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PROCESS FOR THE PREPARATION OF LOW
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4 Claims. (Cl. 208—211)

This invention relates to a process for the preparation of fuel oil of the type burned in industrial furnaces, particularly furnaces located at plants in or near metropolitan areas. More particularly, the invention relates to a process for upgrading high sulfur content petroleum crude residual fractions for use as industrial fuel. Specifically, the invention relates to a multistep process for the preparation of low sulfur fuel oil including HF treating, coking and hydrodesulfurization.

Statutes limiting the sulfur content of residual fuel oil have been enacted in a number of metropolitan areas of the United States (see Chemical Week, July 24, 1965, pp. 20 to 21). Foreign governments, notably Germany, have also acted to impress limits on the quantity of sulfur in fuel oils. The chief disadvantages of most sulfur removal processes are high costs and/or low efficiency. At the present time no generally acceptable sulfur removal process for fuel oil is available.

Sulfur occurs in petroleum stocks in the form of mercaptans, sulfides, disulfides, and as a part of substituted rings, of which thiophene, benzothiophene and dibenzothiophene are the prototypes. Mercaptans are found in the lower boiling fractions, and a number of effective processes have been developed to remove them or to convert them to disulfides. Sulfur removal from higher boiling fractions, however, has been a much more difficult operation. Here the sulfur is present for the most part in the less reactive forms as sulfides, disulfides and as a part of substituted rings, such as thiophenes, benzothiophenes and dibenzothiophenes. These types of organosulfur compounds are not removed by processes applicable to mercaptans. Extraction processes are generally unsatisfactory because high boiling fractions such as petroleum crude residual fractions contain such a high percentage of sulfur-containing molecules. As a result, the yields from a simple extraction process are undesirably low.

Metallic contaminants, such as nickel and vanadium compounds, are found as innate constituents in practically all crude oils associated with the high Conradson carbon asphaltic and/or asphaltenic portion of the crude. When the crude oil is topped to remove the light fractions boiling below about 450–650° F. the metals are concentrated in the residual bottoms. The residual bottoms may also contain nitrogen compounds. The metals, coke formers and nitrogen compounds, all adversely affect catalysts if the residuum is further treated. They also cause poor fuel oil performance in industrial furnaces by forming coke and sludge and by corroding the metal surfaces of the furnace.

It is an object of this invention to provide a process for the preparation of a low sulfur fuel oil which is characterized by a low nitrogen and metals content as well. It is another object of this invention to provide a multistep process for preparing a fuel oil from topped crude which is efficient and economical.

Briefly, the process of the invention involves the steps of sequentially extracting a topped crude oil with substantially anhydrous hydrofluoric acid, coking the extract, hydrodesulfurizing the coked liquid and blending the hydrodesulfurized material with the raffinate from the HF treating step.

The invention will be more fully described with refer-

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ence to the attached drawing which is a flow diagram of one embodiment of the process.

Reference numeral 1 denotes a feed line supplying a high sulfur petroleum residuum to HF extraction zone 2. The term high sulfur in this specification includes petroleum feed stocks which contain more than 2 wt. percent of organosulfur compounds. Oils containing 2 to 10 wt. percent sulfur, preferably 2 to 6 wt. percent sulfur can be processed to yield a fuel oil containing less than 2 wt. percent sulfur, preferably less than 1 wt. percent sulfur. Oils containing 2 to 4 wt. percent sulfur can be processed to yield a fuel oil product containing less than 0.5 wt. percent sulfur and such low sulfur fuel oils meet the requirements of most governments.

Suitable feed stocks include heavy whole crude oils, atmospheric residuums, vacuum residuums, visbreaker bottoms, deasphalted oils and refinery cycle stocks. When required, very viscous oils can be cut back or diluted to a suitable viscosity or gravity with a light diluent oil so that they can be intimately contacted with HF. The preferred feed stocks are atmospheric residuums which have been distilled to yield a bottoms fraction having initial boiling point ranging from 500–650° F.

Liquid, essentially anhydrous HF or hydrofluoric acid is introduced into extraction zone 2 by line 3 and is there countercurrently contacted with the oil feed. The ratio of HF to oil is 50 to 150 wt. percent based on the oil. The time of contact can vary from 2 to 180 minutes, preferably 20 to 60 minutes. The pressure in the contactor may vary from 20 p.s.i.g. to 1000 p.s.i.g., i.e. a pressure sufficient to maintain the HF in a liquid state. The preferred temperature in the contacting vessel is in the range of 100–350° F. The contactor may be provided with a mechanical agitator or agitation can be achieved by means of an inert gas. If desired, the contactor can be packed with inert packing material such as Raschig rings or beryl saddles. Alternately, the contactor can be fitted internally with trays, plates and baffles. Any known means to insure intimate contacting of the oil and HF can be used. Instead of countercurrent contacting a mixer-settler system may be used.

