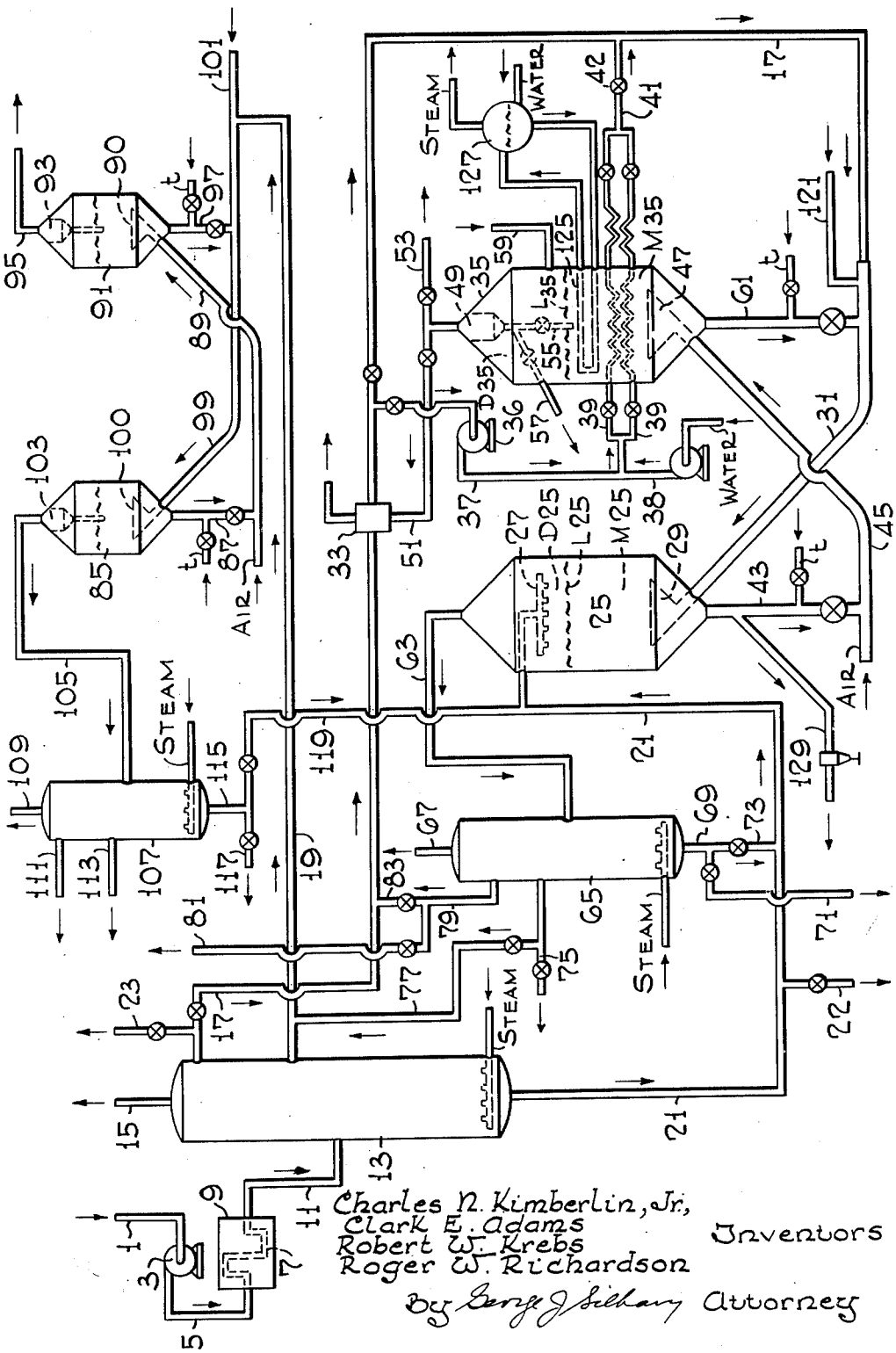
April 28, 1953 C. N. KIMBERLIN, JR., ET AL 2,636,844

PROCESS FOR THE CONVERSION OF REDUCED CRUDES IN THE PRESENCE OF AN ADDED NAPHTHA

Filed Aug. 29, 1950



Charles N. Kimberlin, Jr.,
Clark E. Adams
Robert W. Krebs
Roger W. Richardson
Inventors

By George J. Sibbany Attorney

Patented Apr. 28, 1953 2,636,844

UNITED STATES PATENT OFFICE

2,636,844

PROCESS FOR THE CONVERSION OF REDUCED CRUDES IN THE PRESENCE OF AN ADDED NAPHTHA

Charles N. Kimberlin, Jr., Clark E. Adams, Robert W. Krebs, and Roger W. Richardson, Baton Rouge, La., assignors to Standard Oil Development Company, a corporation of Delaware

Application August 29, 1950, Serial No. 182,036

9 Claims. (Cl. 196—49)

1

The present invention relates to a method of treating hydrocarbons. More particularly, the invention pertains to a method of producing from relatively heavy or high boiling hydrocarbon oils of the type of topped or reduced crude or similar heavy residues increased quantities of motor fuel range fractions of improved quality as well as higher boiling distillate fractions suitable for further cracking. In its broadest aspect, the invention provides for contacting heavy residua of the type mentioned together with a naphtha fraction in a treating zone with hot subdivided fluidized solids at temperatures conducive to the coking of the residua and the reforming of the naphtha.

