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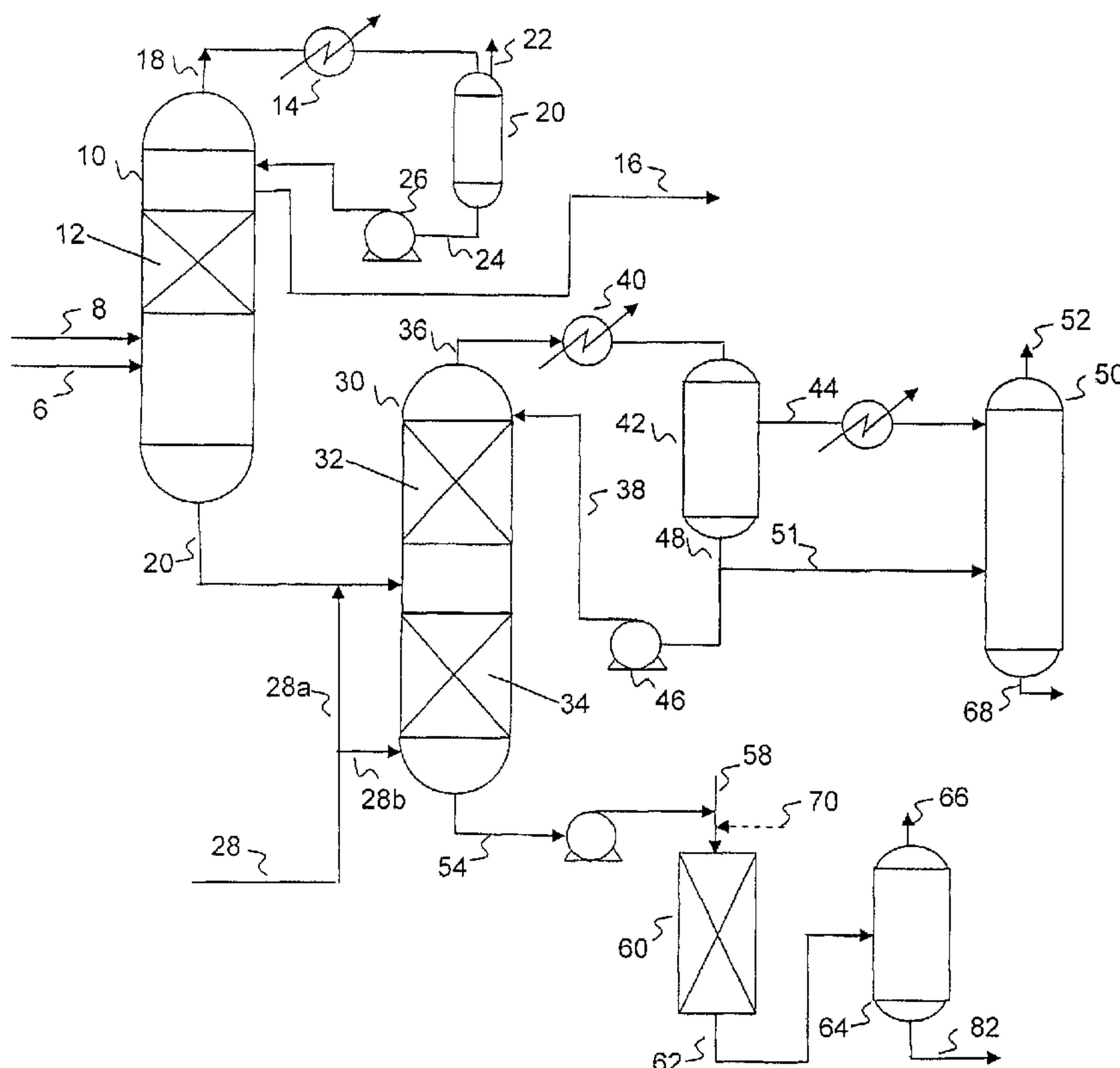
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CATALYTIQUE DU FLUIDE)

(54) Title: SELECTIVE DESULFURIZATION OF FCC GASOLINE



(57) Abrégé/Abstract:

Processes for the desulfurization of high end point naphtha, such as naphtha fractions having an ASTM D-86 end point of greater than 450°F, greater than 500°F, or greater than 550°F, and containing hindered sulfur compounds, are disclosed.



