

[54] **HF EXTRACTION AND ASPHALTENE CRACKING PROCESS**

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[22] Filed: **Dec. 18, 1970**

[21] Appl. No.: **99,386**

[52] U.S. Cl. **208/87, 208/90, 208/115, 208/311**

[51] Int. Cl. **C10g 17/04, C10g 11/0**

[58] Field of Search **208/87, 90, 115, 280**

[56] **References Cited**

UNITED STATES PATENTS

2,495,133 1/1950 Ridgway208/115

2,592,740 4/1952 Ridgway208/115
2,926,129 2/1960 Kimberlin et al.208/87
3,061,539 10/1962 Moritz et al.208/90

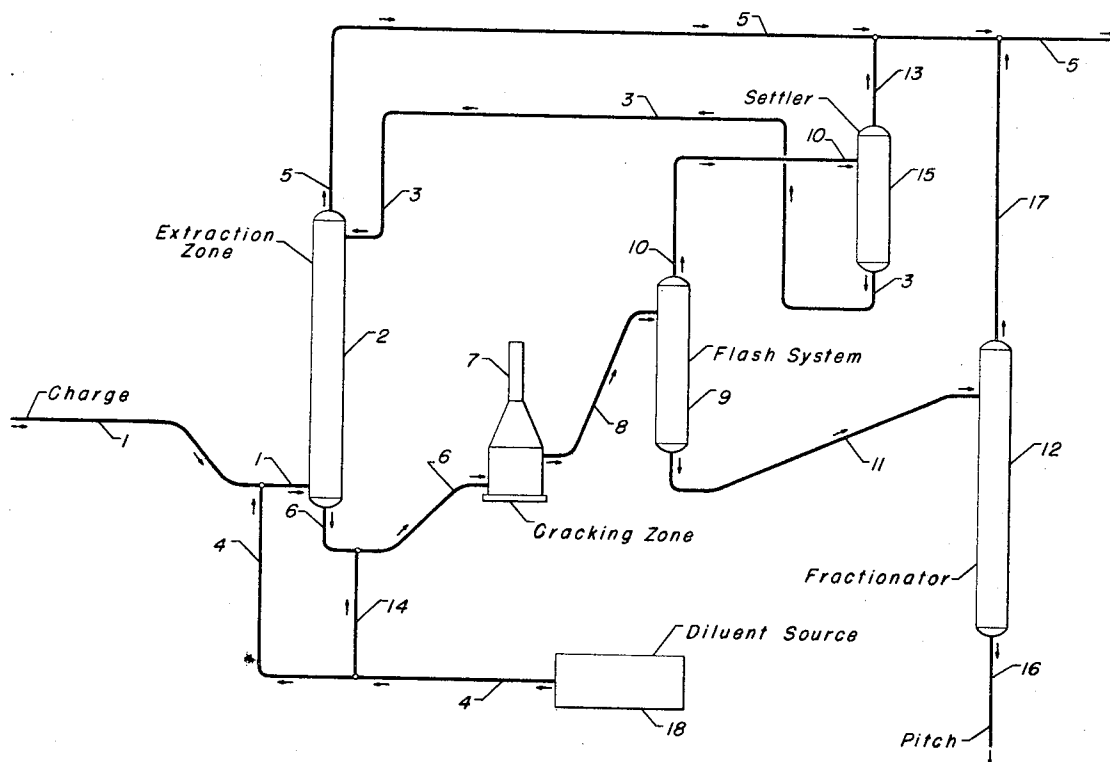
Primary Examiner—Herbert Levine

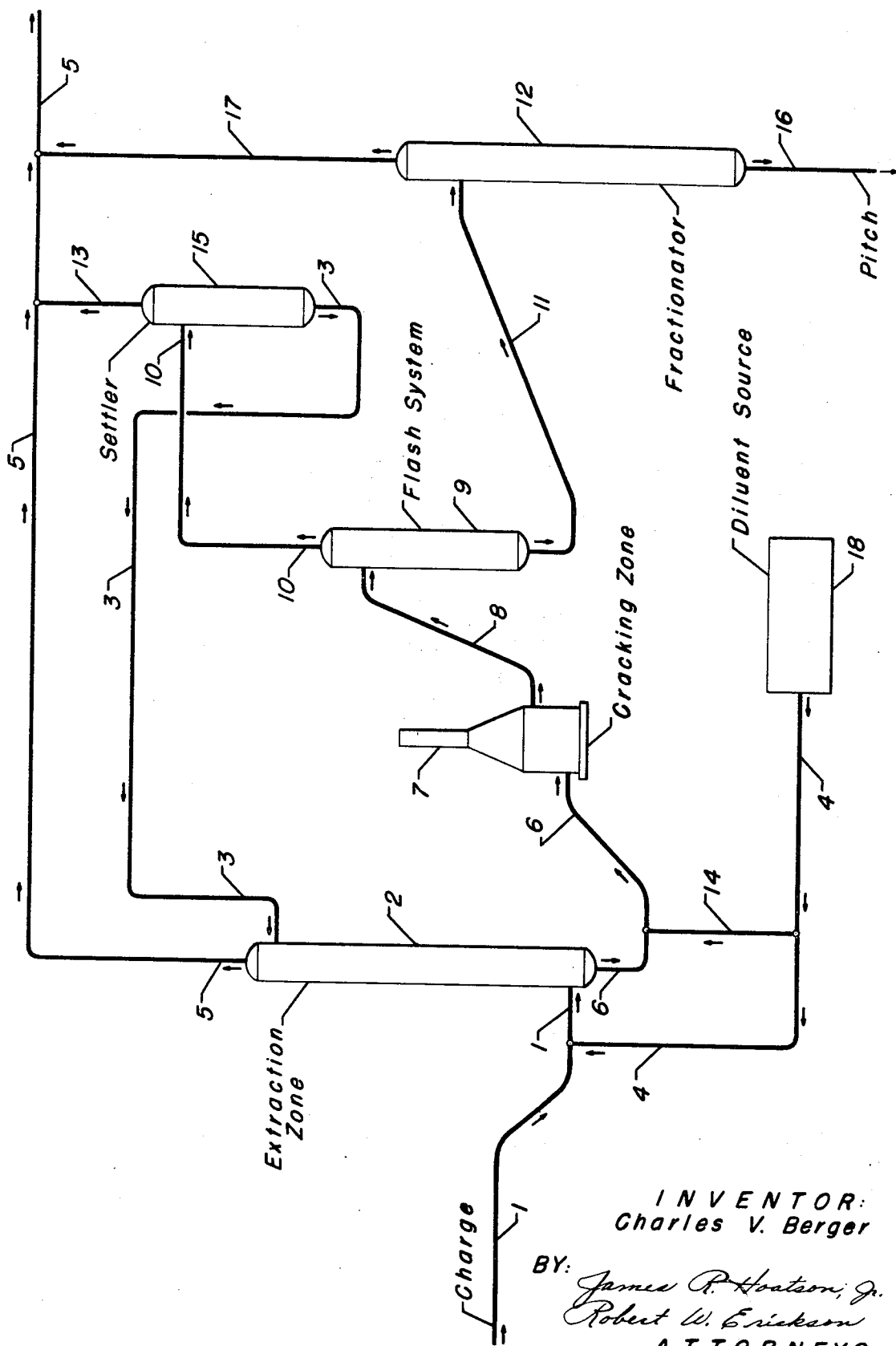
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[57] **ABSTRACT**

A hydrocarbonaceous black oil is subjected to HF extraction for the separation of hetero compounds and highly condensed aromatics from a less soluble raffinate. The extract phase, after separation of the raffinate, but containing HF, is subjected to cracking conditions, and preferably in the presence of a hydrogen donor. The effluent is separated to recover the HF which is recycled to the extraction zone.

6 Claims, 1 Drawing Figure





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HF EXTRACTION AND ASPHALTENE CRACKING PROCESS

APPLICABILITY OF INVENTION

The present invention is applicable as a combination process for the conversion of hydrocarbonaceous black oils. Certain selective fractions (distillates) of full boiling range crude oils, particularly the heavy oils extracted from tar sands and coal oils, as well as atmospheric and vacuum tower bottoms products, etc., are commonly referred to as "black oils," and contain large concentrations of relatively high molecular weight sulfurous and nitrogenous compounds. In addition, these hydrocarbonaceous mixtures contain organo-metallic complexes, principally comprising nickel and vanadium, and asphaltenic compounds, the latter generally found to be complexed with sulfur. An abundant supply of such material currently exists, and virtually demands conversion to the greatest possible extent—to minimum pitch or bottoms—for the purpose of satisfying the ever-increasing need for greater quantities of lower boiling products.

