

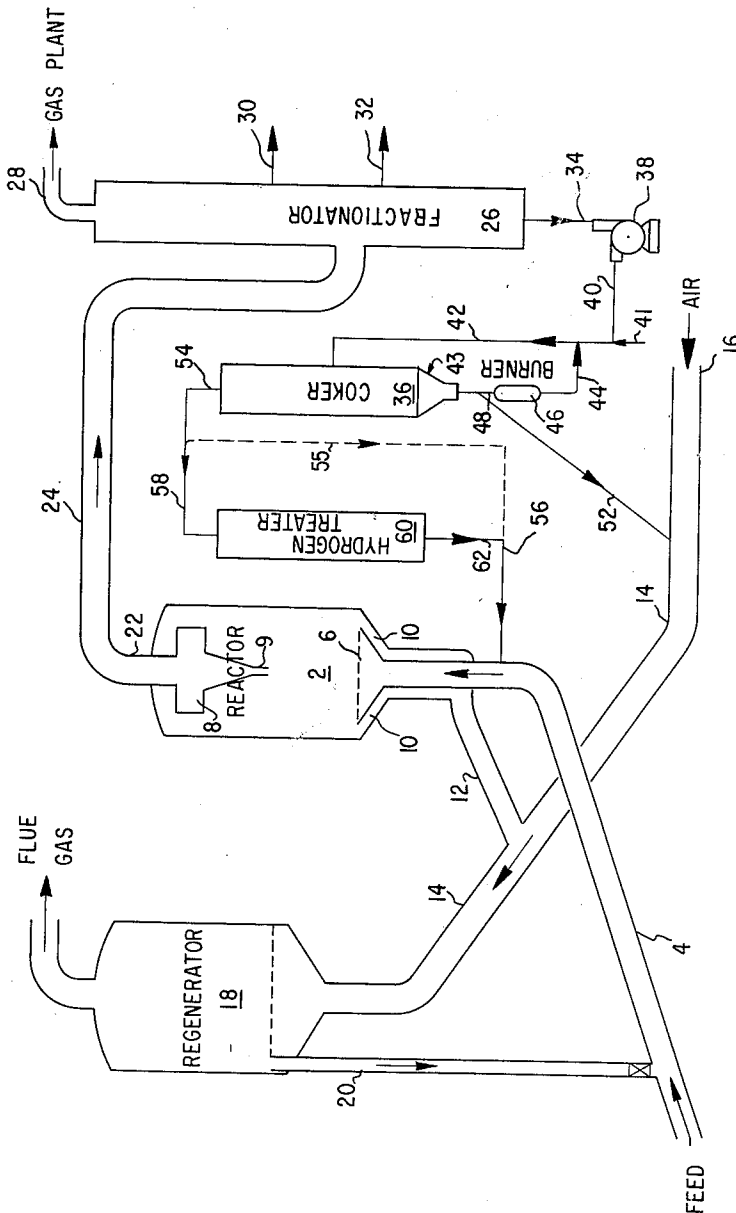
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PROCESS FOR RECOVERING CATALYST PARTICLES IN RESIDUAL
OILS OBTAINED IN THE CONVERSION OF HYDROCARBON OILS
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PROCESS FOR RECOVERING CATALYST PARTICLES IN RESIDUAL OILS OBTAINED IN THE CONVERSION OF HYDROCARBON OILS

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This invention relates to an improved method for the catalytic cracking of mineral hydrocarbon oils. Particularly, the present invention relates to the catalytic cracking of a mineral hydrocarbon oil where the cracking unit has associated with it a coking operation. Specifically, the present invention relates to a process for the catalytic cracking of a mineral hydrocarbon oil and coking of fractionator bottoms to provide process heat, improved product yield and catalyst recovery.

