

Aug. 25, 1936.

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2,052,148

PROCESS FOR THE CONVERSION OF HEAVY HYDROCARBON OILS
INTO LOWER BOILING POINT HYDROCARBON PRODUCTS

Filed Dec. 27, 1933

2 Sheets-Sheet 1

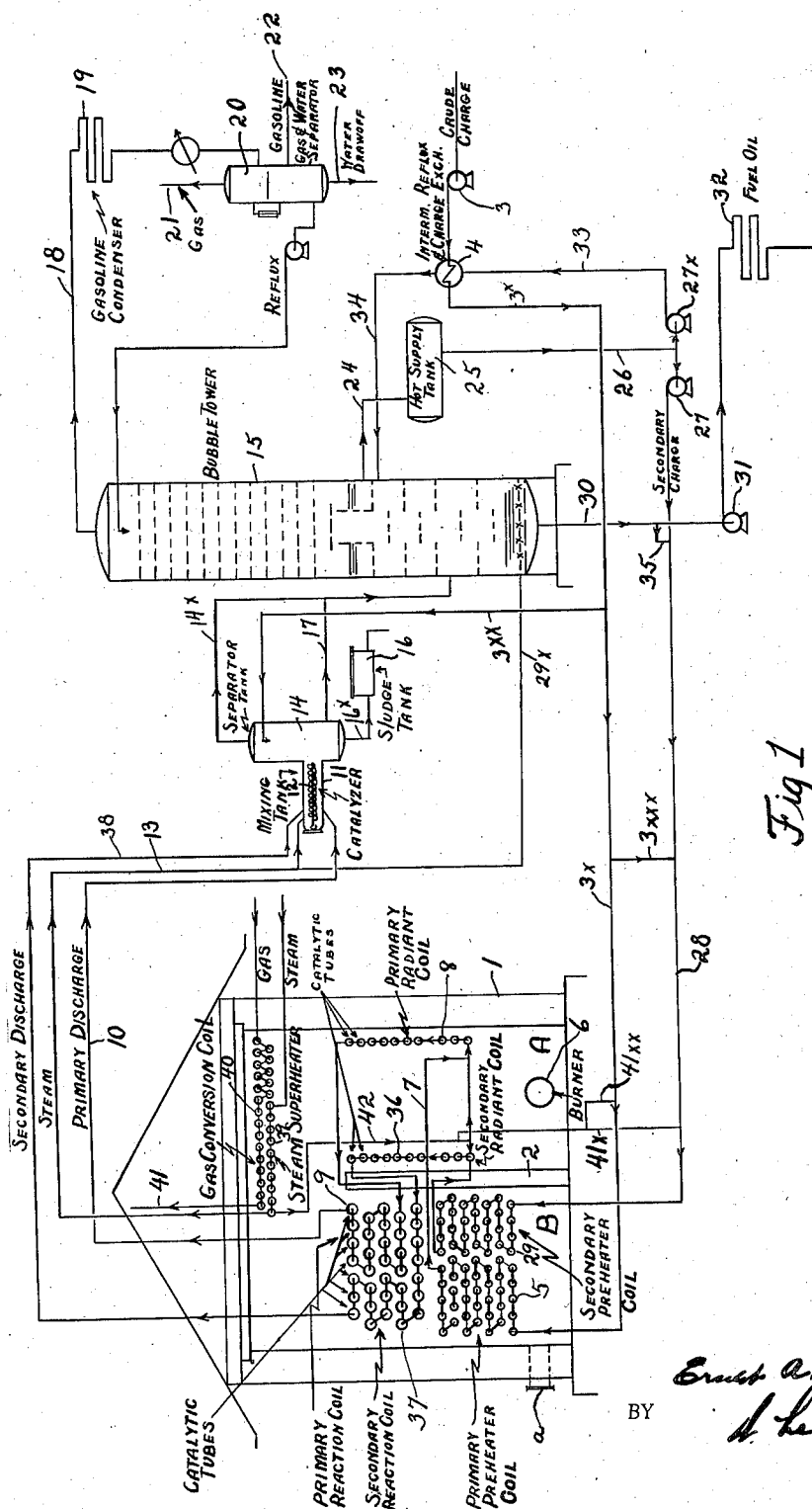


Fig 1

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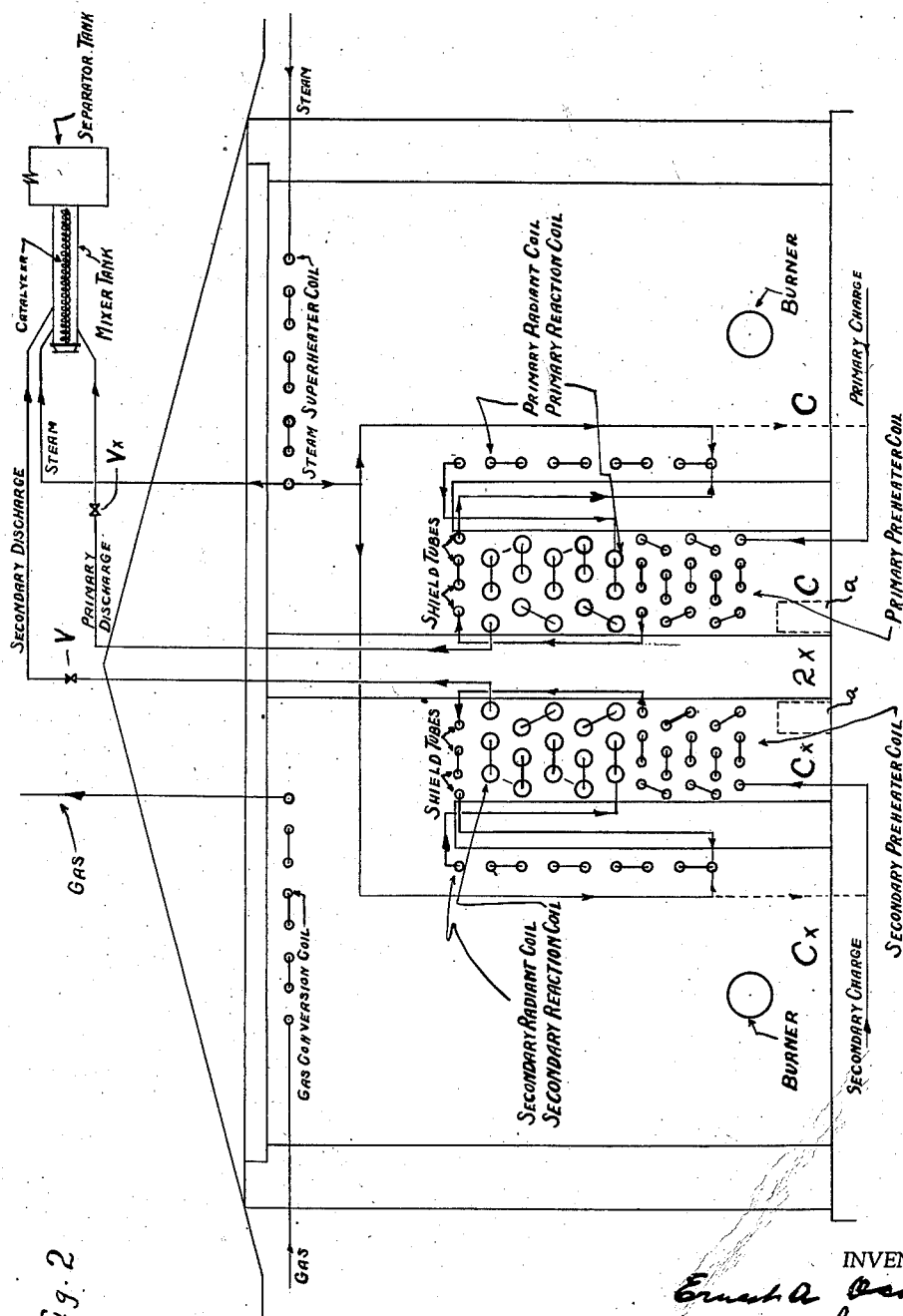


Fig. 2

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UNITED STATES PATENT OFFICE

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PROCESS FOR THE CONVERSION OF HEAVY
HYDROCARBON OILS INTO LOWER BOIL-
ING POINT HYDROCARBON PRODUCTS

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9 Claims. (Cl. 196—63)

The object of the present invention is to provide an efficient and economical process and apparatus for the production of low boiling point hydrocarbon products from heavy petroleum oils and allied hydrocarbons such as liquefied coal or asphalt, shale, etc.

