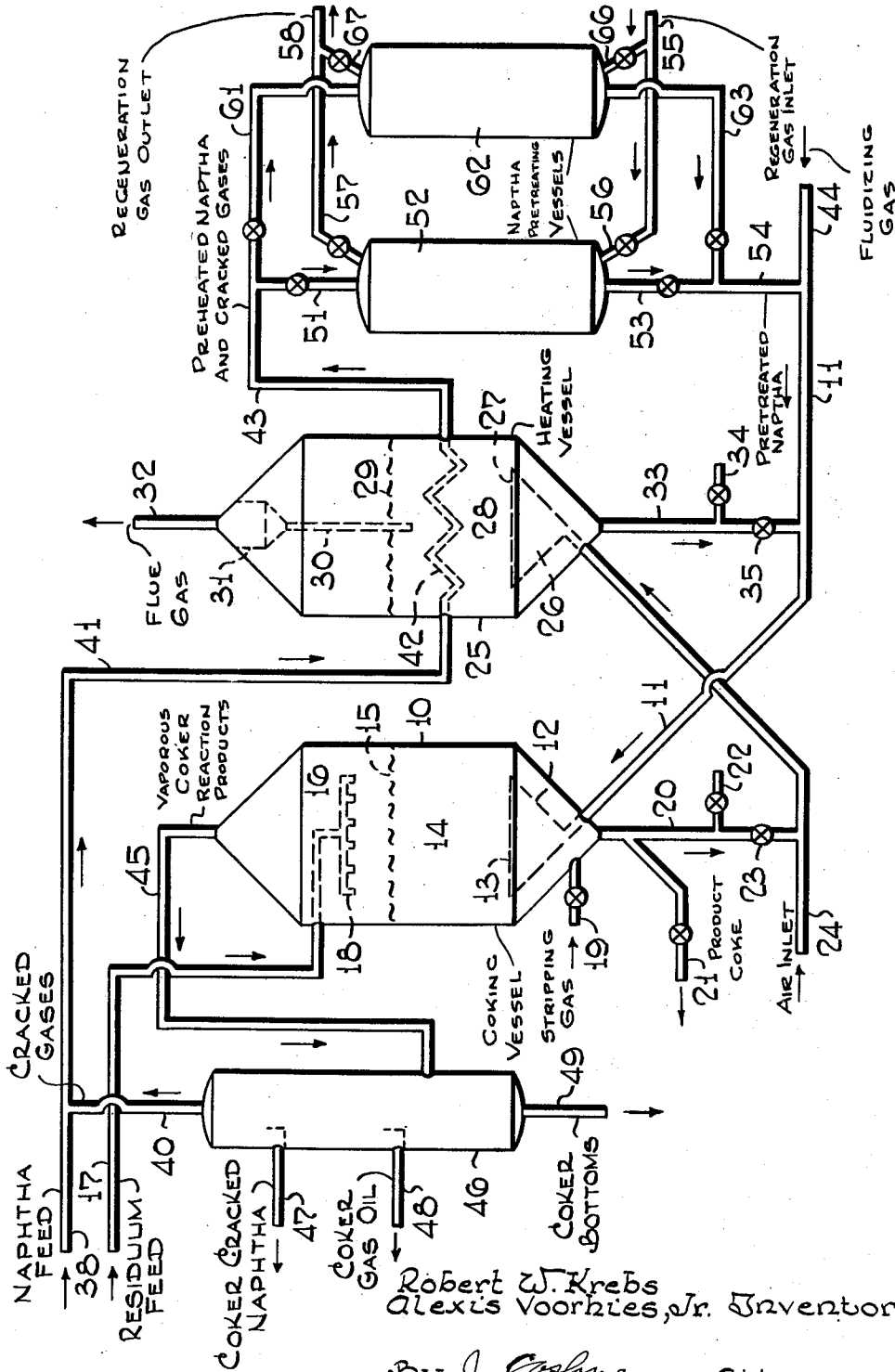


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R. W. KREBS ET AL
NAPHTHA REFORMING PROCESS

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NAPHTHA REFORMING PROCESS

Robert W. Krebs and Alexis Voorhies, Jr., Baton Rouge, La., assignors to Standard Oil Development Company, a corporation of Delaware

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The present invention pertains to naphtha improvement and more particularly to the catalytic reforming of hydrocarbon fractions boiling within the motor fuel boiling range to convert said hydrocarbon fractions into motor fuels of improved anti-knock quality. Specifically, this invention pertains to the upgrading of petroleum naphthas by treating the same with certain gaseous olefins in the presence of hydrogen transfer catalysts under conditions which will convert the naphthenes to aromatics and then combining the reformed naphtha with a residual stock in a high temperature fluidized coking zone wherein the residual stock is converted to more valuable lower boiling products.