In refining crude oil it is standard practice first to subject the crude to simple distillation or "topping" to produce various distillate fractions such as naphtha, heating oil and gas oil cuts, boiling up to about 800°–950° F. Most of these distillate fractions are normally converted into high quality gasoline range motor fuels by such conventional treatments as thermal and/or catalytic reforming and cracking, or similar operations.

The residue from the crude distillation may be processed to yield valuable high molecular weight materials including lubricating oils, waxes, resins, fuel oils, asphalt, etc. depending on the origin and character of the crude. More recently, however, the demand for motor fuels has increased so greatly that it has become extremely difficult to satisfy the motor fuel market by merely processing crude distillates in the manner indicated above. This situation has prompted considerable research and development work directed toward an efficient conversion of crude residua into additional quantities of motor fuels. The two most common methods used for this purpose in current practice are viscosity-breaking and coking of reduced crude.

Viscosity-breaking involves a treatment of reduced crude or the like at elevated temperatures for a short period of time adequate for the formation of an additional quantity of gas oil and about 5–15% of gasoline. The gas oil forms a suitable feed stock for thermal or catalytic cracking and may be converted into gasoline in this manner. However, extensive cracking facilities in addition to the crude still and vis-breaking units are indispensible for the production of satisfactory quantities of gasoline by vis-breaking of reduced crude.

The other method, i. e., coking of reduced crude, is a much more drastic heat treatment usually carried out at higher temperatures of, say, about 800°–1000° F. and for longer times. It results in direct production of increased proportions of gasoline of, say, about 15–35% in addition to gas oil and hydrocarbon gases together with solid coke. This process lends itself more readily than vis-breaking to the purpose of producing maximum amounts of gasoline from reduced crude in the most economic manner, particularly in view of the fact that sufficient coke is produced to supply by combustion the heat requirements of the process. Therefore, the research efforts of the industry most recently have concentrated on improvements of this type of operation. Broadly the present invention is concerned with such improvements.

2

One of the major difficulties complicating a successful coking operation results from the heavy deposition of coke in the coking vessels and transfer lines requiring frequent and time-consuming cleaning periods. This problem has been solved or at least greatly alleviated prior to the present invention by admixing with the residuum to be coked substantial proportions of a subdivided inert adsorbent solid such as petroleum or other coke, pumice, kieselguhr, spent clay, sand, or the like, which serves primarily as a carrier for the coke formed so as to prevent coke deposition on equipment walls and also as a scouring agent removing coke deposits from the walls. The high surface area provided by these solids also accelerates and intensifies the cracking reaction whereby larger yields of gasoline within shorter holding times may be obtained without any danger of deactivation of the solids by carbon deposits or ash constituents of the feed. The coke deposited on the solids may be burnt off in cyclic or continuous two-vessel operation to generate and supply to the coking vessel the heat required for coking.

While fixed bed and suspensoid systems have been suggested for this type of operation, the so-called fluid solids technique offers greatest advantages with respect to temperature control, heat economy, ease and continuity of operation and equipment dimensions. This technique in its application to the coking of reduced crude involves the injection of the feed into a relatively dense highly turbulent bed of hot subdivided solids having a particle size of about 300–400 mesh, fluidized by a gas flowing upwardly through the bed at a linear superficial velocity of about 0.3–5 ft. per second to give the bed the appearance of a boiling liquid separated by a definite interface from an upper dilute suspension of solids-in-gases and gasiform products. Volatile coking products are removed overhead and further treated after the removal of entrained solids. Coke carrying solids are continuously passed to a fluid-type combustion zone wherein they are fluidized by a combustion-supporting gas and coke is burnt off to heat the solids to a temperature higher than coking temperature. Hot solids

are continuously recirculated to the coking zone in amounts sufficient to supply most of the heat required therein.

While this procedure affords excellent heat control and utilization as well as better yields of desirable products as compared to other systems, it does not avoid certain disadvantages inherent in reduced crude coking as such. One of these disadvantages resides in the fact that the gas oil produced by coking has a low quality as a catalytic cracking feed stock due to its high content of condensed ring aromatics which produce excessive amounts of coke on the cracking catalyst. It would be highly desirable, therefore, if the coking operation could be run to more severe conditions in such a manner as will produce very little gas oil and correspondingly increased amounts of gasoline. However, when conditions are used which are adapted drastically to reduce the gas oil yield, most of the additional conversion normally goes to gas and coke, rather than to gasoline. Another drawback not overcome by fluid operation as such is the low octane number of the gasoline produced by coking in the most usual coking temperature range of 800°–1000° F., which rarely exceeds about 75 as determined by the research method so that extensive reforming is required to render the gasoline useful as a basis for a fuel for modern high compression engines. The present invention substantially alleviates these difficulties.

It is, therefore, the principal object of the present invention to provide an improved fluid-type process of coking crude residuum or similar materials which affords increased yields of motor fuel range products of better quality.

Other and more specific objects and advantages will appear from the description of the invention given below with reference to the accompanying drawing, the single figure of which is a schematical flow plan of a system adopted to carry out a preferred embodiment of the invention.

