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CATALYTIC DESULFURIZATION OF BLEND OF A REFORMER FEED AND A FURNACE OIL

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Fig. 1

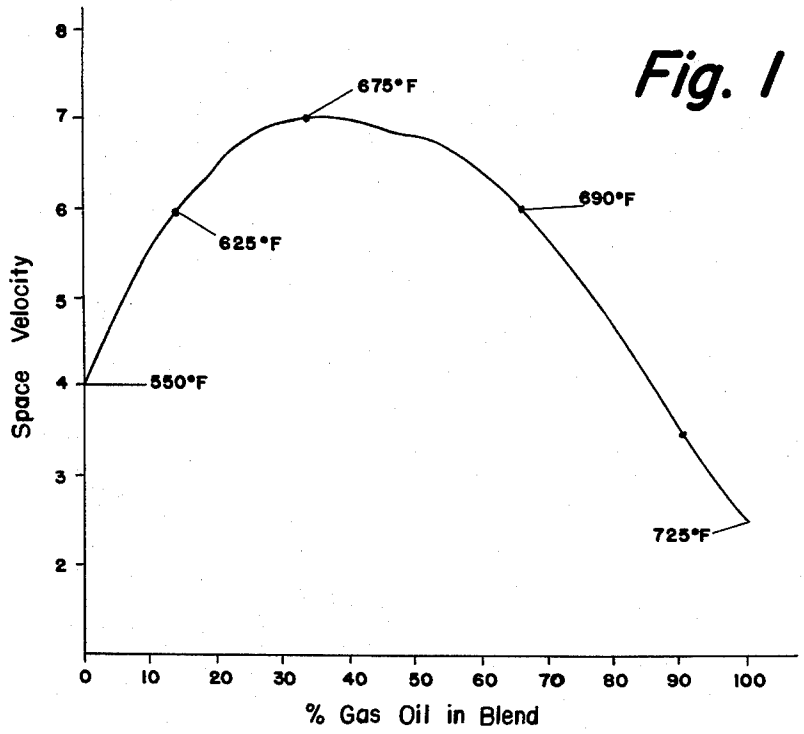
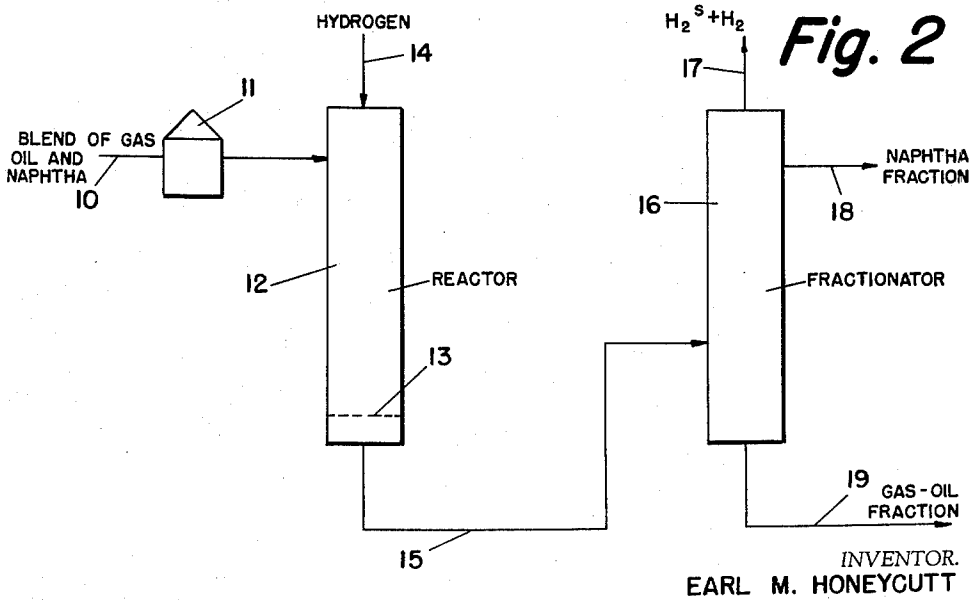


Fig. 2



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CATALYTIC DESULFURIZATION OF BLEND OF A REFORMER FEED AND A FURNACE OIL

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This invention relates to a process for the catalytic desulfurization of hydrocarbon fractions, and is more particularly concerned with the liquid phase catalytic desulfurization of a blend of a light straight run naphtha and a gas oil, whereby the capacity of a desulfurization plant may be substantially increased.

