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CHEMICAL PROCESS

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This invention relates to procedure for preparing a desulfurized hydrocarbon mixture from a straight run and catalytically cracked hydrocarbon both of which contain sulfur.

It is common practice in petroleum refining operations to mix straight run and catalytically cracked stocks used for various purposes. For instance, in preparing furnace oils it is general practice to mix straight run furnace oil with catalytically cracked furnace oil. Similarly it is common practice to mix straight run gas oil with cycle stock before catalytically cracking. The straight run and catalytically cracked stocks frequently contain sulfur compounds and removal of such sulfur compounds is desirable.

My invention has for its object to provide improved procedure for removing sulfur compounds from straight run and catalytically cracked hydrocarbon fractions. Another object is to provide improved procedure for preparing a fuel oil from straight run and catalytically cracked hydrocarbons which contain sulfur compounds. A still further object is to provide improved procedure for preparing a mixture which is low in sulfur compounds from straight run and catalytically cracked stocks which contain sulfur compounds. Other objects will appear hereinafter.

These and other objects are accomplished by my invention which includes separately extracting with sulfur dioxide a straight run hydrocarbon which contains sulfur compounds and a catalytically cracked hydrocarbon which contains sulfur compounds, separating the raffinate phase from both extractions and combining the two raffinate phases to produce a mixture of straight run and catalytically cracked hydrocarbon having a lower sulfur content.

In the following examples and description I have set forth several of the preferred embodiments of my invention but it is to be understood that they are given for the purpose of illustration and not in limitation thereof.

My invention is applicable to the preparation of any mixture of straight run and catalytically cracked hydrocarbons, the components of which mixture contain sulfur compounds in undesirable amounts. Thus the invention may be applied to the preparation of a furnace oil or No. 2 fuel oil from a straight run hydrocarbon and a catalytically cracked hydrocarbon boiling in the furnace oil or No. 2 fuel oil range and containing undesirable amounts of sulfur compounds. The invention is also applicable, for instance, to the preparation of an improved kerosene, Diesel fuel or catalytic cracking charge stock (gas oil) from straight run and catalytically cracked hydrocarbons having appropriate distillation characteristics for the product in question and containing sulfur compounds. The invention is applicable to preparing a final product containing any ratio of the straight run and catalytically cracked hydrocarbons. This ratio usually depends upon the amount of these stocks which are available in the refinery. In general the mixture contains about 1 to 99 percent of either component.

The extraction with sulfur dioxide should be carried out at a temperature and pressure such that the sulfur dioxide is in liquid phase. Temperatures below about ambient temperature are generally used. Temperatures below about 15° F. give highest selectivity. A temperature between about —20° and ambient temperature and especially about 10° to 15° F. is preferred. While lower temperatures than —20° F. may be employed, the cost of operation is increased by the additional refrigeration required. Higher temperatures than ambient temperature can be used. However the additional compression necessary to maintain the sulfur dioxide in liquid phase adds to the cost of operation. The sulfur dioxide to hydrocarbon ratio may be between about 0.1:1 and 10:1. A ratio of between about 0.5:1 and 5:1 is preferable.

The extraction may be accomplished by contacting the sulfur dioxide with the individual hydrocarbon components in any known manner which will give intimate contact between the sulfur dioxide and the hydrocarbon. Thus a batch or countercurrent method of contacting may be employed in either single or multi-stage. It is desirable to permit contact between hydrocarbon and sulfur dioxide to continue until approximate equilibrium is reached. For highest efficiency a continuous countercurrent extraction system should be used. The sulfur dioxide is heavier than the hydrocarbon so that it is introduced into the top of the countercurrent extractor. It will sink to the bottom of the continuous countercurrent extractor from which point it may be withdrawn and separated into extracted hydrocarbon and sulfur dioxide. The sulfur dioxide may be recycled for further use in the process. The charge stock is introduced into the bottom of the countercurrent extractor and the raffinate is removed from the upper portion of the continuous countercurrent extractor. After separation of the small amount of absorbed sulfur dioxide the raffinate is ready for the final step, i.e. intermixture with the other hydrocarbon component to produce the straight run-catalytically cracked hydrocarbon mixture containing a smaller amount of sulfur compounds.

EXAMPLE

Virgin and catalytically cracked No. 2 furnace oils having the properties shown in the first and second columns respectively of the accompanying table were mixed in the ratio of 77 percent by volume Kuwait No. 2 straight run furnace oil and 23 percent by volume Kuwait catalytically cracked No. 2 furnace oil. This mixture was then extracted with sulfur dioxide in a sulfur dioxide-hydrocarbon ratio of 2:1 and 5:1. The results of these extractions are given in the fourth and fifth columns of the accompanying table. In another experiment the same straight run Kuwait No. 2 furnace oil and the same Kuwait catalytic No. 2 furnace oil were extracted separately with liquid sulfur dioxide in a sulfur dioxide-hydrocarbon ratio of 2:1 and 5:1. The raffinates from these extractions were then blended. The proportions of this blend corresponded to the yield of raffinate which would be obtained when 77 parts by volume of Kuwait #2 furnace oil and 23 parts by volume of Kuwait catalytic #2 furnace oil are separately extracted. The results of these extractions are given in the sixth and seventh columns of the accompanying table.