It has now been found that increased yields of gasoline range hydrocarbons of satisfactory octane rating may be obtained directly by coking residual oils such as topped or reduced crudes on fluidized catalytically inert solids such as sand, petroleum coke, pumice or the like when the coking treatment is carried out at temperatures in excess of 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 naphtha boiling within the range of about 120°–430° F. and serving as a fluidizing medium replacing or supplementing steam or other conventional fluidizing gases. Total hydrocarbon feed rates of about 0.5–5 w./hr./w. are suitable for these operations. While appreciable improvements, particularly with respect to gasoline yields, are obtainable when using naphthas of any origin, it has been observed that excellent results are secured when highly saturated naphthas of the type of virgin naphtha are employed.

Prior to the present invention it has been suggested to add various gas oil fractions to crude residua undergoing coking in fixed bed, fluid or suspensoid operation, chiefly for the purpose of fluxing the residuum and aiding in its vaporization while taking advantage of the cracking conditions prevailing in the coking zone for a production of additional gasoline by cracking the gas oil. As far as is known, no beneficial influence of this gas oil addition on the yield and quality of the gasoline produced from the residual oils proper has been observed heretofore. The naphtha fractions added in accordance with this invention, on the other hand, are highly refractory and not subject to much cracking at the coking conditions, such cracking products as may be formed being less desirable than the naphtha feed. Their use in place of gas oils, therefore, appeared undesirable prior to the discovery of their beneficial synergistic effect resulting from their use in accordance with the present invention.

This synergistic effect is illustrated by the following experiments.

EXAMPLE I

In a 1.6" diameter fluid-type laboratory unit externally heated to coking temperatures, sand having a particle size of about 70–180 microns was fluidized with steam or naphtha vapors at a linear superficial vapor velocity of about 2.8–3 ft./second. Crude residuum preheated to about 700°–800° F. was injected into a lower portion of the fluidized bed separately from the fluidizing vapors. The naphtha used was a heavy virgin naphtha (boiling range 250°–430° F.) obtained from East Texas and Coastal crudes. The oil residuum was a 2.4% So. Louisiana vacuum residuum inspecting as follows:

Gravity, °API	11.9
Conradson carbon, wt. per cent	12.8
Furol viscosity at 210° F., sec.	396
H/C atomic ratio	1.56

The conditions and results of these coking experiments are summarized in the table below.

Table I

Run No	I	II	III	IV		V
Feed Mixture:						
Vol. percent Residuum	100	50	34	34		0
Vol. percent Naphtha	0	50	66	66		100
Temperature, ° F	1,100	1,121	1,130	1,100		1,138
Feed Rate, wt. of oil per hr. per wt. of solids	1.05	1.33	2.15	2.22		1.37
Steam Diluent, wt. percent Feed	74	35	[1] 0	[1] 0		0
				Obs.	Calc.[3]	
Product Distribution:						
Coke, wt. percent	10.8	7.4	5.8	5.2	4.2	0.3
C_1-C_3 Gas, wt. percent	19.3	24.9	27.6	22.3	23.0	30.5
C_4/430° F. Gasoline—						
Vol. percent on Feed	33.4	55.2	59.7	67.6	61.6	70.5
CFR-Res., Oct. No.	92.2	87.5	89.5	84.5	84.5	87.8
430/700° F., Vol. percent	13.0	8.9	5.9	2.7	4.4	------
700° F.+Btms., Vol. percent	31.6	9.6	4.9	6.6	10.7	------

See footnotes at end of table.

Table I—Continued

Run No.	I	II	III	IV	V
Yields from Residuum:[2]					
Coke, wt. percent	10.8	14.5	16.5	14.7	------
C_1–C_3 Gas, wt. percent	19.3	17.2	14.9	12.4	------
C_4/430° F., Vol. percent	33.4	40.4	45.6	56.2	------
Research Blending No. Bbls./100 Bbls.[4]	2,120	2,460	2,820	3,340	------
430/700° F., Vol. percent	13.0	17.8	17.4	7.9	------
700° F.+Btms., Vol. percent	31.6	19.2	14.4	19.4	------

[1] Naphtha fed equivalent to about 29 wt. percent steam diluent.
[2] Deducting gasoline produced from naphtha using thermal yields at octane number of total gasoline and assuming 430° F.+products derived from residuum only.
[3] Calculated from data of run No. I combined with naphtha yields from thermal correlations to give observed octane number in run IV.
[4] Research Blending Number bbls. of gasoline per 100 bbls. of residuum fed, indicates quantitatively the effectiveness of the product for blending into the gasoline pool in order to establish a standard higher octane number.

The above data demonstrate that replacement of steam by naphtha as the fluidizing agent has marked synergistic effects in the form of increased conversion of the residuum and of increased blending values for the C_4/430° F. gasoline product. The data from run No. I (no added naphtha) combined with those obtained from thermal conversions of naphtha, of the type of run No. V were calculated for the octane number level obtained in run No. IV. These calculated data are listed next to the observed data in run No. IV. A comparison of the calculated data with those observed in run No. IV shows that a much higher conversion was obtained by the simultaneous use of residuum and naphtha in accordance with the invention than could be expected on the basis of the individual conversions of the residuum and naphtha. The "Yields from Residuum" included in Table I for runs in which residuum and naphtha were fed further demonstrate the improved conversion and product distribution for the operation in accordance with the invention. The conversion of residuum constituents boiling above 700° F. ("700° F.+bottoms") is extremely high for the naphtha runs as compared with run No. I. The enhanced production of C_4/430° F. gasoline when using naphtha is also shown by the Research Blending Numbers which indicate that a greater gasoline value is obtained from the residuum as such when coked in the presence of naphtha than by treating the residuum alone, in spite of the slightly lower octane number. The above data also show that this improvement is enhanced as the naphtha proportion is increased from 50 to 66 vol. per cent and as the temperature is decreased from 1130°–1100° F. For best results, the naphtha feed should, therefore, not be less than 50% and may be as high as 75 vol. per cent while the temperature should not substantially exceed 1130° F. The lower temperature limit is drawn by the fact that the octane values of the gasoline drops off sharply at temperatures substantially below 1100° F. and particularly below 1050° F.

