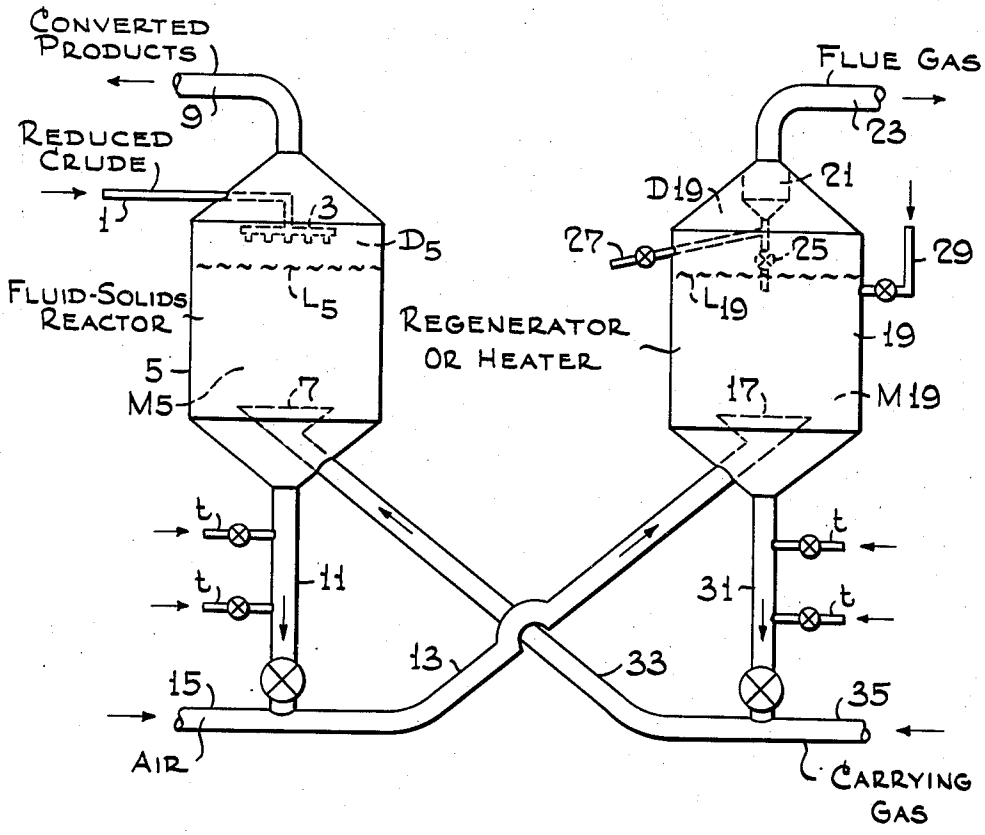
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CONVERSION OF HEAVY HYDROCARBON OILS

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CONVERSION OF HEAVY HYDROCARBON OILS

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4 Claims. (Cl. 196—52)

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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 residua 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 at relatively high coking temperatures with hot subdivided catalytically inert fluidized solids to which a small proportion of a cracking catalyst has been added.

In refining crude petroleum the crude is normally first subjected to distillation or "topping" to produce various distillate fractions and a residue boiling upwards of, say, about 950° F. In standard practice motor fuels are produced almost exclusively from the distillate fractions by suitable refining processes such as thermal or catalytic cracking, reforming, dehydrogenation, isomerization, alkylation, etc. The residue usually has been processed to yield valuable high molecular weight products such as lubricating oils, waxes, asphalt, fuel oils, etc. More recently, however, the demand for motor fuels has increased so greatly that it has become desirable to use the crude residua extensively as an additional source for motor fuels.

It has been known for a long time that substantial yields of motor fuel range hydrocarbons may be obtained by "coking" crude residua which involves subjecting the feed stock to severe cracking at high temperatures and for long holding times. One of the major difficulties encountered in this type of operation resides in the heavy deposition of coke in the coking vessels and transfer lines requiring frequent cleaning periods. This high rate of coke formation combined with the high ash content of the feed stock also renders crude residua highly undesirable as charging material to conventional catalytic cracking processes because of the resulting contamination of the cracking catalyst with difficultly removable impurities and the detrimental effects on cracking selectivity toward motor fuel range products.