In general, black oils are categorized as heavy hydrocarbonaceous mixtures of which at least about 10.0 percent by volume, and often more, boils above a temperature of about 1,050° F. Exemplary of those black oil charge stocks, to the conversion of which the present invention is adaptable, are a vacuum tower bottoms product having a gravity of 7.1° API, and containing 23.7 percent by weight of asphaltics, and 4.1 percent by weight of sulfur; a topped Middle-East Kuwait crude oil having a gravity of 11.0° API, and containing 10.1 percent by weight of asphaltics and 5.2 percent by weight of sulfur; and a vacuum residuum containing about 3.0 percent by weight of sulfur and more than 4,000 ppm. by weight of nitrogen, and having a 20.0 percent volumetric distillation temperature of about 1,055° F. principal difficulties accompanying the conversion of such hydrocarbonaceous black oils stems from the fact that the highest boiling components thereof are generally the most contaminated from the point of hetero molecules and are, therefore, the most difficult to process. Catalytic processes, for converting these materials to more volatile and more useful products, suffer from metallic and/or carbonaceous contamination of the catalytic composite, the consequence of which is frequent regeneration and a high catalyst replacement rate.

In essence, the present invention involves an integrated combination process for converting asphaltene-containing hydrocarbonaceous black oils. The black oil is initially subjected to HF extraction, conducted under conditions of temperature and pressure which permits the extraction of the contaminated feed, but does not produce excessive cracking of the charge stock. The extract phase, containing the HF, is removed from the extraction zone, separately from the raffinate phase, and, without further intermediate separation, subjected to cracking conditions including an increased temperature.

In both the extraction and the cracking step, the presence of a light hydrocarbon component is highly desirable. This component ideally serves to aid in the separation of the phases as a result of density exaggeration, and to surrender a limited amount of hydrogen to the heavy black oil components, thus furthering conversion. Low molecular weight isoparaffins such as isobutane and isopentane are particularly useful for this purpose. In another embodiment, the cracking of the extract phase is effected in a hydrogen atmosphere. This accomplishes the conversion of carbon- and metal-rich high boilers into hydrogen-rich, more volatile fragments. The acid is recovered from the cracked products, and recycled to the extraction zone wherein it countercurrently contacts additional charge stock.

OBJECTS AND EMBODIMENTS

A principal object of the present invention is to provide a combination process for the conversion of asphaltene-containing hydrocarbonaceous black oils. A corollary objective

resides in the conversion of non-distillable high boilers including asphaltenes and high molecular weight sulfurous and nitrogenous compounds.

Another object of my invention is to eliminate the difficulties encountered in the fixed-bed catalytic processing of black oil charge stocks.

Therefore, in a broad embodiment, my invention provides a process for the conversion of an asphaltene-containing hydrocarbonaceous charge stock, which process comprises the steps of: (a) treating said charge stock with hydrogen fluoride in a contacting zone, at conditions of temperature and pressure selected to produce a raffinate phase and an HF extract phase containing asphaltenes; (b) increasing the temperature of said extract phase to a level at which the cracking of hydrocarbons is effected; (c) separating the resulting cracked effluent to provide (i) a volatile hydrocarbon phase, (ii) an asphaltic pitch and, (iii) hydrogen fluoride; and, (d) recycling at least a portion of said hydrogen fluoride to said contacting zone and recovering said raffinate phase and said volatile hydrocarbon phase as the product of the process.

In a preferred embodiment, the extraction and the cracking steps are conducted in the presence of a light hydrocarbon fraction comprising isobutane and/or isopentane. Other embodiments of my invention are directed toward preferred processing techniques and operating conditions, and will become evident from the following, more detailed description.

PRIOR ART

Convention compels recognition of the fact that both hydrogen fluoride extraction and hydrogen fluoride cracking of hydrocarbonaceous material are well known in the art pertaining to petroleum processing and refining techniques. For example, U.S. Pat. No. 2,546,916 is typical of the technology involved with a process for the hydrogen fluoride extraction of a hydrocarbon charge stock. In this instance, sludge-like material is removed from lubricating oil fractions in order to effect the refining thereof. The alleged improvement resides in the elimination of a two-step procedure involving propane deasphalting and sulfuric acid treatment. A combination process is disclosed in U.S. Pat. No. 3,061,539, wherein a feedstock is subjected to treatment with hydrogen fluoride prior to introduction into a coking zone which prepares a purified gas oil fraction suitable as the feed to a catalytic cracking unit. Contrary to the present combination process, however, the disclosed combination utilizes intermediate separation consisting of a settler and flash vessel in order to insure that the charge to the coking reactor is free from hydrogen fluoride.

