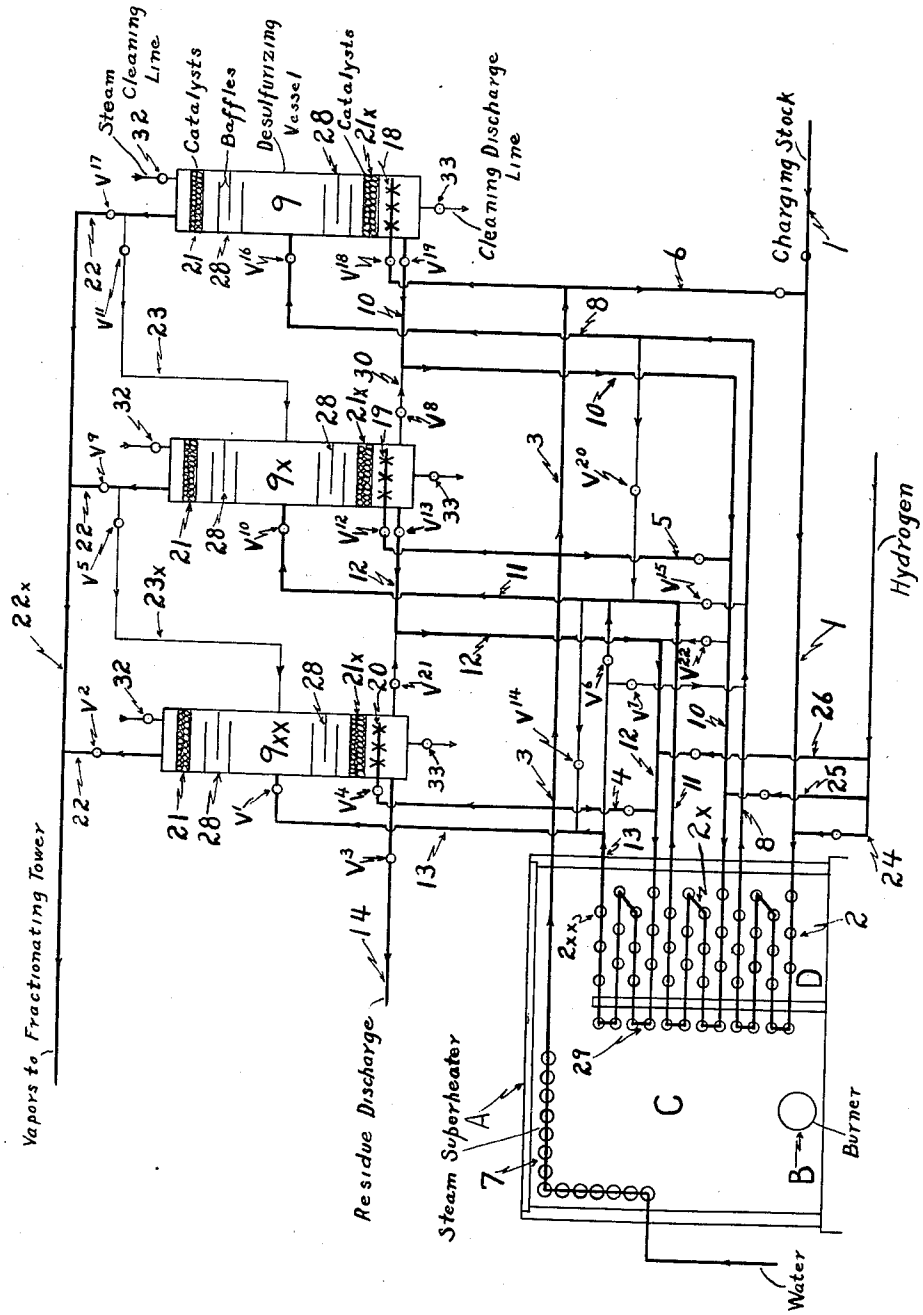
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PROCESS AND APPARATUS FOR DESULPHURIZATION AND CONVERSION OF OILS OF DIFFERENT CHARACTERISTICS INTO LOWER BOILING POINT HYDROCARBON PRODUCTS

