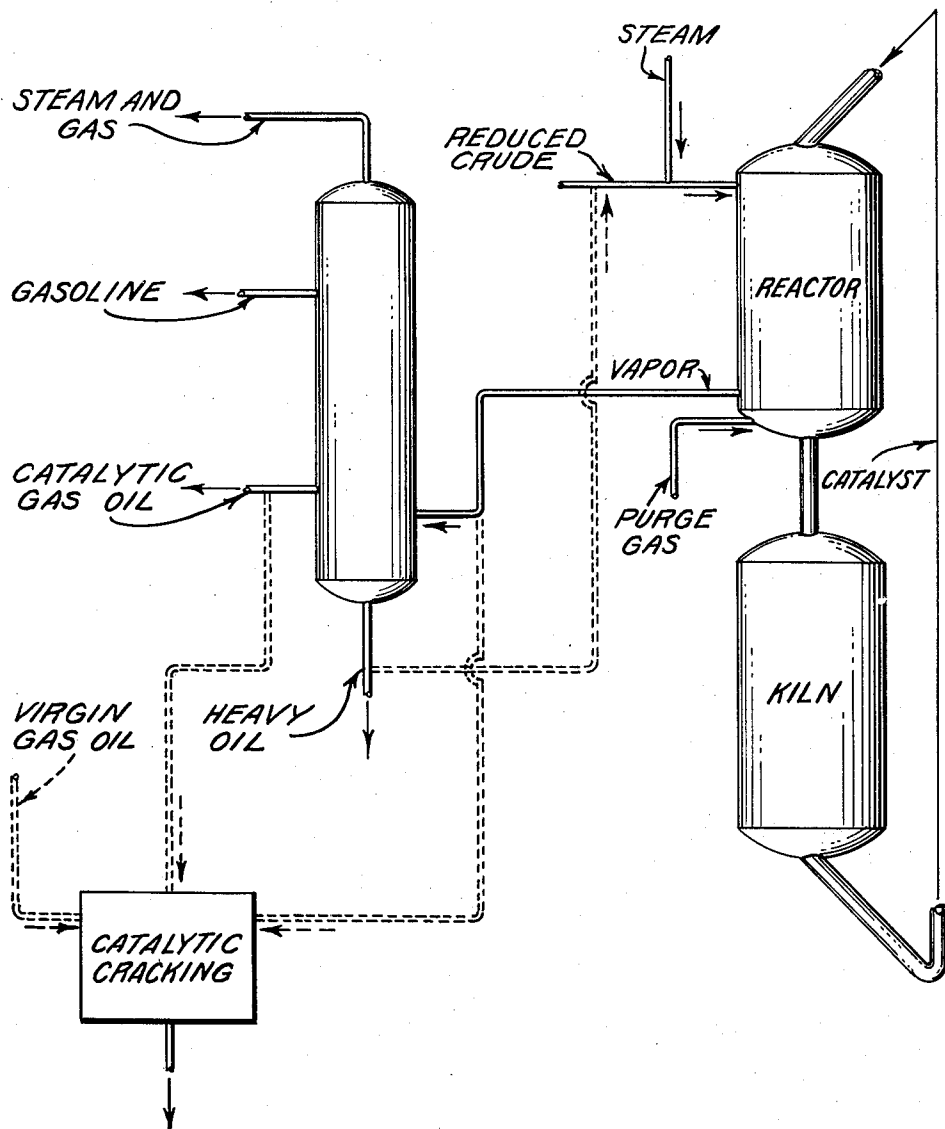


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CRACKING OF RESIDUAL OILS CONTAINING ASPHALTIC AND METALLIC CONTAMINANTS

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The present invention relates to the cracking of heavy oils to more desirable and useful products and is particularly concerned with the catalytic cracking of crude oil bottoms or other heavy oils containing asphaltic residua.

