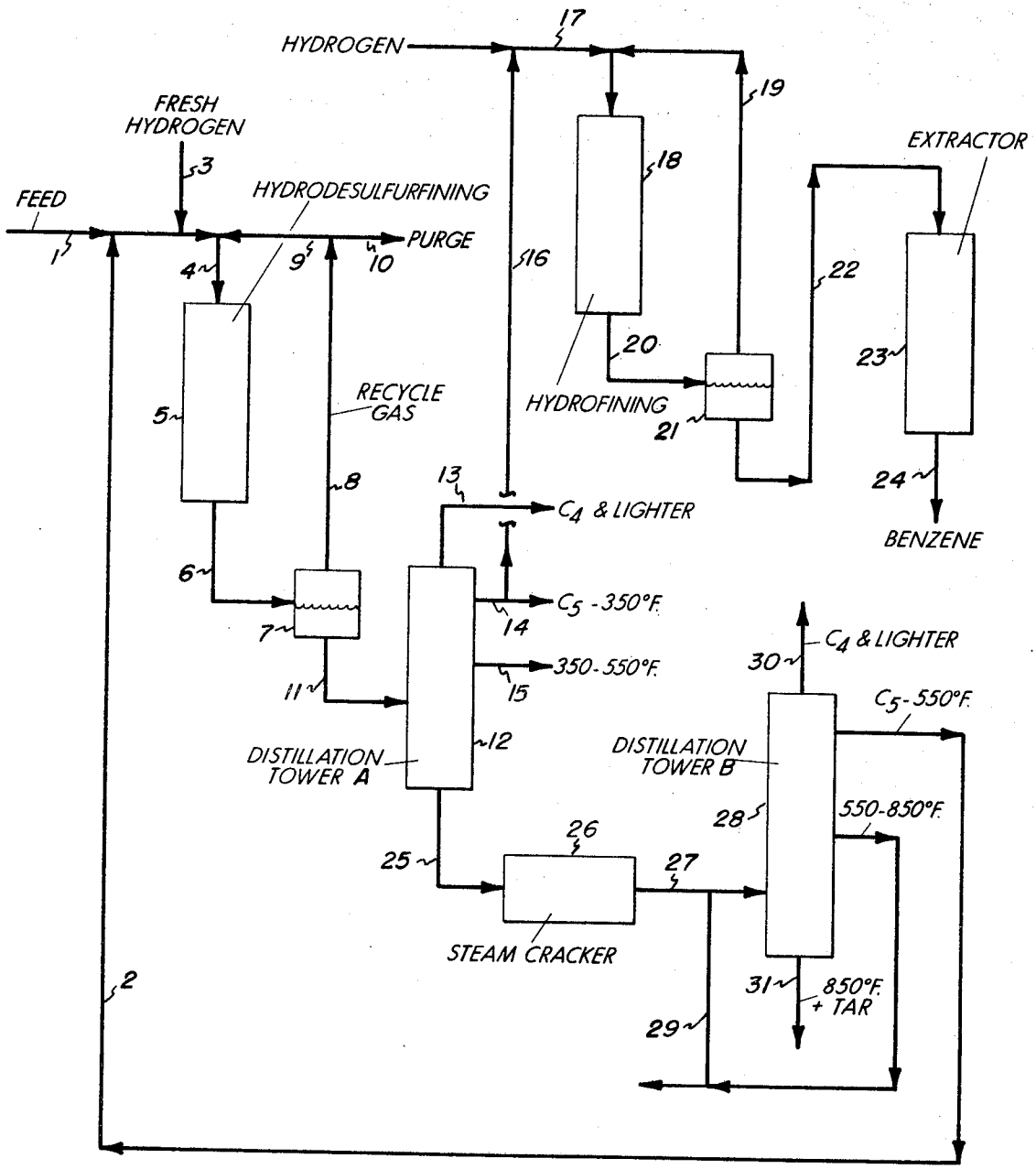
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INTEGRATED HYDROFINING, HYDRODESULFURIZATION AND STEAM CRACKING PROCESS

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INTEGRATED HYDROFINING, HYDRODESULFURIZATION AND STEAM CRACKING PROCESS

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ABSTRACT OF THE DISCLOSURE

In a single reaction zone a liquid petroleum steam cracking feed is hydrodesulfurized prior to steam cracking and an unstable, unsaturated steam cracker product fraction is simultaneously hydrofined.