A further advantage resides in the fact that coking in the presence of naphtha reduces coke formation on total feed as likewise shown in Table I which greatly facilitates a heat balanced operation because heat produced by combustion of the coke can be entirely utilized by the process without the need of resorting to steam generation or other waste heat recovery procedures. At the same time the naphtha is thermally reformed. Furthermore, with naphtha replacing the steam as the fluidizing agent the expense of steam production is saved and the amount of energy required to heat and vaporize the naphtha is utilized in the processing of this fraction and is not lost.

A possible explanation of the synergistic effects afforded by the process of the invention is the availability of hydrogen in the naptha for hydrogen transfer. Any such hydrogen transfer, however, appears to be directed toward the heavier fractions as acceptors which are thereafter further cracked because no appreciable reduction in the unsaturation of the lighter fractions has been observed.

It has been indicated above that the use of gas oils in coking crude residua as suggested in the prior art affords no advantages with respect to motor fuel yields from the residuum as such. This is borne out by the experimental work reported below.

EXAMPLE II

The laboratory unit described in Example I was operated at the fluidization conditions set forth in Example I. However, instead of naphtha a clarified catalytic cycle gas oil (boiling range 700°–970° F.) was injected into the fluidized sand bed. About 75 wt. per cent of steam on total hydrocarbon feed was used for fluidization in all runs. The coking temperature was uniformly 1100° F. The residual oil was a 16% West Texas residuum of the following inspection.

Gravity, °API	11.0
Conradson carbon, wt. per cent	15.0
Furol viscosity at 210° F., sec.	96.6
H/C atomic ratio	1.53

The results obtained are summarized in the table below.

Table II

Feed	16% W. Tex. Residuum	Cycle Oil	50/50 Mixture Residuum/Cycle Oil	
Run No.	VI	VII	Calc. from VI and VII	Observed VIII
Feed Rate of Coke, Wt. Percent	9.8	2.9	6.4	5.2
C_3-Gas, Wt. Percent	24.9	20.1	22.5	17.4
C_4/430° F., Vol. Percent	37.2	30.3	33.7	31.9
CFR-Res. Octane No.	96.5	96.8	----------	95.3
430° F.+Bottoms, Vol. Percent	35.4	49.7	42.6	49.1
Gravity, ° API	−1.9	4.8	----------	----------

A comparison of the observed results of run No. VIII with those to be expected from calculation on the basis of the combined data of run Nos. VI and VII carried out, respectively, with residuum alone and gas oil alone, shows that there was a decrease in conversion as well as in the production of

C_4/430° F. gasoline for the run carried out with residuum + gas oil as compared with those to be expected on the basis of the separate performance of these materials. On the other hand, when operating in accordance with the invention, both conversion and gasoline yield are substantially increased as shown in Example I.

In carrying out the present invention, in practical operation greatest advantages are secured when the naphtha feed and the residuum feed are charged separately to the bottom and top, respectively, of the fluidized bed of hot carrier solids. The naphtha feed may be supplied in liquid or vapor form to the bottom of the reactor. Upon contacting the hot solids the naphtha is vaporized and partially cracked to form a limited amount of normally gaseous hydrocarbons. The combined vapors and gases serve simultaneously as a sole or supplementary fluidizing agent and as a synergistic reactant in the coking operation. The reduced crude is preferably sprayed in the liquid state on top of the dense fluidized solids bed through a substantial portion of the disperse phase above the fluidized bed.

The liquid residuum falling through the disperse phase is heated by the rising gaseous effluents from the bed which are in turn cooled by the falling liquid feed stock. The hot liquid feed then enters the bed at the top and behaves in a conventional manner. Some of the oil is cracked and vaporized in the bed, leaves the bed in a gaseous state and is cooled by the incoming feed. Another portion of the oil is converted to coke deposited on the surface of the inert solids of the bed. The coked solids are transferred to a combustion zone or regenerator wherein the coke is consumed and the solid is heated and returned to the reactor at a rate to maintain the desired high bed temperatures. This type of operation permits, therefore, the coexistence of a hot bed and a relatively cool disperse phase above the bed which provides substantial advantages over conventional operation.

The cold residuum feed being heated by exchange with gaseous bed effluents will undergo some cracking to lighter or lower boiling compounds which assume the gaseous phase. These compounds will then disengage from the liquid and pass upward and be quenched by cold feed prior to any additional cracking. Similarly those materials that are cracked at successively higher temperatures will be liberated and then quenched by incoming feed while the highly refractory compounds that reach the bed will be cracked at the high bed temperatures in a short time. Thus, in effect the individual hydrocarbons are cracked as they reach a given temperature and then are quenched immediately to lower temperatures to avoid further cracking and quality degradation. In conventional operation with the feed entering at the bottom of the bed, cracked materials must pass through the entire bed and hot disperse phase before quenching and this long contact time at high temperatures causes further cracking and seriously degrades the distillate quality with the formation of high gas yields, particularly in the case of high temperature coking.