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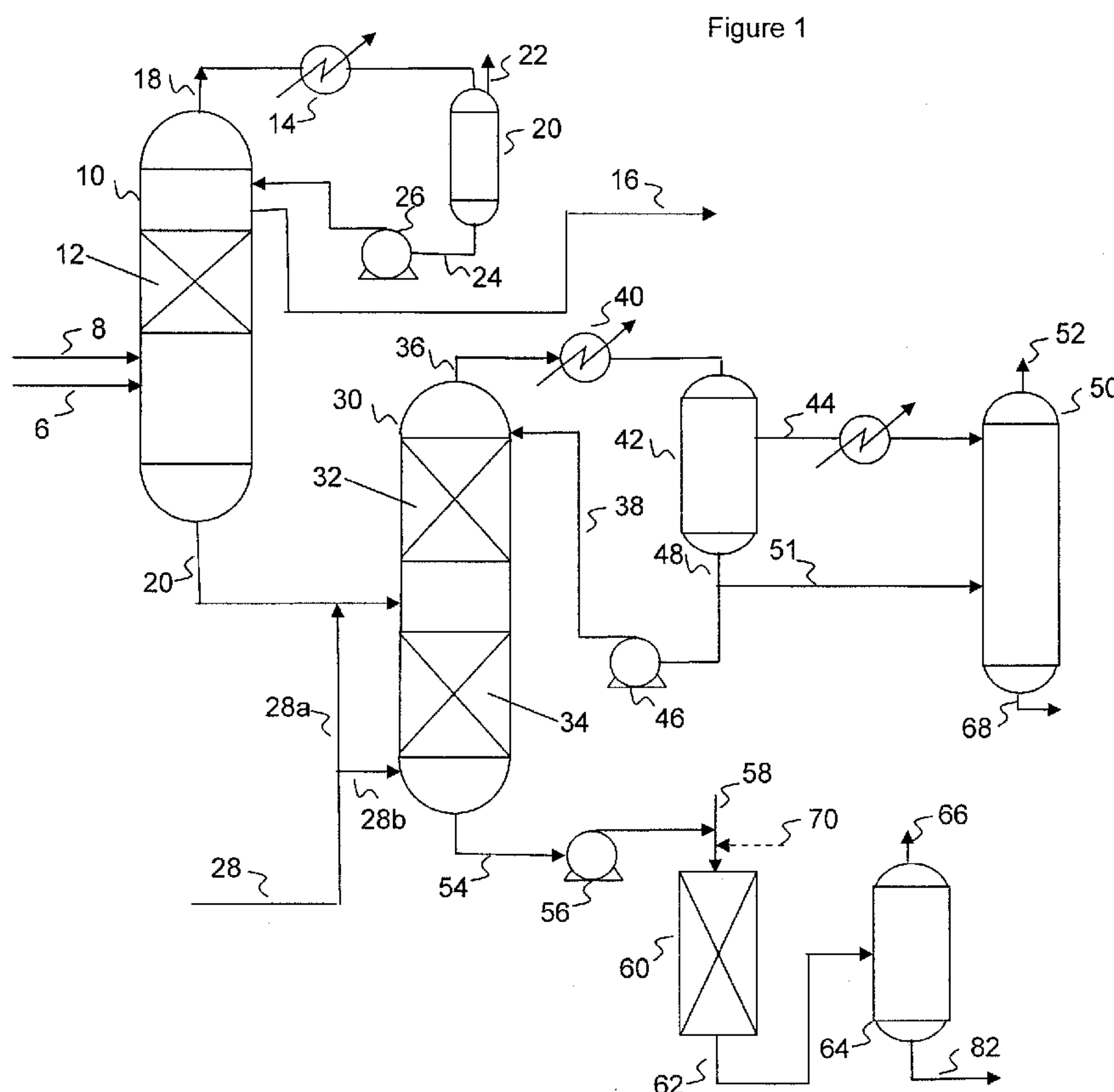
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(54) Title: SELECTIVE DESULFURIZATION OF FCC GASOLINE