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PROCESS AND APPARATUS FOR DESULPHURIZATION AND CONVERSION OF OILS OF DIFFERENT CHARACTERISTICS INTO LOWER BOILING POINT HYDROCARBON PRODUCTS

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In the processing of heavy boiling point hydrocarbon oils for the production of low boiling point products such as high anti-knock non-corrosive fuel of gasoline range, it has been considered commercially impossible to treat in the same unit and process charging materials of such different characteristics as crude oils of various types, gas oil, topped oil, hydrocarbon materials of semi-refined nature, and more particularly, heavy high carbon oils of high viscosity and sulphur content, such as Mexican and Venezuelan crudes, shale oil and liquefied coal.

By means of the present invention, a process and apparatus is provided to commercially and economically produce a superior type of motor fuel almost free from sulphur, if not entirely, from any charging stock regardless of its characteristics and sulphur-content. This motor fuel unlike straight run and cracked gasoline commonly sold, does not produce detonations or carbon deposits during combustion.

A high yield of the most desired products cannot be obtained by subjecting the hydrocarbon charging stock to conditions of a single operation or control. Some of the most highly desirable and valuable products are the results of a chain of reactions and recombinations from intermediate products and not directly from the initial charging stock and in my process I obtain the desired results through a plurality of successive and independent processes of reactions under the influence of gradually increased heat and pressure, regulated and controlled by the general and novel design of the apparatus. By this process 60 to 90% or more of the heavy oil is converted into hydrocarbon products of low boiling points of the gasoline range.

The characteristics of the process are: The initial step of subjecting the heavy oil to heat in the presence of steam and heated to a temperature below its cracking point, even though it may reach a point of incipient cracking, between 600 to 700° F. and under the influence of pressure between 50 to 250 lbs. per sq. inch, to obtain those desired products which a low heat and low pressure would induce, then removing the gases and liquid in a single stream under expansion and reduced heat, and then subjecting the gases and liquid products, preferably separated, to chemical (or catalytic) reactions. The reduced catalytic treated oil of lower viscosity and lower sulphur content is returned to the heating zone, and subjected to a plurality of alternative stages of cracking and heated in each stage of cracking to higher heat and under the influence of higher pressure than in the preceding stage, the heat being between 775 to 1000° F. and the pressure not in excess of 1000 pounds per sq. inch, but not less than 250 pounds per sq. inch.

Any of the stages of cracking or all, may be influenced by hydrogenation by means of the action of steam or, if desired, of steam and hydrogen, or hydrogen bearing or yielding gases directly applied to the charging stock, and preferably in the presence of a suitable catalyst of the hydrogenation type; the resulting mixture of gases and vapors, and liquids from the first stage of cracking are removed in a single stream and subjected, preferably separated, to the action of chemical (or catalytic) desulphurizing reactions and preferably in the presence of additional steam, the gases and vapors are allowed to leave the catalytic zone and subjected preferably to further purification and then to fractionating, and from which is obtained a low boiling point hydrocarbon product of the gasoline range of unusually high anti-knock character and the unvaporized oil of lower viscosity and lower sulphur content is returned, substantially free of tar and tarry materials, to the heating zone and subjected to the succeeding cracking stage.

The proportion of steam to oil preferably will be increased in each succeeding stage of cracking to increase the hydrogenation and reformation of the reactive elements of the oil-steam mixture, the steam being heated to a temperature of not less than the critical temperature of the water, and preferably heated to a temperature in which the absorption of heat by the steam permits it to maintain latent heating conditions.

The process and apparatus will be described in connection with the accompanying drawing, in which—

The figure illustrates in schematic elevation an apparatus adapted for carrying the process into effect. Variation of all or part or modification of changes may be made within the scope of my process and apparatus without affecting the rights of my claims.