It frequently happens that at the optimum conditions for coking, a particular residuum, the severity of reforming of the naphtha feed, is substantially below optimum. Thus, it has been found that the optimum naphtha feed rate for best residuum processing is not necessarily the best from the standpoint of reforming the naphtha. For example, when the naphtha feed rate is high enough to afford efficient residuum coking, the reforming severity may be rather low. This difficulty may be overcome in accordance with a specific modification of the invention by partially reforming the naphtha portion of the feed in a coil prior to its being contacted with the residuum undergoing coking. The reforming coil may be heated by immersing the same in the fluidized bed of hot solids either in the reactor or the regenerator portion of the system or both. Since highest temperatures of about 1100°–1300° F. prevail in the regenerator, at least a portion of the reforming coil is preferably located therein. It may be desirable to provide several reforming coils in parallel so that the residence time of the naphtha in the coils may be varied by varying the number of coils placed in service. In this manner, the reforming severity of the naphtha portion of the feed may be varied over a wide range and controlled within narrow limits while still maintaining the coking reactor under optimum conditions for upgrading the residuum portion of the feed. For example, at optimum residuum coking temperatures of 1050°–1150° F. and a total hydrocarbon feed rate of about 0.5–5 w./hr./w. the naphtha should be reformed at conditions including 1050°–1200° F. coil outlet temperature, 0–1,000 p. s. i. g. pressure and contact times of 5 seconds to 2 minutes. Water or steam may be mixed with the naphtha feed to aid in adjusting the contact time and partial pressure of the oil.

A further modification of the invention which may be adopted for the same purpose involves recycling of a portion of the naphtha fractions recovered from the coking zone, with a corresponding reduction in the feed rate of fresh naphtha. The higher this recycle rate the greater the reforming severity so that by proper selection of the recycle rate the reforming severity may be controlled at any desired value. Naphtha recycle rates of about 10–50% of fresh residuum are normally suitable for this purpose at the coking conditions of the invention. Instead of recycling a portion of the total naphtha it may be desirable in many cases to recycle all or a part of some particular cut from the naphtha boiling range. For example, the naphtha product from the coking zone may be fractionated into a light naphtha cut and a heavy naphtha cut, and the recycle stream taken from only one of these cuts. In this way the boiling range of the naphtha produced may be likewise controlled.

Having set forth its objects and general nature, the invention will be best understood from the following more detailed description of a specific example and preferred modification of the invention wherein reference will be made to the accompanying drawing.

Referring now in detail to the drawing, a mixed South Louisiana crude oil of about 38° API gravity or a similar material is introduced into the system through line 1 by means of pump 3 and discharged via line 5 into a coil 7 disposed in furnace 9. The oil is heated in coil 7 to a temperature within the range of from about 500°–1000° F. under a gauge pressure of 5–500 p. s. i. g. The heated oil is withdrawn from coil 7 through line 11 and discharged into crude distillation still 13 from which a normally gaseous overhead amounting to about 0.1–1.0 wt. per cent on feed is withdrawn via line 15, a naphtha cut boiling up to about 430° F. and amounting to about 30–35 vol. per cent on feed is drawn off through line 17, a

gas oil fraction boiling within the range of about 430°–915° F. and amounting to about 45–60 vol. per cent on feed is recovered through line 19, and crude residuum boiling upwards of about 915° F. having a gravity of about 10–20° API and amounting to about 5–25 vol. per cent on feed is drawn off the bottom via line 21. The hydrocarbon gases recovered through line 15 may be used as fuel or for any other conventional purpose. A portion of the naphtha cut in line 17 may be recovered through line 23 to be further processed or utilized outside the system in any suitable manner. The remainder of the naphtha cut is passed on through line 17 to the coking portion of the system to be treated therein in accordance with the present invention as will be presently described. The gas oil cut in line 19 is preferably subjected to catalytic cracking as will appear more clearly hereinafter.

The heavy bottoms in line 21 constitute the residuum portion of the feed for the coking process of the invention. This reduced crude is passed in the liquid state and at a temperature of about 500°–800° F. to a suitable spraying nozzle 27 arranged in the upper portion of coking vessel 25. The design of vessel 25 may be that of conventional fluid solids contacting vessels suitable for dense phase bottom drawoff operation comprising a substantially cylindrical shell with a conical bottom containing a gas-solids feeding and distributing device 29 in the form of an inverted cone having a perforated top. Vessel 25 contains a dense turbulent mass M_{25} of subdivided catalytically substantially inert solids such as sand, pumice, coke, clay, etc. having a particle size of of about 30–400 mesh and fluidized by upflowing vapors entering through device 29, to form an interface L_{25} separating mass M_{25} from an upper disperse phase D_{25}. The design of vessel 25 and the fluidizing conditions maintained therein are preferably such as will permit a residence time of the upflowing vapors in mass M_{25} of about 3–60 seconds and a descending time of the liquid residuum through dispersed phase D_{25} of about 0.5–10 seconds, depending on the degree of dispersion of the spray and the velocity of the upflowing gases. In commercial operation the distance over which the liquid residuum descends through the disperse phase may be about 5–20 ft., preferably upwards of 10 ft. Dense phase linear superficial gas velocities of about 0.3–5 ft./sec. may be maintained to establish apparent densities of about 20–60 lbs /cu. ft. in mass M_{25} and about .001–0.1 lbs./cu. ft. in phase D_{25}, depending on the composition and particle size of the inert solid and the fluidizing gas velocity. The liquid residuum feed rate may be about 0.15 to 3 w./hr./w. The temperature within mass M_{25} is preferably maintained at about 1050°–1150° F. by circulating hot solids as will appear more clearly hereinafter.