Numerous processes have been proposed for the conversion or reforming of hydrocarbon fractions boiling within the motor fuel or naphtha range to increase the aromaticity and improve the anti-knock characteristics of said hydrocarbon fractions. Reforming processes employing catalysts, especially hydroforming and aromatizing are widely used in the petroleum industry to upgrade or improve the anti-knock characteristics of motor fuels. It has also been proposed to subject naphthenic petroleum fractions to hydrogen transfer with liquid olefinic hydrocarbons whereby the naphthenic constituents are converted to aromatics and the olefinic hydrocarbons are converted to paraffinic hydrocarbons by the hydrogen removed from the naphthenic constituents. It has also been proposed to convert residual stocks into lower boiling or motor fuel components by a coking operation utilizing the fluidized solids technique with steam or naphtha as a fluidizing agent. In view of the increasing demands for greater volumes of motor fuel of improved anti-knock properties, these processes have been the subject of intensive investigation in an effort to find new catalysts or new conditions or techniques for carrying out the coking of residual stock and the reforming or upgrading of motor fuel or naphtha fractions to increase yields and/or improve the anti-knock characteristics of the motor fuel product.

It is the object of this invention to provide an improved process for catalytically reforming hydrocarbon fractions boiling within the motor fuel boiling range to form motor fuels of higher anti-knock ratings in high yields.

It is also the object of this invention to prepare motor fuels of good anti-knock properties and in good yields by reforming a naphtha under hydrogen transfer conditions with the olefinic gases from a high temperature coking of residua.

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It is a further object of this invention to subject a naphtha fraction to hydrogen transfer conditions in the presence of the C₂, C₃ and C₄ gases formed in the fluid coking of residual stocks at high temperatures and then to combine the resultant treated naphtha with the residual stock in the high temperature fluid coking zone.

These and other objects will appear more clearly from the detailed specification and claims which follow.

In accordance with the present invention a residual stock or a hydrogen deficient residual or cycle stock such as a topped or reduced crude is coked on fluidized, catalytically inert solids such as sand petroleum coke, pumice or the like at temperatures above 1000° F., preferably between 1050 and 1150° F. in the presence of substantial proportions, at least 25% and preferably about 50–75 vol. per cent on total hydrocarbon feed of a naphtha boiling within the range of about 120–430° F. which has been subjected to hydrogen transfer, preferably in the presence of activated carbon catalyst using as the hydrogen acceptors the olefins contained in the cracked gases from the high temperature fluid coking operation. The pretreated naphtha serves as a fluidizing medium replacing or supplementing steam or other conventional fluidizing gas and exerts a synergistic effect upon the coking of the residual stock, giving less byproduct formation and higher yields of products of improved properties.

Reference is made to the accompanying drawing illustrating diagrammatically one embodiment of the present invention.

In the drawing, 10 is a coking vessel similar to conventional dense bed, bottom drawoff fluidized solids contacting vessels. 11 is a transfer line for the introduction of finely divided solids in admixture with fluidizing gas or vapors. The transfer line 11 discharges into a suitable distributing inlet chamber 12 comprising an inverted conical member superposed by a perforated grid member 13 which serves to distribute the incoming solids and vapors uniformly over the entire cross section of the coking vessel 10. The coking vessel is charged with finely divided substantially inert solids such as sand, pumice, coke, clay, etc., having a particle size of about 30–400 mesh which are maintained as a dense, fluidized, turbulent bed 14 having a definite level 15 or interface separating the turbulent bed or dense phase 14 from an upper dilute or disperse phase 16. Linear superficial gas velocities through the coking vessel may be varied between about 0.3 to about 5.0 ft. per second to establish apparent densities of about

20 to 60 lbs. per cu. ft. in dense bed 14 and about 0.001 to 0.1 lb. per cu. ft. in disperse phase 16.