Prior to the present invention it has been suggested to avoid these difficulties by coking crude residua in a dense turbulent bed of hot subdivided catalytically inert solids such as coke, pumice, kieselguhr, spent clay, sand, or the like, fluidized by upwardly flowing gases or vapors. These solids serve primarily as carriers 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 of the solids also intensifies the cracking reaction whereby larger yields of gasoline may be obtained within shorter holding times without

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the danger of deactivation of the solids by ash constituents of the feed and coke deposits. The coke deposited on the solids may be burnt off in a separate fluid type heater vessel from which hot solids may be returned to the coking vessel to supply heat required for coking. Fluid operation affords substantial advantages with respect to temperature control, heat economy, ease and continuity of operation as well as equipment dimensions.

While procedures of this type provide substantial improvements over other coking systems the yield and quality of the motor fuels produced are still sufficiently low unfavorably to affect the economics of this way of supplementing the supply of motor fuels. The present invention greatly alleviates this drawback.

It is, therefore, the principal object of the invention to provide means for improving the yield and quality of motor fuels produced by coking heavy residua on hot fluidized solids.

Other objects and advantages will appear from the description of the invention given below wherein reference will be made to the accompanying drawing, the single figure of which illustrates schematically a system suitable to carry out a preferred embodiment of this invention.

It has now been found that substantially increased yields of motor fuels of improved quality may be obtained by coking heavy residua on hot fluidized catalytically inert solids when a subdivided cracking catalyst is added to the solids in specific relatively small proportions and the coking temperature is maintained at a relatively high level within a specific narrow range. The catalyst concentration of the fluidized solids should be kept within the range of about 1–10 weight per cent, preferably within the range of about 3–6 weight per cent. However, the most critical condition is temperature which must be kept substantially above 1000° F., temperatures of 1000° F. and below having been found to be ineffective with respect to the improvements contemplated by the invention. Best results are obtained at temperatures within the range of 1050°–1150° F., particularly in the neighborhood of 1050° F.

Catalytically inert solids such as sand, pumice, spent clay, kieselguhr, petroleum coke, or the like are suitable for the purposes of the invention in fluid operation of the type described above. Sand is particularly useful because of its availability in fluidizable size ranges and its mechanical strength. While all conventional cracking catalysts may be used, synthetic composites of silica gel with alumina, magnesia and/or boria, particularly composites of this type consisting of silica gel and about 10–15 weight per cent of alumina, afford greatest advantages. Certain catalytically active clays, such as acid treated bentonites, may also be used. The cata-

lyst may be added to the inactive solids in any desired manner, such as impregnation, mulling, physical mixing, etc. The simple method of physically mixing the catalyst and inactive solids has been found to be highly effective. In this manner, spent and disintegrated catalyst particles may be elutriated from the fluidized bed without removing inert solids from the bed.

The inert solids take the place of a major proportion of the catalyst used in conventional cracking and may perform an essential part of the function of said replaced catalyst portion namely their function as a heat transfer medium, while sufficient catalyst is provided for the desired catalytic effect. The catalyst may be continuously subjected to regeneration conditions simultaneously with the burning and reheating of the inactive carrier solids in a separate fluidized combustion zone. The catalyst ultimately becomes deactivated and distintegrates into small fines which may be removed overhead from the fluidized bed, fresh catalyst being added continuously or periodically as required, within the proportions specified above. The inert solids normally have a higher resistance to attrition than the catalysts used and, therefore, retain their original size for a longer time.

The fluidization conditions may be those known in the art of similar processes. The inactive solids and the cracking catalyst may be employed originally in substantially the same fluidizable particle size range of about 50–400 mesh. Fluidization may be accomplished at superficial linear gas velocities of about 0.3–5 ft. per second using steam, gasiform hydrocarbons, or the like as the fluidizing medium to establish bed densities of about 20–60 lbs. per cu. ft.

The advantageous effects of the invention are illustrated by the following comparative experiments. In a 1.6" diameter, fluid type experimental unit externally heated to coking temperature, sand having a particle size of about 70–180 microns was fluidized with steam at a linear superficial velocity of about 3 ft. per second. Crude residuum preheated to about 700°–800° F. was injected into a lower portion of the fluidized bed at a feed rate of 2.0–2.3 w./hr./w. and admixed with part of the steam used for fluidization. The oil residuum used in all experiments was a 16% West Texas residuum having the following characteristics:

Gravity, ° API	11.0
Conradson Carbon, weight per cent	15.0
Furol viscosity at 210° F., sec	96.6
H/C atomic ratio	1.43

In some of the experiments 5 weight per cent or 10 weight per cent of a commercial silica-alumina cracking catalyst containing about 13 weight per cent of alumina and having a particle size of about 20–120 microns was mixed with the sand. This catalyst may be prepared by the conventional method of allowing an acid silica sol to set to a hydrogel, washing the hydrogel to low soda and sulfate contents, impregnating the washed hydrogel with aluminum sulfate, adjusting the pH of the impregnated hydrogel to about 4–8 to precipitate alumina, washing, drying and sizing the material.