A further object of my invention is to provide a novel process and apparatus for the continuous treatment of recycling of heavy hydrocarbons under substantially similar conditions as those of the first cycle or run.

A characteristic of the process is the initial subjection of the charging stock to heat above the boiling point temperature of the least volatile constituent of the charging stock and preferably below its critical cracking point and preferably in the presence of a hydrogenating medium such as superheated steam, hydrogen or hydrogenous gas, and under pressure, so as to change the physical character of the heavy charging stock to a vapor-phase and then subjecting the said hydrocarbon material, in the presence of superheated steam, to rapid cracking treatment by the subjection thereof to higher heat, for example, from 1000 to 1500° F. and for a period of time sufficient for sudden breaking down of the high boiling point hydrocarbons, then subjecting the hydrocarbons immediately upon reaching or passing their cracking temperature to sudden expansion and to reduced heat, from 900 to 1100° F. and preferably in the presence of catalytic material and maintaining this condition for a time sufficient to secure a desired hydrogenation and catalytic cracking reaction.

The vapors are then passed to a mixer tank where they are preferably admixed with superheated steam and subjected to the action of a desulfurizing agent, then are passed to an expansion tank where the light vapors are separated from the heavy residue and sulfur emulsion and are fractionated. The condensed steam refined gas oil and other condensates being drawn off from the bottom of the bubble tower and continuously sent back into the heating zone for similar processing as described.

The invention will be described with reference to the accompanying drawings, in which—

Fig. 1 is a schematic view in elevation of an apparatus adapted for carrying the process into effect.

Fig. 2 is an enlarged schematic elevation showing a modified form of kiln and coil placement.

In the drawings, I have shown at 1 a kiln

constructed of usual heat insulation material which is divided by wall 2 into two sections A, B. The charging stock is passed by pump 3 to an intermediate reflux and charge exchange chamber 4 where it absorbs heat and is then led to the primary preheater coil 5 within section B of the kiln.

In this specification, suitable dimensions are given for an apparatus of 1,000 barrels daily capacity, and the primary preheater "coil" may comprise connected tubes having an aggregate length of about 600 feet and of 3½ inch internal diameter.

Within section A of the kiln is the primary heating element, as, for example, a burner 6, and it is intended that coil 5 receive heat below the critical cracking point temperature of the charging stock, yet above its boiling point, such temperature varying with the character of the charging stock being treated and the charging stock having a general range of 300 to 700° F. under pressure from 60 to 600 pounds per square inch, and generally substantially below 100 pounds per square inch. The heat, pressure, and time of treatment in the traverse of the charging stock through the primary preheater coil, is sufficient to place the charging stock in condition for instant action by additional heat treatment, it, for the most part, comprising thoroughly mixed vapors, representing the various fractions, and entrained unvaporized particles. The charging stock in its said condition is discharged from the primary preheater coil 5 into a discharge pipe 7 leading to the primary radiant coil or cracking coil 8. However, immediately prior to or after its discharge into primary cracking coil 8, the charging stock in vapor phase is subjected to a blast of steam superheated to a point preferably at least equal to the temperature of the hydrocarbons, the mixture of superheated steam and hydrocarbon vapor and any entrained liquid being admitted to the lowermost of the tubes comprising the primary cracking coil 8.

The primary cracking "coil" 8 may comprise interconnected tubes having an aggregate length of about 300 feet with an internal diameter of 3½ inches.

The temperature within section A of the kiln is above the critical cracking temperature of the hydrocarbon vapors within the primary cracking coil 8 and therefore the temperature may be from 1400 to 2000° F., normally 1600 to 1700° F., under the heretofore stated pressure range which

generally may be 100 to 300 pounds per square inch.

Some of the tubes of coil 8, preferably two at the top or discharge end thereof are preferably of catalytic material, and/or tubes which contain catalytic material. I prefer that the said two tubes be constructed of palladium-molybdenum-chromium-nickel alloy or other recognized catalytic alloy to accelerate cracking.