The value of hydrocarbons, particularly those obtained from natural sources such as crude petroleum or from oil shale or indirectly as from the destructive hydrogenation of coals, is greatly enhanced by various methods of refining these hydrocarbons. In their raw state or even in a more or less refined condition these hydrocarbons are often unsuited for many purposes because of lack of conformity to certain requirements. Failure to meet these requirements arises from causes which may include unsuitable boiling range, excessive amounts of deleterious materials which are not hydrocarbons, but which are present all too frequently in natural or partly refined hydrocarbons, or from the very nature of the hydrocarbons which, however, may be altered to more desirable form with appropriate treatment or treatments such as pyrolytic or catalytic procedures.

In heavy petroleum oils such as crude oils, tar and asphalt-like materials are often present in considerable and serious amounts. It is the usual practice to separate and remove these materials from the heavy oils when the oils are employed in the normal manner, for example, as the starting materials for cracking operations for the production of gasoline and fuel oils. Present refinery practice is to dispose of these removed tarry or asphaltic materials either as low grade fuels or as road surfacing agents or in other ways. In any case, such materials are considered at present of little value as starting or charge materials for economic production of more valuable hydrocarbons by customary cracking operations, particularly in view of the disproportionately large amounts of coke and gas formed therefrom.

Another problem confronting refiners in using heavy hydrocarbon oils is that of contaminants, such as various nitrogen compounds, metallic compounds and the like. These contaminating materials may either corrode or plug up the pipes and other pieces of the refining equipment; they may pass through the refining operation either in a quantity or quality such that the value of the finished product is considerably impaired; they may be deposited on the surface of the catalyst and rapidly inactivate the catalyst or they may inhibit, to a marked degree, the desired reaction leading to the refined product. Usually, there exists a combination of two or more of these objectionable features.

In any attempt to crack the heavy bottoms portion of petroleum stocks by catalytic methods, the metallic contaminants—which are concentrated in such residues—present a serious and heretofore unsurmountable problem from the standpoint of their deleterious effects on the activity and/or selectivity of cracking catalysts. Thus, it was found, for instance, that the deposition of even relatively small amounts of such metal or its salts on the catalyst, in the order of about 0.05% by weight thereof, increased the light gas make and more than

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doubled the amount of coke produced in cracking of a hydrocarbon charge. Since the heavier hydrocarbons of themselves, when subjected to cracking inherently tend to form comparatively large amounts of coke even in the absence of these metallic substances, the problem is all the more further multiplied.

Among the objects of the present invention is to provide an improved process for cracking of residual petroleum fractions and other heavy hydrocarbon oils containing asphaltic or tarry residua, which oils may include metallic components and other contaminants of the kind above described, to obtain high yields of desired liquid product of enhanced value including greater or less quantities of gasoline, and without disproportionate loss of valuable hydrocarbon material by accompanying excessive formation of coke and/or low molecular weight gases.

The above object is attained and other beneficial advantages realized in accordance with the present invention by contacting the heavy hydrocarbon oil containing such asphaltic residua and possible contaminants of the type hereinabove referred to, with a continuously moving mass of catalyst particles in the presence of at least 25% by weight steam under selected operating conditions hereinafter set out. The described operation can successfully be applied to petroleum distillation residues composed essentially of high boiling hydrocarbons, as those boiling above active cracking temperature (about 850° F.), as well as to wider cut hydrocarbon fractions containing unremoved or added lower boiling hydrocarbons in addition to the higher boiling material comprising all of or part of the asphaltic materials, metallic components and other contaminants found in the crude oils from which these fractions are derived. By the methods of the present invention these charge stocks are readily converted to produce high yields of desired liquid products with surprisingly low loss of charge by accompanying formation of coke and light gases. The liquid effluent provides a fairly clean product of lowered coking characteristics suitable for catalytic cracking or for other desired uses such as furnace oil, having a drastically reduced content of coke-forming materials as determined by Ramsbottom and Conradson methods. While it will be understood that the method of the invention is not so limited, for convenience of description it will be hereinafter referred to as catalytic "residuum cracking" to distinguish from ordinary catalytic cracking as usually applied to gas oils or other hydrocarbon distillates.

In the preferred practice of the invention the catalyst employed is of granular size, as distinguished from powdered material, and moves through the hydrocarbon conversion zone as a compact gravitating bed.