To accomplish the synergistic effects described above and to provide vapors for the fluidization of mass M_{25}, virgin naphtha is passed from line 17 to vapor-solids feed line 31 of coking vessel 25. This naphtha may be fed from line 17 directly into line 31, if desired after preheating to about 400°–800° F. in preheater 33 in heat exchange with flue gases from a generator or heater 35. However, preheating in this manner is not essential. Immediately upon contact with the hot solids in line 31 which are preferably at a temperature of about 1150°–1300° F. the naphtha is vaporized and slightly cracked to become suitable as a fluidizing medium. Preferably, however, at least a portion of the naphtha in line 17 is passed by pump 36 via line 37 to either one or more of several reformer coils imbedded in a fluidized solids mass M_{35} maintained at a temperature of about 1150°–1300° F. in heater 35 as will be presently described. Water may be added from line 38 in amounts of up to about 10 wt. per cent of the naphtha. Coils 39 are so designed and operated that the naphtha is heated to a temperature of 1050°–1200° F. during its passage through coils 39 and is maintained therein for about 5–120 seconds, including residence time outside heater vessel 35 whereby extensive thermal reforming is accomplished. Elevated pressures of, say, about 200–1000 p. s. i. g. may be applied in coils 39, if desired. The naphtha leaving coils 39 through line 41 may, after pressure release in valve 42, reenter line 17 and pass to line 31 as previously described. In any case, the naphtha feed rate to line 31 may be maintained at about 0.25–4 w./hr./w. for the purposes here involved.

The amount of coke deposited on the solids is only one-third to two-thirds as much as when feeding residuum alone at the same solids to oil rate; however this does not necessarily mean that the coke make based on residuum alone has been reduced (there may actually be even a slight increase) but that there is a reduction in coke based on total oil feed. This reduction of coke on total feed aids in obtaining a heat balanced operation while still burning coke as fast as it is made. Expressed another way, coking of the residuum alone produces an excess of coke over that required to furnish heat for the coking; in the present process this excess is utilized to supply heat for upgrading the naphtha.

The contact solids may be coke itself in which case this material will, of course, be essentially 100% coke at all times. In case a material like sand is used the coke content may be maintained at a fairly high level, say 5–20%. This has the effect of giving good burning rates and good utilization of the air in heater-vessel 35. The solids leaving the reactor may have a coke content that is 0.5% to 10% 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 of oil feed rate. Fluidized solids carrying about 5 to 100 wt. per cent of coke may be withdrawn downwardly from vessel 25 through a conventional standpipe 43 at a rate of about 1–10 times the total oil feed rate by weight. Small amounts of an aeration and/or stripping gas such as air, flue gas, steam, etc. may be supplied to standpipe 43 through one or more taps *t* in a conventional manner. The withdrawn solids pass from standpipe 43 to line 45 wherein they are picked up by air to form a relatively dilute suspension which is passed through a distributing device similar to device 29 into the lower portion of heater 35 to form therein dense fluidized mass M_{35} separated by an interface L_{35} from a disperse phase D_{35} substantially as described with reference to coking vessel 25. As a result of the combustion of coke taking place in heater 35, the solids in mass M_{35} may be reheated to a temperature of about 1150°–1300° F. which should be at least about 50° higher than the temperature of mass M_{25}. About 1,000–6,000 cu. ft. of air per barrel of total feed are normally sufficient to burn off all the coke formed in vessel 25 and to maintain the system in heat balance at the conditions specified. Flue gases containing entrained solids fines may be passed through a gas-solids separator 49 and thence via line 51 to preheater 33

or via line 53 to any desired purpose. Separated solids may be returned to mass M_{35} via line 55 or, if of undesirable size, discarded via line 57. Make-up solids may be supplied via line 59.

Fluidized solids at the temperature of mass M_{35} are withdrawn from vessel 35 through standpipe 61 aerated and/or stripped with steam or inert gas etc. via tap or taps *t*. The reheated solids pass from standpipe 61 into pipe 31 wherein they are picked up by the naphtha from line 17 and returned via device 29 to vessel 25 substantially at the rate at which they were withdrawn therefrom, so as to supply heat required in vessel 25 as sensible heat of reheated solids.

Vaporous coking products containing entrained solids fines in a concentration as indicated above are passed upwardly through disperse phase D_{25} countercurrently to descending liquid residuum feed which is preheated and pretreated thereby to give off relatively low temperature coking constituents. Simultaneously, the coking products are quenched to a temperature approximating or somewhat above the feed temperature of the residuum feed and most of the solids entrainment is scrubbed out so that no special gas-solids separation equipment is required and excessive cracking is avoided.