Fluid catalytic cracking processes are generally operated with a bottom draw from the primary fractionator. These bottoms contain heavy cracked oil and suspended catalyst which was not removed from the cracking effluent by the cyclone separators in the cracking reactor. This fractionator bottoms product is either generally recycled to the reactor or processed through a settler to concentrate the catalyst into a slurry. The slurry is usually sent to the catalytic reactor and the clarified oil used as a heavy residual fuel. The latter procedure is generally preferred because the liquid fractionator bottoms has high coking and low cracking tendencies under the usual catalytic cracking conditions. As a consequence cracking operations necessarily produce substantial amounts of high carbon-residue materials from which entrained catalyst must be separated by costly operations.

It has now been found that when a fluidized coking unit is combined with a catalytic cracking unit, to which unit the fractionator bottoms containing suspended cracking catalyst is fed there results improved product yield and catalyst recovery while providing means for adding process heat to the cracking operation. The coker is operated to form coke on the catalyst in the fractionator bottoms and to produce an overhead product. Coke laden catalyst particles can then be fed to a regenerator for their heating value and for catalyst recovery, and the overhead fraction from the coker may be further treated to yield light gases, gasoline and gas oil suitable as a feedstock to the cracking unit or the overhead fraction may be sent directly to the cracking unit without further processing.

The feeds to the present process are those materials which boil primarily above the gasoline range. Advantageous feedstocks are the petroleum gas oils which may be straight run or previously cracked stocks or their mixtures. Gas oils include any fraction distilled from petroleum or other mineral oil which has an initial boiling point of at least about 400° F., say up to about 850° F., and an end boiling point of at least about 600° F., and boiling substantially continuously between the initial boiling point and the end boiling point. Usually the boiling range extends over at least about 100° F.

Catalytic cracking is ordinarily effected to produce gasoline as the most valuable product and is generally conducted at temperatures of about 750 to 1050° F., preferably about 850 to 975° F., at pressures up to about 100 p.s.i.g., preferably about atmospheric to 5 or 15 p.s.i.g., and advantageously without substantial addition of free hydrogen to the system. In the cracking operation, a batch, semicontinuous or continuous system may be used but most often is a continuous fluidized system.

The cracking catalyst is of the solid refractory metal oxide type known in the art, for instance silica, alumina, magesia, titania, etc., or their mixtures. Of most importance are the synthetic gel-containing catalysts, such as the synthetic and the semi-synthetic, i.e., synthetic gel supported on a carrier such as natural clay, cracking catalysts. The cracking catalysts which have received the widest acceptance today are usually predominantly silica, that is silica-based, and may contain solid acidic oxide promoters, e.g. alumina, magnesia, etc., with the promoters usually being less than about 50% of the catalyst, preferably about 5 to 25%. These compositions are calcined to a state of very slight hydration. The catalytic cracking process involves using a finely divided form or fluidized solid catalyst; in a highly preferred form of this invention finely divided (fluidized) catalyst, for instance having particles predominantly in the 20 to 80 or even 150 micron range, is disposed as a fluidized bed in the reaction zone to which the feed is charged continuously and is reacted essentially in the vapor phase.

Vaporous products are taken overhead and a portion of the catalyst is continuously withdrawn and passed to a regeneration zone where coke or carbon is burned from the catalyst in a fluidized bed by contact with a free oxygen-containing gas before its return to the reaction zone. In cracking, coke yield may be held to a minimum through the use of good steam stripping and a high steam partial pressure and removal of coke from the catalyst is performed by regeneration. Regeneration of a catalyst to remove carbon is a relatively quick procedure in most commercial catalytic conversion operations. For example, in a typical fluidized cracking unit, a portion of catalyst is continually being removed from the reactor and sent to the regenerator for contact with air at about 950 to 1200° F., more usually about 1000 to 1150° F. Combustion of coke from the catalyst is rapid, and for reasons of economy only enough air is used to supply the needed oxygen. Average residence time for a portion of catalyst in the regenerator may be on the order of about six minutes and the oxygen content of the effluent gases from the regenerator is desirably less than about ½%. The regeneration of any particular quantum of catalyst is generally regulated to give a carbon content of less than about 1.0%, generally less than about 0.5%.