(57) Abstract: Processes for the desulfurization of high end point naphtha, such as naphtha fractions having an ASTM D-86 end point of greater than 450°F, greater than 500°F, or greater than 550°F, and containing hindered sulfur compounds, are disclosed.

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SELECTIVE DESULFURIZATION OF FCC GASOLINE

FIELD OF THE DISCLOSURE

[0001] Embodiments disclosed herein generally relate to processes for the desulfurization of gasoline fractions, such as FCC naphtha, having a high ASTM D86 end point. More particularly, embodiments disclosed herein relate to processes for the desulfurization of high end point naphthas to produce gasoline fractions having a total sulfur content of less than 20 ppm, by weight. In some embodiments, the total sulfur content of the gasoline fraction may be less than 10 ppm, by weight. Other embodiments disclosed herein may additionally provide for control of the end point of the gasoline product.

BACKGROUND

[0002] Petroleum distillate streams contain a variety of organic chemical components. Generally the streams are defined by their boiling ranges, which determines the composition. The processing of the streams also affects the composition. For instance, products from either catalytic cracking or thermal cracking processes contain high concentrations of olefinic hydrocarbons (alkenes, alkynes, and polyunsaturated compounds such as diolefins) as well as saturated hydrocarbons (alkanes). Additionally, these components may be any of the various isomers of the compounds.

[0003] The composition of untreated naphtha as it comes from the crude still, or straight run naphtha, is primarily influenced by the crude source. Naphthas from paraffinic crude sources have more saturated straight chain or cyclic compounds. As a general rule most of the "sweet" (low sulfur) crudes and naphthas are paraffinic. The naphthenic crudes contain more unsaturated and cyclic and polycyclic compounds. The higher sulfur content crudes tend to be naphthenic. Treatment of the different straight run naphthas may be slightly different depending upon their composition due to crude source. FCC gasoline is the product of catalytic cracking and is also referred to as catalytically cracked naphtha, which may be further processed. Cracked gasolines, especially catalytically cracked gasolines, ordinarily have a sufficiently high octane, and one of the most important objectives in refining these involves the removal of sulfur compounds.

- [0004]** Reformed naphtha or reformat generally requires no further treatment except perhaps distillation or solvent extraction for valuable aromatic product removal. Reformed naphthas have essentially no sulfur contaminants due to the severity of their pretreatment for the process and the process itself.
- [0005]** Cracked naphtha as it comes from the catalytic cracker has a relatively high octane number as a result of the olefinic and aromatic compounds contained therein. In some cases this fraction may contribute as much as half of the gasoline in the refinery pool together with a significant portion of the octane. Although olefin concentration in gasoline increases the octane number, olefins are often limited in their concentration in gasoline as they are a known contributor to smog formation. An attractive alternative to increased olefin content is the addition of alcohols to the gasoline product to raise the octane number. Alcohols such as methanol and ethanol can be used as additives.
- [0006]** Catalytically cracked naphtha (gasoline boiling range material) currently forms a significant part ($> 1/3$) of the gasoline product pool in the United States and it provides the largest portion of the sulfur. The sulfur impurities may require removal, usually by hydrotreating, in order to comply with product specifications or to ensure compliance with environmental regulations. Some users require the sulfur of the final product to be below 50 ppm or at or below 10 ppm.
- [0007]** Various processes for the desulfurization of gasoline boiling range hydrocarbon fractions may include U.S. Patent Nos. 5,510,568, 5,595,634, 5,779,883, 5,597,476, 5,837,130, 6,083,378, 6,946,068, 6,592,750, 6,303,020, 6,413,413, 6,338,793, 6,503,864, 6,495,030, 6,444,118, 6,824,676, 7,351,327, 7,291,258, 7,153,415, 6,984,312, and 7,431,827, among others.
- [0008]** High end point FCC gasoline typically has a higher sulfur concentration than normal boiling range catalytically cracked gasoline, requiring a higher conversion of the sulfur compounds to meet the sulfur requirements. However, due to a higher concentration of multi-substituted benzothiophenes (versus methylbenzothiophenes in normal boiling range catalytically cracked gasoline), hydrotreating high end point naphthas becomes more challenging. This is due to the fact that sulfur atoms in multi-