Without being bound by any particular theoretical explanation thereof, it is believed that the unusually small production of coke and light gas from such heavy charge containing residual bottoms and metal compounds is brought about by the use of the described large quantities of steam, in that the addition of the prescribed large quantities of steam operates not only to reduce the partial pressure of the hydrocarbons present in the reaction zone, but the added steam also functions as a medium which preferentially displaces incipient coke-forming hydrocarbon materials from the catalyst. In addition to these salient benefits, the steam apparently also serves to overcome the tendency to promote coke production otherwise exhibited by the metal and/or salt deposit in the catalyst, as is evidenced by the fact that the large successive increase in coke make heretofore observed does not take place when cracking such metal-containing residues in the presence of the stated quantities of steam.

It has previously been observed, based on experiences in the catalytic cracking of gas oils, that the nature of

the conversion reactions encountered and the general effects of changes in operating variables are essentially the same whether such cracking takes place over a fixed bed of catalyst which is periodically regenerated in situ or over a moving bed of catalyst which passes sequentially through the hydrocarbon conversion zone and a separate regeneration zone. It has now been found that in the cracking of residua and heavy hydrocarbon oils of the type described above, however, that the moving bed technique offers certain important special advantages over the fixed bed operation, which were not fully realized and which do not apply with equal force in the use of the moving catalyst bed for cracking of lighter and/or cleaner hydrocarbon fractions such as gas oil. For instance, since in the case of the residual hydrocarbon material the predominant part or essentially all of the oil is charged in liquid phase, the moving catalyst operation permits a more uniform distribution of the oil over the entire mass of catalyst avoiding preferential adsorption in the upper layer of the catalyst bed which would be the tendency when using a fixed mass of catalyst. Because of the better oil distribution in the moving catalyst system and equalized coke distribution resulting, more uniform temperatures are had during conversion as well as during regeneration of the catalyst, largely avoiding the problems created by thermal effects. The over-all coke make, for this and other reasons, has been found to be considerably less for substantially the same degree of oil conversion when effected in a moving catalyst bed.

There is another important advantage of the moving bed particularly as applied to the catalytic cracking of residual bottoms containing a high concentration of metallic contaminants. Such contaminants play an important role in determining the active life of the catalyst, since the metal thus deposited in or on the catalyst not only of itself reduces the activity or selectivity of the catalyst for the desired cracking operation, but even the presence of very small amounts of such metal in the catalyst raises the coke-making propensities several fold. In the presence of the described large proportions of steam it has been found, that the coke-promoting tendency of the metal-contaminated catalyst is largely overcome. Moreover, it has been observed, in operations employing a moving bed of granular catalyst that only a comparatively small portion of the metal expected to be present is actually retained by the catalyst. It appears that the predominant portion of the metal compound is adsorbed on the external surface of the granular catalyst particles as a thin layer, which layer apparently is abraded by impact and attrition in the moving bed and in transport to and from such bed, and a large part of the metal is thus removed from the system as fines.

In the foregoing description reference has been made to the presence of metallic contaminants in the residuum fraction. It is not intended to be inferred thereby that such contaminants are necessarily present in the oil as free metals, since it is known that these contaminants may appear in the oil in a variety of different chemical and physical states and forms, including: in addition to the free metals and/or oxides, certain so-called metal soaps, particularly those of the naphthenic acids; chelates and other organo-metallic complexes which may be present as true or colloidal solutions or as finely divided solid particles; inorganic salt forms, and the like. The term "metallic contaminants" and similar terms employed in the present description and claims are to be accordingly understood as including all such compounds and complexes as well as free metals. The principal metals which have been found to adversely affect cracking catalyst include iron, nickel, and vanadium.