In a typical operation the catalytic cracking of the hydrocarbon feed would normally result in the conversion of about 40 to 70%, preferably about 50 to 60%, of the feedstock into a product boiling in the gasoline range. The effluent from the cracker, containing a minor amount, for instance, about 0.6 to 2 lbs./gal. of the cracking catalyst which was not removed by the cyclone separator in the reactor, may be conveniently distilled to remove materials boiling below the gasoline range; gasoline boiling in the range up to about 430° F., and cycle oil fractions boiling up to about 950° F. which may be recycled to the cracking reactor. The fractionator bottoms usually boiling primarily above about 750° F., comprise a heavy oil slurry stream containing entrained catalyst particles primarily of a size up to for instance about 80 microns, is removed and charged to the coking unit. The distillation is preferably carried out at near atmospheric pressure.

Coking processes of one type or another have been practiced in the petroleum refining art for many years. A primary objective in all these processes has been to convert as large a proportion as possible of the feedstock to the coker to lighter hydrocarbon fractions while keeping coke formations to a minimum. In the present invention fluidized coking apparatus is used, such as disclosed

in U.S. Patents 2,707,202, 2,366,055, 2,340,974, etc. These patents disclose continuous coking processes which are characterized by the formation of relatively small amounts of coke and improved yields of lighter hydrocarbon products. In the present case the fractionator bottoms containing the suspended catalyst is charged to the coking unit. The charge feed may be mixed with a dispersion medium such as steam or the latter may be separately applied to give a compact fluidized bed or dispersed fluidized system. The pressure to be employed in the coking zone is conventional and atmospheric, sub-atmospheric or superatmospheric pressures can be used. Preferably, however, the pressure is advantageously kept low ranging from atmospheric up to about 75 p.s.i.g. Temperatures prevailing in the coking zone should be sufficiently high to effect coking of the fractionator bottoms on the suspended catalyst particles before the bottoms feed comes in contact with the walls of the coker in order to prevent the coke from collecting along the walls and not on the catalyst particles. These temperatures will vary depending on the composition of the bottoms fraction as well as the physical conditions prevailing in the system, i.e. the diameter of the reaction zone, the size of the spray particles as they are fed into the coking unit, and other related factors. In general, the temperatures in the reactor should be sufficiently high to effect readily coking of the feed particles on the suspended catalyst particles, but not appreciably higher since the use of unduly high temperatures leads to an undesirable increase in thermal cracking of the hydrocarbon products recovered from the fractionator bottoms. The temperature in the coking unit will usually vary from about 800 to 1200° F., preferably from about 900 to 1000° F. The heat to the coke can be supplied by a coke burner which burns a portion of the coke to provide heat and/or catalyst from the regenerator standpipe.

The fractionator bottoms can be supplied to the coking zone at rates varying within a relatively wide range. The bottoms from the fractionator will generally supply essentially all of the feed to the coking unit, but if desired petroleum residua, as for instance, vacuum residua, atmospheric residua, tars, pitches, etc. boiling primarily above about 950° F. may be supplied to the coking unit from an outside source. Dispersion steam superheated to about the same temperature as maintained in the coking reactor can be used to improve distribution. The fluidizing steam flow will of course, depend on the coke particle size with higher steam velocities being avoided on account of economic reasons. Generally the steam flow may be in the range of about 20 to 100 lbs./bbl. of hydrocarbon feed with a preferred steam flow rate being about 30 to 45 lbs./bbl. of feed to yield coke laden catalyst particles having a size of about 20 to 80 or even 150 microns. The coke laden catalyst particles are removed from the bottom of the coker and transferred to the regeneration zone where these particles are subjected to regenerating conditions described above to supply heat to the cracking system. The catalyst particles after the coke has been removed can be recycled to the catalytic cracking zone for further use.

A portion of the coke laden catalyst can be withdrawn from the return line to the regenerator and sent to a burner where the coke is burned off and hot catalyst is added to the incoming fractionator bottoms feed to maintain a desired range of catalyst to oil ratio of 10:1 to 40:1 and provide the additional heat required for the process. Alternatively, if extra catalyst particles are needed in the coking reaction a slip stream of regenerated catalyst from the regenerator may be introduced to the feed line to the coker.

