

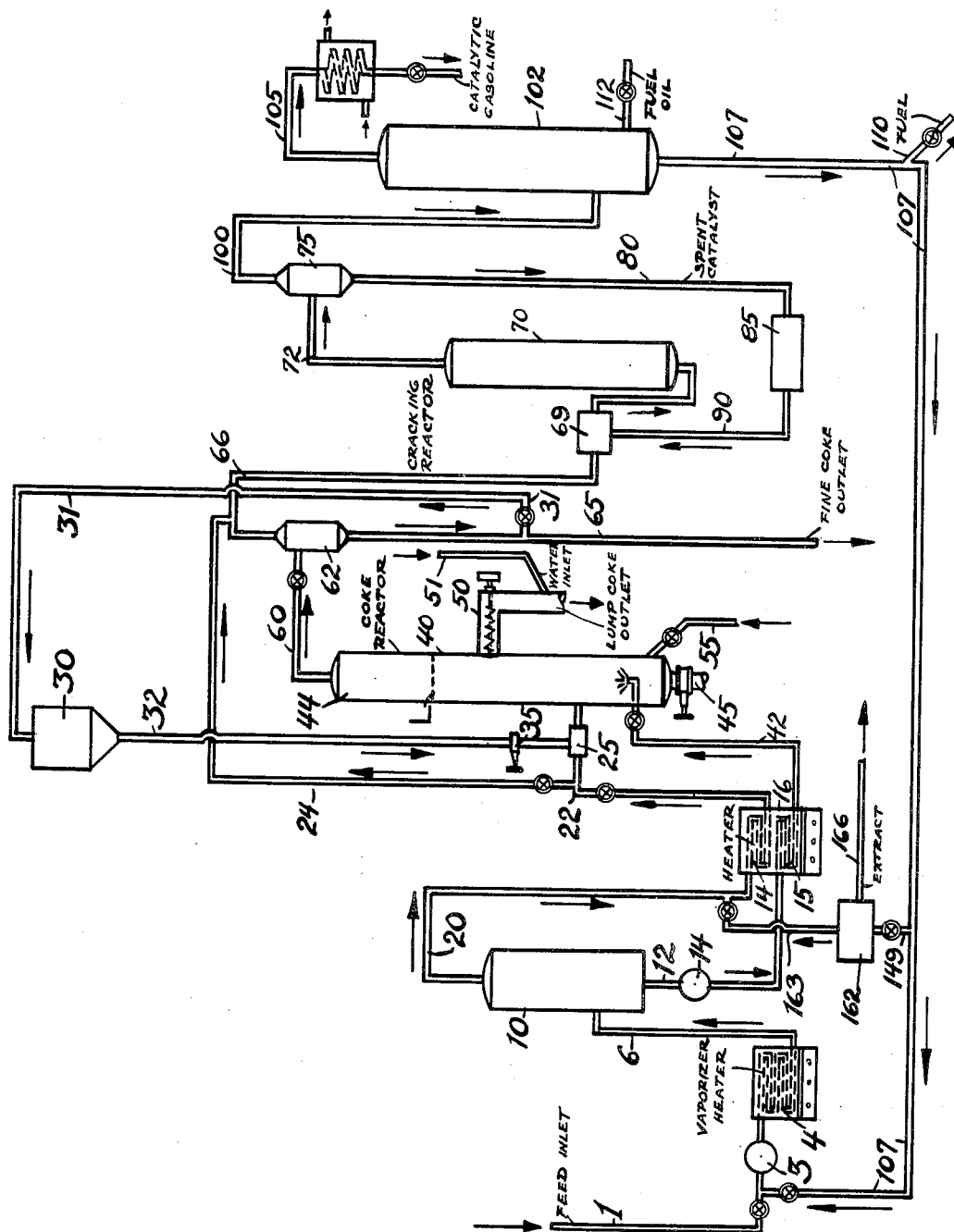
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REFINING PROCESS

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REFINING PROCESS

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The present invention relates to improvements in the art of refining hydrocarbon oils, and more particularly it relates to a continuous process of treating heavy petroleum oils, such as topped crudes, heavy pitches, oxidized asphalts, cracked residua, etc., in order to form maximum quantities of hydrocarbons boiling substantially within the gasoline range of improved octane ratings and continuously produced solid coke.

