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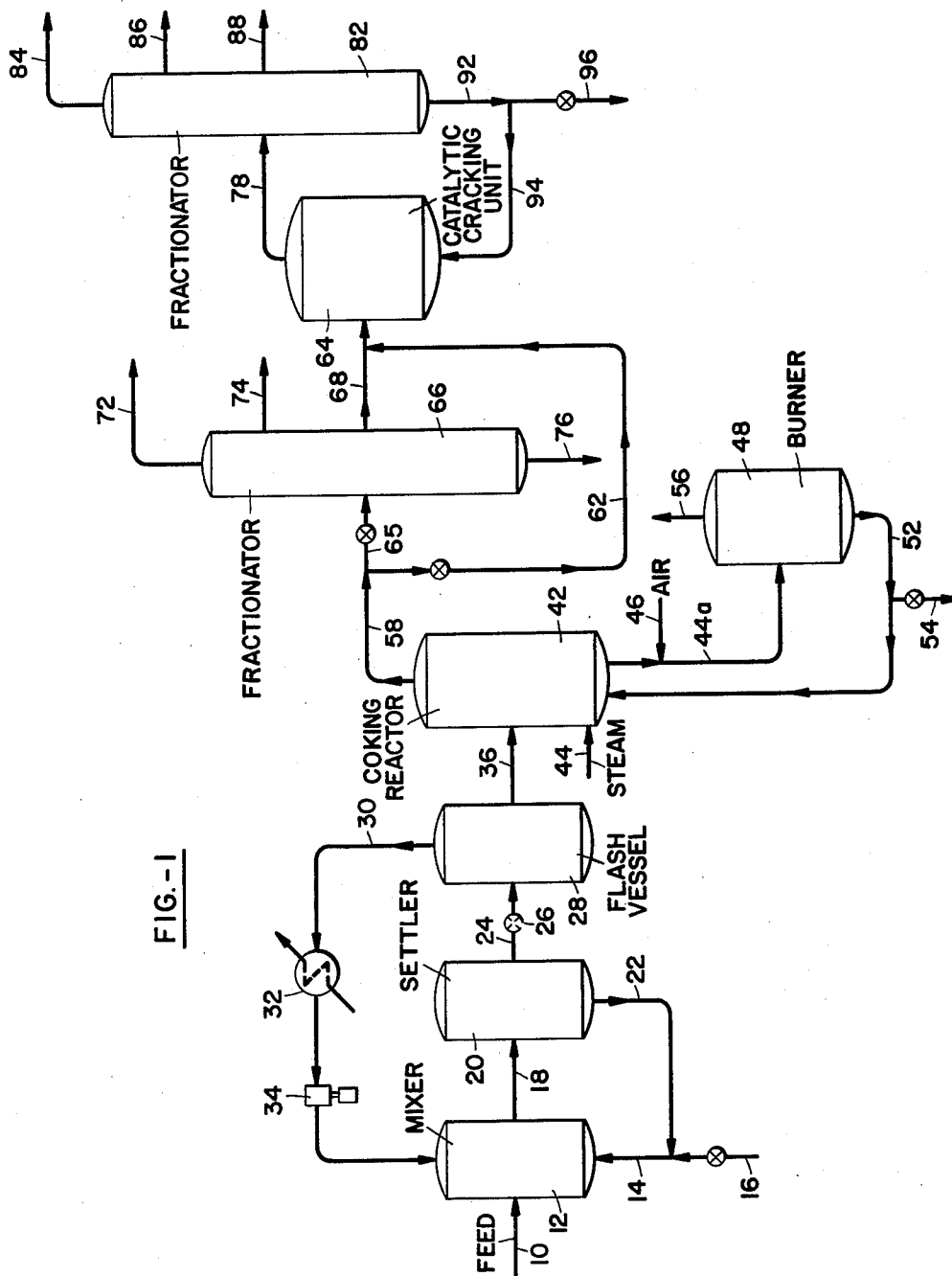
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3,061,539