The cracking coil 8 is so proportioned and heated that the hydrocarbons are rapidly broken down or cracked in the presence of superheated steam, which is partly decomposed under the influence of the cracking reactions, causing what appears to be carbon oxidation reactions from the liberated oxygen and carbon released during the cracking and absorption of some hydrogen by the hydrocarbons in their re-formations. The catalytic tubes accelerate the cracking reactions and, in effect, the cracking reactions need not be completed at the time the vapors are discharged from the primary cracking coil 8.

The cracked hydrocarbons are passed from primary cracking coil 8 to a primary hydrogenation reaction coil 9 which may comprise connected tubes having an aggregate length of 600 feet with an internal diameter of 5½ inches, and located at the upper part of kiln connection section B.

When an apparatus such as illustrated in the drawings is employed, it will be desirable to shield the uppermost tubes of the convection sections, as by superposed tubes communicating with and forming a part of the primary and/or secondary coils, which will be understood by those skilled in the art.

It is desired that the primary hydrogenation reaction coil be subjected to a temperature from 900 to 1200° F., normally 1050° F., and that the tubes, at the discharge end of the coil, as, for example, the four tubes shown in the drawings, be constructed of catalytic material such as chromium-nickel-iron, or contain a recognized hydrogenation catalytic material. Thus, in the primary hydrogenation reaction coil, the hydrocarbons, in the presence of catalytic material and under reduced pressure and temperature, are permitted to complete their reactions and reformations sufficiently to secure desired hydrogenation and catalytic reactions.

The hydrocarbons are discharged from the primary reaction coil through pipe 10 to a mixing tank 11 which may be 10 to 30 feet in length and 10 to 20 inches diameter. Within the mixing tank may be disposed a suitable desulfurizing catalyzer indicated at 12, and steam may be led to the mixing tank through pipe 13. The mixing tank discharges into separator tank 14. In the mixing and expansion tanks further desulfurizing reactions may be effected in the presence of suitable desulfurizing chemical materials such as alcoholic solution of lead, acetate or sodium plumbite, or the catalyzer may be of tungsten-molybdenum-iron. The function of the mixing and separator tanks is to remove the sulfur, incidentally further final reactions of the hydrocarbons, and to separate the heavy residues, the lighter vapors being led through pipe 14x to a fractionating column such as bubble tower 15, the sulfur emulsions and heavy residues passing through pipe 16x to sludge tank 16 and the condensed synthetic crude or gas oil passing through pipe 17 for further treatment as hereinafter explained.

To aid the separation of the light vapors and facilitate clear-cut fractionation, fresh oil may be

sprayed into the upper part of the expansion tank by passing the same through pipe 3xx.

The gasoline and lighter fractions are led from the bubble tower through pipe 18 to condenser 19 and the condensate with any entrained gas is led to separator tank 20 from which the gas may be discharged through pipe 21 to a suitable gas-holder, or, directly to a gas conversion coil within the kiln, as later to be explained. The gasoline may be led off from separator tank 20 by means of pipe 22. Water may be drained from separator tank 20 by means of pipe 23 for re-use in the system, if desired. The steam refining condensate of the bubble tower may be led through pipe 24 to a hot supply tank 25 for recycling, tank 25 discharging into pipe 26 communicating with pump 27 which forces oil through pipe 28 leading to secondary preheater 29 within the kiln section B.

Means may be employed for revaporizing within the bubble tower so as to act primarily upon the heaviest condensates therein. For this purpose, I have shown a steam inlet pipe 29x for superheated steam which will be discharged upwardly near the base of the bubble tower, and the steam may be superheated to a point where it will serve to bring or reform some of the said condensates up to the gasoline point. If desired, all or part of the steam refined condensates may be discharged from the base of the bubble tower through pipe 30 leading to pump 31 which will pass condensates to a fuel oil container. A condenser 32 may be interposed between the container and the pump, if desired. Part of the condensate led from the hot supply tank may pass to a pump 27x which will discharge upwardly through pipe 33 into the intermediate reflux and charge exchanger 4, and thence through pipe 34 back into the bubble tower where it will be subjected to the action of the steam. All or part of the steam refined condensates at the base of the bubble tower may be by-passed from pipe 30 by pipe 35 to the pipe line 28 leading to the secondary preheater coil 29.