This invention relates to an integrated steam cracking process. More particularly the invention relates to a process for steam cracking heavier petroleum feedstocks to produce ethylene and a plurality of coproducts ranging from propylene to tar.

The steam cracking process has traditionally been used to crack gases and light naphthas to produce the maximum quantity of ethylene. Recently refiners have been considering heavier feeds because of the market demand for such coproducts as propylene, stable steam cracker gasoline, and aromatic hydrocarbons, particularly benzene.

The use of heavier feeds such as gas oil as steam cracking feeds gives rise to a number of processing problems. For example many gas oils have a high sulfur content and the sulfur creates difficulties in the steam cracking step and in the use and further processing of steam cracker products. The liquid fractions from gas oil cracking contain diolefins, monoolefins and gum forming components which must be removed if the fractions are to be used as fuels or as feeds to benzene recovery processes.

I have found that many of these problems and difficulties can be mitigated or eliminated by means of an integrated process. Briefly summarizing the process involves the steps of hydrodesulfurfining a blend of a sulfur-containing liquid petroleum fraction and an ustable, unsaturated cracked fraction recovered from the subsequent steam cracking step, separating a stabilized fraction, recovering a bottoms fraction of substantially reduced sulfur content, steam cracking the bottoms fraction and recovering an unstable cracked fraction for recycle to the hydrodesulfurfining step.

Hydrodesulfurfining is a coined term in which the terms hydrofining and hydrodesulfurizing are combined. In this treatment step the sulfur-containing liquid petroleum fraction is hydrodesulfurized to render it suitable for steam cracking and concurrently the unstable cracked fraction is hydrofined (hydrogenated) to convert the diolefins to olefins and at least a part of the olefins to paraffinic hydrocarbons.

Further details of the process will be described below with reference to the drawing which is a flow sheet illustrating a preferred embodiment of the invention.

The sulfur-containing liquid petroleum component of the feed to the process is a petroleum fraction boiling in the range of from about 350 to about 1000° F., containing from about 0.1 to 3.0 wt. percent sulfur. A major amount, i.e., 60–95 vol. percent of this material is used in preparing the blended feed to the hydrosulfurfining step. Specific materials include naphtha fractions, kerosene, virgin gas oils, cracked gas oils, and blends of these fractions. The preferred feed component is a virgin gas oil

having a boiling range of 500–1000° F. Inspections of some typical gas oils are set forth below in Table 1.

TABLE 1.—TYPICAL GAS OIL FEEDSTOCKS

	A*	B*	C
ASTM Atmospheric Distillation, ° F.			
IBP	577	598	524
5%	691	706	------
10%	716	732	586
20%	742	756	------
30%	761	771	------
40%	784	781	------
50%	800	798	614
60%	818	814	------
70%	842	830	------
80%	871	846	------
90%	907	871	656
95%	932	888	666
FBP	992	945	676
Sulfur, Wt. percent	0.33	2.73	1.73
Gravity, ° API	26.7	22.9	30.4
Conradson Carbon Residue, Wt. percent	0.11	0.09	0.05
Conradson Carbon Residue on 10% Bottoms, wt. percent	0.99	1.30	------
Type Analysis, Wt. percent:			
Paraffin+Naphthenes	66.8	48.8	75
Aromatics	32.9	51.0	25

*10 mm. distillation converted to atmospheric equivalent.

Referring to the drawing, a major amount of a gas oil is blended in line **1** with a minor amount of a C_5–550° F. boiling range steam cracked fraction from recycle line **2**. The boiling range of the recycle fraction is intended to be exemplary for this particular embodiment. A narrow or wider boiling range cut can be used. The recycle fraction is an unstable, unsaturated material containing 5.0–25.0 wt. percent diolefins, 5–50 wt. percent olefins and 5–50 wt. percent aromatics. The bromine number (ASTM D–1159) of this fraction is usually greater than 50, but it can range from 30–140. As a narrow cut boiling in the range of C_5–350° F. the fraction is known as steam cracked naphtha. The blend is heated to a temperature in the range of 400 to 700° F. Fresh makeup hydrogen is added to the blend from line **3**. The reaction mixture is passed by line **4** into hydrodesulfurfining zone **5** for liquid phase contacting with a suitable catalyst. Suitable reaction conditions are set forth below in Table 2.