It is, of course, generally known that in modern refinery practice, the residual oil remaining after the crude oil has been distilled at relatively low pressure as say at about atmospheric pressure, to remove naphtha, gasoline, kerosene, and the like, or, in other words, that portion of the original crude boiling up to about 800° F., if a greater quantity of gas oil is required, is subjected to either a viscosity reducing operation or a coking operation. In the first of these operations, the oil is heated to about cracking temperatures and then is discharged into a reaction zone where it is permitted to remain or react for a sufficient period of time to effect a conversion of the charged oil to substantial quantities of gas oil and tar.

In the second type of operation, the conditions are more drastic and the oil is transformed into readily volatilizable products (gas oil, gasoline, gas, etc.) and solid coke. In coking oils, the oil heated to 800° to 950° F. or thereabouts is discharged into a drum where the reaction proceeds until the drum becomes practically filled with coke whereupon the operation is discontinued, the oil is removed, the drum is permitted to cool and the coke is removed.

The usual coking practice is to employ two or more coking drums, one of which is in the "on-stream" or coking operation, while the other or others is or are being decoked. The decoking operation is a laborious and time-consuming one, since in the ordinary refinery practice, the coking operation is carried out until a thick layer of coke is deposited on the bottom and the side walls of the coking vessel. When it becomes necessary to decoke the vessel, the usual procedure, as stated, is to draw off the oil, permit the vessel to cool, and then to remove the coke manually. In order to aid in the removal of the coke, it is customary to insert cables or chains in the coking vessel prior to the coking operation, upon which the coke as formed deposits. The cables or chains when drawn out of the vessel at the end of the coking operation break up the coke and facilitate its removal. However, this particular expedient

does nothing more than to break up the masses of coke, still leaving considerable coke adherent to the side walls and bottom of the vessel, and of course this adherent coke must be removed before the vessel is put back in the onstream operation.

Another method of coke removal is by means of hydraulic drilling. Hydraulic drilling is however, an expensive process and therefore not generally practiced. Thus, we observe that the decoking of a coking drum is a laborious and time-consuming operation, in the usual practice.

My present invention is primarily directed toward a combined coking and catalytic cracking operation in which I form a high octane number gasoline and a hard, friable, relatively oil-free coke which may be continuously removed from the system thus obviating the necessity of intermittent shut-downs.

Further, my present invention not only differs from the prior practice in the details enumerated hereinbefore, but it further differs in that I conduct the coking operation in the presence of a powdered material, which powdered material forms nuclei about which the formed coke may be built up to form granules or lumps.

Another important object of my invention is that I produce a gas oil by coking which is particularly suitable as a catalytic cracking stock because of the fact that the coke-forming constituents are substantially removed during the coking operation.

In general then, the objects of this invention include treating a residual petroleum oil to: (a) secure maximum quantities of high octane gasoline, (b) desired quantities of gas oil, either for sale as a fuel or for catalytic cracking, and (c) continuously produce high quality coke of saleable quantity.

Other and further objects of my invention will appear from the following more detailed description and claims.

In order to afford a better understanding of my present invention reference is had to the accompanying drawing which contains a flow diagram indicating diagrammatically the various steps performed in a preferred modification of my present invention.

I shall refer to the drawing in detail and shall set forth a specific example in which I describe the manner of processing a given feed stock.

A topped or reduced West Texas crude petroleum oil having an A. P. I. gravity of about 18° is charged to the system shown in the drawing through line 1 and thereafter pumped by pump

