

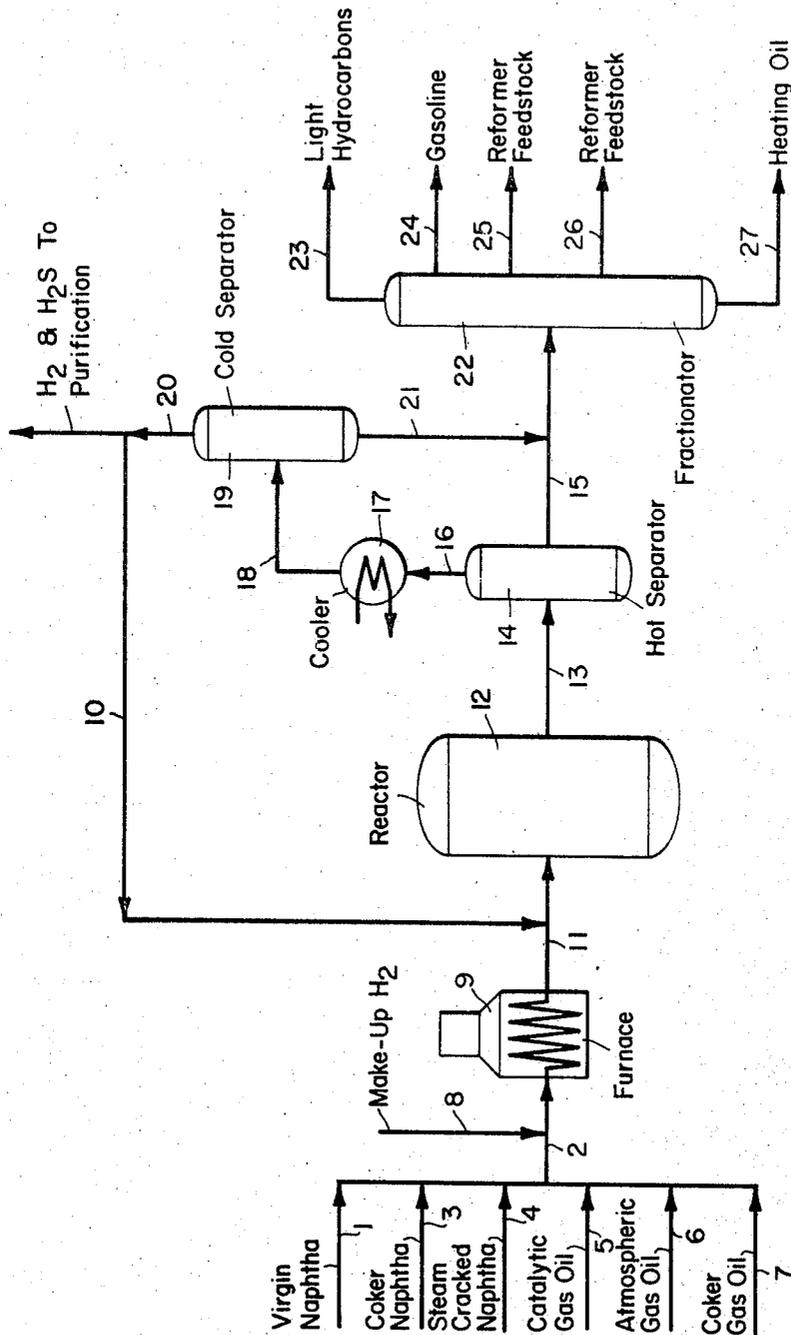
Oct. 28, 1969

J. ENG ET AL

3,475,327

HYDRODESULFURIZATION OF BLENDED FEEDSTOCK

Filed Oct. 28, 1966



J. ENG, G. H. THOMSON
and R. C. VANDERLINDEN INVENTOR

BY *C. W. Crady Jr.*

PATENT ATTORNEY

1

3,475,327

HYDRODESULFURIZATION OF BLENDED FEEDSTOCK

Jackson Eng and Gordon H. Thomson, Sarnia, Ontario, and Ronald C. Vanderlinden, Sarnia Township, Ontario, Canada, assignors to Esso Research and Engineering Company, a corporation of Delaware
 Filed Oct. 28, 1966, Ser. No. 590,288

Int. Cl. C10g 23/00

U.S. Cl. 208—211

13 Claims

ABSTRACT OF THE DISCLOSURE

Unstable naphthas are concurrently hydrofined with stable and unstable gas oils in a single reactor with consequent savings in investment and operating costs.