To obtain the full advantages of the present invention the catalyst employed should be a solid granular material of fairly large particle size, as above about 40 mesh and preferably at least 1 and up to 5 or more milli-

meters length and thickness. Particles of predominantly this size range flow easily without excessive packing and gases can flow through a compact bed of such particles quite readily without disturbance of the bed. More important, however, as applied to the cracking of residual petroleum fractions and other heavy oils charged in liquid state and containing metallic and other contaminants, particles of granular size, as distinguished from fine or fluidizable powders, provide ample exterior surface per particle on which the liquid oil and accompanying metallic and other contaminants can be absorbed or collected. It will be understood that the area of the external surface of a particle increases directly with the square of its radius; moreover, since the liquid oil penetrates only a small distance through and below the exterior surface of the particle, and accompanying salts and metals, deposit largely on and a short distance below the external surface, in the larger particle size material a substantial portion of the interior of the particle remains uncontaminated and fully active in catalytic conversion of hydrocarbon molecules which penetrate thereto. In repeated use of the catalyst, as this surface is gradually worn off in successive laminae, new surfaces are continuously presented over a long period of use until the catalyst granule is ultimately reduced to a core of very small size and is removed from the system.

The contact material employed in the residuum cracking operation may be any siliceous adsorptive material having catalytic cracking properties and may be one having an activity up to that ordinarily selected for conventional gas oil catalytic cracking, or it may be even lower than such activity. Thus, there can be used not only the conventional siliceous cracking catalysts such as acid-activated clays and dried gels comprising composites of silica with alumina and/or other of the known refractory metal oxides, but also certain other cheap and abundant common clays and other minerals which cannot or have not been brought to activated state by acid-treatment, including clays of the kaolin and montmorillonite types, spent decolorizing clays, as well as "spent" catalysts of the activated clay and synthetic gel types which are discharged or recovered from conventional catalytic cracking units.

The catalytic activity of the contact mass largely determines the product distribution including the composition of the gas oil, and the relative quantity of gasoline produced as well as the anti-knock characteristics thereof. Thus with a relatively inert contact material the gas oil formed contains a considerable quantity of high boiling range hydrocarbons (above about 1000° F.), and comparatively little or no gasoline is formed at temperatures within the described operating range. With contact materials having appreciable or higher cracking activity the extent of cracking of the heavy oil and asphaltic components is considerably increased over that obtained with relatively inert materials, as evidenced by higher conversion to liquid products boiling below about 1000° F. and highly increased production of gasoline. The gasoline formed, moreover, has the high anti-knock characteristics of usual catalytically cracked gasoline. Such higher conversion or more extensive cracking with a catalyst of increased activity may lead to somewhat increased production of gas and coke, but this is more than offset by the quality of the obtained liquid product, particularly as to its much lower Conradson carbon values. Cracking catalysts of moderate activity, for example, such as those showing an activity of 25-30% gasoline by the standard "CAT-A" method (see J. Alexander and H. G. Shimp, National Petroleum News, August 2, 1944, at pages R537 and 538 and J. Alexander, Proc. Am. Petroleum Inst., III, 27, 51 (1947)) employed in cracking of petroleum residua (13-14% bottoms of mixed Coastal crude, 63% boiling above 1000° F.) in the presence of the prescribed quantities of steam, showed a production in the order of up to 25% gasoline (and higher) at tem-

peratures of 800–850° F., which gasoline had an octane rating of over 85 (F1 clear); the Ramsbottom carbon of the 400° F. + gas oil was no more than about 1%.

The choice of contact material, accordingly, is fairly flexible and will be governed largely by the requirements of the individual refiner based largely on balance of economics and the nature of the heavy oil or other charge, the other facilities of the refinery and the ultimate products marketed. As a general rule, the use of contact materials of higher than moderate cracking activity, as above about 30 CAT-A index, is not recommended in the process of the invention; since these catalytic materials of high activity are higher in initial cost and tend to be more easily deactivated by steam and by contaminants present in the heavy oil charge, there is ordinarily no over-all advantage obtained by their use. As contrasted with catalytic materials, however, the desired results are not obtained with relatively inert materials, since with the latter as much as 50% or more of the gas oil produced from conversion of the residua is in the higher boiling range (a considerable portion thereof boiling above 1000° F.), is of high coking tendency, and does not have the quality and properties of desired gas oil feed to ordinary catalytic cracking facilities. For instance, the Ramsbottom carbon of the gas oil obtained when cracking over such inert materials runs considerably higher than that of the product produced with contact masses of even low to moderate catalytic cracking activity. For these reasons contact materials having at least appreciable cracking activity are selected in practice of the invention, such as those having CAT-A gasoline yield indexes of above ten and preferably at least about 20.