The secondary preheater coil may receive a charge from the following sources; (a) from the hot supply tank; (b) from the heavy condensates from the base of the bubble tower; (c) fresh oil from any desired source. The secondary preheater coil thus is primarily intended for recycling condensates remaining from the first cycle above described. The secondary preheater coil discharges into a secondary radiant coil or secondary cracking coil 36 within section A of the kiln. The secondary preheater coil may consist of connected tubes aggregating 600 feet with an internal diameter of 3½ inches, and the cracking coil 36 may comprise connected tubes aggregating 300 feet with an internal diameter of 3½ inches.

From the secondary cracking coil 36 the hydrocarbons are passed to the secondary hydrogenation reaction coil 37 in Section B which may comprise connected tubes aggregating 600 feet and of 5½ inches internal diameter, the uppermost tubes of which are formed of catalytic material, being similar to tubes 9 in construction, or contain catalytic material. The action of the secondary hydrogenation reaction coil is the same as that heretofore described with regard to the primary hydrogenation reaction coil. The secondary hydrogenation reaction coil discharges through pipe 38 into the mixing tank and thus meets therein the vapors from the primary hydrogenation reaction coil 9.

The steam employed in the process may be superheated by a coil of suitable length and internal diameter within kiln 1 and indicated at 39. Adjacent the steam heated coil is a metal alloy gas-conversion coil 40 of sufficient length to insure fixing of the gas as it passes through the coil and is discharged through pipe 41 to a suitable gas holder (not shown).

To avoid carbonization of the preheater coils, steam may be led from pipe 41 to a branch pipe 41x communicating with the pipe 28 near that end thereof discharging into the secondary preheater coil, the steam also passing through a branch pipe 41xx communicating with the charging stock supply pipe 3x leading to the primary preheater coil 5. The steam appears to form a thin film of black iron oxide on the walls of the tubes preventing the deposit of carbon.

In the process, the charging stock prior to its passage into the primary cracking coil 8 has been brought to a temperature approximating, while generally yet below, cracking temperature, and the cracking is immediately instituted within the primary cracking coil and proceeds to the point where the action of catalytic material may be had with greatest efficiency, the vapors being immediately discharged into a hydrogenation reaction coil where they are expanded and somewhat reduced in temperature and caused to follow a lengthy path with unchanged conditions as to heat until the point is reached where the hydrogenation and cracking reactions are substantially completed and desulfurization and separation may properly take place, the heavier condensates being carried back into separate preheating, cracking and reaction coils in the same heating zones as the initial and primary corresponding elements. If desired, a proportion of fresh oil may be carried with the heavy condensates into the recycling elements, as, for example, by a controlled branch pipe 3xx leading from charging stock pipe 3x to secondary charging pipe 28.

The increase of low boiling point motor fuel in this process in contrast with previously employed cracking methods does not affect the required end point of the fuel, and the finished product requires no further treatment. The high anti-knock characteristic of the motor fuel is the result of the hydrogenation and catalytic reactions of the process itself, and the value of the product for blending is similar to benzol.

The condensed steam refined heavier fractions condensed during the first run of the process is fuel oil of Diesel oil type which has distinctive characteristics of its own. It is not heavy and sticky, is of low viscosity, has more B. t. u. value per gallon, above 10 Baumé, and can be used directly as a fuel without further treatment and can, of course, be altered to suit a specification required by a user of a particular grade.

Petroleum oils when subjected to high temperature with absence of substantial pressure, follow the gas laws and the amount of cracking depends upon the time the oil is subjected to heat. The yield of gasoline and gas depends on the time the oil is subjected to the cracking temperature and to the pressure applied. In my process, the elements time, heat and pressure are regulated and controlled as to avoid over-reactions and these elements may be varied independently one from the other to produce the greatest percentage of the desired products. Hydrogen or hydrogen-containing gases may be in-

jected into the preheater or cracking coils, or either, if desired.

To produce fuel oil, a portion or all of the steam refined hydrocarbon oil is drawn off at the bottom of the fractionating tower and its gravity controlled by means of superheated steam and oil reflux led into the tower.

In Fig. 2 of the drawings, I have shown a modification of the apparatus in that the primary preheater and reaction coils are in a zone separate from the zone in which the secondary preheater and reaction coils are located. However, the operation and effect of the arrangement is the same as that shown in the preceding figure and hence the same numerals are employed to designate the elements shown in Fig. 2. In Fig. 2, the kiln is constructed with primary and secondary heating zones C, Cx, which are separated by a wall 2x, the primary preheater and reaction coils being located, respectively in said zones C, Cx. Outdraft may be provided at or toward the base of each zone, as indicated by the dotted lines a, Figs. 1 and 2.