The vaporous products amounting to about 90/95 wt. per cent on total feed pass through line 63 at a temperature of about 700°–1000° F. into a fractionating column 65. About 20–30 wt. per cent of product gases based on total feed may be taken overhead from fractionator 65 through line 67 and used for any desired purpose. For example, this gas may contain 25–40 wt. per cent propylene which can be converted into high quality gasoline by polymerization by well known means. Fractionator bottoms boiling upwards of about 950° F. and amounting to about 1–10 vol. per cent on total feed are withdrawn through line 69 either to be passed through line 71 to tankage for fuel oil use or to be recycled via lines 73 and 21 to the top of coking vessel 25 to be retreated as described above. A gas oil cut boiling within the range of about 430°–950° F. and amounting to about 5–15 vol. per cent of the total naphtha plus residuum feed may be withdrawn via line 77 and combined with the virgin catalytic cracking feed stock flowing through line 19 to be treated therewith as will appear hereinafter. Any desired portion of this cut may be withdrawn through line 75 to be passed to tankage or further fractionated into narrower cuts for use as kerosene, heating oils, diesel fuel, and the like.

A naphtha cut boiling up to about 430° F. and amounting to about 50–70 vol. per cent on total feed is recovered through line 79. It may be passed to tankage or gasoline blending via line 81. If desired, a proportion of this naphtha amounting to about 10–15% on the residuum feed may be returned va lines 83 and 17 to coking vessel 25 to be retreated and further reformed therein as described above.

When operating in the manner described above, about 40–60 vol. per cent of gasoline range naphtha may be produced from the reduced crude portion of the feed as compared with only about 30–40 vol. per cent when operating in the absence of naphtha added to the coking zone. These naphtha yields do not include the additional naphtha that is obtainable by polymerization of the propylene in the gas.

Returning now to the catalytic cracking feed stock in line 19, this may be catalytically cracked in any conventional manner, that is in fixed bed, moving bed, fluid solids or suspensoid operation. By way of example, a conventional fluid catalyst dense phase type of operation has been schematically illustrated in the drawing. The operation of a system of this type is well known to those skilled in the art and will only be briefly described for the sake of completeness.

A cracking catalyst of fluidizable size such as a synthetic composite of silica gel with alumina and/or magnesia, or any other conventional cracking catalyst is fluidized in reactor 85 and circulated via standpipe 87, air feed line 89 and distributing device 90 to regenerator 91 wherein coke deposits are burned off in the fluidized state, flue gases being withdrawn via cyclone 93 and line 95. Hot regenerated catalyst is returned at a temperature slightly above cracking temperature through standpipe 97, oil feed line 99 and distributing device 100 to reactor 85 at a rate adequate to vaporize the feed and to supply the heat required for cracking. The cracking feed stock from line 19 is supplied to line 99 as indicated. Any desired amount of steam may be added via line 101 to assist in fluidization and to control cracking conditions.

Suitable conditions for running a cracking system of this type are well known in the art. They include cracking temperatures of about 800°–950° F., pressures of about 0–50 p. s. i. g., regenerator temperatures of about 1000°–1100° F., superficial linear fluidizing gas velocities of about 0.3–3 ft. per second at catalyst particle sizes of about 50–400 mesh, and oil feed rates of about 0.5–10 w./hr./w.

Cracked products are withdrawn overhead from reactor 85 via cyclone 103 and may be passed through line 105 to a fractionator 107. Normally gaseous hydrocarbons may be withdrawn from fractionator 107 through line 109. They are suitable as feed materials for alkylation or polymerization processes. Catalytically cracked naphtha boiling within the range of up to about 430° F. may be recovered through line 111 and passed to gasoline blending. Heating oil may be withdrawn via line 113 and then passed to storage or recycled to reactor 85 for further cracking at recycle ratios of about 10–50 volumes per volume of fresh cracking feed. Catalytically cracked heavy bottoms boiling upwards of about 700° F. are drawn off through line 115. They may be either passed to fuel oil storage via line 117 or added to the residuum feed of coking vessel 25 via line 119 to be coked in vessel 25 as described above. The ultimate residuum feed to cracking vessel 25 may contain any virgin and cracked residues in any desired proportion but the concentration of cracked residuum will usually be limited to about 25–40%, because that is about the production ratio of heavy catalytically cracked residues to virgin residuum that will be produced in usual refinery practice.

The system illustrated in the drawing permits of various modifications. If desired, small amounts of steam or other additional fluidizing gas may be added to vessel 25 through line 121. Catalytically cracked naphtha from line 111 may be added via line 17 to the naphtha feed of vessel 25 in any desired proportion. Fractionators 13, 65 and/or 107 may be operated in such a manner as to yield two separate fractions of different boiling range within the naphtha range and either one of the two fractions may be used in coking vessel 25. Distributing grids extending over the entire cross-section of vessels 25, 35, 85

and 91 may be used in combination with suitable solids withdrawal wells to replace distributing cones 29, 47, 90 and 100. If desired, steam generating coils 125 may be inserted in heater 35 and steam recovered via a conventional recovery system 127. In case petroleum coke is used as the inert solid, product coke may be recovered from reactor 25 via line 129.

The crude distillation shown is an atmospheric distillation only, giving an atmospheric residuum. Where modern distillation equipment is available the bottoms from this still may go to a second still operated under 25–30 inches of vacuum where an additional amount of virgin gas oil may be removed and sent to catalytic cracking. The bottoms from this second still constitute a vacuum residuum and may serve as the feed to the coking vessel 25.

Virgin residuum may, if desired, be drawn off line 21 through line 22 for use in fuel oils, asphalts, and the like. Other modifications may appear to those skilled in the art.

The above description and exemplary operations have served to illustrate specific embodiments of the invention but are not intended to be limiting in scope.