The utilization of hydrogen fluoride as a cracking catalyst is also described in the prior art. For example, U.S. Pat. No. 2,454,615 discloses the use of an anhydrous liquid hydrofluoric acid for the cracking of gas oils having a boiling range of about 350° F. to about 650° F. A result of processing the gas oils, in accordance with the techniques disclosed, is the production of significant quantities of asphalt, tar or other heavy, high boiling conversion products. There is, therefore, no recognition that hydrofluoric acid can be utilized for the cracking of asphaltenes and other non-distillables. Similarly, U.S. Pat. No. 2,495,133 discloses the cracking of gas oil boiling range mixtures, while being specifically directed toward a method for separating and recovering the hydrogen fluoride for recycle to the conversion zone.

As hereinabove stated, it must be recognized that HF extraction and HF cracking techniques are known in the prior art pertaining to petroleum refining processes and techniques. Significantly, however, none of the foregoing specifically discloses the combination process of the present invention wherein the hydrogen fluoride employed in the extraction zone is utilized to crack asphaltenes and other non-distillables with which it is admixed upon emanating from the extraction zone.

SUMMARY OF INVENTION

A preferred method for treating the asphaltene-containing hydrocarbonaceous black oils with hydrogen fluoride utilizes a countercurrent extraction zone with the charge stock passing therethrough in upward flow. As previously noted, a particularly preferred mode of operation involves the use of a light hydrocarbon added to the black oil to aid in separation efficiency. The descending hydrogen fluoride effectively extracts the non-distillables from the charge, thereby forming an extract phase which is removed from a lower portion of the extraction zone. Extraction conditions include a temperature in the range of about 100° F. to about 250° F., and a pressure sufficient to maintain a liquid phase. The conditions of temperature and pressure are, however, selected to produce an operating severity level below that at which the cracking of hydrocarbons will be effected. The relative rates of addition of the black oil charge stock and hydrogen fluoride to the extraction zone lies in the range of about 0.2 to about 5.0. Although anhydrous hydrogen fluoride is preferred, aqueous hydrogen fluoride having a maximum water content of 2.0 percent by weight may be utilized. In addition to avoiding an operating severity which fosters the cracking of hydrocarbons, conditions are selected to maintain the hydrogen fluoride in liquid phase. The addition of light hydrocarbons, such as isobutane, is generally in the range of from 0.1 to about 2.0 by weight, based upon the quantity of black oil charge.

The hydrogen fluoride phase, containing extracted asphaltenes and other polar molecules, is introduced, in admixture with a light paraffinic diluent, into a cracking zone, wherein cracking reactions are effected at a temperature in the range of about 250° F. to about 450° F. The pressure is selected to maintain a mixed phase reaction system, and generally varies from 400 psig. to about 2,000 psig. in the aforesaid temperature range. As a result of the presence of the paraffin diluent, the cracked products will be substantially more saturated than would obtain in the absence thereof.

The effluent from the cracking zone passes into a suitable flash system, functioning at a lower pressure wherein the unconsumed paraffin diluent, distillable cracked products and HF are separated from the viscous heavy bottoms which remain. Additional volatile products may be removed by fractionation from these heavy bottoms, leaving a still higher boiling pitch. The volatile products are introduced into HF recovery facilities from which the separated hydrogen fluoride is recycled to the upper portion of the extraction zone, and the light paraffin diluent is recycled to both the extraction and cracking zones. It is understood that the design of the cracking zone, extraction zone, flash chamber, settler, product fractionator and HF recovery system forms no essential part of the present invention. Various configurations of such mechanical equipment can be readily found in the prior art relating thereto.

The raffinate phase removed from the extraction zone may be combined with volatile hydrocarbons recovered from the flash system and product fractionator, and the mixture treated for the purpose of removing trace quantities of hydrogen fluoride. Alternatively, these streams may be treated separately for HF recovery.

DESCRIPTION OF DRAWING

In further describing the present process, reference will be made to accompanying drawing which is presented for the sole purpose of illustration. In the drawing, the embodiment is presented by means of a simplified flow diagram in which such details as pumps, instrumentation and controls, heat-exchange, and heat-recovery circuits, valving, start-up lines and similar mechanical hardware have been eliminated as non-essential to an understanding of the techniques involved. The use of such miscellaneous appurtenances, to modify the illustrated embodiment, will be evident to those possessing expertise in the art.