A line 17 is provided for supplying residual stock for coking to the coking vessel 10. The line 17 connects to suitable spray nozzles mounted on manifold 18 arranged in the disperse phase 16 in the upper part of coking vessel 10. The distance of travel of the droplets of residuum through the disperse phase, i. e. before contacting the main body of fluidized solids should be about 5 to 20 feet, preferably about 10 feet. Design of the coking vessel and the fluidizing conditions maintained therein should be such as will permit a residence time of the upflowing vapors in the dense bed 14 of about 3 to 60 seconds and descending time of liquid residuum through the disperse phase 16 of about 0.5 to 10 seconds depending upon the degree of dispersion of the spray and the velocity of upflowing gases. The liquid residuum feed rate may be about 0.3 to 5.0 wt./hr./wt. (lbs. of residuum per hour per lb. of solid contact material in the coking vessel). The temperature within the dense bed 14 should be maintained at about 1050-1150° F. by circulation of the contact solids as will now be described.

Contact solids from the dense bed 14 pass downwardly around inlet chamber 12 at the bottom of the coking vessel 10 to an outlet pipe 20. Stripping gas, preferably steam, is introduced into the lower part of the coking vessel to minimize the amount of hydrocarbon entrained or adsorbed on the solids leaving the coker vessel. Part of the coke-carrying solids passing into outlet pipe 20 may be withdrawn from the system through valve controlled discharge line 21. The remainder of the contact solids pass down through conduit 20 in fluidized state. A stream of steam or other stripping or fluidizing gas is supplied through one or more taps 22 on conduit 20, fluidizing the solid particles and removing further amounts of vaporizable material from the contact solids before admixture of said solids with air or combustion gas.

The stripped contact solids are discharged from conduit 20 through control valve 23 into transfer line 24 where they are picked up by a stream of air or combustion gas and conveyed to heater vessel 25. The transfer line 24 discharges the suspension of contact solids and air into inlet chamber 26 arranged adjacent the bottom of heater vessel 25. The inlet chamber comprises an inverted conical section superposed by a horizontally disposed perforated plate or grid 27 which serves to distribute the incoming solids and air uniformly over the entire cross section of the heater vessel 25. The linear superficial velocity of the air passing through the heating vessel 25 similarly to the gas velocities through coking vessel 10 may be varied between about 0.3 to about 5.0 ft. per second and forms therein a dense, fluidized, turbulent bed 28 of contact solids having a definite level 29 or interface separating it from the dilute or disperse phase 30 in the upper part of the heater vessel. The combustion gases are withdrawn from the heater vessel 25 through a cyclone separator 31 or the like which serves to separate most of the entrained solid particles which may be returned to the dense bed 28 via the dip leg attached to the separator 31. The combustion gases pass to the atmosphere via stack 32 or, if desired to heat recovery equipment and then to the at-

mosphere or to storage for use as stripping gas or the like.

In the event that petroleum coke is used as the contact solid the solid material withdrawn from the coking vessel and supplied to the heater will be essentially 100% coke. In case a material such as sand is used as the contact material it is advisable to maintain the coke content at a relatively high level, for example about 5 to 20% at all times in order to maintain good burning rates and to achieve good utilization of the air supplied to the heater vessel. The solids leaving the coking vessel will ordinarily have a coke content that is about 0.5 to about 10 wt. per cent higher than that of the solids leaving the heater vessel. This figure depends upon the amount of coke deposited by the particular feed used and the ratio of solids circulation rate to oil feed rate. Fluidized solid contact material carrying about 5 to 100 wt. per cent of coke may be withdrawn from the coking vessel for circulation to the heater vessel 25 at a rate of about 1 to 20 times the total oil feed rate to the coking vessel. The suspension of withdrawn contact material in air passes through the transfer line 24 and distributor plate 27 to form a dense fluidized bed in which the desired amount of coke is burned off of the contact particles. As a result of the combustion of the coke taking place in the transfer line and heater vessel 25, the solid contact materials are heated to temperatures of about 1150 to 1300° F. Ordinarily the temperature of the dense bed of contact material in heater 25 should be at least about 50° F. higher than the temperature of the dense fluidized bed 14 in coking vessel 10. About 1000 to 6000 cu. ft. of air per barrel of total feed to the coking vessel will suffice to burn off all the coke formed and maintain the system in heat balance at the conditions specified.

Fluidized solid contact material at the temperature of the dense bed 28 is withdrawn through standpipe 33 connected to the bottom of the heater vessel 25. The solid contact materials are aerated and/or stripped with steam or inert gas supplied through one or more taps 34. The reheated contact particles are discharged through control valve 35 into transfer line 11 where they are picked up by a stream of naphtha which is given a pretreatment as will be described immediately below, and conveyed through line 11 to coking vessel 10 at substantially the same rate at which they were withdrawn therefrom, so as to supply heat required in coking vessel 10 as sensible heat of the reheated contact solids.