TABLE 2.—HYDRODESULFURFINING CONDITIONS

	Broad Range	Preferred Range
Temperature, ° F	450–750	500–700
Pressure, p.s.i.g	200–1500	400–1000
LHSV, v./v./hr.	0.2–5.0	0.5–2.0
H_2/Oil Ratio, s.c.f./b	1,000–10,000	2,000–5,000

Conditions are adjusted in accordance with the characteristics of the individual components of the feed blend; however, in all cases cracking conditions are avoided. The object of the treatment is to hydrofine the cracked fraction without forming polymers from the unstable components and to simultaneously desulfurize the material which will be steam cracked.

Suitable hydrodesulfurfining catalysts comprise a hydrogenating component in which the metal is selected from the group consisting of Groups VI–B and VIII–B of the Periodic Table and mixtures of these metals, preferably distended on a support material. Such metals as platinum, palladium, nickel, tungsten, cobalt and molybdenum are effective hydrogenating components and they are used in elemental form or as salts such as oxides, sulfates, nitrates, etc. Specific examples include reduced nickel, nickel tungstate, nickel molybdate, and cobalt molybdate. Suitable supports include alumina, clays, bauxite, kieselguhr, molecular sieves, silica promoted alumina having a silica content of 0.1 to 8.0 wt. percent, silica promoted magnesia, charcoal, etc. The catalyst is preferably sulfided prior to use or in situ with H_2S or CS_2. The preferred catalysts are sulfided cobalt molybdate on silica stabilized alumina and sulfided nickel molybdate on alumina.

Effluent from reaction zone **5** is passed by line **6** to high pressure separator **7**. Recycle gas comprising hydrogen

id H_2S is recycled via lines **8** and **9**. When required, a irge gas stream is removed by line **10**. The gas flow managed so that the treat gas in reactor **5** contains)–100% hydrogen. A liquid stream is passed by line **11** a separation zone such as distillation tower A desig-ted by reference numeral **12**. In this embodiment four actions are recovered from the separation zone; how-er, any desired number of fractions can be recovered th cut points established to conform with the require-ents of subsequent treating steps and the type of prod-ts desired.

A C_4 and lighter gas and vapor stream is recovered line **13**. A C_5–350° F. naphtha fraction from gas ending is recovered by line **14**. A middle distillate frac-n boiling in the range of 350–550° F. is recovered by e **15**. When the naphtha fraction in line **14** contains a fficient quantity of aromatic hydrocarbons it may be sirable to further treat the fraction to recover aro-tics. In this variation of the process the naphtha frac-n is further hydrogenated if necessary to saturate the fins and then solvent extracted to separate benzene, uene and xylene from the paraffinic materials. The uration of the olefins can be done by catalytic hydro-ating or by reforming. In this particular embodiment naphtha is passed by lines **16** and **17** to hydrogenation ne **18**. If the olefin content of the fraction is low enough s step may be eliminated and the fraction can be sed directly to solvent extraction, but this is not usually case. Fresh hydrogen from line **17** and recycle hydro-from line **19** are mixed with the naphtha and the ction mixture is passed through reactor **18** in contact h a suitable hydrogenation catalyst. Catalysts like se mentioned previously in connection with the hy-desulfurfining step can be used for the saturation type lrogen step in reactor **18**. Preferred catalysts are nickel, tinum, palladium, cobalt molybdenum and mixtures these metals on a suitable support material such as mina or silica alumina. Typical hydrogenation condi-ns are set forth below in Table 3.

TABLE 3

	Broad Range	Preferred Range
perature, ° f.	200–700	400–650
ssure, p.s.i.g.	200–1000	400–800
SV, v./v./hr.	0.5–5.0	1–2
Oil Ratio, s.c.f./b.	500–5,000	1,000–2,500

he saturated naphtha fraction now containing paraf- and naphthenes and 15 to 75 vol. percent aromatic lrocarbons is passed by line **20** to high pressure separa-**21**. Recycle treat gas is passed to reactor **18** by line The liquid fraction is passed by line **22** to solvent ex-tion zone **23**. Extraction is carried out at conventional ditions with solvents selective for aromatics such as ylene glycols, dimethyl-sulfoxide and sulfolane. Udex raction with a mixture of alkylene glycols and water he preferred extraction technique. An aromatic prod-such as benzene is recovered by line **24**.

Returning to distillation tower A of the drawing at bot-s fraction for steam cracking is removed from the er by line **25**, and passed to steam cracking zone **26**. onventional steam cracking reaction is carried out on 550° F.+ bottoms fraction in zone **26**. Typical stem cking conditions are set forth below in Table 4.