This invention relates to the hydrodesulfurization of blended feedstocks. More particularly the invention relates to the hydrodesulfurization of a blend of fractions boiling in the range of 50–1200° F. derived from petroleum. Specifically the invention relates to the hydrodesulfurization of a plurality of sulfur-containing petroleum derived hydrocarbon fractions including unstable, olefinic fractions which are rich in diolefins such as those derived from coking and/or steam cracking.

Many large petroleum refineries are equipped with processing units integrated to produce a wide variety of petroleum and petrochemical products including gasoline, kerosene, jet fuel, ethylene, propylene, acetylene, benzene, fuel oil and petroleum coke. These units produce a multitude of sulfur-containing fractions as major products and as by-products. It is desirable to remove as much sulfur from the fractions as possible because of end use specifications and also for further treatment in the refinery in contact with sulfur sensitive catalyst. For example, the sulfur content of motor gasoline must be reduced to a few parts per million. The sulfur content of reformer feedstocks must be very low because of the extreme sensitivity of the platinum-containing catalyst to sulfur. Fuel oils must be desulfurized to meet increasingly lower sulfur content requirements.

In conventional hydrodesulfurization or hydrofining operations naphthas, straight run gas oils, coker naphthas, coker gas oils and steam cracked fractions are processed separately in individual units. One of the reasons for this practice, particularly where steam cracked or other pyrolysis fractions and coker fractions are involved, is the general feeling that these unstable fractions must be processed in a very specific manner and that they cannot be processed along with conventional naphthas and gas oils at ordinary hydrofining conditions in the presence of conventional hydrofining catalysts.

The prior art practice results in the use of a large number of hydrofiners of varying capacity as well as an equal number of separators and stripping towers to remove H₂S and light ends. In the case of olefinic feeds, facilities must also be available for controlling the heat of reaction. This can be accomplished by recycle of cool reacted product or by the use of specially designed multiple catalyst bed reactors utilizing cold product or hydrogen quenches injected between the beds to cool the reaction mixture. These facilities are cumbersome to operate and they are expensive because of increased size and heat requirements.

The object of the present invention is to provide a hydrodesulfurization process which will provide adequate desulfurization of a plurality of feedstocks in a single unit employing the same conditions and catalyst for all certain quantities and processed at certain hydrodesulfur-

2

ization conditions, excellent sulfur reduction is obtained for all fractions of the product slate. The invention will be further described below in conjunction with the drawing which is a diagrammatic flow sheet of a preferred embodiment of the process.

Reference numeral 1 refers to a line supplying 70 vol. percent 92–382° F. virgin naphtha as a preferred feed to line 2 where the fractions are blended. By virgin naphtha or straight run naphtha we mean a non-olefinic hydrocarbon fraction boiling in the range of about 50–400° F. obtained by atmospheric distillation, vacuum distillation or flashing of a petroleum crude oil. Since virgin naphtha does not present too much of a processing problem, relatively large quantities can be present in the blend, i.e. 20–80%, preferably 40–80% of the blend. Virgin naphthas contain about 100–800 p.p.m. sulfur.