In order to facilitate the coking of the residuum and to provide vapors for fluidization of the dense bed of contact solids in coking vessel 10, a naphtha feed stock is used after suitable pretreatment. The naphtha feed stock, which may be a virgin naphtha, a catalytically cracked naphtha, or the like having a boiling range between about 120 and 430° F., is supplied through inlet line 38 and is contacted with a hydrogen transfer catalyst in admixture with the C₂, C₃ and C₄ fraction from the coker cracked products in a fixed bed, moving bed, fluidized bed or suspension type operation. Suitable hydrogen transfer catalysts include activated carbon, vanadium oxide on alumina, alumina on silica, molybdenum oxide on alumina or the like.

In some installations, activated carbon catalyst may be added directly to the naphtha and passed along with it directly into the coking zone without adversely affecting the subsequent coking

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operation. In the embodiment of the invention shown on the drawing the hydrogen transfer catalyst is contained in two fixed bed reactors 52 and 62 wherein the naphtha is treated. Only one of the reaction vessels is used at a time. For example, the heated naphtha may be introduced through line 43 into line 51 and the reactor 52, out through line 53 and 54 to line 11. Meanwhile the alternate reactor 62 is being regenerated or freed from carbonaceous deposits by the introduction of air or other combustion gas from line 55 through line 66 and out through lines 67 and 58. When the catalyst in vessel 52 becomes fouled, the valving of the two vessels is reversed.

In accordance with this invention there is also added to the naphtha feed prior to the pretreatment, the highly olefinic cracked gases or C₂, C₃ and C₄ fraction from the coker cracked products. These cracked gases are taken overhead from the fractionator 46 through line 40 and are intermixed with the naphtha-catalyst mixture and the resultant mixture is heated to the desired reaction temperature of about 800 to about 1000° F. as by passage in indirect heat exchange with the reaction products from coker vessel 10 and/or by passage through line 41 through heater coils 42 arranged in the dense, fluidized bed 28 in heater 25. The feed rate of naphtha and the size of vessels 52 and 62 are so adjusted as to give a space velocity of 0.2 to 2.0 volumes of naphtha per volume of catalyst per hour to obtain the desired conversion of the naphtha. If desired, elevated pressures of about 200-1000 lbs. per sq. in. may be applied in coils 42 and vessels 52 or 62. The naphtha passing through line 11 serves to pick up and convey the reheated contact solid particles back into the coking vessel 10. If necessary, or desired, steam or other fluidizing gas may also be supplied to line 11 through inlet line 44.

Vaporous coking products containing small amounts of entrained solid particles pass into the disperse phase 16 in the upper part of coker vessel 10 and pass therethrough countercurrently to descending droplets of residuum feed. In this way the said feed droplets are preheated and pretreated to give off relatively low temperature coking products. Simultaneously the vaporous coking products are quenched to temperatures approximating or somewhat above the temperature of the residuum feed thereby avoiding excessive cracking. At the same time most of the solid particles entrained with the vaporous coking products are scrubbed out so that no special gas solids separation equipment or cyclones are required at the vapor outlet of the coking vessel.

The vaporous coking products amounting to about 80-95 wt. per cent on total feed pass overhead from coking vessel 10 through line 45 at temperatures of about 700-1000° F. into fractionating column 46. About 10-25 wt. per cent of product gases based on total feed are taken overhead from fractionator 46 through line 40 for admixture with the feed naphtha as described above. If desired, part of the cracked gases may be withdrawn from the unit and passed to suitable processing or recovery equipment.

Coker cracked naphtha boiling up to about 430° F. amounting to about 50-80 vol. per cent based on total feed is recovered through line 47 and passed to gasoline storage or blending. Coker gas oil boiling within the range of about 430-950° F. and amounting to 5 to 20 vol. per cent of the total feed is withdrawn from fractionator 46 through line 48 and may be blended with virgin gas oil and passed to a catalytic cracking opera-

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tion. Coker bottoms boiling above about 950° F. and amounting to about 1-5 vol. per cent of the total feed is withdrawn through line 49 and passed to fuel oil storage, or the like or, if desired, it may be recycled to the coking vessel for re-treatment therein.