HYDROGEN FLUORIDE TREATMENT OF COKING AND CRACKING FEED STOCK

Filed May 25, 1960

2 Sheets-Sheet 1



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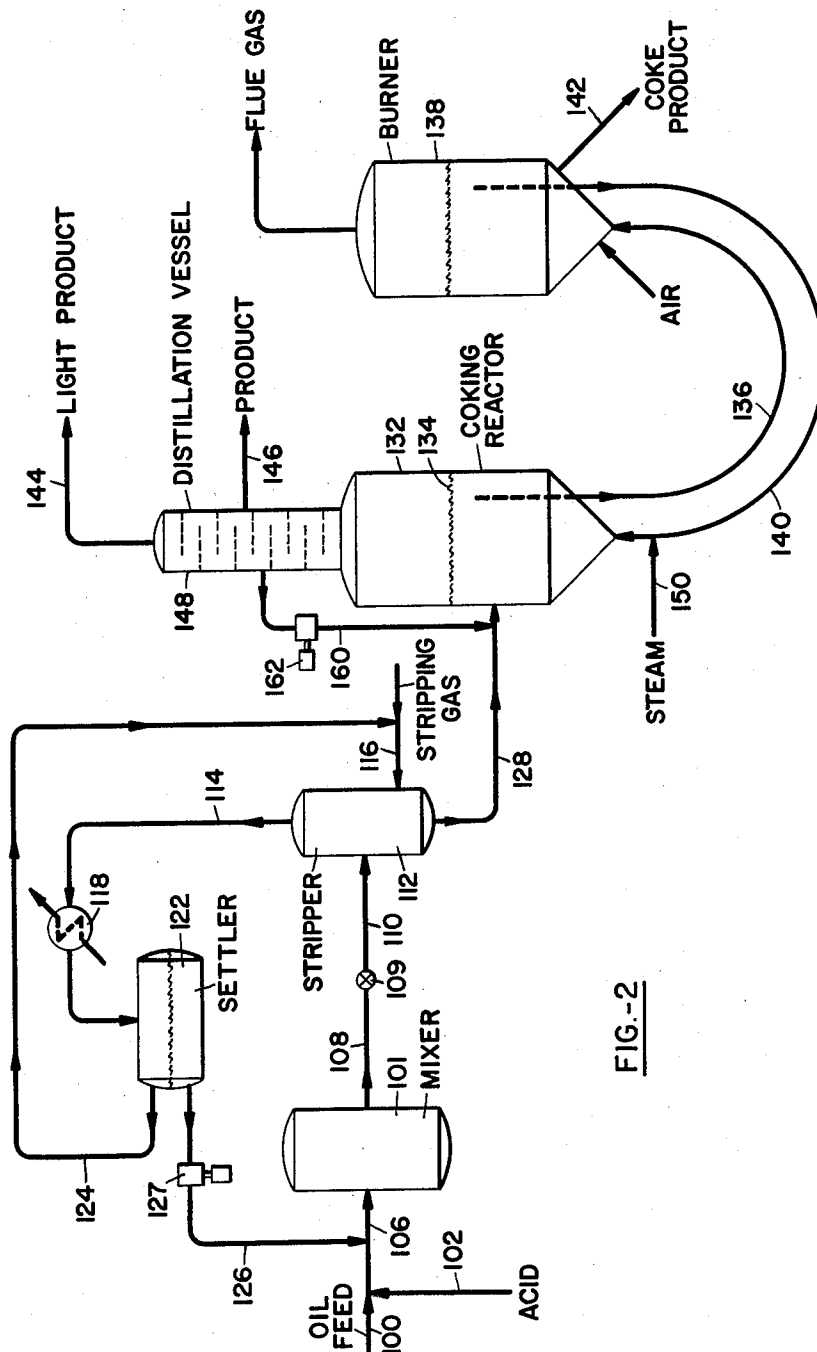


FIG.-2

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HYDROGEN FLUORIDE TREATMENT OF COKING AND CRACKING FEED STOCK

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This invention relates to the conversion of hydrocarbons and more particularly relates to the conversion of high boiling hydrocarbons to lower boiling hydrocarbons.

In the catalytic cracking of hydrocarbons it is known that metal contaminants such as compounds of iron, nickel, vanadium etc. in very small concentrations in the oil feed lead to poisoning or contamination of the cracking catalyst with a decrease in yield of desired products and an increase in gas and coke yields. This is true if the gas oil is derived by fractionation from a crude petroleum oil or if it is derived by coking a residual oil.

No satisfactory method has heretofore been disclosed for removing metallic contaminants from the oil cracking feed stock. The removal of contaminants is largely unaffected by conventional desalting techniques, solvent extraction, chemical treatments and other methods heretofore proposed.

According to the present invention coker oil feeds such as residual oils are treated with aqueous and/or anhydrous hydrofluoric acid or hydrogen fluoride and the so-treated residual oil is passed to a coking unit to obtain higher yields of low metals gas oils for use in catalytic cracking than would be obtained by coking alone without the hydrofluoric acid treatment.

Normally, catalytic cracking feedstocks are limited by two quality specifications: Conradson carbon and metals content. The Conradson carbon specification will vary from unit to unit, but because of carbon burning limitations a catalytic cracker can tolerate feeds only up to a certain maximum Conradson carbon. The limitation on metals, especially nickel, must be met for any catalytic cracking feedstock because metals contaminate the catalysts.

Coking operations, such as fluid coking, are used in refineries where it is desired to upgrade residual feedstocks of high Conradson carbon and/or metals content to provide feedstocks for catalytic cracking units. Fluid coking operations are normally conducted at about 950 to 980° F. The products are taken overhead as vapor and normally the heavy portion boiling above 1015° F. is recycled to extinction. The recycle cut points may be lower than 1015° F. if a gas oil of lower Conradson carbon is desired, but it cannot usually be extended above that temperature because volatile or vaporous metal compounds of the nickel and vanadium type will be carried over into the product. Thus the metals level in the gas oil sets the maximum for the coker recycle cut point.