The catalytic cracking of heavy bottoms by the process of the invention provides considerable flexibility of operation. The effluent from such cracking will comprise steam, fixed gases, good quality gasoline, and a gas oil suitable for further catalytic cracking; which can be fractionated or separated, if desired, by known methods to provide the charge sent to the gas oil catalytic cracking operation.

Those products which do not go off in the vapor effluent from the residuum cracking reactor become deposited as a hydrocarbonaceous mass in the contact material, and in the proposed commercial operation would be periodically removed. Since the contact material is of catalytic nature subject to impairment in various ways, and it is desired to maintain catalytic activity over a long useful period, care must be taken in the removal of the hydrocarbonaceous deposit to insure minimum depreciation of the catalytic activity. To this end also, the coke content of the catalyst as subjected to combustive regeneration is maintained as low as possible. Thus, in practice of the invention it is important that the catalyst remain in the hydrocarbon conversion zone for a sufficient period that the heavy hydrocarbons thereon can be converted to full extent by cracking to lower boiling vaporized products, inasmuch as such heavy hydrocarbons are not removable by usual purging with steam or other inert gas. In certain instances it will be found desirable also to effect the subsequent purging employing steam or other inert gas at elevated temperature whereby the catalyst is thereby raised to higher temperature, as 50° F. or more above that employed during the hydrocarbon conversion reaction and desirably to above 900° F. or up to about a temperature of 1000° F. or above under non-oxidizing conditions, thereby volatilizing or decomposing at least a portion of the hydrocarbonaceous deposit. Thereafter the remainder of the deposit may be wholly or partially removed by oxidative combustion in air or other oxygen-containing regenerating gas.

The quantity of steam employed in the catalytic cracking of residua, to obtain the desired yields of liquid effluent having low Conradson carbon and other advantages described, should comprise not less than about 25% steam by weight of the normally liquid hydrocarbons

charged as fresh feed and preferably in the order of about 40 to 50% in the case of a narrow range high boiling bottoms cut. Above the described minimum, increased quantities of steam are beneficial from the standpoint of enhanced yield and/or quality of the desired conversion products obtained, as will appear below. Amounts of steam in excess of about 150% by weight of the oil are not recommended in practice because any possible advantage thereof would be largely overcome by the increased operating costs in handling such quantities of steam.

The preferred operating temperature lies in the range of about 800–1000° F. With increasing temperature more extensive cracking takes place with the formation of increased quantities of gasoline but also larger quantities of light gas. The quantity of "coke" produced in the cracking of residua usually approaches a minimum at cracking temperatures above about 800° F.

The effects of changes in operating variables on the distribution and yields of the cracked products obtained which have heretofore been observed in the customary catalytic cracking of lighter hydrocarbon charge fractions, such as gas oils, do not necessarily apply in cracking of heavy residua in accordance with the present invention. For example, in cracking of a gas oil increasing the severity of operation by lowering the space velocity of the hydrocarbon feed generally results in increased coke production; on the other hand in practice of the present process of catalytic cracking of oils containing heavy bottoms in the presence of the indicated quantities of steam, it has been found that increase of severity by lowering space rate results in a lowered coke production. This difference in behavior appears to be associated with the requirement of an adequate period of contact of the heavy oil on the catalyst to permit the potential coke-forming material to be converted to lower boiling vaporized hydrocarbons. Based on present observations it appears that a catalyst residence time in the reactor of not less than about ten minutes should be provided to assure adequate conversion and low coke production from charges containing considerable amounts of refractory heavy hydrocarbons. With certain less refractory charge stocks and/or with increase in operating temperature as above about 875° F., a catalyst residence time of as low as 5 or 6 minutes may be adequate, but in no event should the residence time be less than 5 minutes.