substituted benzothiophenes are more hindered and slower to react with hydrogen than the sulfur atoms in methylbenzothiophenes.

[0009] In addition to supplying high octane blending components, the cracked naphthas are often used as sources of olefins in other processes such as etherifications, oligomerizations and alkylations. The conditions of hydrotreating of the naphtha fraction to remove sulfur will also saturate some of the olefinic compounds in the fraction, reducing the octane and causing a loss of source olefins. Severe operating conditions typically used to remove sulfur from high end point fractions may cause an excessive loss of olefins.

[0010] Accordingly, there exists a need for processes for the hydrodesulfurization of high end point FCC gasoline, including processes which preserve, to an extent, the olefinic content of the naphtha, minimizing olefins lost to hydrogenation and recombinant mercaptan formation during the processing of the naphtha.

SUMMARY OF CLAIMED EMBODIMENTS

[0010a] Certain exemplary embodiments provide a process for the desulfurization of a high end point sulfur-containing petroleum fraction comprising the steps of: (a) feeding (1) a sulfur-containing petroleum fraction containing C5 hydrocarbons, olefins, diolefins, mercaptans, other organic sulfur compounds, and hindered sulfur compounds and having an ASTM D86 end boiling point of at least 450°F, and (2) hydrogen to a first distillation column reactor, wherein the hydrogen is fed to the first distillation column reactor at a rate of 10 to 1000 scf/bbl of the sulfur-containing petroleum fraction; (b) concurrently in the first distillation column reactor, (i) contacting the diolefins and the mercaptans in the presence of a Group VIII metal catalyst in the rectification section of the first distillation column reactor, at a temperature in the range of 260°F to 400°F, a pressure in the range of 75 to 300 psig, and a WHSV in the range of 1 to 5, thereby reacting: (A) a portion of the mercaptans with a portion of the diolefins to form thioethers, and/or (B) a portion of the dienes with a portion of the hydrogen to form olefins; and (ii) fractionating the sulfur-containing petroleum fraction into (A) a distillate product containing C5 hydrocarbons having a total sulfur content of less than 10 ppm S, by weight and (B) a first heavy

fraction containing C7+ hydrocarbons, sulfur compounds, and hindered sulfur compounds; (c) recovering the first heavy fraction from the first distillation column reactor as a first bottoms; (d) feeding the first bottoms and hydrogen to a second distillation column reactor, wherein the hydrogen is fed to the second distillation column reactor at a rate of 10 to 1000 scf/bbl of the sulfur-containing petroleum fraction; (e) concurrently in the second distillation column reactor, (i) reacting at least a portion of the organic sulfur compounds in the first bottoms with hydrogen in the presence of a hydrodesulfurization catalyst in the rectification section of the second distillation column reactor at a temperature in the range of 300°F to 700°F, a pressure in the range of 75 to 300 psig, and a WHSV in the range of 1 to 5, to convert a portion of the other organic sulfur compounds to hydrogen sulfide, and (ii) separating the first heavy fraction into a first intermediate fraction having an ASTM D86 end point in the range from 270°F to 400°F and a second heavy fraction; (f) recovering the first intermediate fraction, unreacted hydrogen, and hydrogen sulfide from the second distillation column reactor as a second overheads, where a total sulfur content in the first intermediate fraction is in the range from about 50 ppm S to about 100 ppm S, by weight; (g) recovering the second heavy fraction containing the hindered organic sulfur compounds from the second distillation column reactor as a second bottoms; (h) feeding the second bottoms and hydrogen to a first fixed bed reactor containing a hydrodesulfurization catalyst; (i) contacting the second bottoms and hydrogen with the hydrodesulfurization catalyst in the first fixed bed reactor at a temperature in the range of 500°F to 700°F, a pressure in the range of 50 to 500 psig, a hydrogen partial pressure in the range of 25 psi to about 350 psi, and a WHSV in the range of 0.5 to 10 to convert at least a portion of the hindered organic sulfur compounds to hydrogen sulfide; (j) recovering an effluent from the first fixed bed; (k) separating unreacted hydrogen and hydrogen sulfide from the effluent from the first fixed bed reactor to recover a desulfurized heavy fraction having a total sulfur content of less than 50 ppm S, by weight; (l) separating unreacted hydrogen and hydrogen sulfide from the second overheads; (m) feeding at least a portion of the second overheads and hydrogen to a second fixed bed reactor containing a hydrodesulfurization catalyst at a temperature in the range of 400°F to 600°F, a pressure in the range of 50 to 350 psig, and a WHSV in the range of 5 to 10 to convert at least a portion of the sulfur