As the recycle cut point in coking is lowered the product distribution deteriorates into higher gas and coke make and lower gas oil yields. Thus, where higher Conradson carbon in the gas oil can be tolerated (and this is often the case, because coker gas oils are usually low in Conradson carbon and because in most refinery situations coker gas oils are only incremental catalytic cracking feedstocks, so that the percentage contribution of the coker gas oil Conradson carbon to the total pool Conradson carbon is only small) it would be desirable to increase the recycle cut point to maximize the gas oil yield, or to operate the coker completely without recycle. This method of operation has the additional advantage that higher steam dilutions can be used in the reactor which

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has the effect of lowering the per-pass conversion and thus further increases the gas oil yield.

During treatment with hydrofluoric acid, the contaminating volatile metal compounds are selectively changed to a solid form. After this conversion, these metal compounds do not vaporize and do not come overhead with coker vapors but are deposited on the coke during the coking step. Because the coker vapors are substantially free of contaminating metals when using the present invention, the entire vaporous overhead from the coking reactor in one form of the invention may be passed directly to a catalytic cracking unit and in another form of the invention the coker vaporous overhead products may be first fractionated to separate a high boiling gas oil fraction which is then passed to a catalytic cracking unit.

With the present invention, coking is used to crack a hydrogen fluoride treated residual oil to produce a greater volume of gas oil suitable as catalytic cracking feedstock than is obtained only by coking without HF pretreatment and, if desired, the entire vaporous overhead cracked products from the coker reactor may be passed directly to a catalytic cracking unit without fractionation into several fractions. The application of this invention allows much greater flexibility in the operation of the coker, and in addition, the coker can be operated more cheaply. Operation with limited recycle or completely without recycle, as well as decreased per-pass conversion adds to the flexibility of the coker. Economic benefits are obtained from operating the coker at minimum or zero recycle because of lower investment and operating costs.

The hydrofluoric acid may be used repeatedly in the process since little or no acid is consumed by reaction with the oil.

The metals content of any distillate fraction will depend upon the type and concentration of contaminants in the crude oil from which the fraction was distilled, the boiling range of the fraction, and the amount of entrainment which took place during the distillation of the crude oil. Heavy gas oils in the range of 900° to 1200° F. distilled from typical crudes may contain from about 1 to about 20 pounds of metallic contaminants per 1000 barrels. Residual fractions (1000° F.+) and gas oils (900° F. to 1200° F.) derived from crudes which are particularly high in contaminants may contain as much as 200 pounds of metal per 1000 barrels.

The treating temperature, the volume of aqueous hydrofluoric acid employed and the intensity with which the oil and the acid are mixed in carrying out the process of the invention may be varied considerably. It is preferred to treat at temperatures between about 100° and about 450° F., although in some cases temperatures as high as 550° F. may be employed. The temperature employed depends, of course, upon other operating conditions. The volume of acid employed may range between about 0.01 and about 2 volumes, preferably 0.1 to 1.0 volume, per volume of oil treated.

In another form of the invention the residual oil feed is treated with anhydrous hydrogen fluoride at a temperature between about 250° F. and 400° F., preferably between about 300° F. and 350° F., then water washed to remove water soluble salts or compounds, filtered to remove any solids and the resulting oil then coked to produce an increased yield of demetalized coke. The treated oil before coking can be separated into an asphaltene fraction which is coked and a deasphalted oil which is a good catalytic cracking feedstock substantially free of catalyst contaminating metals.

In the drawing;

FIG. 1 diagrammatically represents one form of apparatus adapted to practice the present invention; and

FIG. 2 diagrammatically represents a modified form of apparatus for practicing the present invention.

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Referring now to FIG. 1 of the drawing, the reference character 19 designates a line through which the oil to be treated is passed into mixing vessel 12. The oil feed may be a residual petroleum oil or any other metal containing oil fraction from petroleum, shale, coal or other sources. The residual oil fraction usually boils above about 900° F. The mixing vessel 12 is provided with suitable means (not shown) for agitating or mixing the contents of the vessel and is provided with heating coils and jacketing or other means (not shown) for maintaining the desired temperature within the mixing vessel 12.

The preferred temperature in the mixing vessel is in the range between about 100° F. and 450° F. It is an important feature of the present invention that improved results are obtained at these lower temperature levels. Above about 550° F., depending on the concentration of the hydrofluoric acid, less satisfactory results are obtained because gas oil fractions normally recovered as catalytic cracking feeds may be converted to coke (or Conradson carbon material) due to the action of the acid at these temperatures.

Aqueous hydrofluoric acid in a concentration of about 50% by weight and higher, or anhydrous hydrofluoric acid, is introduced into the mixing vessel 12 through line 14 and is there mixed with the oil introduced through line 10. The aqueous hydrofluoric acid solution may be used in a concentration between about 50 and 100% by weight. The ratio of acid solution to oil, that is, the acid dosage is determined by the acid concentration, the temperature and the contact time and may be between about 1 and 200% by weight, preferably 10 to 100% by weight of the oil. The time of contact within the mixing vessel 12 may vary between about 2 and 120 minutes. The pressure in the mixing vessel 12 may be between about 100 and 1800 p.s.i.g. or at a pressure sufficient to maintain the hydrofluoric acid in liquid state.