3 into a furnace 4 where the residual oil is heated to a temperature of from about 800° F. to 850° F. under a pressure preferably in the range of from 10 lbs. to 20 lbs./square inch gauge, but in any event below 100 lbs./square inch gauge, with optional use of steam. During this heating, a maximum quantity of superheated heavy gas oil vapors are produced and the entire product is then discharged through line 6 into a separator 10. From separator 10 the bottoms fraction was withdrawn from line 12 carrying pump 14 and then discharged into coil 15 in a furnace 16, where the said liquid fraction was further heated to a temperature of from about 850° F. to 925° F. During this heating, the heavy oil undergoes viscosity reducing to produce further quantities of gas oil, which gas oil was then superheated to the range indicated. The overhead fraction from separation drum 10 was withdrawn through line 20 and discharged into coil 14 of furnace 16, as is indicated in the drawing. The superheated vapors originating in line 20 were withdrawn from furnace 16 through line 22 and thence discharged into an injector 25 where they were mixed with a non-catalytic powdered material withdrawn from the supply hopper 30 through a standpipe 32 carrying a sliding valve 35 adapted to control the flow of material in said standpipe. Instead of injection means 25, any other suitable mixing means may be provided. The solid material mixed in 25 with the oil vapors may be powdered carbon in the form of charcoal, or it may consist of wood flour, coal dust, powdered petroleum coke and the like. Preferably this material has a particle size of from 20-100 mesh.

A suspension of the powdered solid material in the oil vapors is formed in mixer 25, and this suspension is then discharged into a reactor 40. The powdered material and oil vapors are mixed in such proportions that within the reactor the concentration of the solid material in the vapors is from about 15 to 35 lbs./cu. ft., taking into consideration the vapors released from line 42 within the said reactor. The oil in line 42 is that formed in the previously mentioned viscosity reducing operation and normally will have intermixed therewith oil vapors. The combined liquid oil and vapors in line 42 are discharged into a point near the bottom of reactor 40 in the form of a spray or mist formed by an atomizer 44, spray head or the like, as indicated in the drawing. Within the reactor 40, the oil introduced through line 42 undergoes coking and the coke which is produced forms particles about the solid material originating in hopper 30, the latter serving as a sort of nuclei about which the formed petroleum coke coats or deposits to form "pea" size lumps or larger aggregates. In the coking operation, the material originating in hopper 30, if it be cellulosic, say sawdust, etc., undergoes carbonization so that with respect to the operations in reactor 40 both organic and petroleum coke may be formed. The coke formed in reactor 40 may, for the most part, be withdrawn through an outlet pipe 50 in the form of lumps having a particle size of say about $\frac{1}{4}$ inch to $\frac{1}{2}$ inch on the average. The discharging coke is preferably sprayed with water from pipe 51 to cool it so that it will not ignite upon contact with the atmosphere. This coke, because of the manner in which it is produced, is hard, friable, substantially ash-free and dry and provides a saleable fuel. It may be necessary periodically to discontinue the operation to withdraw coke

which has become too massive to be carried up to the level of draw-off 50 and in that event, the coke may be withdrawn through manhole 45, or this massive coke may be withdrawn continuously without shutting down the coking drum operation by substituting for manhole 45 a gas seal through which the coke may be withdrawn. These gas seals are well known and include liquid pumps, etc., through which the coke gravitates and is withdrawn from the bottom while vapor escape is prevented at this point by said seal. It should be pointed out that in order to assist in the operation carried out in reactor 40 superheated steam or heated hydrocarbons from some source, say at temperatures of 850° F. or higher may be discharged into the bottom of reactor 40 through line 55. This superheated steam aids in the vaporization of the vaporizable portions of the oil in reactor 40.

A portion of the vapors in line 22 may be bypassed around the coking vessel 40 and mixer 25 and discharged directly to the catalytic cracking step, hereinafter more fully explained.

The vapors formed in reactor 40 are withdrawn overhead through line 60 and discharged into cyclone separator 62 where coke particles, if any, entrained in the vapors are separated and withdrawn through pipe 65. The coke fines in line 65 after drying the same with steam or the like may be recycled to hopper 30 through line 31. The vapors, on the other hand, are withdrawn through line 66. If these vapors still contain particles of carbon or coke, it is advisable to pass them through one or more additional separators, such as cyclone separators or electrical precipitators, to substantially free vapors of solid material. The vapors in line 66 were discharged into a reaction vessel 70 after first mixing therewith in mixer 69, a cracking catalyst, preferably in the form of a powder to form a suspension. The catalyst may be an acid treated clay such as "superfilitrol," bauxite, bentonite, or synthetic gels, alumina and silica or magnesia. The catalyst preferably has a particle size of 100 or 400 mesh. The amount of catalyst mixed with the vapors in line 66 should be so proportioned as to provide a suspension for reactor 70 having a density of about 1-5 lbs./cu. ft. In reactor 70 the vapors undergo cracking to form substantial quantities of gasoline having a high octane number. The operating conditions prevailing within reactor 70 in order to effect the desired result were as follows:

Temperature.....	degrees F.	850 to 950
Pressure.....	lbs./sq. in.	0 to 10
Residence time of vapors in reactor	seconds..	5 to 25

After being subjected to the foregoing conditions, the reaction products were withdrawn through line 72 and discharged into cyclone separator 75 where the catalyst is separated from the reaction products, withdrawn through line 80, thence regenerated in regenerator 85 preferably by combustion with air or other regeneration gas of tarry and cokey constituents formed thereon as a result of the operation taking place in reactor 70.

The method of regenerating catalyst of the kind here in question is well known to the art and need not be described in detail. It may merely be stated that the catalyst is regenerated by mixing it with air or other free-oxygen-containing gas under conditions of temperature and pressure and time of exposure or contact be-

tween the fouled catalyst and regenerated gas to effect the desired regeneration or revivification. The art also is well aware that certain precautions must be observed in order to prevent injury to the catalyst, these precautions involving essentially the steps of diluting the regeneration gas (if it is air or oxygen) with inert gas to prevent the acquisition of such temperatures by the catalyst as will cause baking or fusing, or it might involve carrying out regeneration under super-atmospheric pressure to cause the regeneration gas to promote active combustion of the catalyst contaminants at a substantially lower temperature than may be had at normal atmospheric pressure. The regenerated catalyst is reintroduced into line 66 through line 90. Conservation of energy may be effected by mixing hot uncooled catalyst recovered from the regeneration zone with the vapors in line 66, thus providing at least a portion of the superheat necessary to effect the desired conversion in reactor 70 and also to compensate, at least in part, for the heat absorption resulting from the endothermic nature of the reaction in vessel 70.

Reaction products are recovered from cyclone separator 75 through line 100 and, as before, these vapors are passed through additional separators to free the vapors completely of solid material. The vapors are then discharged into a fractionating column 102. In the drawing I have shown a catalytically cracked gasoline withdrawn overhead through line 105 and a cycle stock withdrawn through line 107 which latter may be returned to the inlet side of pump 3 for further treatment.

The cracked gasoline in 105 is discharged into equipment (not shown) to refine and recover a finished gasoline of proper volatility, etc. This product may be used as such, or it may be blended with other stocks to form a finished gasoline. It is also pointed out that highly refractory material may be withdrawn from the system through line 110 or may be withdrawn directly from the fractionator through line 112. The cycle stock in line 107 may be recycled to line 20 and in this modification of my invention, it is usually advisable to solvent treat the cycle oil to remove polynuclear aromatics such as naphthalene, its derivatives, etc., since such compounds cause excessive coke formation. I have indicated diagrammatically a solvent treater 162 in line 149. The process of solvent treating is itself well known and involves treating the material with a selective solvent for the aromatic compounds to form a raffinate which is richer in paraffinic constituents and therefore more suitable for further cracking than the untreated stock. The raffinate is withdrawn through line 163 and discharged into line 20 for further treatment. The solvent extract is withdrawn through line 166. Also I may hydrogenate the material in line 149 preferably catalytically and under superatmospheric pressure according to standard methods to render the cycle stock more suitable as a cracking stock.

To recapitulate, my present invention relates to the method of producing from residual petroleum oils by a continuous method commercially saleable coke fuels with a minimum cost of handling and, at the same time, to produce maximum quantities of high quality anti-knock gasoline from the balance of the charging material not reduced to coke.