Should, after a long period of time, the catalytic tubes of the coil of either section become inactive or of reduced inactivity, heat may be discontinued in the corresponding zone and the flow through the coils of the zone likewise discontinued, for reactivation or replacement of said catalytic tubes or other changes within the zone, while the operations within the second zone may continue unaffected. Also, should it be desired to employ zone Cx for the primary purpose of producing fixed gas, the heat therein may be increased to the desired point without affecting the thermal condition of zone C. A further advantage is that the thermal effects of the two zones may be varied as desired in the action upon the hydrocarbon material for specifically desired effects. Also, by controlling valves V and Vx located, for example, one in the primary discharge line and the second in the secondary discharge line, the pressures within the tubes of the primary and secondary elements may be varied to correspondingly vary the treatment of the hydrocarbons passed through said tubes.

An additional and important advantage of the structure shown in Fig. 2, is that it enables the operation of my process as adapted for the production of saturated and unsaturated hydrocarbons of low boiling point from a given charging stock or different charging stocks suitable, as to their cracked products, for blending.

It is now recognized that pressure largely controls the production of saturated hydrocarbon cracked products, as shown by the fact that under low or moderate pressure, as in vapor-phase cracking, the relative proportion of unsaturates, as compared with high pressure cracking operation, is substantially increased. It is generally desirable to blend a saturated motor fuel product with a motor fuel of high unsaturated content in order to secure an anti-knock characteristic by the blend, and for other reasons recognized in the art. Thus, by running a charging stock through the coils of the heating chambers C, Cx of Fig. 2, or through the two independent series of coils of chambers A and B of Fig. 1, under substantially different conditions of pressure, the product from one coil series may be largely saturated by heat reactions under the influence of high pressure, whilst the cracked vapors from the second coil series will be of high unsaturated characteristic. Inasmuch as the blending is effected under ideal conditions,

through the mixing of the vapors and the condensation of the mixed vapors into a stable blend not only may the desired blend be obtained most economically, but efficiency and stability of the blend will be obtained.

Features of my process and apparatus, compared with standard cracking methods are as follows:

- (a) Hydrogenation and catalytic cracking without formation of carbon.
- (b) High yield of gasoline, 70 to 85% of (70-80) octane number.
- (c) Large capacity and yield in proportion to size and cost of the unit.
- (d) Greatest absorption of heat with less consumption of fuel in proportion to capacity and yield.
- (e) Less cost of maintenance, labor and production.
- (f) Flexibility to control the percentage of a given product such as gasoline, fuel oil or fixed illuminating oil gas.

Although in the description of my process and apparatus, I stated that the vapors of the hydrogenation and catalytic cracking coils of the two sections discharge simultaneously and are mixed into the mixer container, if desired, I can use a separate mixer for each section of coils.

It is to be understood that the apparatus shown in the drawings is schematic and may be substantially modified without deviating from the scope of my invention.

The gas conversion coil, disposed in the uppermost part of section Cx in Fig. 2, may be used as a supplementary steam superheater when the unit is primarily operated for the production of motor fuel.

It is to be understood that the tubes may be disposed horizontally, vertically or spirally, and that their size as well as the tanks, etc., will depend on the capacity of the unit.

Having described my invention, what I claim and desire to secure by Letters Patent, is as follows:—

1. In the conversion of high boiling point hydrocarbons into lower boiling point products which comprises passing a stream of high boiling point hydrocarbons substantially in the vapor phase and under superatmospheric pressure through a primary conversion coil in less than thirty seconds, rapidly heating the vapors to above their critical vapor phase cracking temperature by heat conduction through the coil to the vapors and by injection of steam superheated to above the temperature of the vapors at the point of injection of the steam, expanding the stream of vapors from the primary coil into a lower pressure zone in which heat is conducted to the vapors but in less degree than in the primary coil, so as to maintain a temperature of between 900 and 1200° F., and maintaining the vapors in the lower pressure zone for a period of time longer than they were maintained in the primary conversion zone.