In the drawing, A indicates a kiln having a burner B, located in its combustion section C. The charging stock is pumped through pipe 1 to an externally heated coil 2 disposed in the lower part of the convection section D of furnace A, by which means the charging stock is heated to a temperature of incipient cracking, under a pressure range of not less than 50 pounds per square inch, but not in excess of 250 pounds, depending upon the characteristics of the charging stock used and products desired.

Heat is applied to the interior of coil 2 by means of steam passed through pipe 3 and branch pipe 6 leading from the steam coil 7 disposed in the combustion section C of furnace A and superheated to a temperature preferably in which the absorption of heat by the steam vapor permits it to maintain latent heating conditions and preferably in the presence of hydrocarbon gases and any metallic material capable of reacting with the water and vapors to produce nascent hydrogen, such as finely divided iron, or such as hydrides of zinc, iron or other metallic material.

Coil 2 is of such size as to maintain the oil-steam mixture within the heating zone for an insufficient time to exceed the incipient cracking stage of the mixture, say 600 to 700° F. The heavy reduced oil-steam mixture of coil 2 passes through pipe 8 into a desulphurizing catalytic vessel 9 wherein the said oil-steam mixture expands under reduced heat. Desulphurizing vessel 9 discharges condensate or unvaporized treated oil by pipe 10, either directly or through a heat exchanger, into a highly externally heated coil 2*x*, centrally located in section D, and the oil heated to a temperature from 775° F. to 875° F. in the presence of additional steam applied internally by means of pipe 5, and subjected to pressure higher than coil 2, coil 2*x* discharges through pipe 11 into desulphurizing vessel 9*x* centrally thereof wherein the gases and vapors expand under reduced heat. Vessel 9*x* discharges condensate and unvaporized treated oil through pipe 12, directly or through a heat exchanger, with fresh charging stock, if desired into coil 2*xx*, disposed in the uppermost part of convection section D and subjected to pressure higher than coil in 2*x*, and heated to a temperature of about 875° F. to 1000° F. in the presence of steam applied internally by pipe 4, coil 2*xx* discharges through pipe 13 into desulphurizing vessel 9*xx* wherein the gases and vapors expand under reduced heat and vessel 9*xx* discharges the residue through pipe 14 into a residue tank (not shown) or can be recycled practically free of tar and tarry materials, jointly with fresh charging stock.

The proportion of steam to oil by weight fed into the cracking coils is adjusted to the temperature used to regulate the time of contact and extent of reactions of the reactive elements of the mixture, but below the ratio of twelve pounds of steam to one gallon of oil.

The vapors and fixed gas separated from the unvaporized oil within the desulphurizing vessels 9, 9*x* and 9*xx* pass upward concurrent with the additional steam injected below the catalyzers 21*x* through steam spiders 18, 19, and 20 and in direct contact with catalyzers 21, and are drawn off through pipes 22 and manifold pipe 22*x* and diverted to a condenser and condensate tank (not shown) or pass directly to the fractionating apparatus, or may be passed from one vessel to the other through pipes 23 and 23*x* and drawn off from vessel 9*xx* and subjected to fractionation. The condensed steam will be returned without substantial loss of heat to the heating zone and superheated for re-use in the process.

Superheated steam from coil 7 or any other suitable source is injected upwardly from the lower part of each desulphurizing vessel through steam spiders 18, 19, and 20, the steam passing counter-current to the condensate and unvaporized treated oil to secure an intimate contact with the oil as it passes through the catalyzers 21*x*. Catalyzers or catalytic material of the vessels 9, 9*x*, and 9*xx* may be of the same type of reactions, or the type of catalyzers of each vessel may differ from one vessel to another and preferably catalyzer 21 being of stronger material than catalyzers 21*x* in accordance with specific reactions desired.