The specific conditions and the results of these expirements are tabulated below:

Run No	I	II	III	IV	V	VI
Temperature, ° F	1,000	1,000	1,000	1,100	1,050	1,050
Steam Diluent, Wt. percent on Feed	75	75	75	75	75	75
Feed Rate, W./Hr./W	2.0	2.2	2.3	2.0	2.1	2.2
Percent Catalyst in Sand	0	5	10	0	0	5
Product Distribution:						
Coke, Wt. Percent	8.6	8.1	10.3	9.8	9.1	10.2
C_3— Gas, Wt. percent	10.8	10.6	9.9	24.9	15.5	19.2
C_4/430° F., Vol. percent	31.1	32.3	32.7	37.2	38.6	45.8
Naphtha Aniline Point, ° F	68	61	61	40	46	32
430/650° F., Vol. percent	22.9	22.8	22.4	10.0	22.7	11.0
650° F.+Bottoms, Vol. percent	34.3	34.1	33.7	25.4	22.6	19.2
Gravity, ° API	6.8	1.0	0.9	3.6	−4.7	−6.3

It will be observed that the addition of 5 or 10% of catalyst to the fluidized sand contacting medium showed no noticeable effect on the product distribution obtained at 1000° F. At 1050° F., however, the addition of 5% of cracking catalyst to the inert contacting medium caused an increase in the C_4/430° F. gasoline yield of about 20%. An appreciable increase in the octane number of the gasoline formed in the presence of the cracking catalyst is indicated by the lowered aniline point of the naphtha. Runs Nos. IV and V show that merely increasing the temperature within the range effective for catalyst addition affords no comparable advantages.

The invention will be further illustrated by setting forth a specific example with reference to the accompanying drawing.

Referring now in detail to the drawing, reduced crude such as 16% West Texas residuum of the type specified above may be supplied in the liquid state and at a temperature of about 500° to 900° F. through line 1 to a suitable spraying nozzle 3 arranged in the upper portion of coking vessel 5 which may have the design of a conventional fluid solids contacting vessel used in dense phase bottom drawoff operation. It may consist of a substantially cylindrical shell with a conical bottom containing a gas-solids distributing device 7 in the form of an inverted cone having a perforated top.

Vessel 5 may contain a dense turbulent mass M_5 of subdivided solids comprising about 95% by weight of inerts such as sand admixed with about 5% by weight of a cracking catalyst of the silica gel-alumina type. The solids may have a particle size of about 20–250 microns. They are fluidized by means of steam and/or gasiform hydrocarbons entering through device 7 to establish within mass M_5 a linear superficial vapor velocity of about 0.3–5 ft. per second. At these conditions mass M_5 may have an apparent density of about 20–60 lbs. per cu. ft. and it forms an interface L_5 separating it from a disperse phase D_5 having a solids concentration of about .001–0.1 lb. per cu. ft. The liquid residuum may be fed through nozzle 3 at a rate of about 0.2–5 w./hr./w. (weight of oil per hour per weight of solids) and, in descending to mass M_5, may exert a scrubbing and quenching action on dispersed

phase D_5. This type of feeding this residuum is broadly claimed in the copending Kimberlin et al. application, Serial No. 182,036, filed of even date herewith, now Patent No. 2,636,844 and assigned to the same interests. The temperature in mass M_5 is preferably maintained at about 1050°–1100° F. by circulating hot solids from heater-regenerator 19 as will be presently described. Vaporous coking products of low solids content and containing about 35–55 weight per cent of gasoline range hydrocarbons are withdrawn overhead through line 9 to be passed to conventional product recovery and processing equipment (not shown).