Reference numeral 3 refers to a line supplying 3 vol. percent of 220–356° F. heavy coker naphthas derived from coking of petroleum residuum. The coking process converts heavy residual fuel oil into gasoline, gas oil and petroleum coke. Delayed coking and fluid coking processes are in general use in the United States today. These processes are well described in a review by S. W. Martin and L. E. Wills titled Coking Petroleum Residues appearing in Advances in Petroleum Chemistry and Refining, vol. II, 1959, pp. 357–433. Coker gasoline has an end point of about 400° F., however, it is not always necessary to desulfurize and stabilize the entire fraction. The process of the invention is particularly applicable and beneficial to so-called heavy coker naphtha having a boiling range of about 200–400° F. Coker naphthas contain 0.5–4 wt. percent sulfur and contain large quantities of olefins and diolefins, i.e., 30 to 70 vol. percent resulting in Bromine Numbers of 40–140 (ASTM method). When refinery contains a fairly large coker, correspondingly large quantities of coker naphthas are produced and they must be treated to make them suitable for blending into the gasoline pool. The processing usually involves hydrodesulfurization and reforming. Our process provides a simple and inexpensive means of preparing coker naphtha for subsequent upgrading. From 1 to 40 vol. percent preferably 1–10 vol. percent coker naphtha can be included in the blend.

Reference numeral 4 denotes a line supplying 2 vol. percent of 136–256° F. steam cracked naphtha derived from pyrolysis of petroleum fractions boiling in the range of 80–1100° F. The best known process of this type is steam cracking of naphtha to produce a maximum amount of ethylene, propylene and/or acetylene. Steam cracked naphtha or pyrolysis gasoline is produced as a by-product of these processes in amounts ranging from 1–20% depending on feed characteristics and cracking conditions. Typical commercial processes are described in Hydrocarbon Processing, November, 1965, vol. 44, No. 11, pp. 165–166 and 203–208. Steam cracked naphthas, especially those derived from cracking heavier feedstocks are extremely unstable due to the presence of monolefins and conjugated diolefins, i.e., 20–60 percent and a correspondingly high Bromine Number of 40–150 (ASTM method). Steam cracked naphthas boil in the range of 100–400° F. From 0.5 to 40 vol. percent preferably 0.5 to 15 vol. percent steam cracked naphtha can be hydrotreated along with the other material in the blend.

Reference numeral 5 denotes a line supplying 10 vol. percent 408–656° F. catalytic gas oil to common line 2. Cat. gas oil is a fraction produced in the catalytic cracking of petroleum fractions. This material boils in the range of 300–800° F. depending on the cut points used in fractionating the products of catalytic cracking. Catalytic cracking is a conventional process and constitutes no part of this invention. Cat. gas oils contain from 0.5 to 3% sulfur depending on the sulfur content of the crude oils from which they are derived. From 5–40 vol. percent,

preferably 10–25 vol. percent of cat gas oil is included in the blend.

Reference numeral 6 refers to a line supplying 8 vol. percent 462–654° F. straight run (virgin) gas oil to line 2. This component is obtained by atmospheric or vacuum distillation of crude oil. The oil contains from 0.5 to 3% sulfur and boils in the range of 300–800° F. depending on the cut points used in distillation. From 5 to 40 vol. percent, preferably 10–25 vol. percent straight run gas oil can be supplied to line 2.

Reference numeral 7 refers to a line supplying 7 vol. percent 360–710° F. coker gas oil to line 2. Coking has been discussed above with respect to coke naphtha. Coker gas oil is difficult to desulfurize because of its high sulfur content, i.e., 1–5%, and also because of its high olefinic content, 30–60 vol. percent and its relatively high instability towards heat. From 5 to 40 vol. percent, preferably 10–25 vol. percent coker gas oil is included in the blend in line 2. The coker naphtha and coker gas oil can be derived from coking bitumen derived from tar sands such as the Athabaska tar sands of Canada.

