thereof below effective cracking temperature while leaving a high-boiling portion including contained tarry matter substantially in unvaporized condition but commingled with the vapors, separating out the unvaporized portion, further heating said vapors to a temperature in excess of that required for effective cracking but so rapidly that said vapors leave this stage of the process largely uncracked, then

maintaining said vapors in a cracking zone kept at effective cracking temperature substantially only by the superheat of said vapors for a period of time long enough to effect extensive cracking, and recovering a relatively low-boiling condensate from the cracked vapors.

2. The process of converting mineral oil into lower-boiling products which comprises heating relatively heavy mineral oil in the form of a rapidly flowing stream of small diameter to a temperature sufficiently high to vaporize a substantial portion of the oil while leaving unvaporized a high-boiling portion including tarry constituents, discharging the heated stream of vaporized and liquid oil into a separator to separate vapors from liquid, superheating said vapors while they travel at high velocity in a stream of small diameter to a temperature above that required for cracking but within a period of time so short that they remain largely uncracked, then reducing the velocity of the vapors and maintaining them at cracking temperature substantially only by the superheat of said vapors for a period of time sufficiently long to effect extensive cracking, and recovering a relatively low-boiling condensate from the cracked vapors.

3. The process of converting mineral oil into lower-boiling products, which comprises subjecting mineral oil traveling in a stream of relatively small thickness to heat at temperatures below cracking temperatures but sufficiently high to vaporize a desired portion of said oil while leaving heavy constituents of the oil as liquid commingled with the vapors, separating such liquid from the vapors, passing said vapors at high velocity through a heated coil until they attain a temperature in the neighborhood of 600° C., but within a period of time so short that no cracking occurs sufficient to cause substantial deposition of carbon, discharging the vapors into a cracking chamber wherein the temperature is below 600° C. but is maintained high enough for effective cracking substantially only by the superheat of said vapors, allowing said vapors to travel through said chamber slowly enough to permit extensive cracking to occur, and recovering a relatively low-boiling condensate from the cracked vapors.

4. The process defined in claim 1, further characterized by the fact that in said cracking zone the oil vapors pass through a mass of porous adsorptive contact material.

5. The process defined in claim 2, further characterized by the fact that the cracking of the oil vapors is effected with the aid of porous adsorptive contact material inert to sulfur, nitrogen and carbon under the conditions of operation.

6. The process defined in claim 3, further characterized by the fact that in traveling through said cracking chamber, said vapors pass through a mass of lump pumice.

7. A process of oil conversion which includes heating heavy mineral oil to a temperature sufficiently high to vaporize a substantial portion thereof while leaving unvaporized a high-boiling point portion thereof, including tarry constituents, separating therefrom the vaporized portion, and subjecting the latter to superheating to a temperature above that required for the cracking reaction but within a period of time so short that no cracking occurs sufficient to cause substantial deposition of carbon, passing the superheated vapors through a mass of porous adsorptive material, said vapors being superheated sufficiently to maintain by their contained heat the desired cracking reaction of the vapors when passed through said material while maintaining said material at the required temperature for said reaction, the duration of such passage being long enough to effect extensive cracking, and separating a condensate of the motor fuel type from the resultant vapors.

8. A process of oil conversion which includes heating heavy mineral oil to a temperature sufficiently high to vaporize a substantial portion thereof while leaving unvaporized a high-boiling point portion thereof, including tarry constituents, separating therefrom the vaporized portion, and subjecting the latter to superheating to a temperature above that required for the cracking reaction but within a period of time so short that no cracking occurs sufficient to cause substantial deposition of carbon, passing the superheated vapors into a decomposition chamber wherein said vapors are retained at cracking temperature for a period of time long enough to effect extensive cracking, said vapors being heated sufficiently to maintain by their contained heat the desired cracking reaction of the vapors while in said chamber, and separating a condensate of the motor fuel type from the resultant vapors.