In order to provide adequate surface for distribution of the liquid oil and to limit the quantity of coke formed in or on the catalyst, it is also important that high catalyst to oil ratios be employed as above about 5:1 by weight. It will be understood that at the indicated minimum catalyst to oil ratios and the above-stated minimum catalyst residence time the corresponding space rates of the oil feed will be no more than about two parts of oil per hour for each part of catalyst in the reactor; and in general, space rates of about one or less will be used in preferred operation. Under the described conditions the catalyst will contain less than about 2%, and preferably in the order of about 1%, by weight of carbonaceous deposit (after purging) when subjected to oxidative regeneration.

Example I

In this run of synthetic silica-alumina gel catalyst was employed having a bulk density of 640 grams per liter and an activity index of 27 by the CAT-A method. To the catalyst there was charged a 13% bottoms fraction of a mixture of essentially East Texas type crude oils, which fraction had an API gravity of 18.4 and a Conradson carbon value of 6.7%, substantially all of the fraction boiling above 850° F. and 40% boiling above 1000° F.

The catalyst temperature was held at 850° F. and the oil fraction charged thereto at the rate of one volume

(as liquid) of oil per hour per volume of catalyst together with about 75% steam by weight of oil.

As products from the above cracking operation there were obtained by weight of oil charged 72.6% gas oil boiling over the range of 400 to 1000° F., 9.1% of liquid product boiling above 1000° F., 9.2% gasoline, 3.0% gas; 4.3% by weight of the charge was deposited as coke on the catalyst.

The liquid boiling above 400° F. had a Ramsbottom carbon value of 1.06% and was found to be highly suitable as gas oil charge stock to conventional catalytic cracking.

Example Ia

In other run made on the same charge stock employing approximately the same quantity of steam addition as before but using an inert material (quartz) instead of the catalyst in the reactor, only about 55% by weight of the charge could be recovered as gas oil, no gasoline was produced, and the Ramsbottom carbon of the liquid product was 2 to 3 times that of the corresponding product obtained when catalyst was employed.

Example II

There was charged to moving bed of commercial silica-alumina bead cracking catalyst a 14% bottoms fraction from a mixture of Texas Pipe Line crude oils, having an API gravity of 14.9° and a Ramsbottom carbon value of 9.7%, of which charge 63% boiled above 1000° F. The following results were obtained at the conditions tabulated below:

Operating conditions:

Oil space rate, v./hr./v.	1.0
Cat./oil ratio, v./v.	6.0
Steam wt. percent of oil	97.5
Operating pressure, p.s.i.g.	10
Catalyst temp. (bed avg.), ° F.	855

Yields (on charge):

Gasoline, vol. percent	30.4
Light gas oil, vol. percent	11.8
Heavy gas oil, vol. percent	47.6
C ₄ Fraction, vol. percent	6.7
Dry gas, wt. percent	4.0
Coke, wt. percent	9.8

Inspection:

C ₅ +gasoline—F-1 clear octane No.	91.5
Light gas oil—	
Ramsbottom C, percent	1.0
Gravity, API°	22.0
50% point ° F. (ASTM)	572
Heavy gas oil—	
Ramsbottom C, percent	2.3
Gravity, API°	18.3
50% point ° F. (VA)	875
90% point ° F.	1032

The total gas oil fractions from the above run were charged to a conventional catalytic cracking unit operating at 875° F. (bed temperature), at a catalyst to oil ratio of 7 and at a space rate of 0.86 volume of oil per hour per volume of catalyst. At a conversion level of 47.2% by weight of charge there was obtained 36.2% by volume gasoline having an F1 clear octane rating of 90.4.

Example III

The effect of residence time (or space rate) on products distribution is evident from the table below showing the yields obtained in cracking of a heavy charge composed of the 10% bottoms fraction from the Texas Pipe Line crude above described, adding 50% by weight steam and over the same commercial silica-alumina catalyst as in the previous example. The charged fraction had an API gravity of 12.5 to 13.5°, and a Ramsbottom carbon of 12%.