The overhead fraction from the coker is removed and may be treated with molecular hydrogen in the presence of a sulfur resistant hydrogenation catalyst prior to charging the overhead or a fraction thereof, to the catalytic cracking operation alone or in combination with other

feedstock constituents. Such catalysts usually have as an active component a so-called metal, for instance, selected from the group consisting of tin, vanadium, metals of Groups VB and VIB in the Periodic Table and metals of the iron group, frequently disposed as inorganic components, for instance, oxides, sulfides or other compounds, supported on a solid carrier exemplified by alumina, silica, etc. The amount of catalytically active metal in the supported catalysts is usually about 1 to 30 weight percent of the catalyst and preferably about 3 to 20 weight percent, with there being at least about 1%, preferably at least about 2%, of each catalytically active metal when combinations are used. The hydrotreating is conducted at a temperature of about 600 to 900° F., preferably about 650 to 750° F., pressures of about 300 to 3000 p.s.i.g., preferably about 500 to 2000 p.s.i.g.; weight hourly space velocities (WHSV) of about 0.1 to 10, preferably about 0.5 to 5; molecular hydrogen is provided in amounts of about 500 to 10,000, preferably about 1000 to 7500 standard cubic feet of hydrogen per barrel of oil.

By so treating, the hydrocarbon overhead fraction may be given an improved hydrogen-to-carbon ratio and the amount of contaminants, such as coke-formers, sulfur and nitrogen may be reduced. Alternatively, the coker overhead fraction may be fed directly to the catalytic cracking unit without pretreating and recovery of all the products may be made in the cracking units recovery system.

The present invention may be illustrated by reference to the accompanying schematic of the preferred embodiment of the present invention.

A typical Mid-Continent gas oil having an API gravity of about 27, a Conradson carbon of about 0.3 weight percent, a kinematic viscosity of about 5.5 centistokes at 210° F., and an initial boiling point above about 450° F. at atmospheric pressure is preheated to about 600 to 700° F. and introduced into catalytic cracking unit 2, via line 4, mixed with a finely divided cracking catalyst. The catalyst introduced into feed line 4 is a "Nalcat" synthetic gel cracking catalyst containing 25% Al_2O_3 , the balance silica, and having fluidizable particle size.

The reactor 2 is an elongated vessel having disposed in its lower portion, grid 6, for supporting the fluidized catalyst bed. The overhead from the catalytic reactor passes through the cyclone separator 8 with catalyst fines being returned to the fluidized bed by the cyclone dip leg 9. Coked catalyst particles from the reaction bed are removed via annulus 10 to line 12 to catalyst riser 14 and conveyed by the action of dry air entering line 14 at 16 to regenerator 18. In regenerator 18, the catalyst is decoked and then passed through standpipe 20 and recycled to the reaction zone 2, by feed line 4.

The cracking conditions in the reactor 2, comprise a temperature of about 915° F. and a pressure of about 10 p.s.i.g. The feedstock mixture is conveyed to the cracker at a weight hourly space velocity of about 3 and a catalyst to oil ratio of about 7. The catalyst is withdrawn via annulus 10, and lines 12 and 14 to regenerator 18 and is contacted with air at 1050° F. to burn off the carbon. The overhead from reaction vessel, 2, passes through cyclone separator 8 to line 22 and conveyed via line 24 to fractionating column 26. Pressures of about 10 to 80 p.s.i.g. are maintained in the fractionating column. Line 28 provides for the removal of fixed gases and gasoline, e.g. boiling up to about 430° F., for further processing for fuel recovery and separation. Line 30 provides for the removal of light cycle oils, e.g. boiling up to about 600 to 650 which may be used for fuel. Gas oil fractions of the catalytically cracked product, usually boiling up to about 850-950° F. may be removed from fractionator 26 through line 32 for fuel, thermal cracking, etc. or may be recycled to the catalytic cracking unit 2 by means not shown.