In catalytic reforming using a platinum catalyst, it is necessary to reduce the sulfur content of the feed to less than 0.01% and preferably to less than 0.005% in order to avoid poisoning the catalyst. It has been the practice to desulfurize light straight run petroleum naphthas by passing them in liquid or vapor phase over a hydrogenation catalyst such as cobalt molybdate supported on alumina, in the presence of hydrogen. When the term "cobalt molybdate" is used herein, it denotes a mixture of cobalt and molybdenum oxides which may or may not be in whole or in part chemically combined. Liquid phase operation is preferred since the cost of the necessary equipment is very much smaller than in vapor phase processes. While the rate of desulfurization increases rapidly with increasing temperatures, it is necessary, in liquid phase desulfurization, to operate at temperatures below the critical temperature of the naphtha, so that, in practice, 550° F. is about the highest temperature that can be used. At this temperature the liquid hourly space velocity of the feed (volumes of feed/volume of catalyst/hour) must be 4 or less in order to achieve satisfactory desulfurization.

Another stock which is troublesome due to high sulfur content is the cracked gas oil produced by refineries processing high sulfur crudes such as Kuwait crudes. The sulfur content of these cracked gas oils may be as high as 2% or higher, and the sulfur should be reduced to around 0.3% before they are salable as furnace oils. These gas oils may also be desulfurized in liquid phase, but temperatures in excess of 700° F. are required, together with pressures of from 650 p.s.i.g. and up. Even at these high temperatures and pressures it is necessary to hold the liquid hourly space velocity to 2.5 or less in order to secure a satisfactory degree of desulfurization.

It is an object of this invention to provide a method for increasing the rate of desulfurization of straight run naphtha fractions and gas oils, so as to permit the use of greater space velocities in processing these fractions, and thereby permit the processing of greater quantities of oil in an existing piece of equipment.

I have found that the foregoing object may be attained by blending a straight run naphtha fraction with a sulfur-containing gas oil, and contacting the blend in liquid phase with a sulfur-resistant hydrogenation catalyst at a temperature slightly below the critical temperature of the blend and under a sufficient pressure of hydrogen to hold the blend in liquid phase. Even a very small proportion of either component in the blend will permit the space velocity to be markedly increased, and at optimum proportions it has been found that the reactor volume required for processing the blend to a satisfactory sulfur level is less than that required for processing the

naphtha fraction alone. Fig. 1 of the accompanying drawings illustrates the effect of the proportion of gas oil in the blend on the permissible temperatures and space rates which may be used in effecting desulfurization. In obtaining the data on which the graph is based the naphtha fraction boiled from 220° F. to 425° F., containing 0.035% sulfur, and the gas oil was a cracked gas oil boiling from 435° F. to 650° F., and having a sulfur content of about 1.8%. The hydrogenation catalyst was a commercial cobalt molybdate catalyst, and the hydrogen pressure was sufficient to keep the blend in liquid phase. At the temperatures and space rates shown on the curve in Fig. 1 the product could be fractionated to yield a naphtha fraction containing 0.005% sulfur and a furnace oil containing 0.3% sulfur. It will be noted that when desulfurizing the naphtha fraction alone it was necessary to keep the temperature down to 550° F. at 500 p.s.i.g. in order to maintain the feed in liquid phase, and at this temperature the space velocity required to bring the sulfur content of the product down to 0.005% was 4. With no naphtha fraction in the blend, at 725° F. and 650 p.s.i.g. (pounds per square inch gauge) reduction of sulfur in the gas oil to 0.3% could not be obtained at a space rate greater than 2.5.

With various blends of the naphtha and the gas oil, however, it was found that the space velocity could be considerably increased while still obtaining satisfactory desulfurization of both fractions. Referring again to Fig. 1, it will be noted that a blend of 15% gas oil and 85% naphtha can be processed at 625° F. and a space velocity of 6, a blend of naphtha and gas oil in a ratio of 2:1 can be processed at 675° F. and a space velocity of 7, and a blend of 35% naphtha and 65% gas oil can be processed at 690° F. and space velocity of 6. At the higher allowable temperatures at which the blend may be processed, as compared to the allowable temperature when processing the naphtha fraction alone, it is understood why the naphtha fraction may be desulfurized at a higher space rate, but the fact that the gas oil fraction may be adequately desulfurized at these low terperatures and high space rates would appear to be most surprising.

In order that the invention may be more fully understood by those skilled in the art, a specific example of a process in accordance with the invention will be described in connection with Fig. 2 of the drawings, which is a diagrammatic flow sheet of the process.