The blend in line 2 contains from 10–70 vol. percent of the unstable components described above, i.e., the group consisting of coker naphtha, steam cracked naphtha, coker gas oil and mixtures thereof. Preferably the blend contains 10–70 vol. percent of a gas oil selected from the group consisting of straight run gas oil and catalytic gas oil. In a particularly preferred embodiment at least four of the five fractions listed below are present in the total blend in amounts within the ranges set forth opposite the particular fraction:

	Volume Percent	
	Suitable	Preferred
(a) Coker naphtha.....	1–40	1–10
(b) Steam cracked naphtha.....	0.5–40	0.5–15
(c) Catalytic gas oil.....	5–70	5–25
(d) Virgin gas oil.....	5–70	5–25
(e) Coker gas oil.....	5–40	5–25

If a particular component such as steam cracked naphtha is not to be included in the blend, increased quantities of any or all of the other components can be employed to bring the quantity of blend up to 100 vol. percent, the operating charge required for optimum hydrodesulfurization. Selection of the blend component is based upon availability of components, the characteristics of each component, the hydrodesulfurization catalyst, the scope of hydrodesulfurization conditions which can be used effectively, and the type of product slate desired. The blend has a boiling range of 50–1200° F., preferably 70–1000° F., and more preferably 85–750° F.

The components are mixed and blended in line 2 and makeup hydrogen is added by line 8. The reaction

mixture is heated to a temperature of about 600 to 750° F. and then passed by line 11 to hydrodesulfurization reactor 12. Recycle hydrogen is added by line 10 to line 11.

Hydrodesulfurization is carried out in any suitable, conventional hydrodesulfurization reactor. Product recycle and multi-bed reactors are not required. The reactor system may include a plurality of reactor and a catalyst regenerator but these have not been shown. The reaction is carried out at conventional conditions including a temperature in the range of 500–950° F., preferably 600–750° F.; a pressure in the range of 300–1000 p.s.i.g., preferably 350–600 p.s.i.g., a space velocity of 0.5 to 5 v./hr./v. and a hydrogen to blend ratio of 250–3000 s.c.f./bbl. preferably 300 to 700 s.c.f./bbl. A hydrogen containing gas containing 70 to 100 vol. percent H₂ is used.

Suitable conventional catalysts include a mixture of a member of the group consisting of Group VI oxides and sulfides with a member of the group consisting of iron, cobalt and nickel oxides and sulfides deposited upon a porous carrier such as alumina, silica-alumina, bauxite, kieselguhr, magnesia, zirconia, etc. The preferred catalyst is cobalt-molybdate on silica stabilized alumina. The catalyst may be sulfided with H₂S if it desired.

Hydrodesulfurized reaction products are passed by line 13 to hot separator 14. This separation is carried out at 300 to 500° F. and 350 to 600 p.s.i.g. By employing a hot separation of this type we are able to conserve heat. The reaction products are passed by line 15 to the distillation zone 22 at a temperature of 300 to 500° F., and thus less heat is required for distillation. A gas containing light hydrocarbons, hydrogen and H₂S is passed by line 16 to cooler 17 and thence by line 18 to cold separator 19. The cold separator operates at a temperature of 80 to 150° F. and a pressure of 350 to 600 p.s.i.g. Hydrogen and H₂S are passed to a purification system not shown; however, part of the gas is recycled by line 10. Liquefied light hydrocarbons from the cold separator are passed by line 21 to line 15 for distillation in fractionation column 22. The number of cuts and the specific cut points is a matter of choice, however in a preferred embodiment a light hydrocarbon fraction is recovered by line 23, a C₅–160° F. gasoline fraction is recovered by line 24, a 160–250° F. C₆ naphthene-rich fraction for reforming is recovered by line 25, a 250–350° F. fraction for reforming into a gasoline component is recovered by line 26 and a 350–700° F. premium heating oil is recovered by line 27. These fractions are all substantially reduced in sulfur content and they are in condition for use as end products or for further processing in contact with sulfur sensitive catalysts.

Table 1 shows typical feedstock inspections for the components which make up the hydrodesulfurization feed.