The heavy material boiling above about 750° F. and

containing the entrained catalyst particles is removed from the bottom of the fractionator tower 26 by line 34. The bottoms, from fractionation tower 26, containing the entrained cracking catalyst particle, represents the feed to coking reactor 36 and is charged through pump 38 and lines 40 and 42. Residual hydrocarbon oil may be added by line 41. The bottoms amounting to, for instance, about 3 to 15% by volume of the hydrocarbon cracked product may have an API gravity of up to about 25 and a Conradson carbon residue in the range of about 1.5-2.5% or more. The coking temperature is maintained in the reaction vessel at about 975° F. Dispersion steam, superheated up to about 1000° F. or more is introduced into the coker through line 43. As the coke particles on the entrained catalyst in the bottoms feed grow larger they are discharged through line 52 to line 14 where these coke laden catalyst particles are conveyed to regenerator 18 to remove the coke. A slip stream may be withdrawn from line 52 and passed to unit 46 via line 48 where the coke is burnt off and hot catalyst is added to the incoming fractionator bottoms feed to the coking unit. Unit 46 is a burner of any conventional type where coke is heated in combustion gases such as an oxygen-containing gas, to reaction temperatures of about 1200 to about 1500° F. Flue gases are removed and the coke free catalyst particles are added to the fractionator bottoms via line 44. The heating in unit 46 may take place by means of burning of the carbon or by means of hot flue gases or the combustion of combustible gases in the heater in the presence of the coke laden catalyst particles. The overhead from vessel 36 passes via lines 54, 55 and 56 to feed line 4 where it is carried into reactor 2. Alternatively the overhead fraction removed by line 54 may be passed by line 58 to hydrogen treater 60 in order to improve its hydrogen-to-carbon ratio. The treated overhead is then removed via line 62 and passed by line 56 to feed line 4.

An analysis of the yield from the process of the method of the present invention is as follows:

Table I

Coke	wt. percent	14.7
Gas (FOE) ¹	vol. percent	12.9
C ₃ + products:		
Propylene	vol. percent	3.0
Propane	vol. percent	2.0
Iso-butane	vol. percent	2.0
Butylene	vol. percent	5.5
n-Butane	vol. percent	1.7
Gasoline stocks	vol. percent	52.6
Distillate stocks	vol. percent	35.0

¹ Fuel oil equivalent.

It can be readily seen that by the method of the present invention the coke make is minimized, and the production of usable products is maximized from the fractionator bottoms material. The method of the present invention provides increased process heat by utilizing the heat contained in the recovered coke particle in the regeneration zone, and also for the recovery of catalyst lost from the reactor cyclone separator.

I claim:

1. A process for treating a hydrocarbon oil boiling above the gasoline range comprising contacting said hydrocarbon oil in a cracking zone with a cracking catalyst having a particle size of about 20 to 150 microns under fluidized cracking conditions, removing the cracking effluent containing a small amount of said cracking catalyst, fractionating the cracking effluent containing said effluent catalyst particles to recover gasoline and materials in the gas oil range, removing from the fractionator residual material higher boiling than said gas oil and containing said effluent cracking catalyst, conveying said residual and effluent catalyst to a coking zone where said material is subjected in a fluidized state to temperatures of about 800 to 1200° F. to coke said residual on said effluent catalyst particles, recovering an overhead product, removing coke from said coke-bearing catalyst by burning and passing resulting decoked catalyst particles to said cracking zone; said overhead product from the coking zone being passed to said cracking zone.

2. The method of claim 1 wherein said cracking catalyst is synthetic gel silica-alumina.

3. The method of claim 1 wherein the overhead product from the coking zone is contacted with a sulfur resistant hydrogenation catalyst in the presence of molecular hydrogen at a temperature of about 600 to 900° F. prior to charging to said cracking zone.

4. The method of claim 1 wherein a portion of the coked catalyst is burned and passed to the coking zone to provide heat.

5. The method of claim 3 wherein a portion of the coked catalyst is burned and passed to the coking zone to provide heat.

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