An example of a typical embodiment of this invention is as follows:

Example

In a plant handling 10,000 B./D. of a 10° API pitch, the pitch feed is preheated to 750° F. and fed into a fluid coking reactor over fluidized coke particles in the range of 20 to 200 mesh size at a weight space velocity of one weight of feed per hour per weight of solids in the reactor vessel. The coking takes place at 1100° F. in which the pitch is converted largely to distillate fuels, coke and gas. The coke formation is 15 per cent on feed. The fluidized solids are circulated between a burner vessel and the reactor at a solids-to-pitch ratio of about ten to one. In the burner, about four per cent on feed of carbon is burned off to supply heat for the process and about eleven per cent must be drawn off. The amount burned, representing about one-tenth per cent of the circulating stream, increases the temperature of the solids stream to about 1200° F. About 20 weight per cent of the pitch is converted to light gases which are fed along with 10,000 B./D. of extraneous virgin naphtha to vessels containing a hydrogen transfer catalyst in the form of pills or granules. The naphtha is fed at a volumetric space velocity of 0.5 v./v./hr. and the catalyst bed is maintained at an average temperature of around 900° F. Pelleted catalyst containing 10 per cent vanadium oxide on alumina is used as the catalyst. In this reactor, a large share of the naphthenes in the naphtha (which may amount to 10-20 volume per cent of the naphtha) are converted to aromatics and the olefins and the gases become saturated. The treated naphtha is then conducted to the injector at the base of the burner solids standpipe and serves as carrying gas for conducting that material to the coker reactor. All of the reactions described are conducted at substantially atmospheric pressure.

The foregoing description contains a limited number of embodiments of the present invention. It will be understood that numerous variations are possible without departing from the scope of the following claims.

What is claimed is:

1. A process for naphtha improvement which comprises pretreating a naphtha with olefinic cracked gases in contact with a hydrogen transfer catalyst under hydrogen transfer conditions, passing the treated naphtha in admixture with finely divided hot inert contact solids into a coking zone where the inert contact solids are maintained as a dense fluidized bed having a level, spraying a residuum into the coking zone above said dense bed and converting the residuum to volatile products and coke, recovering olefinic cracked gases from the vaporous reaction products and recycling the recovered olefinic cracked gases to said naphtha pretreating step.

2. A process for naphtha improvement which comprises pretreating a 130-430° F. naphtha with olefinic cracked gases in contact with a hydrogen transfer catalyst under hydrogen transfer conditions, passing the treated naphtha in admixture with finely divided inert contact solids at a temperature of 1150-1300° F. into a coking zone wherein the inert contact solids are maintained

as a dense fluidized bed having a level, introducing a petroleum residuum in the form of droplets into said coking zone above said dense bed, maintaining the droplets in the coking zone at temperatures of between 1050 and 1150° F. for a period sufficient to convert the residuum into volatile products and coke, recovering olefinic cracked gases from the vaporous reaction products and recycling the recovered olefinic cracked gases to said naphtha pretreating step.

3. A process for naphtha improvement which comprises pretreating a 130-430° F. naphtha with olefinic cracked gases in contact with a hydrogen transfer catalyst under hydrogen transfer conditions, passing the treated naphtha in admixture with finely divided inert contact solids at a temperature of 1150-1300° F. into a coking zone wherein the inert contact solids are maintained as a dense fluidized bed having a level, introducing a petroleum residuum in the form of droplets into said coking zone above said dense bed, maintaining the droplets in the coking zone at temperatures of between 1050 and 1150° F. for a period sufficient to convert the residuum into volatile products and coke, recovering olefinic cracked gases from the vaporous reaction products, recycling the recovered olefinic cracked gases to said naphtha pretreating step, withdrawing a stream of contact solids directly from the dense bed in the coking zone, transferring the withdrawn contact solids to a heater vessel, burning carbonaceous deposits from said contact solids to heat the same to 1150-1300° F. recycling said heated solids to said coking zone.

4. The process as defined in claim 1 wherein the hydrogen transfer catalyst is activated carbon.

5. The process as defined in claim 2 wherein

the hydrogen transfer catalyst is activated carbon.

6. The process as defined in claim 3 wherein the hydrogen transfer catalyst is activated carbon.

7. The process as defined in claim 1 wherein the hydrogen transfer catalyst is vanadium oxide on alumina.

8. The process as defined in claim 2 wherein the hydrogen transfer catalyst is vanadium oxide on alumina.

9. The process as defined in claim 3 wherein the hydrogen transfer catalyst is vanadium oxide on alumina.

10. The process as defined in claim 1 wherein the hydrogen transfer catalyst is molybdenum oxide on alumina.

11. The process as defined in claim 2 wherein the hydrogen transfer catalyst is molybdenum oxide on alumina.

12. The process as defined in claim 3 wherein the hydrogen transfer catalyst is molybdenum oxide on alumina.

ROBERT W. KREBS.

ALEXIS VOORHIES, JR.

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