TABLE 1.—FEEDSTOCK INSPECTIONS

Inspections	Naphthas			Gas Oils		
	Virgin	Steam Cracked	Heavy Coker	Virgin	Coker	Cat. Cracked
Gravity, ° API.....	63.6	37.4	54.2	32.2	27.4	20.3
Sulfur.....	¹ 630	¹ 2,223	¹ 6,150	² 1.10	² 2.16	² 1.93
Mercaptan No.....	27	0.2	12.2	15.2	21.6	25.9
Bromine No. (ASTM Method).....	1.3	140	118	7.4	53.6	16.7
Basic N, p.p.m.....	<1	-----	44	71	641	56
Total N, p.p.m.....	<1	13	75	169	1,400	400
ASTM Distillation:						
IBP, ° F.....	92	136	220	462	360	408
10%.....	145	168	247	550	462	483
50%.....	235	188	270	592	550	570
90%.....	321	218	306	624	668	649
FBP.....	382	256	356	654	710	656
Composition, vol. percent ³ :						
Aromatics.....	11	48	14	35	51	67
Monoolefins.....	Nil	37	34	Nil	28	6
Diolefins.....	Nil	14	12	Nil	10	Trace
Saturates.....	89	1	40	65	11	27

¹ Parts per million.

² Weight percent.

³ Typical values for these types of feedstocks.

It can be seen that all of the unstable fractions, i.e., steam cracked naphtha, coker naphtha and coker gas oil contain high levels of olefins and diolefins. Bromine Numbers are also high.

In this specification and claims an unstable fraction or the mixture of unstable fractions is one which contains 10-50 vol. percent olefins and 1-20 vol. percent diolefins. The Bromine Number of the fraction ranges from 40-140.

Table 2 below shows the results of desulfurizing the six component feed shown on lines 1 and 3-7 of the drawing. The hydrofining conditions were: 650° F., 2 v./v./hr., 500 p.s.i.g. and 500 s.c.f. 85% H₂ per bbl. The catalyst was cobalt molybdate on silica stabilized alumina.

TABLE 2

	Volume Percent	Sulfur Content
Feed Components:		
92-382° F., Virgin Naphtha.....	70	¹ 630
220-356° F., Heavy Coker Naphtha.....	3	¹ 6, 150
136-256° F., Steam Cracked Naphtha.....	2	¹ 2, 223
408-656° F., Cat. Cracked Gas Oil.....	10	² 1.93
462-654° F., Heavy Atmosphere Gas Oil.....	8	² 1.10
360-710° F., Coker Gas Oil.....	7	² 2.16
Total.....	100	
Hydrofined Product, Fractions:		
C ₁ to C ₄	5	¹ ~1
C ₅ /160° F.....	10	¹ ~1
160/250° F.....	30	¹ 1-2
250/350° F.....	30	¹ <5
350/700° F.....	25	² 0.12
Total.....	100	

¹ Parts per million.

² Weight percent.

It can be seen that the C₅-160° F. fraction which is used in motor gasoline is entirely suitable for that use because the sulfur content has been reduced to about 1 p.p.m. The 160/250° F. and the 250/350° F. are in suitable condition for reforming since the sulfur content of these fractions is low enough that they can be contacted with a platinum catalyst without any danger that the catalyst will be fouled by the reforming feed. The heating oil fraction has a sulfur content of 0.12 wt. percent making it suitable for use as a premium fuel oil or for use as a blending stock with fuel oil components having a higher sulfur content.

Since no steam strippers are used in the process the products are dry. Since no product recycle is required, no heat is needed to reheat the recycle stream. Also, heat requirements are reduced by passing the total hydrofined blend to a hot separator before fractionation. By processing in this manner the light ends and hydrogen are removed and a hot liquid steam is provided which will require very little if any further heating prior to fractionation into the various product fractions. In addition to heat savings, there is also a sizeable reduction in heat exchanger equipment. Savings of 20-40% are achieved over the cost of a plurality of specialized conventional hydrofining units.

It is to be understood that the foregoing detailed description is given merely by way of illustration and many alterations may be made therein without departing from the spirit of the invention. This applies particularly to the proportions of feed components used to formulate the blends treated.