The reduced oil passed to the cracking coils 2*x* and 2*xx* from vessels 9 and 9*x* is subjected to internally applied heat by means of the injected steam and the reactions within the coils 2*x* and 2*xx* may be influenced by pressure, preferably increasing as the heat increases in each successive cracking coil disposed in the heating zone. The pressure may range preferably from 250 to 1000 pounds per square inch.

Each of the coils 2*xx*, 2*x*, and 2, are located in the convection section D and subjected to a gradual reduction of external heat supplied by the flue gases from the combustion section C, may have one or a number of tubes 29, disposed in the combustion section C to heat the oil to the temperature required.

By disposing one or more tubes 29 in the combustion section C, as required to insure the necessary gradually increased temperature of the oil in coils 2, 2*x* and 2*xx*, not only does it insure the desired cracking reactions within the coils, but also insures a greater efficiency in the unit and economy in the construction costs.

If one or more of the vessels 9, 9*x*, and 9*xx* were shut down for cleaning or to reactivate the catalytic material whose activity may have been reduced or lost, or for any other reason, the apparatus would continue in operation without any interruption, as, for example, if vessel 9*xx* is to be shut down for reactivation of the catalyzers, then by closing the valves V1, V2, V3, V4 and V5 to stop all the flows into and out of the vessel and by opening valves V6 and V7, the discharge from coil 2*xx* is diverted to the vessels 9 and/or 9*x* to join the flow from coils 2 and 2*x*. If vessel 9*x* is to be shut down, then by closing valves V8, V9, V10, V11, V12, and V13 to stop all flows into or out of the vessel 9*x* and by opening valves V14 and V15, the discharge from coil 2*x* is diverted to the vessel 9 and/or 9*xx* to join the flow from coils 2 and 2*xx*. If vessel 9 is shut down, then by closing valves V16, V17, V18, and V19, to stop all flows into or out of the vessel and by opening valve V20, the discharge from coil 2 is diverted into vessel 9*x* to join the flow from coil 2*x*, and by opening valve V8 in branch pipe 30, the coil 2*x* will receive unvaporized oil from vessel 9*x*.

If vessels 9*x* and 9*xx* are shut down simultaneously then by closing all valves to shut off all flows into or out of the vessels 9*x* and 9*xx*, and by opening valves V7, V15, and V22 all the coils within the heating zone remain unaffected and discharge simultaneously into vessel 9 by means of by-passes. If vessel 9*xx* is the only vessel in operation, the coils 2*x* and 2*xx* would receive their supply of unvaporized oil by opening valves V21 and V22 although in the latter cases the feed to the coils is preferably reduced.

Pipes controlled by valves 33 disposed at the bottom of each vessel can be used for the ejection of any tar or tarry materials deposited at the bottom of the desulphurizing vessels, and can be used jointly with pipes controlled by valves 32 disposed at the top of each vessel for cleaning purposes and for the reactivation of the catalytic materials.

When the catalyzers within the vessel or vessels have been reactivated, then by reversing the op-

eration of the valves herein described, to their original positions, the flows will continue as originally stated in the description of my process and apparatus.

The catalytic desulphurizing vessels may be preferably 20 to 30 feet long and 15 to 25 inches in diameter and may be one or a plurality of such structures or may be units of 2 or 3 or more vessels, the number used depending upon the capacity of the unit and extent of catalytic treatment and reactions desired.

Hydrogen or gases containing or yielding hydrogen can be desirably injected into the heating coils **2**, **2***x*, and **2***xx*, or into one or more of them, through pipes **24**, **25**, and **26** respectively.

The catalyzers or catalytic material used in my desulphurizing-cracking process can be solid metallic bodies in the form of beads, mesh, layers on baffles, etc., or they may be of any suitable form to give the greater contact surface and have double function, as, for example, the baffles **28** and catalysts **21** and **21***x* may be of catalytic material or an alloy of two or more catalytic materials, such as metallic oxides, as, for example, molybdenum, tungsten, iron, chromium, copper, etc. and may be incorporated with a promotor or a carrier such as oxides of zinc, silicate alumina, infusorial earth, bentonite, or instead of the oxides, sulphides of said metals may be used or the vessels themselves can be of chromium-nickel-iron-alloy or lined or coated inside with one or a combination of two or more desulphurizing catalysts such as those named above.