compounds in the second overheads to hydrogen sulfide; (n) recovering an effluent from the second fixed bed reactor; (o) separating at least a portion of the hydrogen sulfide from the effluent from the second fixed bed reactor to form a desulfurized intermediate fraction having a total sulfur content of less than 50 ppm S, by weight; wherein a combined olefin content of the distillate product, the desulfurized heavy fraction, and the desulfurized intermediate fraction is at least 60% of the olefin content of the sulfur-containing petroleum fraction.

[0011] In one aspect, embodiments disclosed herein relate to a process for the desulfurization of a full boiling range catalytically cracked naphtha including the steps of: (a) feeding (1) a full boiling range naphtha containing olefins, diolefins, mercaptans and other organic sulfur compounds and having an ASTM D86 end boiling point of at least 350°F, and (2) hydrogen to a first distillation column reactor; (b) concurrently in the first distillation column reactor, (i) contacting the diolefins and the mercaptans in the full boiling range naphtha in the presence of a Group VIII metal catalyst in the rectification section of the first distillation column reactor thereby reacting: (A) a portion of the mercaptans with a portion of the diolefins to form thioethers, and/or (B) a portion of the dienes with a portion of the hydrogen to form olefins; and (ii) fractionating the full boiling range cracked naphtha into a distillate product containing C5 hydrocarbons and a first heavy naphtha containing sulfur compounds; (c) recovering the first heavy naphtha from the first distillation column reactor as a first bottoms; (d) feeding the first bottoms and hydrogen to a second distillation column reactor; (e) concurrently in the second distillation column reactor, (i) reacting at least a portion of the organic sulfur compounds in the first bottoms with hydrogen in the presence of a hydrodesulfurization catalyst in the rectification section

of the second distillation column reactor to convert a portion of the other organic sulfur compounds to hydrogen sulfide, and (ii) separating the first heavy naphtha into a first intermediate naphtha having an ASTM D86 end point in the range from 270°F to 400°F and a second heavy naphtha; (f) recovering the first intermediate naphtha, unreacted hydrogen, and hydrogen sulfide from the second distillation column reactor as a second overheads; (g) recovering the second heavy naphtha containing hindered organic sulfur compounds from the second distillation column reactor as a second bottoms; (h) feeding the second bottoms and hydrogen to a first fixed bed reactor containing a hydrodesulfurization catalyst; (i) contacting the hindered organic sulfur compounds and hydrogen with the hydrodesulfurization catalyst in the first fixed bed reactor to convert at least a portion of the hindered organic sulfur compounds to hydrogen sulfide; and (j) recovering an effluent from the first fixed bed reactor. In some embodiments, the second bottoms may be combined with a diesel hydrocarbon fraction for processing in the first fixed bed reactor.