At the conditions specified about 8–20 weight per cent of coke based on residuum feed is deposited on the solids in mass M_5. The amount of coke deposited is dependent almost entirely on the quality of the feed, particularly the Conradson carbon of the feed. The coke deposit will be of the order of about two-thirds of the Conradson carbon content of the feed. The coked solids may be withdrawn downwardly from vessel 5 through a conventional standpipe 11 at a rate of about 2–20 times the weight rate at which the residuum is fed. The solids in standpipe 11 may be aerated and/or stripped by small amounts of suitable gases such as flue gas, steam, etc., admitted through taps *t* in a conventional manner. The withdrawn solids pass to line 13 into which air is blown from line 15 in such a manner that a relatively dilute suspension of solids in air is formed. This suspension flows upwardly through line 13 and a distributing device 17 into a lower portion of heater-rerenegator 19. Device 17 and heater-regenerator 19 may be similar in design to device 7 and vessel 5. A fluidized mass M_{19} similar to mass M_5 is formed in heater-regenerator 19 at similar fluidization conditions. Mass M_{19} is separated by interface L_{19} from disperse phase D_{19}.

Combustion of coke takes place in heater-regenerator 19 with the result that the solids are reheated to a temperature of about 1150°–1200° F. but higher than the temperature of mass M_5 and that the activity of the catalyst is restored. About 3,000 to 10,000 cu. ft. of air per bbl. of residuum fed may be used for this purpose. Flue gases containing entrained solids fines may be passed through a cyclone or similar gas-solids separator 21 and via line 23 to any desired use. Separated solids may be returned to mass M_{19} through line 25 or discarded through line 27. Make up inert solids and/or catalyst may be supplied via line 29.

Highly heated inert solids admixed with regenerated catalyst may be withdrawn from heater-regenerator 19 through a conventional standpipe 31 which may be stripped and/or aerated through taps *t* with steam, flue gases, etc. The solids mixture passes substantially at the temperature of mass M_{19} into line 33 wherein it is picked up by the fluidizing gas such as steam, hydrocarbons, etc., which may be preheated, if desired, and supplied from line 35. A dilute suspension of solids-in-gases is formed which passes through line 33 and device 7 to vessel 5 so as to supply heat required therein as sensible heat of reheated solids returned from heater-regenerator 19 at substantially the same rate at which they are withdrawn from vessel 5.

The system illustrated in the drawing permits of various modifications. Instead of spraying the liquid residuum on the top of mass M_5 it may be introduced, preferably admixed with a diluent such as steam or hydrocarbons directly into mass M_5 at any desired location. Distributing cones 7 and 17 may be replaced by grid plates extending over the entire cross-section in the bottom portions of vessels 5 and 19, and combined with suitable withdrawal wells in a manner well known in the art of fluid solids handling. 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. The process of producing gasoline from heavy residual hydrocarbon oils which comprises contacting said oils at a temperature of about 1050°–1110° F. with a dense turbulent fluidized mass of subdivided solids composed of about 94–97 weight per cent of catalytically inactive solids physically admixed with about 3–6 weight per cent of a solid cracking catalyst, said inert solids and said catalyst having particle sizes within the general range of 50 to 400 mesh, said contacting being continued for a time sufficient to effect coking of said oils.

2. The process of claim 1 in which said cracking catalyst is a silica-alumina composite containing about 10–15% alumina.

3. The process of claim 1 in which said temperature is about 1050° F. and said mass contains about 5 weight percent of a cracking catalyst.

4. The process of producing gasoline from heavy residual hydrocarbon oils which comprises maintaining in a coking zone a dense turbulent fluidized solids mass composed of about 94–97 weight per cent of catalytically inert solids physically admixed with about 3–6 weight per cent of catalytically active solids, maintaining said mass at a coking temperature of about 1050°–1150° F., contacting said oils with said mass for a time sufficient to effect coking of said oils and deposit coke on said solids, withdrawing vaporous coking products upwardly from said coking zone, withdrawing coke-carrying mixed catalytically active and inactive solids downwardly from said mass, subjecting said withdrawn solids to combustion in the fluidized state in a separate combustion zone at a temperature of about 1100°–1200° F. but higher than that coking temperature to remove coke and regenerate said catalytically active solids, and returning mixed solids substantially at said combustion temperature from said combustion zone to said coking zone at a rate sufficient to maintain said coking temperature.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
2,229,353	Thomas et al.	Jan. 21, 1941
2,323,501	Tuttle	July 6, 1943
2,406,555	Martin	Aug. 27, 1946
2,441,170	Rose et al.	May 11, 1948
2,464,616	Schwarzenbek et al.	Mar. 15, 1949
2,485,315	Rex et al.	Oct. 18, 1949
2,573,906	Huff	Nov. 6, 1951

FOREIGN PATENTS

Number	Country	Date
118,399	Australia	Apr. 12, 1944