The raffinate from the extraction is passed by line 4 to HF stripper 5. Stripping can be accomplished by lowering pressure until the HF boils out of solution or by any other suitable means. HF is returned to the HF contacting zone by lines 6 and 3. A low sulfur fuel oil constituting about 60 to 80 wt. percent of the feed to zone 2 is recovered by line 7.

The HF extract constituting about 20 to 40 wt. percent of the feed to zone 2 is recovered as bottoms by line 8 and passed to stripper 9 in which HF is stripped overhead by line 10 and returned to contactor 2 by lines 6 and 3. The extract in line 8 contains a major proportion of the organosulfur compounds and metals present in the feed to HF contactor 2.

Data on a typical HF extraction according to the invention are tabulated below. These data are for the extraction of a West Texas atmospheric residuum with 100% HF (on feed) at 200° F.

TABLE I

	Feed	Raffinate	Extract
Yield, percent.....	100	74	26
Gravity, ° API.....	19.5	23.7	1.2
Con. Carbon, wt. percent.....	5.5	1.8	20
Sulfur, wt. percent.....	2.2	1.0	5.0
Vanadium, p.p.m.....	24	0	95
Nickel, p.p.m.....	12	1	46

The above extraction was a single stage operation. Improved results can be obtained by multiple stage contacting.

It can be seen that the raffinate now contains 1% sulfur

and needs no further treatment for most fuel oil uses. If desired, all or part of the raffinate can be hydrodesulfurized. The extract contains the bulk of the coke formers, sulfur, metals and nitrogen compounds. This material is passed by line 11 to coking unit 12. Preferably unit 12 is a fluid coker, although delayed coking can be used. In the case of a fluid coker, the temperature in the reactor is maintained in the range of from about 900 to about 1025° F., preferably 950–990° F. Superheated steam is introduced into the coking unit through line 13 in an amount between about 20 to 60 pounds per barrel of coker feed.

Coke particles are withdrawn from unit 12 by line 14 and mixed with air introduced through line 15, and the resulting suspension is introduced into the burner or combustion vessel 16 where at least part of the coke is burned to raise the temperature of the coke particles to between about 100–250° F., higher than that in the coking reactor. The burner temperature is about 1050 to 1250° F. The pressure in the coker 12 and the burner 16 is about 10 to 60 p.s.i.g. Hot coke particles are withdrawn from the burner through line 17 and returned to the coker in an amount sufficient to maintain the desired temperature therein. 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 of 75 to 200 microns. Combustion gases pass overhead from the burner through line 18 and may be used for heat exchange. Excess coke is removed as a product by line 19.

The vaporous products of coking are passed overhead from coker 12 by line 20 to fractionator 21 to separate coker vapors into desired fractions. A gas fraction is carried overhead from the fractionator by line 22. This gas can be run through a hydrocarbon separation plant and reforming to recover its hydrogen content. A naphtha fraction can be recovered by line 23. The bulk of the coker product is passed by line 24 to hydrodesulfurization zone 25. The feed to zone 25 is low in coke formers, i.e. high Conradson carbon hydrocarbons, metals and nitrogen compounds. For this reason, the hydrodesulfurization catalyst can be used without regeneration for a longer period of time than would otherwise be the case. Another advantage of HF treating and coking prior to hydrodesulfurization is that the volume of the feed to the hydrodesulfurization zone is smaller and less hydrogen is required.

The hydrodesulfurization step is carried out at mild conditions. Reactor temperatures ranging from 600–800° F. and pressures ranging from 500 to 2000 p.s.i.g. are employed. Hydrogen gas is supplied at a rate of 1000 to 5000 std. cu. ft. per bbl. by line 26. Hydrogen is recycled by lines 27 and 28. The oil is fed to the reactor at a rate of 0.5 to 3.0 v./v./hr. Preferred catalysts are 5 to 15 wt. percent molybdena on porous alumina and mixtures of cobalt oxide (3 to 6 wt. percent) with molybdenum oxide (6 to 12 wt. percent) on adsorptive alumina. Catalysts containing nickel, chromia, platinum and tungsten in the form of metals, oxides and sulfides on alumina, charcoal, Kieselguhr and bauxite can be used as well.

A gas comprising H₂ and H₂S is carried overhead by line 27 and the H₂S is removed by a conventional gas scrubbing process such as amine scrubbing. The scrubbing unit is not shown in the drawing.

Low sulfur fuel oil is removed by line 28 and blended in line 7 with the raffinate from the HF treating unit. If desired, all or part of the raffinate in line 7 can be passed by lines 29 and 24 to the hydrodesulfurization step. The latter embodiment will provide a fuel oil product having an extremely low sulfur content.