After the oil and acid have been mixed the mixture is passed through line 18 to the settling vessel 20. The acid is withdrawn from the settling vessel 20 through line 22 and recycled through line 14 to the mixing vessel 12. With certain heavy oil feeds and certain acid concentrations, the acid phase may be lower in density than the oil phase and in this case will rise to the upper part of the settling vessel 20. The oil phase, which contains some residual acid and the metals as compounds dispersed as oil-insoluble solids, is passed through line 24 and pressure release valve 26 to flash vessel 28 where the acid vapors are flashed overhead and passed through line 30, condenser 32 and compressor 34 to the mixing vessel 12. The flash vessel 28 may be operated at any pressure below the operating pressure of settler 20 to obtain good HF separation by flashing.

The above oil phase, which contains the metal conversion products as an oil-insoluble solid dispersion, is withdrawn from flash vessel or tower 28 and passed through line 36 without filtration or any solids separation directly to at coking unit in which the reference character 42 designates a coking reactor. The coking unit is diagrammatically shown and preferably a fluid coking unit is used. In the case of a fluid coking reactor, the temperature in the coking reactor 42 is maintained between about 950° F. and 980° F. Superheated steam is introduced into the coking reactor 42 through line 44 in an amount between about 20 and 50 lbs. per barrel of oil feed.

Coke particles are withdrawn from the coking reactor 42 through line 44a and mixed with air introduced through line 45 and the resulting suspension is introduced into the burner or combustion vessel 48 where at least part of the coke is burned to raise the temperature of the coke particles to between about 100° F. and 250° F. higher than that in the coking reactor 42. The temperature during burning or combustion in the heater vessel 48 is between about 1000° F. and 1200° F. The pressure in the reactor 42 and heater vessel 48 is between about

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10 and 60 p.s.i.g. This invention should not be limited by these coker conditions, since for other coking units, such as delayed cokers, other operating conditions may be applicable.

Hot coke particles are withdrawn from the heater vessel 48 through line 52 and returned to the coking reactor 42 in an amount sufficient to maintain the desired temperature in the reactor 42. Part of the coke is withdrawn through line 54 as product coke from the process.

The particle size of the fluidized coke particles is between about 30 and 600 microns with most of the particles being of an average size between about 75 and 200 microns. Combustion gases pass overhead from the heater vessel 48 through line 56 and may be passed through heat exchangers or waste heat boilers to recover heat therefrom.

The vaporous products of coking are passed overhead from coker reactor 42 through line 58 and the total vaporous overhead product may be passed through line 62 to a catalytic cracking unit 64 diagrammatically shown in the drawing. Or the vaporous overhead products passing through line 58 may be passed through line 65 into fractionating tower 66 to separate coker vaporous products into desired fractions. One of these fractions is a gas oil fraction withdrawn through line 68 as a side stream and this gas oil fraction is passed to the catalytic cracking unit 64. A gaseous fraction is taken overhead through line 72 and a gasoline fraction is withdrawn as a side stream through line 74. The bottoms fraction is withdrawn through the bottom line 76 and may be recycled to the coking unit and coking reactor 42, or it may be combined with the gas oil fraction leaving through line 68 and used as incremental catalytic cracking feed, or it may be used as a fuel oil.

The catalytic cracking unit 64 is preferably of the fluidized catalytic cracking type but other catalytic cracking processes may be used. In the fluid cracking reactors the temperature is maintained between about 890° F. and 1000° F., the catalyst to oil ratio is between about 5 and 20 and the w./hr./w. in the cracking reactor is between about 5 and 12. The pressure in the cracking reactor is preferably atmospheric but may be as high as 75 lbs. p.s.i.g. The size of the catalyst particles is between about 20 and 150 microns with most of the particles being between a size of about 40 and 70 microns.

The regenerator which forms part of the cracking unit 64 but not shown in the drawing is maintained at a temperature between about 1000° F. and 1150° F. and a sufficient amount of the hot regenerated catalyst is recycled to the reactor to maintain the desired cracking temperature therein.

Cracked vapors pass overhead from the cracking unit 64 through line 78 and are passed into fractionator 82 wherein the cracked products are separated into a gaseous fraction which passes overhead from fractionator 82 through line 84, a gasoline fraction withdrawn through top withdrawal line 86, a gas oil or fuel oil fraction withdrawn through line 88 and a bottoms fraction withdrawn from the bottom of fractionator through line 92. The bottoms from the fractionator 82 may be at least in part recycled to the cracking unit 64 through line 94 and may be at least in part discarded from the system through line 96.

According to this invention, the coker gas oil final boiling point during fractionation in tower 66 can be increased substantially without carrying contaminating metal compounds into the gas oil fraction. One form of the present invention includes the combination of hydrofluoric acid treating of residual oil and coking of the treated oil. This combination of steps permits a higher end point cut for the gas oil fraction so that a higher yield of gas oil substantially free of the contaminating metals and lower coke and gas yields are obtained.

The following correlated data give a specific illustration of the advantages which may be gained by the present

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invention. The feed to the fluid coking unit is about 925° F.+ residium and the temperature of the coking operation is about 950° F. For the HF treatment about 1 weight of aqueous HF of 95% concentration per weight of residium is mixed with the residium feed at a temperature of about 250° F., a pressure of about 300 p.s.i.g. and a time of contact of about 60 minutes. In the table I p.p.m. means parts per million by weight.