Operating Conditions:

Space rate, vol. cat./hr./vol. oil.....	0.75	1.0	1.5	2.0
Catalyst/oil, v./v.....	13.1	11.6	12.5	12.4
Catalyst res. time (min.).....	6.1	5.2	3.2	2.4
Temp., ° F.....	885	870	865	870
Product Yields:				
C ₅ + gasoline, vol. percent chg.....	41.9	35.7	37.3	30.4
Cat. gas oil, vol. percent chg.....	41.6	49.7	48.7	51.8
C ₄ cut, vol. percent chg.....	12.5	9.9	8.7	9.4
Dry gas, wt. percent chg.....	7.6	5.4	3.8	4.1
Coke, wt. percent chg.....	12.1	13.4	14.4	16.3
Gasoline Octane No. (F-1 clear).....	89.2	89.0	88.9	87.5

Example IV

A 38% bottoms cut of the above-described crude oil of 22.6° API gravity was cracked over a moving bed of pelleted equilibrium clay catalyst (26 CAT-A) with the addition of 50% steam by weight of the oil charged. The conditions and yields are reported below:

Operating conditions:

Temp., ° F.	910
Space rate (v./hr./v.)	0.68
Cat./oil (v./v.)	11.0
Cat. res. time (min.)	9.7

Product yields:

C ₅ +gasoline (vol. percent chg.)	44.3
Cat. gas oil (vol. percent chg.)	32.4
C ₄ cut (vol. percent chg.)	15.2
Dry gas (wt. percent chg.)	12.2
Coke (wt. percent chg.)	7.8
Gasoline octane No. (F-1 clear)	94

From results observed in a number of runs carried out at different operating levels and on various charge stocks it is apparent that the quantity of steam employed also has an important influence on yield and quality of products. Thus, in a once-through operation on the same charge stock (40% East Texas bottoms) under approximately the same operating conditions except that the quantity of added steam was raised from 20% by weight of oil to 52.5%, the gasoline yield was thereby increased about 9%, the coke reduced about 19%, the gas production decreased about 30%, while the octane rating of the F-1 clear gasoline was raised from 89.8 to 91.6. These effects of increasing quantities of steam are even more pronounced with narrower cut residual fractions. In general with increasing water to oil ratio, there is progressive increase in the recovered liquid hydrocarbon product, while at below about 25-30% by weight steam the quantity of fixed gas produced on cracking of a heavy residual fraction increases quite rapidly as the quantity of steam is lowered.

It will be seen from the foregoing that the process of the invention is applicable to the cracking of narrow cut high boiling residua essentially all of which boils above cracking temperature, such as a 10-15% bottoms cut, as well as to wider cut fractions containing greater or less quantities of lower boiling hydrocarbons in addition to the asphaltic and tarry residua. While not limited thereto the advantages resulting from the use of the advocated large quantities of steam are particularly beneficial in the catalytic cracking of fractions containing metallic components which when deposited in the catalyst tend to impair desired activity and/or selectivity.

In the accompanying drawing there is illustrated a general processing scheme that can be employed in practice of the invention. As shown the reduced crude, which may be a heavy bottoms fraction, together with added steam is cracked in a moving bed catalytic reactor. The cracked effluent therefrom may be fractionated or the total vapor effluent may be sent directly to further catalytic cracking together with virgin gas oil from any other source. The heavy oil from the fractionator may be separately recovered or recycled to the residuum cracking reactor, while the separated catalytic gas oil is sent to the gas oil catalytic cracking system or recovered in part as a desirable furnace oil.

It will be understood that in practice of the invention so-called "purging" of the catalyst with steam before the catalyst is subjected to regeneration will ordinarily be carried out at the bottom of the hydrocarbon conversion reactor; if desired, however, purging may be effected in a separate vessel. Since at the prevailing temperature during the purging action at least a portion of the heavy hydrocarbon material on the catalyst is being subjected to further cracking, the term "reaction zone" as employed in the specification and claims is intended to include such purging zone whether in the same or in a separate vessel.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What is claimed is:

1. The method of cracking residual hydrocarbon fractions containing heavy hydrocarbon materials which are liquid at 850° F., which method comprises introducing such a fraction including unvaporized hydrocarbons into a reaction zone, contacting such fraction including unvaporized hydrocarbons in said reaction zone with a non-turbulently gravitating mass of solid adsorptive cracking catalyst particles having minimum dimensions greater than 1 mm., adding to said reaction zone at least 25% steam by weight of fresh hydrocarbon feed, withdrawing condensable hydrocarbon vapors from the reaction zone, subjecting catalyst particles withdrawn from the reaction zone to a flowing gas in a purging step at a temperature higher than that of the catalyst admitted to the purging step, subjecting the purged catalyst particles to oxidizing conditions to burn the carbonaceous deposit and to regenerate said catalyst particles and returning the regenerated catalyst particles to the reaction zone.