In its essence, my new process is preferably a multi-stage operation, in the one stage of which

I coke a viscosity reduced petroleum oil residuum, and in another stage thereof, I catalytically crack the readily vaporizable products formed in the viscosity reducing stage, as well as virgin gas oil, etc., to form high yields of high quality gasoline. As hereinbefore enumerated, the major features of my improved process include the following: (1) continuity of operation with respect to the coking phase; (2) an integrate vis-breaking, coking and cracking operation all contributing toward the end result, namely, the production of commercially saleable coke and high quality gasoline; (3) the advantages of heat conservation made possible by an uninterrupted chain of operations, including viscosity reducing, coking, and cracking, and the transfer of heat from a catalyst regeneration zone which operates under exothermic conditions, to zones where endothermic reaction takes place, such as for instance cracking operations; (4) a compact unitary system which, because it operates continuously, eliminates the necessity for intermediate storage tanks or other vessels common in interrupted or non-integrating systems. The production of a gas oil by viscosity reducing and coking is particularly suitable for catalytic cracking because of its low content of coke-forming constituents.

Many modifications of my invention falling within the spirit thereof will be apparent to those familiar with this particular art. In the first place, obviously I may use a feed stock of higher or lower gravity from any domestic or foreign source. I may charge into the system a whole crude, or I may limit the charging stock to a heavy gas oil. Depending of course upon the nature of the charging stock, the operating conditions will vary. In a word, the specific example which I have hereinbefore set forth is purely illustrative of my invention and does not impose any undue restrictions thereon. It is my intention to claim as my invention, the subject matter expressed in precise details which I have set forth hereinbefore and all reasonable modifications thereof which are included therein by necessary implication, except matter excluded by the terms of the appended claims.

What I claim is:

1. A continuous operation for treating a relatively heavy hydrocarbon oil to produce a hard, friable coke and a maximum quantity of high anti-knock gasoline which comprises heating the said oil, separating the oil into a vapor fraction and a liquid fraction, superheating the vapor fraction and separately heating the liquid fraction, mixing a powdered non-catalytic solid material with the vaporized fraction, discharging both fractions into a coking zone, recovering a sensibly dry coke from said coking zone, simultaneously recovering a vapor fraction from said coking zone, mixing the vapor fraction with a cracking catalyst, conducting the mixture to a catalytic cracking zone, permitting the mixture to remain in said last-named zone for a sufficient period of time to effect the desired conversion, recovering reaction products from the cracking zone, separating the catalyst therefrom, fractionating said reaction products and recovering a gasoline of high octane rating from the said fractionation.

2. The method set forth in claim 1 in which the powdered solid material used in the coking operation is of organic origin.

3. The method set forth in claim 1 in which the liquid fraction recovered from the separation

zone is subjected to viscosity reducing conditions prior to introduction into the coking zone.

4. The method of treating a crude petroleum oil which comprises heating the said oil to vaporize constituents boiling up to and including the gas oil range, separating the heated oil into a vapor fraction and a liquid fraction, subjecting the liquid fraction to viscosity reducing temperatures, superheating said vapor fraction to cracking temperatures, mixing the said vapor fraction with a powdered non-catalytic solid material to form a suspension, discharging the latter suspension into a coking zone, discharging the viscosity reduced oil at coking temperatures into said coking zone in the form of droplets, permitting the suspension and the droplets of oil to intermix and undergo conversion in said coking zone, forming and withdrawing continuously a lump coke in said coking zone, recovering a vapor fraction containing gas oil from said coking zone as an overhead vapor fraction, suspending a powdered catalyst in last-named vapor fraction and

subjecting the suspension thus formed to catalytic cracking temperatures, to form a quantity of high octane rating gasoline and a gas oil.

5. The method set forth in claim 4 in which the powdered material mixed with the first-named vapor fraction is a powdered petroleum coke.

6. The method set forth in claim 4 in which the gas oil formed in the catalytic cracking phase is separated from the gasoline fraction and recycled to be mixed with crude oil.

7. The method set forth in claim 4 in which the gas oil formed in the catalytic cracking is separated from the gasoline and recycled to the vapor superheating step.

8. The method set forth in claim 4 in which coke fines are present in the vapor fraction recovered from the coking zone, which fines are separated from the said vapors, dried and resuspended in the vapor fraction discharged into said coking zone.

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