What is claimed is:

1. In a process for cracking heavy residual oils to form gasoline and lower boiling hydrocarbons the improvement which comprises introducing a stream of said residual oil into a turbulent fluidized bed of subdivided solids in a conversion zone, maintaining said conversion zone at a temperature between about 1050° F. and 1150° F., circulating a stream of solids from said conversion zone through an extraneous heater and back to said conversion zone to maintain said temperature, maintaining said residual oil within said conversion zone and in contact with said hot fluidized solids for a period sufficient to convert at least 40% by volume of said residual oil into gasoline, and passing a stream of virgin naphtha boiling within the range of about 250 to 430° F. into the bottom portion of said fluidized bed in an amount sufficient to maintain said bed in a fluidized state.

2. The process defined in claim 1 wherein said naphtha stream is utilized to return solids from said heating zone to said conversion zone.

3. The process defined in claim 1 wherein said heavy oil is sprayed into the top of said conversion zone above the level of said bed.

4. A process for cracking heavy residual oils to form gasoline and low boiling hydrocarbons which comprises introducing a stream of said oil into a turbulent fluidized bed of finely divided solids maintained in a conversion zone, circulating said solids from said conversion zone through an extraneous heater and back to said conversion zone to keep said conversion zone at a temperature between 1050° and 1150° F., maintaining said residual oil within said conversion zone for a period sufficient to convert at least 40% of said oil into gasoline, introducing a stream of virgin naphtha boiling within the range of about 250° F. to 430° F. into the bottom portion of said conversion zone in an amount sufficient to maintain said bed in said turbulent fluidized state, removing vaporous products from the upper end of said conversion zone, separately fractionating said products to segregate a gasoline fraction, a gas oil fraction and a residual fraction, returning said residual fraction to said conversion zone, withdrawing said gasoline fraction as a product of the process and subjecting said gas oil fraction to further cracking treatment in a zone separate and independent from said conversion zone.

5. The process of producing gasoline from heavy residual hydrocarbon oils which comprises maintaining a dense turbulent mass of subdivided solids fluidized by an upflowing gasiform medium to form an interface separating said mass from an upper disperse phase of substantial height, in a coking zone, maintaining said mass at a coking temperature of about 1050°–1150° F., spraying said oils in the liquid state into an upper portion of said disperse phase, supplying vapors of virgin naphtha boiling within the range of about 250°–430° F. to a lower portion of said mass in amounts of about 25–75% of the total hydrocarbon oil feed to said mass, said vapors forming at least a major proportion of said gasiform medium whereby vaporous coking products including gasoline are formed in said coking zone and coke is deposited on said solids, withdrawing vaporous products through said disperse phase countercurrently to said sprayed liquid oil to preheat and pretreat the latter and scrub entrained solids from said products, withdrawing coke-carrying solids from said mass, subjecting said withdrawn solids to combustion in the fluidized state in a separate combustion zone at a temperature of about 1150°–1300° F. but higher than said coking temperature, returning solids substantially at said combustion temperature from said combustion zone to said coking zone to supply heat thereto.

6. The process of producing gasoline from crude petroleum which comprises subjecting crude petroleum to distillation to produce a virgin naphtha fraction, boiling within the range of about 250°–430° F.; a gas oil fraction and a heavy residue, passing at least a portion of said naphtha fraction to a lower portion of a coking zone, passing at least a portion of said heavy residue substantially in the liquid state to an upper portion of said coking zone, maintaining in said coking zone a dense turbulent mass of subdivided solids fluidized by upflowing vapors of said naphtha fraction to form an upper interface at a point intermediate the feed points of said naphtha fraction and said residue, maintaining said mass at a coking temperature of about 1050°–1200° F. in contact with said vapors and said residue, passing gasiform coking products upwardly from said interface countercurrently to and in direct contact with downwardly flowing liquid residue in said coking zone, withdrawing gasiform products from the top portion of said coking zone, fractionating said withdrawn products to produce a second naphtha fraction, a second gas oil fraction and a second heavy residue, returning a portion of said second naphtha fraction to said lower portion of said coking zone, withdrawing coke-carrying solids downwardly from said mass, passing said withdrawn solids to a heating zone, subjecting said solids in said heating zone to a combustion reaction in the form of a second dense turbulent mass of solids fluidized by upwardly flowing combustion-supporting and flue gases, maintaining said second mass at a temperature higher than said coking temperature and returning highly heated solids from said second-named mass to said first-named mass at a rate sufficient to maintain said first-named mass at said coking temperature.

7. The process of claim 6 in which at least a portion of the naphtha passed to said coking zone is subjected to reforming conditions of tem-

perature and pressure in indirect heat exchange with said second-named mass, prior to the passage of said naphtha to said coking zone.

8. The process of claim 6 in which at least a portion of said second residue is passed substantially in the liquid state to said upper portion of said coking zone.

9. The process of claim 6 in which at least a portion of said gas oil fractions is subjected to catalytic cracking, cracking products being fractionated to produce cracked naphtha, heating oil and cracked heavy residue, and in which at least a portion of said cracked heavy residue is passed in the liquid state to said upper portion of said coking zone.

CHARLES N. KIMBERLIN, JR.
CLARK E. ADAMS.
ROBERT W. KREBS.
ROGER W. RICHARDSON.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,073,456	Sachs	Mar. 9, 1937
2,101,641	Cooke et al.	Dec. 7, 1937
2,289,839	Herthel	July 14, 1942
2,309,540	Rollman et al.	Jan. 26, 1943
2,388,055	Hemminger	Oct. 30, 1945