2. The method of converting petroleum which comprises the steps of: removing volatile components therefrom, thereby preparing a residual hydrocarbon fraction containing all of the asphaltic, metallic and other contaminants occurring in said petroleum, said fraction comprising hydrocarbon materials which are liquid at 850° F.; contacting said residual fraction as the sole fresh hydrocarbon feed in a reaction zone within the range from 800° F. to 1000° F. with a moving mass of solid granular adsorptive cracking catalyst having a cracking activity corresponding to at least 10% gasoline by the CAT-A method, said granular catalyst being passed through said reaction zone at a rate such that the catalyst traverses said reaction zone in not less than five minutes, the weight of the granular catalyst in said reaction zone being at least five times the weight of the hydrocarbons in said zone; adding to said reaction zone at least 25%, but not more than 150% steam by weight of said fresh hydrocarbon feed; and withdrawing volatile cracked products comprising high octane gasoline components from the reaction zone.

3. The method of converting petroleum which comprises the steps of: removing volatile components there-

from, thereby preparing a residual hydrocarbon fraction containing all of the asphaltic, metallic and other contaminants occurring in said petroleum, said fraction comprising hydrocarbon materials which are liquid at 850° F.; contacting said residual fraction as the sole fresh hydrocarbon feed in a reaction zone at cracking conditions with a compact, gravitating bed of granular siliceous cracking catalyst having a cracking activity corresponding to at least 10% gasoline by the CAT-A method, said granular catalyst being passed through said reaction zone at a catalyst to oil weight ratio in excess of 5:1 and said catalyst being retained in said reaction zone for at least five minutes and said cracking being conducted in the presence of at least 25% but not more than 150% steam by weight of said fresh hydrocarbon feed; and withdrawing volatile cracked products comprising high octane gasoline components from the reaction zone.

4. The method of converting petroleum which comprises the steps of: removing volatile components therefrom, thereby preparing a residual hydrocarbon fraction containing all of the asphaltic, metallic and other contaminants occurring in said petroleum, said fraction comprising hydrocarbon materials which are liquid at 850° F.; contacting said residual fraction as the sole fresh hydrocarbon feed to contact in a reaction zone at temperature above 750° F. and under catalytic cracking conditions with granular particles of regenerated silica-alumina cracking catalyst having a cracking activity corresponding to at least 10% gasoline by the CAT-A method, said granular catalyst being passed through said reaction zone at a catalyst to total oil weight ratio of not less than 5 and at rates whereby said catalyst remains in said reaction zone for not less than five minutes, in the presence of at least 25% but not more than 150% steam by weight of said fresh hydrocarbon feed, thereby producing volatile cracked products containing gasoline and higher boiling hydrocarbons; and thereafter subjecting at least a portion of said volatile cracked product freed from gasoline and lighter hydrocarbons to further catalytic cracking in a separate reaction zone.

References Cited in the file of this patent

UNITED STATES PATENTS

45	2,089,616	McKee	Aug. 10, 1937
	2,209,973	Houdry et al.	Aug. 6, 1940
	2,348,156	Sheppard	May 2, 1944
	2,342,983	Thomas	Feb. 29, 1944
	2,428,532	Schulze et al.	Oct. 7, 1947
50	2,437,222	Crowley	Mar. 2, 1948
	2,448,922	Simpson et al.	Sept. 7, 1948
	2,560,433	Gilbert et al.	July 10, 1951
	2,676,909	Bethea	Apr. 27, 1954
	2,683,109	Norris	July 6, 1954
55	2,770,582	Eastwood	Nov. 13, 1956

OTHER REFERENCES

Mills: Aging of Cracking Catalysts, Ind. Eng. Chem., 42 (1950), pages 182 to 187.