2. In the conversion of heavy hydrocarbon oils containing sulfur compounds into refined valuable hydrocarbon products, a dual two-stage treatment which comprises subjecting the initial material to vaporization, subjecting the substantially vaporized material under pressure to vapor-phase substantial conversion, subjecting the products of conversion to successive desulfurizing and fractionation to obtain a purified condensate recycle stock comprising the heavier fractions resulting from said treatment, then

separately subjecting said recycle stock in the presence of steam to vapor phase conversion, and to common desulfurizing and fractionation with the vapors of the initial two-stage treatment.

3. In the conversion of high boiling point hydrocarbons into lower boiling products, a dual two-stage conversion process which comprises subjecting a charging stock of the high boiling point hydrocarbons substantially in the vapor phase to a rapid vapor phase cracking treatment under superatmospheric pressure within the range of 100 to 600 pounds per square inch in the presence of superheated hydrogenous gas, passing the vapors from the vapor phase cracking treatment through a hydrogenating zone maintained under low pressure and with heat input of less amount than in the preceding treatment but with longer reaction time, subjecting the products of the hydrogenation to fractionation, then subjecting a reflux condensate to the same steps of cracking and hydrogenation in a separate stream and separately controlled, and subjecting the vapor products of this latter treatment to common fractionation with the products of the hydrogenation of the initial material to produce a valuable blended anti-detonating motor fuel.

4. A process in accordance with claim 1, in which the cracked charging stock vapor mixture within the lower pressure zone is subjected under expansion and reduced applied heat to the action of a metal catalyst of the hydrogenation type, and the reflux condensate is mixed with the charging stock, and subjecting the mixture to vaporization and two-stage cracking and hydrogenation reactions as described.

5. A process in accordance with claim 1, in which hydrogen is passed into the primary conversion coil simultaneously with the steam.

6. In the conversion of heavy hydrocarbon oils containing sulfur compounds into refined valuable hydrocarbon products, a dual two-stage and cracked vapor blending process which comprises the subjection of a plurality of streams of liquid oil charging stocks separately to a progressive heat action in separate heating coils to raise the temperature of the stock to above the boiling point of the least volatile constituent and preferably below its cracking temperature and thereby effecting substantial vaporization thereof, subjecting the plurality of streams of substantially vapor phase charging stock separately, each to a primary stage of rapid cracking action and under superatmospheric pressure, maintaining the vapor in said condition for a short period of time, the pressure of one stream being varied substantially from the pressure at which the other stream is subjected, and within the range of 100 to 600 pounds per square inch, the primary stage of rapid cracking action being effected by the simultaneous absorption of heat applied externally to the coils and by the injection into the oil vapor of steam superheated to a temperature substantially above the temperature of the oil vapor at the point of injection, passing the plurality of streams of oil-steam cracked mixture, each into its respective hydrogenation reaction zone under reduced pressure and heat, the temperature being from 900 to 1200° F., and the period of time that the substantially cracked mixture is subjected to the reduced heat and pressure within the hydrogenation reaction zones being greater than that of within the primary stages of rapid cracking and less than one minute, and blending the products of such treatments.

7. A process in accordance with claim 6, in which the highly saturated and highly unsaturated cracked oil vapors leaving the lower pressure zone are blended under expansion, and during the blending process are subjected to the action of a desulfurizing agent selected from materials such as alcoholic solution of lead acetate and sodium plumbite, allowing the vapors to separate from any residue and entrained liquid, subjecting the vapors to fractionation, and during fractionation allowing the heavier hydrocarbon vapors to separate from the lighter vapors and condense, mixing said purified heavier condensate with the oil charging stock subjected in the cracking action to the lesser pressure and subjecting the mixture to vaporization and two-stages of cracking and hydrogenation and blending as described.

8. A process in accordance with claim 3, in

which the time and pressure of cracking and hydrogenation reactions to which one of the plurality of streams of oil charging stock is subjected is greater than the time and pressure of cracking and hydrogenation reactions at which the other stream is subjected to secure highly saturated cracked oil vapors and highly unsaturated cracked oil vapors that by blending and fractionating will result in the production of a stable, homogeneous and highly anti-knock condensate of motor fuel type.

9. A process in accordance with claim 1, in which the oil-steam mixture within the lower pressure zone is subjected under expansion and reduced applied heat to the action of a metal catalyst of the hydrogenation type.

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