The use of steam in the coils and desulphurizing vessels not only supplies additional heat but acts as a diluent and effectively retards polymerization reactions. By regulating the intake of steam and oil, polymerization can largely be controlled and the desired temperature within the coils and vessels can be effectively and efficiently controlled. The steam assures delicate adjustment of time, temperature and cracking.

It will be understood that in this process with its extreme flexibility and many independent reactive stages, the control conditions can be varied as desired to vary the reactions to suit the nature of the final products desired with the maximum results. For example, the valve arrangement applied to each one of the desulphurizing vessels is such that the vapors received within any vessel may be returned with the liquid to the following corresponding set of cracking tubes.

In this process, I do not limit the use of the liberated oxygen of the steam to react with the free carbon, other oxygen bearing gas vapors or liquids may be introduced with the steam or separated for reacting with the carbon and to obtain specific reactions due to their composition.

The exact size of the furnace length of tubes, pipes, vessels, height of towers, etc. depend on the capacity of the unit, character of the charging stock and final products desired.

In the claims "oil" is used as meaning crude oil, gas oil, topped oil, shale oil, liquefied coal, allied hydrocarbon products or hydrocarbon products of semi-refined nature except gasoline or naphtha; by the words "heating zone" I mean a furnace subjected to heat in which a plurality of reaction, heating, cracking coils are disposed within different zones of heat; the word "coil" is used as meaning one or a plurality of such coils, and the word "vessel" as meaning one or a plurality of such structures or may be in units composed of two or more vessels.

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

1. Apparatus for desulphurizing and converting oils into lower boiling point hydrocarbon products, comprising a kiln, means dividing the kiln into combustion and convection sections plurality of sets of heating tubes comprising preheating tubes primarily disposed in the convection section of lowest heat, a set of tubes primarily disposed in the convection section of intermediate heat, and a set of tubes primarily disposed in the convection section of highest heat, each set of tubes including an area thereof disposed within the combustion section of the kiln a burner in the combustion section of the kiln, a plurality of desulphurizing members disposed exteriorly of the combustion and convection sections of the kiln, means for leading a mixture of oil and steam to the set of tubes of lower heat adapted to preheat said mixture, means for discharging the treated mixture from said tubes in a single stream to one of said desulphurizing members, means for leading the liquid from said desulphurizing member to the set of tubes receiving an intermediate and cracking heat, means for discharging the treated mixture from said intermediate tubes to a second of said desulphurizing members, means for leading liquid from said second desulphurizing member to the set of tubes having higher temperature than the second named sets, means for leading the treated materials from said set of tubes of higher heat to one of said desulphurizing members, and means for discharging vapors from said desulphurizing members.

2. Apparatus in accordance with claim 1, in combination with means for leading the vapors from one desulphurizing chamber to a second desulphurizing member preliminary to discharge of said vapors from areas of desulphurization.

3. A process for treating heavy hydrocarbon oil to produce liquid lower boiling point products, which comprises the initial heating of a mixture of oil and steam in proportion below 12 pounds of steam per gallon of oil to a temperature not in excess of 700° F. under pressure not exceeding 250 pounds per square inch, removing the heated mixture and subjecting the same to expansion and the action of catalytic materials of the desulphurizing type, under reduced heat and pressure, returning the heavier fractions of the mixture to a heating zone and subjecting the same together with additional steam to a plurality of stages of cracking, the stages of cracking being under the influence of successively higher heat and higher pressure than that of the initial heating stage, and following each stage of cracking removing the vapors and unvaporized liquid products and subjecting the same separately to catalyzation under expansion and reduced heat and under superatmospheric pressure, the catalytic materials in at least one stage of catalytic action following a cracking stage being of the desulphurization type, and the remaining catalytic materials being of the hydrogenation type.