TABLE 4.—STEAM CRACKING CONDITIONS

	Broad Range	Preferred Range
perature, ° f.	1,150–1,500	1,200–1,400
sure, p.s.i.g.	0.5–50	5–15
e, sec.	0.05–1.0	0.1–0.5
m, Mol. percent	20–150	50–100

team cracker effluent is removed from the reactor by **27** and passed to distillation tower B designated by

reference numeral **28**. The effluent is quenched with an oil recycled by line **29** from the distillation tower. A C_4 and lighter fraction is recovered from tower **28** by line **30** and ethylene is recovered from the fraction by means not shown. In this embodiment a C_5–550° F. fraction characterized by olefinic unsaturation is recovered by line **2** for blending with the gas oil component of the process feed. A part of the 550–850° F. fraction recovered by line **29** can be recovered from the process. This material is a suitable feed for making carbon black. A bottoms fraction comprising material boiling above 850° F. is recovered from the process by line **31** and this tar is suitable for use as a binder oil in the preparation of carbon electrodes or as a premium feed to a coker.

It should be understood that the fractionation of the steam cracker products can be conducted in any manner consistent with the characteristics of the feed to the process and the end use requirements of the products. For example if the feed to the process is a sulfur containing kerosene fraction and it is desired to obtain a maximum quantity of motor gasoline from the coproduct fraction recycled by line **2** for blending, conditions throughout the process would be adjusted to that end. By the same token, if the feed to the process is a relatively high sulfur gas oil and it is desired to obtain a maximum quantity of benzene from the coproduct recycled by line **2** for blending, process conditions would be adjusted for this feed and this product.

EXAMPLE

A 100–1000° F. Kuwait virgin gas oil containing 2.73 wt. percent sulfur is combined with a C_5–550° F. steam cracked fraction in a 80/20 weight ratio, respectively. The 20% stem cracked fraction is produced from the steam cracking step of the hydrodesulfurized gas oil feed. To the above blend hydrogen is added at the rate of 5000 s.c.f. H_2/bbl. with the hydrogen stream being 25% fresh hydrogen and 75% recycle hydrogen. The combined gas oil, steam cracked fraction and hydrogen mixture is heated to 450° F. prior to introduction to the hydrodesulfurfining reactor. The hydrodesulfurfiner reactor is charged with a sulfided NiMo alumina catalyst and process conditions of 450–550° F., 800 p.s.i.g. and 1.0 v./v./hr. are maintained in order to separate at least 50% of the suflur present in the gas oil feed.

The hydrodesulfurfining product is then freed of hydrogen treat gas for recycle and the liquid product is fed to tower A to remove all traces of C_4 and lighter gases containing H_2S, to recover a sweetened saturated naphtha, fraction for utilization in the motor gasoline pool, to recover a sweetened stabilized middle distillate for prime fuel utilization and the desulfurized gas oil feed is then fed to a steam cracker. The gas oil feed is steam cracked at 1365° F., 8 p.s.i.g. with 90 mole percent steam at an average contact time of 0.28 second. At this condition 36.7 wt. percent C_3 and lighter, 10.3 wt. percent C_4's, 12 wt. percent C_5–430° F. fraction, 6% 430–550° F. fraction and 31 wt. percent 550° F.+ fraction is produced.

The steam cracker effluent is quenched with cycle oil to approximately 800° F. and is fed to tower B and the subsequent recovery system to recover the above steam cracked products. The C_5–550° F. fraction is recycled for admixture with the original gas oil feed for processing in the hydrodesulfurfiner unit and ultimate recovery as finished products from tower A.

The low sulfur 550–850° F. steam cracker product from tower B may be utilized as specialty product (rubber extender oil) or carbon black feed stock and the low sulfur 850° F.+tar from tower B may be utilized as a binder oil and/or premium coker feedstocks.

The foregoing description and example demonstrate the effectiveness of the process as a means of steam cracking heavy oils and recovering useful coproducts in addition to ethylene.