[0012] In another aspect, embodiments disclosed herein relate to a process for the desulfurization of a full boiling range catalytically cracked naphtha including the steps of:

- (a) feeding (1) a full boiling range naphtha containing olefins, diolefins, mercaptans and other organic sulfur compounds and having an ASTM D86 end boiling point of at least 350°F, and (2) hydrogen to a first distillation column reactor;
- (b) concurrently in the first distillation column reactor,
 - (i) contacting the diolefins and the mercaptans in the full boiling range naphtha in the presence of a Group VIII metal catalyst in the rectification section of the first distillation column reactor thereby reacting:
 - (A) a portion of the mercaptans with a portion of the diolefins to form thioethers, and/or
 - (B) a portion of the dienes with a portion of the hydrogen to form olefins; and
 - (ii) fractionating the full boiling range cracked naphtha into a distillate product containing C5 hydrocarbons and a first heavy naphtha containing sulfur compounds;

- (c) recovering the first heavy naphtha from the first distillation column reactor as a first bottoms;
- (d) feeding the first bottoms and hydrogen to a second distillation column reactor;
- (e) concurrently in the second distillation column reactor,
 - (i) reacting at least a portion of the organic sulfur compounds in the first bottoms with hydrogen in the presence of a hydrodesulfurization catalyst in the rectification section of the second distillation column reactor to convert a portion of the other organic sulfur compounds to hydrogen sulfide, and
 - (ii) separating the first heavy naphtha into a first intermediate naphtha having an ASTM D86 end point in the range from 270°F to 400°F and a second heavy naphtha;
- (f) recovering the first intermediate naphtha, unreacted hydrogen, and hydrogen sulfide from the second distillation column reactor as a second overheads;
- (g) recovering the second heavy naphtha containing hindered organic sulfur compounds from the second distillation column reactor as a second bottoms;
- (h) feeding the second bottoms and hydrogen to a first fixed bed reactor containing a hydrodesulfurization catalyst;
- (i) contacting the hindered organic sulfur compounds and hydrogen with the hydrodesulfurization catalyst in the first fixed bed reactor to convert at least a portion of the hindered organic sulfur compounds to hydrogen sulfide;
- (j) recovering an effluent from the first fixed bed reactor;
- (k) separating unreacted hydrogen and hydrogen sulfide from the effluent from the first fixed bed reactor;
- (l) separating unreacted hydrogen and hydrogen sulfide from the second overheads;
- (m) feeding at least a portion of the second overheads and hydrogen to a second fixed bed reactor containing a hydrodesulfurization catalyst to convert at least a portion of the sulfur compounds in the second overheads to hydrogen sulfide;
- (n) recovering an effluent from the second fixed bed reactor;
- (o) separating at least a portion of the hydrogen sulfide from the effluent from the second fixed bed reactor to form a naphtha fraction having a reduced sulfur content.

[0013] In another aspect, embodiments disclosed herein relate to a process for the desulfurization of a full boiling range catalytically cracked naphtha including the steps of:

- (a) feeding (1) a full boiling range naphtha containing olefins, diolefins, mercaptans and other organic sulfur compounds and having an ASTM D86 end boiling point of at least 350°F, and (2) hydrogen to a first distillation column reactor;
- (b) concurrently in the first distillation column reactor,
 - (i) contacting the diolefins and the mercaptans in the full boiling range naphtha in the presence of a Group VIII metal catalyst in the rectification section of the first distillation column reactor thereby reacting:
 - (A) a portion of the mercaptans with a portion of the diolefins to form thioethers, and/or
 - (B) a portion of the dienes with a portion of the hydrogen to form olefins; and
 - (ii) fractionating the full boiling range cracked naphtha into a distillate product containing C5 hydrocarbons and a first heavy naphtha containing sulfur compounds;
- (c) recovering the first heavy naphtha from the first distillation column reactor as a first bottoms;
- (d) feeding the first bottoms and hydrogen to a second distillation column reactor;
- (e) concurrently in the second distillation column reactor,
 - (i) reacting at least a portion of the organic sulfur compounds in the first bottoms with hydrogen in the presence of a hydrodesulfurization catalyst in the rectification section of the second distillation column reactor to convert a portion of the other organic sulfur compounds to hydrogen sulfide, and
 - (ii) separating the first heavy naphtha into a first intermediate naphtha having an ASTM D86 end point in the range from 270°F to 400°F and a second heavy naphtha;
- (f) recovering the first intermediate naphtha, unreacted hydrogen, and hydrogen sulfide from the second distillation column reactor as a second overheads;
- (g) recovering the second heavy naphtha containing hindered organic sulfur compounds from the second distillation column reactor as a second bottoms;