What is claimed is:

1. A process for desulfurizing blended feedstocks comprising the steps of:

(A) blending 20-80 vol. percent of virgin naphtha with 10-70 vol. percent of a gas oil selected from the group consisting of straight run gas oil, catalytic gas oil, and mixtures of these, and with 10-70 vol. per-

cent of an unstable hydrocarbon fraction consisting of coker naphtha, steam cracked naphtha and coker gas oil the total quantity of said gas oil and said unstable fraction representing 80-20% of the total blend,

(B) subjecting the blend to hydrodesulfurization with a catalyst comprising a mixture of a member of the group consisting of Group VI oxides and sulfides with a member of the group consisting of iron, cobalt and nickel oxides and sulfides deposited upon a porous carrier, at temperatures of 600-750° F. and pressures 350-600 p.s.i.g.,

(C) recovering said blend substantially reduced in sulfur content, and

(D) fractionating said blend to recover a gasoline fraction, a reformer feedstock fraction and a heating oil fraction.

2. Process according to claim 1 in which the unstable fraction contains 10-50 vol. percent olefins, 1-20 vol. percent diolefins and has a Bromine Number of 40-140.

3. Process according to claim 1 in which the unstable fraction comprises a mixture of coker naphtha, steam cracked naphtha and coker gas oil.

4. Process according to claim 1 in which the unstable fraction comprises a mixture of coker naphtha and coker gas oil.

5. Process according to claim 4 in which the said mixture is obtained from the coking of bitumen derived from tar sands.

6. Process according to claim 1 in which the gas oil is straight run gas oil.

7. Process according to claim 1 in which the gas oil is a mixture of straight run gas oil and catalytic gas oil.

8. Process according to claim 1 in which the hydrogen containing gas contains 70-100 vol. percent hydrogen.

9. A process for the concurrent desulfurization of a plurality of sulfur containing hydrocarbon fractions comprising the steps of:

(1) preparing a blend of 40-80% straight run naphtha with at least 4 of the 5 fractions listed below in an amount selected from the range set forth opposite the fraction, the total quantity of said fractions being 20-60% of the blend:

Quantity in total blend
(volume percent)

(a) Coker naphtha 1-10
(b) Steam cracked naphtha 0.5-15
(c) Catalytic gas oil 5-25
(d) Virgin gas oil 5-25
(e) Coker gas oil 5-25

(2) subjecting the blend to hydrodesulfurization at a temperature of 600-750° F., a pressure of 350-600 p.s.i.g., a space velocity of 0.5 to 5 v./hr./v., a hydrogen to blend ratio of 300 to 700 s.c.f./bbl. in the presence of a hydrogen-containing gas and a catalyst comprising a mixture of a member of the group consisting of Group VI oxides and sulfides with a member of the group consisting of iron, cobalt and nickel oxides and sulfides deposited upon a porous carrier,

(3) recovering the desulfurized blend,

(4) passing the desulfurized blend to a fractionating zone while maintaining the blend at a temperature above 300° F. and

(5) fractionating said blend to recover a gasoline fraction, a reformer feedstock fraction and a fuel oil fraction.

10. Process according to claim 9 in which the catalyst is cobalt molybdate on silica-alumina.

11. Process according to claim 9 in which the catalyst is nickel tungstate on alumina.

12. Process according to claim 9 in which the said blend has a boiling range of from about 50° F. to about 1200° F.

3,475,327

7

13. Process according to claim 9 in which the said blend has a boiling range of 85-750° F.

References Cited

UNITED STATES PATENTS

2,901,417 8/1959 Cook et al. ----- 208-211
2,958,654 11/1960 Honeycutt ----- 208-216

8

FOREIGN PATENTS

719,231 12/1954 England.

DELBERT E. GANTZ, Primary Examiner

5 G. J. CRASANAKIS, Assistant Examiner

U.S. Cl. X.R.

208-212, 216