The drawing will be described in conjunction with a commercially scaled unit designed to process a Middle-East reduced crude oil having a gravity of 16.6° API, and an ASTM 65.0 percent volumetric distillation temperature of about 1,034° F. The reduced crude oil contains about 3.8 percent by weight of sulfur, 2,032 ppm. of nitrogen, 6.5 percent by weight of heptane-insoluble asphaltenes, about 85 ppm. by weight of nickel and vanadium, and has a Conradson Carbon Residue of 8.0 wt. %.

The charge stock in line 1 is commingled with an equal weight of isobutane in line 4, heated to a temperature of about 205° F., and passes into extraction zone 2. The extraction zone functions at a pressure of about 370 psig. Substantially anhydrous hydrogen fluoride, equivalent in weight to the reduced crude, is introduced into the upper portion of extraction zone 2 by way of line 3; the HF is also at a temperature of about 205° F. A raffinate phase, in an amount of about 70.0 percent by weight of reduced crude, after removal of isobutane, is withdrawn through line 5, and constitutes a portion of the product of the process. This raffinate phase has a gravity of about 21.0° API, a sulfur content of about 0.8 percent, a nitrogen content of less than 30 ppm. and reduced levels of heptane-insolubles, metals and Conradson Carbon. The remainder of the charge stock is withdrawn through line 6 as an extract in HF.

The extract is commingled with additional isobutane, from line 14, in an amount of about 0.5 relative to the original reduced crude, and introduced into thermal cracking zone 7 which functions at a temperature of about 380° F. and a pressure of about 1,800 psig. The cracked product effluent is withdrawn via line 8 and introduced into flash system 9 at a pressure of about 110 psig. Volatile hydrocarbons, excess isobutane diluent and HF are removed by way of line 10 and passed after cooling, into settler 15. Settled HF is returned to the extractor via line 3, while isobutane and cracked products are withdrawn through line 13 and combined with the raffinate in line 5, and are supplied to a suitable system for removal of trace quantities of HF and for recovery of isobutane which is introduced into diluent source 18.

Heavier hydrocarbons are removed from flash system 9 through line 11 and introduced therethrough into product fractionator 12. Additional distillable hydrocarbons are recovered through line 17 and admixed with the raffinate phase in line 5. A heavy pitch, in an amount of about 20.0 percent by weight of the charge stock, is removed from the process through line 16.

The overall liquid hydrocarbon product of the combination process, after removal of unreacted isobutane, is recovered in an amount of about 85.0 percent by weight of the fresh feed charge stock, showing interaction with the isobutane diluent. Approximately 12.0 percent by weight of the hydrocarbon product is gasoline boiling range material, and the overall sulfur concentration is 0.85 percent by weight.

The foregoing clearly demonstrates the utility of the present combination process, and indicates the benefits afforded through the utilization thereof.

I claim as my invention:

1. A process for the conversion of an asphaltene-containing hydrocarbonaceous charge stock which comprises the steps of:
 - a. treating said charge stock with hydrogen fluoride in a contacting zone, at conditions of temperature and pressure selected to produce a raffinate hydrocarbon phase and an HF extract phase containing asphaltenes;
 - b. increasing the temperature of said extract phase, to a level at which the cracking of hydrocarbons is effected and cracking said phase in a cracking zone;
 - c. separating the resulting cracked effluent to provide (i) a volatile hydrocarbon phase, (ii) an asphaltic pitch and (iii) hydrogen fluoride; and,
 - d. recycling at least a portion of said hydrogen fluoride to said contacting zone and recovering said raffinate and volatile hydrocarbon phases as the product of the process.

5

- 2. The process of claim 1 further characterized in that said hydrogen fluoride is substantially anhydrous.
- 3. The process of claim 1 further characterized in that said conditions include a temperature in the range of 100° F. to about 250° F. and a pressure sufficient to maintain said hydrogen fluoride in liquid phase.
- 4. The process of claim 1 further characterized in that the

6

- temperature of said extract phase is increased to a level in the range of about 250° F. to about 450° F.
- 5. The process of claim 1 further characterized in that a light paraffin is admixed with said charge stock.
- 5 6. The process of claim 1 further characterized in that a light paraffin is introduced into said cracking zone.

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