9. A process of oil conversion which includes heat treating the oil to vaporize the fractions to be subjected to cracking reaction, while retaining a high-boiling point portion thereof, including tarry constituents, unvaporized, passing such intermingled vapor and liquid into a separating chamber wherein the liquid portions are retained for sufficient time to permit the evolution of the vapors, withdrawing the vapors therefrom and quickly superheating the same to a temperature above the temperature of the desired cracking reaction but within a period of time so short that no cracking occurs sufficient to cause substantial deposition of carbon, and then passing the largely uncracked superheated vapors through a mass of porous adsorptive material whereby said material is maintained at the required temperature for the desired cracking reaction, the superheat

of the vapors being sufficient to also maintain them by their contained heat at cracking temperatures while they are being passed through said material for a period of time long enough to effect extensive cracking, and separating a condensate of the motor fuel type from the resultant vapors.

10. A process of oil conversion which includes heating heavy mineral oil to a temperature sufficiently high to vaporize a substantial portion of the oil without material cracking or decomposition while leaving unvaporized a high-boiling point portion thereof, including tarry constituents, passing the intermingled vapor and unvaporized oil to a separating chamber wherein the vapors are evolved from said liquid oil, withdrawing the evolved vapors and heating the same to a temperature above that required for the desired cracking reaction but within a period of time so short that no cracking occurs sufficient to cause substantial deposition of carbon, passing the superheated vapors through a mass of porous adsorptive contact material, said vapors being superheated sufficiently to maintain by their contained heat the desired cracking reaction of the vapors when passed through said material, and to maintain said material at the required temperature for said reaction, the duration of such passage of the vapors being long enough to effect extensive cracking, and separating a condensate of the motor fuel type from the resultant vapors.

11. A process of oil conversion which includes heat-treating the oil to vaporize the fractions to be subjected to cracking while retaining a high-boiling portion, including tarry constituents, unvaporized, passing the intermingled vapor and liquid oil to a separating chamber, wherein the same is retained for the desired time for the evolution of vapors, withdrawing the vapors therefrom and superheating the same to a temperature above the temperature of the desired cracking reaction but within a period of time so short that no cracking occurs sufficient to cause substantial deposition of carbon, passing the largely uncracked superheated vapors through a mass of porous adsorptive contact material, said vapors being superheated sufficiently to maintain by their contained heat and without the input of additional heat the desired cracking reaction of the vapors when passed through said contact material and to maintain said material at the required temperature for said reaction, the duration of such passage of the vapors being long enough to effect extensive cracking, and separating a condensate of the motor fuel type from the resultant vapors.

12. In a process of cracking oil in vapor phase to produce lower boiling point products, passing a mineral oil in a relatively small stream through a heating zone, wherein a substantial portion of the oil is vaporized without material cracking or decomposition while a higher boiling point portion thereof, including tarry residuents, is unvaporized, discharging such vapor and liquid oil into a separating chamber, wherein the liquid oil is retained for sufficient time to permit the evolution and withdrawal of the vapors, passing the withdrawn vapors at high velocity through a heated coil, wherein they are rapidly raised to a temperature approximating 600° C., but within a period of time so short that no cracking occurs sufficient to cause substantial deposition of carbon, and discharged therefrom largely uncracked and passed into a cracking chamber, wherein the temperature is below 600° C. but maintained by the contained heat of said vapors sufficiently high for effective cracking, retaining the vapors in said chamber a sufficient time to insure extensive cracking, and recovering a relatively low-boiling point condensate from the removed cracked vapors.

13. Apparatus for converting mineral oil into lower-boiling products which comprises, in combination, means for heating oil to obtain oil vapors mixed with liquid oil, mechanical separating means connected to such heating means and into which such vapor-liquid mixture is discharged, superheater means arranged to receive vapor from said separating means and to heat the same to cracking temperature, and a heat-insulated cracking chamber, containing a mass of porous adsorptive contact material of the character described, connected to said superheater means for receipt of vapors therefrom.

In testimony whereof I hereunto affix my signature.

WILLIAM G. LEAMON.