- (h) feeding the second bottoms and hydrogen to a first fixed bed reactor containing a hydrodesulfurization catalyst;
- (i) contacting the hindered organic sulfur compounds and hydrogen with the hydrodesulfurization catalyst in the first fixed bed reactor to convert at least a portion of the hindered organic sulfur compounds to hydrogen sulfide;
- (j) recovering an effluent from the first fixed bed reactor;
- (k) separating unreacted hydrogen and hydrogen sulfide from the effluent from the first fixed bed reactor;
- (l) partially condensing the second overheads and separating the uncondensed portion of the second overheads including unreacted hydrogen and hydrogen sulfide from the condensed portion of the second overheads;
- (m) feeding at least a portion of the condensed portion of the second overheads to the second distillation column reactor as reflux;
- (n) feeding the separated effluent (k), the uncondensed portion of the second overheads, and at least a portion of the condensed second overheads to a fractionation column for separating unreacted hydrogen and hydrogen sulfide and to recover a bottoms hydrocarbon fraction;
- (o) feeding the bottoms hydrocarbon fraction and hydrogen to a second fixed bed reactor containing a hydrodesulfurization catalyst to convert at least a portion of the sulfur compounds in the bottoms hydrocarbon fraction to hydrogen sulfide;
- (p) recovering an effluent from the second fixed bed reactor;
- (q) separating at least a portion of the hydrogen sulfide from the effluent from the second fixed bed reactor to form a naphtha fraction having a reduced sulfur content; and
- (r) forming a gasoline from one or more of (i) at least a portion of the naphtha fraction and (ii) at least a portion of the distillate fraction, wherein the gasoline has a total sulfur content of less than about 20 ppm S, by weight.

[0014] In another aspect, embodiments disclosed herein relate to a process for the desulfurization of a full boiling range naphtha including the steps of:

- (a) feeding (1) a full boiling range naphtha containing olefins, diolefins, mercaptans and other organic sulfur compounds and having an ASTM D86 end boiling point of at least 350°F, and (2) hydrogen to a first distillation column reactor;

- (b) concurrently in the first distillation column reactor,
 - (i) contacting the diolefins and the mercaptans in the full boiling range naphtha in the presence of a Group VIII metal catalyst in the rectification section of the first distillation column reactor thereby reacting:
 - (A) a portion of the mercaptans with a portion of the diolefins to form thioethers, and/or
 - (C) a portion of the dienes with a portion of the hydrogen to form olefins; and
 - (ii) fractionating the full boiling range cracked naphtha into a distillate product containing C5 hydrocarbons and a first heavy naphtha containing sulfur compounds;
- (c) recovering the first heavy naphtha from the first distillation column reactor as a first bottoms;
- (d) feeding the first bottoms and hydrogen to a second distillation column reactor;
- (e) concurrently in the second distillation column reactor,
 - (i) reacting at least a portion of the organic sulfur compounds in the first bottoms with hydrogen in the presence of a hydrodesulfurization catalyst in the rectification section of the second distillation column reactor to convert a portion of the other organic sulfur compounds to hydrogen sulfide, and
 - (ii) separating the first heavy naphtha into a first intermediate naphtha having an ASTM D86 end point in the range from 270°F to 400°F and a second heavy naphtha;
- (f) recovering the first intermediate naphtha, unreacted hydrogen, and hydrogen sulfide from the second distillation column reactor as a second overheads;
- (g) recovering the second heavy naphtha containing hindered organic sulfur compounds from the second distillation column reactor as a second bottoms;
- (h) feeding the second bottoms and hydrogen to a first fixed bed reactor containing a hydrodesulfurization catalyst;
- (i) contacting the hindered organic sulfur compounds and hydrogen with the hydrodesulfurization catalyst in the first fixed bed reactor to convert at least a portion of the hindered organic sulfur compounds to hydrogen sulfide;
- (j) recovering an effluent from the first fixed bed reactor;