TABLE I

	I Coking	II HF+Coking
Recycle Cut Point, ° F.	1,015	Once-through
Conversion, to 1,015° F.—Percent.....	100	60
Yields:		
C ₂ , wt. percent.....	9	4
C ₃ /430° F., vol. percent.....	20	13
430° F.—gas oil, vol. percent.....	55	74
Coke, Wt. Percent.....	24	14
Gas Oil Quality:		
Con. Carbon, Wt. Percent.....	3	5-8
Vanadium, p.p.m.....	2	2
Nickel, p.p.m.....	1	1

According to the data in Table I it will be seen that there is a 50% increase in gas oil yield for doubling the Conradson carbon content of the gas oil. The Conradson carbon can be controlled by the degree of conversion. The higher the conversion, the lower the Conradson carbon of the product. The data for this example in Table I, column II, represents the maximum gas oil yield advantage that can be obtained or gained, because no recycle at all was employed. Lower yields and lower Conradson carbon can be obtained by recycling any portion of the cracked feed or by increasing the once-through conversion.

The HF treating of coker feeds allows one-through operation which is impossible because of metals contamination in operation without HF treating. Under normal operations, one-through conversion is about 85 vol. percent to 1015° F.— at 10–15 wt. percent steam dilution on feed. With the metals contamination out of the way, the coker can be run at even lower conversions once-through by higher steam dilution. The bottoms in the once-through case are retained in the gas oil. This is the reason for the higher Conradson carbon. In the conventional coker operation these bottoms are cracked to extinction. The point is that even in mild, once-through coking of the present invention most of the carbon forming materials are deposited on the coke (feed Conradson carbon 22 wt. percent) but the severity is low enough so that the product is not nearly so much degraded to coke, gas and naphtha and fairly large quantities of 1015° F.+ material are retained in the gas oil. This is possible because the metals are left behind on the coke.

The following data show that the hydrofluoric acid treatment of residium converts the contaminating metal compounds to non-volatile metal solids so that the originally volatile contaminating metals do not vaporize and come overhead with the vaporous products from the coker. The data show that the HF treatment converts the contaminating volatile metal compounds in the residual oil into solids which subsequently are deposited on the coke particles during the coking operation.

Bachaquero reduced crude (400° F.+) was treated with 0.5 weight of 95 wt. percent HF per weight of residium at a temperature of 250° F., a pressure of 460 p.s.i.g. and a contact time of about 15 minutes. In order to show that certain metal compounds in a particular oil fraction were converted to a different form by the HF treatment, the untreated and treated oils were pentane precipitated. Pentane precipitation is only used as a means to separate low and high molecular weight fractions (less than and greater than 2000 mol. wt.). Metals data on the various fractions are given in Table II. These data show that the pentane soluble fraction or potential volatile fraction

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and the asphaltene fraction of the HF treated oil has been markedly reduced in metals with the subsequent production of approximately 1 wt. percent oil insoluble solids that are concentrated in metals. The untreated oil shows high metals for all fractions. In order to demonstrate what happens to metals in the coke producing portion of the feed, the asphaltenes (Conradson carbon material) from the above solvent precipitation were coked. Data for the various coker products are given in Table III. The gas oil fraction (650° F.+) obtained from the HF treated asphaltenes showed negligible metals while the gas oil from the untreated asphaltenes contained excessive quantity of metals contaminants. This latter gas oil fraction when combined with the metals contaminants present in the volatile portion of the untreated feed is considered unsatisfactory for incremental catalytic cracking feed.

TABLE II

	Pentane Deashing of Coker Feed (3/1 Sol- vent/Oil)	
	Treated Oil	Untreated Oil
Pentane Soluble Fraction, Wt. Percent.....	83	85
Metals Analysis:		
V, p.p.m.....	<5	180
Ni, p.p.m.....	12	25
Asphaltene Fraction, Wt. Percent.....	16	15
V, p.p.m.....	232	2,400
Ni, p.p.m.....	198	265
Solids, Wt. Percent:	1	0
V, wt. percent.....	7.0	
Ni, wt. percent.....	2.4	

TABLE III

	Coking of Asphaltenes +Solids from HF Treat	Coking of Asphaltenes from Un- treated Oil
Coke Yield, wt. percent.....	50-55	45-50
Inspection of Coke:		
V, wt. percent.....	0.43	.245
Ni, wt. percent.....	0.16	.035
Sulfur, wt. percent.....	3.3	3.3
Na, wt. percent.....	1.9	1.9
C, wt. percent.....	90.1	90
H, wt. percent.....	4.9	5
Oil and Gas Yield, wt. percent.....	45-50	50-55
Inspections of Gas Oil Fraction:		
V, p.p.m.....	<10	216
Ni, p.p.m.....	<10	28

According to one form of the present invention a residual oil feed containing between about 100 and 600 p.p.m. of V and between about 20 and 100 p.p.m. of Ni are treated with aqueous hydrofluoric acid as above described and the so treated residual oil is passed directly to a fluid coking unit without the necessity of an intermediate filtering or similar step. The hydrofluoric acid treatment converts the contaminating vaporous nickel and vanadium compounds to a substantially non-volatile form which will deposit on the coke particles to give overhead coker products having substantially no contaminating metal compounds therein. The solid metals are withdrawn with the excess coke from the coker. In this way, higher gas oil yields from a coker operation may be realized because the gas oil fraction or cut may have a higher boiling point than when no treatment with hydrofluoric acid is used without the danger of contaminating metals carryover.