A blend consisting of two volumes of a straight run petroleum naphtha boiling from 220° F. to 425° F. containing 0.035% sulfur and one volume of a cracked gas oil boiling from 435° F. to 650° F. derived from the catalytic cracking of Kuwait virgin gas oil, and containing 1.73% sulfur is taken from storage through line **10** and is passed through furnace **11** in which it is heated to a temperature of 675° F. The heated blend is then passed to reactor **12**, in which it trickles downwardly over a cobalt molybdate catalyst supported on alumina. A hydrogen pressure of 500 p.s.i.g. is maintained in reactor **12** over liquid level **13**, hydrogen being admitted to the reactor through line **14** in an amount sufficient to make up for the hydrogen consumed in the desulfurization of the feed. The feed is passed through reactor **12** at a space velocity (volumes of feed/volume of the reactor/hour) of 7. The reaction products are removed from reactor **12** through line **15** and are passed to fractionator **16** from which hydrogen sulfide and dissolved hydrogen are removed overhead through line **17**, hydrocarbons boiling below 400° F. are removed as a side stream through line **18**, while higher boiling hydrocarbons are removed as bottoms through line **19**.

The results obtained in this run are set forth in the following table, together with results obtained in similar runs on the naphtha alone and gas oil alone.

Table I

	Naphtha alone	Gas Oil alone	67% Naphtha, 33% Gas Oil
Percent S in naphtha	0.035		0.035
Percent S in gas oil		1.94	1.73
Percent S in blend			0.57
Temperature, ° F	550	725	675
Space Velocity	4.0	2.5	7.0
Percent S in product	0.005	0.33	0.1
Percent S in 400° F.+fraction		0.33	0.30
Percent S removed from gas oil		83	83
Percent S in 400° F.—fraction			0.005

It may be observed that when operating at a space rate of 7 on the combined feed, less than half the reactor capacity is needed than when processing the two fractions separately. For example, in a refinery processing 10,000 barrels per day of naphtha, and 5000 barrels per day of gas oil, if the oils are processed separately at a space velocity of 4 for the naphtha and 2.5 for the gas oil, a reactor of 465 cubic feet capacity would be required for processing the gas oil, and a separate reactor of 584 cubic feet capacity would be required for processing the naphtha. When the 2/1 blend of naphtha is desulfurized at a space velocity of 7, a reactor of only 500 cubic feet capacity is required to process the entire 15,000 barrels per day of feed. It is estimated that at present day construction costs a plant to process the two streams separately, including reactors and associated fractionation facilities, would involve an investment of about $1,300,000, whereas a plant for processing the combined streams would cost but $700,000. In addition, important savings are realized from the reduction in the required inventory of catalyst.

While in operating with the specific stocks discussed above, a blend of two-thirds naphtha and one-third gas oil appeared to be the optimum blend, with other gas oils having higher or lower sulfur contents than 1.73%, the optimum blend may not be the same. With any stocks, however, improved results in accordance with the present invention may be obtained by blending sufficient gas oil into the naphtha to raise the critical temperature of the blend to at least 650° F., and sufficient naphtha should

be present in the blend to reduce the sulfur content of the blend to below 1%, and preferably to below 0.75%. Operating temperatures suitable for use in the process are from about 600° F. to about 800° F., it being understood, however, that temperatures in excess of the critical temperature of the particular blend being treated should not be used. The pressure may be from about 500 p.s.i. to about 1000 p.s.i. (pounds per square inch) or over, but in any case should be sufficient to keep the feed in liquid phase at the temperature employed.

When processing very high sulfur gas oils it may not be possible to obtain adequate desulfurization at space velocities as high as 7, and with low sulfur stocks it may be possible to go to even higher velocities. In any event, it will be found that a space velocity may be used which is substantially higher than the over-all space velocity permissible when processing the stocks separately.

The invention claimed is:

1. A process for the simultaneous desulfurization of reformer feed stocks and furnace oils which comprises blending a sulfur-containing straight run petroleum naphtha boiling in the gasoline boiling range with a sulfur-containing gas oil in proportions such that the critical temperature of the blend is at least 650° F., and the sulfur content of the blend is less than 1%, contacting the blend with a sulfur-resistant hydrogenation catalyst, in the presence of hydrogen, at a temperature of from about 600° F. to about 800° F., but less than the critical temperature of the blend, and at a pressure in excess of about 400 p.s.i.g., and sufficient to maintain the blend in liquid phase while in contact with the catalyst, recovering a reaction product, and separating the reaction product into a substantially desulfurized naphtha fraction and a substantially desulfurized gas oil fraction.

2. The process according to claim 1 in which the catalyst is cobalt molybdate supported on alumina.

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