Table

LIQUID SULFUR DIOXIDE EXTRACTION OF KUWAIT VIRGIN AND KUWAIT FLUID CATALYTIC NO. 2 FURNACE OILS

Operation	Charge Stocks			Extraction of Blended Furnace Oils		Separate Extraction Of Furnace Oils Followed by Blending	
	Virgin	Catalytic	Blend [1]				
Liquid Sulfur Dioxide/Oil Ratio	----------	----------	----------	2.0	5.0	2.0	5.0
Temperature, ° F	----------	----------	----------	15	15	15	15
Yield of Raffinate: Percent by Vol. of Combined No. 2 Furnace Oils	----------	----------	----------	65.3	58.9	70.5	63.8
Inspections:							
Raffinate—							
Gravity, ° API	40.3	21.5	35.4	41.7	42.7	43.3	44.7
Mean Molecular Weight	----------	----------	----------	246	----------	242	265
Sulfur, Braun-Shell, Percent	0.93	2.78	1.38	0.58	0.43	0.39	0.25
Sediment, Percent, ASTM D 473-48	----------	----------	----------	0.02	----------	0.01	0.01
Aniline Point, ° F., ASTM D611-51T	----------	----------	140	170	176	175	181
Cetane Number	56	20	36	62	65	67	69
Extract—							
Gravity, ° API	----------	----------	----------	24.8	25.1	18.9	19.1
Mean Molecular Weight	----------	----------	----------	215	213	199	214
Sulfur, Braun-Shell, Percent	----------	----------	----------	2.79	2.72	3.46	3.12
Sediment, Percent, ASTM D473-48	----------	----------	----------	----------	----------	0.03	----------
Aniline Point, ° F., ASTM D611-51T	----------	----------	----------	66	63	<32	<32

[1] Blend of 77% by volume Kuwait No. 2 Furnace Oil and 23% by volume Kuwait catalytic No. 2 Furnace Oil.

The results of the last mentioned extractions when compared with the corresponding extractions of the blend show that the procedure of the invention resulted in a considerably lower sulfur content in the product. Furthermore the procedure of the invention gave a substantially higher yield of final product and the cetane number in every case was improved.

I claim:

1. The process for preparing an improved mixture of a straight run hydrocarbon and a catalytically cracked hydrocarbon both of which initially contain sulfur compounds, the straight run hydrocarbon and the catalytically cracked hydrocarbon being selected from the group consisting of kerosene, diesel fuel, gas oil and fuel oil, said mixture after preparation containing a relatively small amount of sulfur compounds, which comprises in combination separately extracting the straight run hydrocarbon and catalytically cracked hydrocarbon with a liquid comprising essentially sulfur dioxide, separating the raffinate phases from both extractions, and combining the raffinate phases to produce a mixture of said straight run and said catalytically cracked hydrocarbon having a lower sulfur content.

2. The process for preparing an improved hydrocarbon mixture of a straight run hydrocarbon and a catalytically cracked hydrocarbon both of which initially contain sul-sulfur compounds, the straight run hydrocarbon and the catalytically cracked hydrocarbon being selected from the group consisting of kerosene, diesel fuel, gas oil and fuel oil, said mixture after preparation containing a relatively small amount of sulfur compounds, which comprises in combination separately extracting the straight run hydrocarbon and catalytically cracked hydrocarbon with a liquid comprising essentially sulfur dioxide at a temperature below about ambient temperature, at a sulfur dioxide-hydrocarbon ratio between about 0.1:1 and 10:1, separating the raffinate phases from both extractions, and combining the raffinate phases to produce an improved hydrocarbon mixture of said straight run and said catalytically cracked hydrocarbon having a lower sulfur content.

3. The process for preparing an improved furnace oil containing a relatively small amount of sulfur compounds from a straight run furnace oil which contains sulfur compounds and a catalytically cracked furnace oil which contains sulfur compounds which process comprises separately extracting the straight run furnace oil and the catalytically cracked furnace oil with a liquid comprising essentially sulfur dioxide and thereafter combining the raffinates from both extractions to produce a mixed straight run-catalytically cracked furnace oil having a lower sulfur content.

4. The process for preparing an improved furnace oil containing a relatively small amount of sulfur compounds from a straight run furnace oil which contains sulfur compounds and a catalytically cracked furnace oil which contains sulfur compounds which process comprises separately extracting the straight run furnace oil and the catalytically cracked furnace oil with a liquid comprising essentially sulfur dioxide at a temperature between about ambient temperature and —20° F., at a sulfur dioxide-furnace oil ratio between about 0.1:1 and 10:1 and thereafter combining the raffinates from both extractions to produce a mixed straight run-catalytically cracked furnace oil having a lower sulfur content.

5. The process for preparing an improved furnace oil containing a relatively small amount of sulfur compounds from a straight run furnace oil which contains sulfur compounds and a catalytically cracked furnace oil which contains sulfur compounds which process comprises separately extracting the straight run furnace oil and the catalytically cracked furnace oil with a liquid comprising essentially sulfur dioxide at a temperature of about 15° F., at a sulfur dioxide-furnace oil ratio between about 0.5:1 and 5:1 and thereafter combining the raffinates from both extractions to produce a mixed straight run-catalytically cracked furnace oil having a lower sulfur content.

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