4. A process for treating heavy petroleum oil to produce liquid lower boiling point products, which comprises the initial heating of a mixture of oil and steam under a temperature not in excess of 700° F. to incipient cracking under pressure not exceeding 250 pounds per square inch, removing the heated mixture and subjecting the same under expansion and reduced heat to a purifying agent for the removal of sulphur, re-

turning the liquid heavier fractions of the mixture to a heating zone and subjecting the same together with water vapor to a plurality of stages of cracking, the stages of cracking being under the influence of successively higher heat and higher pressure than that of the initial heating stage and following each stage of cracking subjecting the treated mixture to expansion and to a purifying agent, and removing the lighter vapors.

5. A process in accordance with claim 3, in which the lighter vapors of the initial heating and two cracking stages are subjected jointly to fractionation and condensation.

6. A process in accordance with claim 3 in which the cracked vapors and heavier fractions are subjected to direct contact with steam flowing countercurrent to the flow of said unvaporized oil prior to their passage through the desulphurizing treatment, the ratio of steam to oil being from 1 to 4 pounds of steam per gallon of oil.

7. A process in accordance with claim 3, in which vapors substantially composed of gasoline boiling range fractions are led from the initial zone of expansion and action of catalytic materials of the desulphurizing type to a second catalytic zone receiving vapors from one of the plurality of the stages of cracking, and are mixed with said vapors jointly with steam, and the mixed vapors are subsequently subjected to fractionation.

8. Apparatus for desulphurizing and converting petroleum oils into lower boiling point hydrocarbon products and desulphurizing the products, comprising a plurality of cracking tubes, a furnace enclosing the tubes, a plurality of independent desulphurizing chambers disposed exteriorly of the furnace, a heating coil within the furnace, means for leading a mixture of oil and steam to the heating coil, means for discharging the heated mixture from said coil to one of said desulphurizing chambers, means for leading liquid from said desulphurizing chamber to one of said cracking coils receiving an intermediate and cracking heat, means for discharging the treated mixture from said intermediate tubes to a second of said desulphurizing chambers, means for leading liquid from said second desulphurizing chamber to one of said set of cracking tubes receiving a higher temperature than the first named cracking tubes, means for leading the treated materials from said set of tubes of higher heat to one of said desulphurizing chambers, means for discharging vapors from said desulphurizing chambers to a fractionating zone, means for shutting off the connection between one of said desulphurizing chambers and said fractionating zone, and means for directing both liquid and vapors from said shut off desulphurizing member to a set of cracking tubes, having a higher temperature than the set from which the vapors and liquids were previously discharged.

9. A process in accordance with claim 3, in which the additional steam is superheated to a temperature above the critical temperature of the water, and is mixed with the heavier fractions from the first desulphurizing treatment and the mixture subjected to heat above the cracking temperature of said heavier fractions and under the influence of pressure and not in excess of 1000 pounds per square inch and not less than 250 pounds per square inch.

10. A process of producing low boiling point products from heavy petroleum oils, in which cracked vapors of an oil-steam mixture are subjected to a series of consecutive desulphurizing catalysts prior to final fractionation and condensation of the low boiling point products, and in a plurality of independent zones, said vapors being passed through the catalytic material in the zones under progressively increased temperature in the consecutive zones, and fractionating the vapors of the last zone resulting from said consecutive zone treatment, to obtain low boiling point products of motor fuel type.

11. A process in accordance with claim 10, in which the oil-steam mixture comprises not in excess of one gallon of oil to 100 pounds of steam, and the mixture is superheated prior to entering the desulphurizing zones under the influence of a metallic material able to react with the steam and to produce nascent hydrogen, said material being selected from a group comprising zinc hydride, iron hydride, and finely divided iron.

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