The coker overhead products in line 58 may be passed directly to catalytic cracking unit 64 without substantially cooling of the overhead products to effect a heat economy and also to avoid any side reactions or polymerization etc. of the cracked coker vapors before they contact the catalyst in the catalytic cracking unit 64. Or the coker overhead products may be fractionated to

separate a gas oil fraction which is withdrawn through line 68 for passage to the catalytic cracking unit 64 and in this case there will be a smaller volume of gas and vapors passing through the cracking unit 64. With the present invention a higher yield of gas oil is obtained for catalytic cracking and the gas oil is substantially free from contaminating metal compounds containing nickel, vanadium or the like.

Referring now to FIG. 2 wherein the conditions of treatment are substantially the same as in FIG. 1 unless otherwise indicated, the reference character 100 designates a line passing reduced crude or a residual oil to mixer vessel 101. The oil stream is mixed with fresh hydrofluoric acid entering through line 102 and the mixed oil and acid enter the mixing zone 101 through line 106. The mixer vessel 101 is maintained under superatmospheric pressure. The treated oil is removed with the acid from the mixer 101 through line 108 containing a pressure reducing valve 109 whereby the pressure on the mixture is reduced. The mixture under reduced pressure is passed through line 110 to the hydrogen fluoride stripping vessel 112 which is operated to remove hydrogen fluoride as a vapor overhead through line 114. Light naphtha such as pentane, hexane or benzene of 1 to 10% concentration is introduced into the lower portion of the stripper 112 through line 116 to aid in the removal of hydrogen fluoride from the oil.

Some of the hydrocarbon oil and naphtha pass overhead with the hydrogen fluoride through line 114 and this mixture is passed through the condenser 118 to cool and condense the products and cooled mixture is passed to settler vessel 122 where the acid and the naphtha or other hydrocarbons are allowed to separate into two layers. The upper layer comprising naphtha is removed from the settler vessel 122 through line 124 and recycled to line 116. The lower layer containing hydrogen fluoride is returned to line 106 through line 126 by compressor 127. The treated oil now freed of volatile metal compounds but containing metal solids is removed from the bottom of the stripping vessel 112 through line 128 and is processed in a coking unit which is shown as a fluid coker.

The coking reactor 132 is operated at a temperature between about 950° and 1050° F. The coker vessel contains a fluidized bed 134 of fluid coke which is continuously circulated through line 136 to the bottom of the burner vessel 138 for heat balance and returned hot to the reactor 132 through line 140 which introduces the coke into bottom portion of the reactor 132. Excess coke make is withdrawn as product through line 142 from the burner 138.

The overhead coker products are withdrawn through lines 144 and 146 and may be cut in the overhead distillation tower 148 to any fraction desired. Steam is preferably added to the bottom of the reactor 132 through line 150 to provide fluidization gas in the bottom of the reactor. The amount of steam may vary from about 10 to 100% weight on the oil feed. The amount of steam used determines largely the severity of operation, that is, the conversion of the oil feed. The reason for this is that steam dilutes the hydrocarbons and thus reduces the oil feed partial pressure. In once-through operation, 10% steam addition usually results in 90% conversion or better, whereas 50% steam gives only about 60% conversion.

Any desired fraction of the product in the distillation or fractionation tower 148 may be recycled through line 160 by pump 162 to line 128 for recycle to the coker reactor 132 to be coked to extinction. The recycle stream is taken off the tower 148 through line 160 and below the level of product withdrawal through line 146. When coking to extinction, the coke make is raised and the final boiling point of the product is decreased.

The total coker overhead or the product in line 146 may be processed as in FIG. 1, that is, it may be passed directly to a catalytic cracking reactor (not shown in

FIG. 2) like that shown in FIG. 1 or the product from the coker can be fractionated to give a substantially metal free gas oil which is sent to the catalytic cracking step.

Example 1

In a specific example a West Texas vacuum residuum having an initial boiling point of about 1050 F., an API gravity of about 11° and a Conradson carbon of 20 wt. percent, is contacted with an equal weight of 95% by weight of aqueous hydrofluoric acid at 400° F. for one hour at a pressure of about 1000 p.s.i.g. and containing 39 p.p.m. of vanadium and 25 p.p.m. of nickel in a mixing vessel like vessel 12. The entire mixture is passed to a settling vessel like vessel 20 to separate a liquid oil phase from an aqueous acid phase. The acid aqueous phase is withdrawn from the bottom of the settling vessel 20 for recycle to the mixing vessel 12. The oil layer which contains HF treated material in suspension or solution which does not settle out, is sent without filtration or any separation or treating step directly to a coking unit like fluid coking unit 42. The pressure in settling zone 20 is reduced to about 100 p.s.i.g.