In a specific embodiment, about 10,000 bbl./stream day of atmospheric residuum boiling above about 500° F. and having a gravity of about 19.5° API is fed continuously to the bottom section of HF contactor 2. The feed contains about 2.2 wt. percent sulfur, about 0.4 wt. percent nitrogen. Liquid HF is continuously added to the top section of the contactor at the rate of 8,000 bbl./stream day. Extraction is carried out at a tempera-

ture of about 200° F. and a pressure of about 150 p.s.i.g. employing a contacting time of about 40 minutes. About 80 vol. percent of the oil (8,000 bbl./day) is carried overhead. This raffinate boils above about 500° F. and will contain less than about 1% sulfur. The raffinate is stripped of HF in stripper 5 by reducing the pressure to about 20 p.s.i.g. and raising the temperature to about 350° F. The HF extract fraction containing most of the sulfur, metals and nitrogen compounds as well as the high Conradson carbon materials is withdrawn from the HF contactor at the rate of about 2,000 bbl./day. This extract has an initial boiling point above about 500° F. The extract is stripped of HF by pressure reduction and heating and the HF free material is fed to the coker 12 at the rate of 2,000 bbl./stream day. The fluid coker is operated at 970° F. and 15 p.s.i.g. Steam is added by line 13 at the rate of 50 lbs./bbl. of coker feed. The coker contains about 4 lb. of coke particles/lb. of feed per hour. The average particle size of the coke is about 100 microns. About 20 wt. percent of the coke is burned in burner 16 to supply heat for the coker. Air is added by line 15 to support combustion in the burner. About 1,750 bbl./day of coker overhead is passed to fractionator 21. About 6 wt. percent of this material is distilled overhead as gas and gasoline. About 1,630 bbl./day of material is fed by line 24 to hydrodesulfurization unit 25. This feed contains less than about 10 p.p.m. metals and has a sulfur content of about 5.5 wt. percent. Desulfurization is carried out with a CoO-MoO₃ on Al₂O₃ catalyst at 680° F., 1,500 p.s.i.g. and a hydrogen rate of 4,000 c.f./bbl. of feed. Desulfurized fuel oil containing less than about 1.0 wt. percent sulfur is blended in line 7 with the HF raffinate to produce about 9,700 bbl./stream day of fuel oil containing less than about 1.0 wt. percent sulfur and very low metals and nitrogen. Those skilled in the art can then select the optimum feed rates and conditions for the process units for any feed stock depending on the characteristics of the feed stock.

The sequential processing of a high sulfur residuum through HF extraction, coking and hydrodesulfurization as described in the specification provides an efficient and economical solution to the problem of upgrading fuel oil to meet modern requirements.

What is claimed is:

1. In a process for the preparation of low sulfur fuel oil by catalytic hydrodesulfurization, the improvement comprising pretreating the feed by the sequential steps of extracting a high sulfur petroleum residuum with liquid HF, stripping HF from the extract, coking the extract, separating the fraction which boils below about 450° F. from the coker overhead products and employing the remaining coker overhead product as the feed to catalytic hydrodesulfurization.

2. In a process for the preparation of low sulfur fuel oil by catalytic hydrodesulfurization, the improvement comprising pretreating the feed by the steps of extracting a high sulfur petroleum residuum with liquid HF, stripping HF from the raffinate, stripping HF from the extract, coking the extract, separating the fraction which boils below about 450° F. from the coker overhead product, blending the remaining coker overhead product with the said raffinate and employing the blend as the feed to catalytic hydrodesulfurization.

3. A process for the preparation of a low sulfur fuel oil comprising the steps of intimately contacting a high sulfur petroleum residuum with liquid HF in a counter-current contacting zone, separating an overhead raffinate phase, passing the extract bottoms to a coking zone, coking the bottoms at coking conditions, passing the coker overhead to a distillation zone, distilling the 450° F. fraction overhead, passing the distillation bottoms to a desulfurization zone, desulfurizing the distillation bottoms in the presence of a desulfurization catalyst and hydrogen, recovering a desulfurized product and blending the

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desulfurized product with said overhead raffinate phase to produce a low sulfur fuel oil.

4. A process for the preparation of a low sulfur fuel oil comprising the steps of intimately contacting a petroleum residuum containing from 2 to 10 wt. percent sulfur and organometallic compounds with liquid HF in a countercurrent contacting zone at a temperature in the range of 100–350° F., stripping HF from the raffinate, stripping HF from the extract, coking the extract at a temperature in the range of 900–1025° F. and a pressure in the range of 10 to 60 p.s.i.g., distilling the coker overhead to remove the light hydrocarbons, desulfurizing the remaining coker overhead product at a temperature in the range of 600–800° F., a pressure in the range of

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500 to 2,000 p.s.i.g. and a hydrogen recycle rate in the range of 1,000 to 5,000 c.f./bbl., and blending the desulfurized product with said raffinate to produce a low sulfur fuel oil.

References Cited

UNITED STATES PATENTS

2,689,207	9/1954	Gerald	208—211
2,988,501	6/1961	Inwood	208—211
3,061,539	10/1962	Moritz et al.	208—88
3,132,088	5/1964	Beuther et al.	208—216

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