What is claimed is:

1. An integrated steam cracking process comprising the steps of:

(a) mixing a hydrogen-containing gas with a blend of sulfur-containing liquid petroleum feed boiling in the range of from about 350° to 1000° F. and an unstable, unsaturated cracked fraction recovered from steam cracking,

(b) subjecting the blend to simultaneous hydrofining and hydrodesulfurization conditions concurrently in a single reaction zone, in the liquid phase at a temperature in the range of 450–750° F. and a pressure in the range of 200–1500 p.s.i.g., and in the presence of said hydrogen-containing gas and a catalyst comprising a hydrogenating component in which the metal is selected from the group consisting of Group VI–B metals, Group VIII–B metals and mixtures of Group VI–B and Group VIII–B metals distended on a suitable support material,

(c) recovering a recycle gas fraction from the treated mixture,

(d) fractionating the treated blend to recover a stable fraction having a substantially reduced content of unsaturated materials and a bottoms fraction of substantially reduced sulfur content,

(e) steam cracking said bottoms fraction,

(f) recovering an unstable, unsaturated cracked fraction from the steam cracker products.

(g) and passing the cracked fraction to step (a) for blending with said feed.

2. An integrated steam cracking process comprising the steps of:

(a) mixing a hydrogen-containing treat gas with a blend of a sulfur-containing gas oil boiling in the range of 400 to 1000° F. and a cracked fraction recovered from the steam cracking step of the process, said cracked fraction container diolefins, olefins and aromatics and having a bromine number greater than 50,

(b) subjecting the blend to simultaneous hydrofining and hydrodesulfurization in the liquid phase at a temperature in the range of 450–750° F. and a pressure in the range of 200–1500 p.s.i.g. in the presence of said hydrogen-containing treat gas and a catalyst comprising a hydrogenating component in which the metal is selected from the group consisting of Group VI–B metals, Group VIII–B metals and mixtures of Group VI–B and Group VIII–B metals distended on a suitable support material,

(c) separating a recycle treat gas fraction from the liquid products of step (b),

(d) distilling the liquid products of step (b) to recover a stable fraction substantially free of diolefins and having a reduced olefins content and a bottoms fraction of substantially reduced sulfur content,

(e) steam cracking said bottoms fraction at a temperature of 1150–1500 ° F. in the presence of 20–150 mol. percent steam,

(f) recovering a cracked fraction from the products of step (e) having bromine number greater than 50,

(g) and passing the cracked fraction to step (a) for blending with said gas oil.

3. Process according to claim 2 in which the gas-oil is a virgin gas oil.

4. Process according to claim 2 in which the gas oil boils in the range of 400 to 1000° F.

5. Process according to claim 2 in which the cracked naptha fraction boils in the range of 100 to 350° F.

6. Process according to claim 2 in which the catalyst is cobalt molybdate on silica stabilized alumina.

7. Process according to claim 2 in which the catalyst is nickel molybdate on alumina.

8. Process according to claim 2 in which the bottoms fraction subjected to steam cracking boils in the ranges of 350 to 1000° F.

9. An integrated steam cracking process comprising the steps of:

(a) a mixing a treat gas containing 70–100% hydrogen with a blend of a virgin gas oil containing 0.1 to 3.0 wt. percent sulfur and a steam cracked naphtha fraction having a bromine number of 30–140,

(b) subjecting the blend to simultaneous hydrofining and hydrodesulfurizing concurrently in a single reaction zone, in essentially liquid phase at a temperature in the range of 450–750° F. and a pressure in the range of 200–1500 p.s.i.g. in the presence of said treat gas and a catalyst comprising a hydrogenating component selected from the group consisting of sulfided cobalt molybdate and sulfided nickel molybdate distended on a support comprising alumina,

(c) distilling the liquid products of step (b) to recover a stable fraction substantially free of diolefins and having a reduced olefin content and a bottoms fraction of substantially reduced sulfur content,

(d) further hydrofining said stable fraction at catalytic hydrogenation conditions whereby essentially all the olefins in the fraction are converted to paraffins,

(e) contacting the treated fraction of step (d) with a solvent selective for aromatic hydrocarbons,

(f) recovering an aromatic hydrocarbon fraction,

(g) steam cracking the bottoms fraction of step (c),

(h) recovering a steam cracked naphtha fraction from the steam cracker effluent,

(i) and recycling the steam cracked naphtha fraction to step (a) for blending with the virgin gas oil.

10. Process according to claim 9 in which process conditions are adjusted to maximize the recovery of a maximum quantity of benzene from step (e).

References Cited

UNITED STATES PATENTS

3,024,188	3/1962	Yeo et al.	208—264
3,113,097	12/1963	White et al.	208—255
3,190,830	6/1965	Rowland et al.	208—255
3,239,449	3/1966	Graven et al.	208—143
3,281,351	10/1966	Gilliland et al.	208—67
3,340,178	9/1967	Hornaday et al.	208—89

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