The coking step is maintained at a temperature of about 950° F. at substantially atmospheric pressure. The vapor holding time in the coking vessel is 15 seconds. The products of coking are fractionated to separate a gas oil fraction having an end point of about 1300° F. and a Conradson carbon content of 5-8 wt. percent. The gas oil contains less than 0.1 p.p.m. of nickel and less than 0.1 p.p.m. of vanadium. Compared to gas oil obtained from coking the same residuum without the hydrofluoric acid pretreatment and fractionated to an end point of about 1015° F. and a Conradson carbon content of 2 wt. percent, the gas oil from the present process invention is obtained in a 22.5% by volume greater yield than the gas oil from conventional coking. The gas oil from conventional coking contains 0.2 p.p.m. of vanadium and 0.1 p.p.m. of nickel.

Example 2

In another form of the invention, the process is modified to separate metal contaminants from the oil feed so as to provide a stock which on coking will produce a demetalized gas oil feed or a wide cut oil suitable for use in catalytic cracking and also a substantially metal free coke which is useful in the manufacture of electrodes for aluminum manufacture. There is considerable interest in low metals coke for use in electrode manufacture for the aluminum industry.

In this form of the invention residuum or residual oil suitable for use in a thermal cracking or coking process, but containing excessive metal compounds such as vanadium and nickel compounds which degrade the final coke product, is first demetalized by treating with anhydrous hydrogen fluoride at a temperature between about 250° F. and 400° F. under superatmospheric pressure between about 200 and 1000 p.s.i.g. About 0.1 to 2 parts by weight of hydrogen fluoride to 1 part by weight of oil may be used. The hydrogen fluoride is stripped from the treated residual oil by a stripping gas such as a light naphtha, hexane, etc.

The treated residual oil is then thoroughly water washed to remove water soluble metal compounds formed by the hydrofluoric acid treatment. The washed residual oil is then filtered to remove any solid articles such as coke particles that contain contaminating metal compounds.

The demetalized residual oil now contains two to three times the amount of asphaltene fraction present in the untreated residual oil feed and in this way an increase in coke make is made possible. The coke may be produced by a fluid or delayed or any conventional coking process. The demetalized treated residual oil may be separated into an asphaltene fraction and deasphalted oil by conventional precipitation steps prior to the coking

step and the deasphalted residual oil can be used in catalytic cracking or as a low metals fuel oil.

In a specific example a residual oil such as one having an initial boiling point of about 400° F., an API gravity of about 14.5° and a Conradson carbon of about 10.7 wt. percent is mixed with 1 part by weight of anhydrous hydrofluoric acid per part by weight of residual oil at 300° F. at a pressure of about 800 p.s.i.g. in a mixing vessel for about 60 minutes.

The hydrofluoric acid is then stripped from the residual by treatment with a stripping gas such as a light naphtha. Other stripping gases such as pentane, hexane, benzene, etc. may be used. The stripped residual oil is then thoroughly water washed with tap water to remove water soluble metal compounds formed as a result of the hydrofluoric acid treatment. About 3 parts by weight of water to one part by weight of treated oil is used. Following the water washing step, the treated oil is filtered by passing through a 200 mesh filter to remove any solids and coke particles which contain the objectionable metal compounds. The residual oil contains about 18 p.p.m. of vanadium and about 22 p.p.m. of nickel.

The filtered residual oil now contains about three times the amount of the asphaltene fraction present in the untreated residual oil. The filtered oil is then coked in the same way as done in Example 1 to obtain a gas oil fraction boiling up to about 1015° F. and having a Conradson carbon of about 1 to 2 wt. percent. The gas oil contains less than about 1 p.p.m. of vanadium and less than about 1 p.p.m. of nickel. The coke yield is about 30% of residual oil feed and the coke contains about 60 p.p.m. of vanadium and 70 p.p.m. of nickel. The coke yield is greater than that obtained in conventional fluid coking by about 300% by weight. Cokes and/or oils containing less vanadium and nickel can be obtained by the same procedure from feedstocks which have lower concentrations of the same metals.

In a further modification the treated residual oil may be treated at a temperature of about 170° F. with a precipitating agent such as propane using about 4 parts by weight of propane to one part by weight of the treated demetalized residual oil. The pressure is about 450 p.s.i.g. The demetalized asphaltene fraction is separated prior to the coking step. After coking this asphaltene fraction, the resulting coke has a vanadium content of about 60 p.p.m. and a nickel content of about 70 p.p.m. The deasphalted oil is suitable as a catalytic cracking feedstock. Instead of propane other precipitating agents such as butane, pentane, hexane, heptane or mixtures thereof may be used. The temperature of the precipitating treatment may vary between about 100° F. and 300° F. The pressure for the precipitating treatment may be between about 100 p.s.i.g. and 500 p.s.i.g.

What is claimed is:

1. A process for converting high boiling hydrocarbons containing cracking catalyst contaminating materials which comprises treating in a contacting zone such a high boiling hydrocarbon fraction with hydrogen fluoride at an elevated temperature, separating an oil phase substantially free of hydrogen fluoride, passing said oil phase directly without filtration to a coking zone to crack said treated hydrocarbon fraction to vaporous reaction products and coke, and recovering a gas oil fraction from said vaporous reaction products in increased yield and substantially free of catalyst contaminating metals.

2. A process according to claim 1 wherein said hydrofluoric acid is in an aqueous solution.

3. A process according to claim 1 wherein said hydrofluoric acid is in anhydrous form.

4. A process according to claim 1 wherein said coking process is a fluid coking process.

5. A process for converting high boiling hydrocarbons which cannot be distilled under normal temperature and pressure conditions without cracking and which contain

catalyst contaminating materials which comprises treating in a contacting zone such a high boiling hydrocarbon fraction with an aqueous hydrofluoric acid solution at an elevated temperature, separating an oil phase from an aqueous phase, passing said oil phase directly without filtration to a fluid coking zone to crack said treated hydrocarbon fraction to vaporous reaction products and coke, passing said vaporous reaction products with a reduced amount of catalyst contaminating metals directly to a catalytic cracking zone and recovering desired products from the resulting catalytically cracked products.

6. A process for converting high boiling hydrocarbons which cannot be distilled under normal temperature and pressure conditions without cracking and which contain catalyst contaminating materials which comprises treating in a contacting zone such a high boiling hydrocarbon fraction with an aqueous hydrofluoric acid solution at an elevated temperature, separating an oil phase from an aqueous phase, passing said oil phase directly without filtration to a fluid coking zone to crack said treated hydrocarbon fraction to vaporous reaction products and coke, passing said vaporous reaction products to a fractionating zone to separate and recover a gas oil fraction substantially free of catalyst contaminating materials, passing said recovered gas oil fraction to a catalytic cracking unit, and recovering desired products from the catalytically cracked products.

7. A process for converting high boiling hydrocarbons which cannot be distilled under normal temperature and pressure conditions without cracking and which contain catalyst contaminating materials which comprises treating in a contacting zone such a high boiling hydrocarbon fraction with an aqueous hydrofluoric acid solution of a concentration greater than about 50% by weight of HF at a temperature between about 100° F. and 700° F. and using about 0.1 to 2 weights of the hydrofluoric acid solution per weight of the hydrocarbon fraction to be treated, maintaining the contacting time in said contacting zone between about 2 and 120 minutes and the pressure between about 100 and 1800 p.s.i.g., or at a pressure sufficient to maintain the hydrofluoric acid in the liquid phase, separating an oil phase from an acid phase, passing said oil phase, freed of HF without any solids separation step to a coking zone containing a bed of coke particles to crack said treated hydrocarbon fraction to vaporous reaction products with a reduced amount of catalyst contaminating metals, and coke which contains the catalyst contaminating material deposited on the coke particles of said bed, and recovering a gas oil fraction from said vaporous cracked products containing less than 1 p.p.m. of vanadium or nickel contaminating materials.

8. A process according to claim 7 wherein the concentration of the aqueous hydrofluoric acid is between about 95% and 100% by weight, the temperature in said contacting zone is between about 100° F. and 300° F., the weight ratio of aqueous hydrofluoric acid to oil feed is between about 0.12 and 3.5 and the time of contacting is between about 2.0 and 13 minutes.

9. A process for converting high boiling hydrocarbons which contain cracking catalyst contaminating materials which comprises treating in a contacting zone such a high boiling hydrocarbon fraction with anhydrous hydrogen fluoride at an elevated temperature and pressure, stripping hydrogen fluoride from said treated hydrocarbon fraction, water washing the treated and stripped hydrocarbon fraction to remove water soluble metal compounds, then filtering the treated and washed hydrocarbon fraction to remove solids, then coking the treated hydrocarbon fraction to obtain coke having less than about 60 p.p.m. of vanadium and 70 p.p.m. of nickel depending on the feedstock and a gas oil suitable for use as a catalytic cracking feedstock and containing less than about 0.5 p.p.m. of vanadium and 0.2 p.p.m. of nickel.

10. A process according to claim 9 wherein the treated and washed hydrocarbon fraction is treated with a low

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boiling paraffin hydrocarbon to separate an asphaltene fraction from a deasphalted oil and coking said asphaltene fraction to obtain a low metals coke.

11. A process according to claim 9 wherein the treatment with anhydrous hydrogen fluoride is at a temperature between about 250° F. and 450° F.

12. A process for converting high boiling hydrocarbons which cannot be distilled under normal temperature and pressure conditions without cracking and which contain catalyst contaminating materials which comprises treating in a contacting zone such a high boiling hydrocarbon fraction with an aqueous hydrofluoric acid solution of a concentration greater than about 50% by weight of HF at a temperature between about 100° F. and 700° F. and using about 0.1 to 2 weights of the hydrofluoric acid solution per weight of the hydrocarbon fraction to be treated, maintaining the contacting time in said contacting zone between about 2 and 120 minutes and the pressure sufficient to maintain the hydrofluoric acid in

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the liquid phase, separating an oil phase from an acid phase, passing said oil phase, freed of HF without any solids separation step to a coking zone containing a bed of coke particles to crack said treated hydrocarbon fraction to vaporous reaction products with a reduced amount of catalyst contaminating metals, and coke which contains the catalyst contaminating material deposited on the coke particles of said bed, passing the total overhead vaporous reaction products without substantial cooling to a catalytic cracking zone and recovering desired products from said catalytically cracked products.

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