- (k) separating unreacted hydrogen and hydrogen sulfide from the effluent from the first fixed bed reactor;
- (l) separating unreacted hydrogen and hydrogen sulfide from the second overheads;
- (m) feeding at least a portion of the second overheads and hydrogen to a second fixed bed reactor containing a hydrodesulfurization catalyst to convert at least a portion of the sulfur compounds in the second overheads to hydrogen sulfide;
- (n) recovering an effluent from the second fixed bed reactor;
- (o) separating at least a portion of the hydrogen sulfide from the effluent from the second fixed bed reactor to form a H₂S separated naphtha fraction;
- (p) fractionating the H₂S separated naphtha fraction to form a heavy naphtha fraction and a mid-range gasoline fraction; and
- (q) recycling at least a portion of the heavy naphtha fraction to the second fixed bed reactor; and
- (r) forming a gasoline from one or more of (i) at least a portion of the distillate product, (ii) at least a portion of the naphtha fraction, and (iii) at least a portion of the effluent from the first fixed bed reactor, wherein the gasoline has a total sulfur content of less than about 20 ppm S, by weight..

[0015] In some embodiments, the high end point naphtha being treated may have an ASTM endpoint of greater than about 470°F; greater than about 470°F in other embodiments; greater than about 500°F in other embodiments; greater than about 525°F in other embodiments; and greater than about 550°F in yet other embodiments.

[0016] Other aspects and advantages of the invention will be apparent from the following description and the appended claims.

BRIEF DESCRIPTION OF DRAWINGS

[0017] Figure 1 is a simplified flow diagram in schematic form of one embodiment of processes for hydrodesulfurization of naphtha fractions according to embodiments disclosed herein.

[0018] Figure 2 is a simplified flow diagram in schematic form of one embodiment of processes for hydrodesulfurization of naphtha fractions according to embodiments disclosed herein.

[0019] Figure 3 is a simplified flow diagram in schematic form of one embodiment of processes for hydrodesulfurization of naphtha fractions according to embodiments disclosed herein.

DETAILED DESCRIPTION

[0020] In one aspect, embodiments disclosed herein relate to a process for the desulfurization of a high end point FCC gasoline. Embodiments disclosed herein generally relate to processes for the desulfurization of FCC naphtha having a high ASTM D86 end point, such as greater than about 350°F, greater than 400°F, greater than 450°F, greater than 470°F, greater than 500°F, greater than 525°F, or greater than 550°F. More particularly, embodiments disclosed herein relate to processes for the desulfurization of high end point naphthas to produce gasoline fractions having a total sulfur content of less than 20 ppm, by weight. In some embodiments, the total sulfur content of the resulting gasoline fraction may be less than 10 ppm, by weight. Other embodiments disclosed herein may additionally provide for control of the end point of the gasoline product.

[0021] “Recombinant mercaptans,” as used herein, refers to mercaptans that are not in the feed to the present process but are the reaction products of the H₂S generated by the hydrogenation of sulfur-containing compounds in the present process and alkenes in the feed. Thus, the recombinant mercaptans are not necessarily the same as those destroyed by the hydrodesulfurization of a first portion of the present process, although they may be.

[0022] Within the scope of this application, the expression “catalytic distillation reactor system” denotes an apparatus in which the catalytic reaction and the separation of the products take place at least partially simultaneously. The apparatus may comprise a conventional catalytic distillation column reactor, where the reaction and distillation are concurrently taking place at boiling point conditions, or a distillation column combined with at least one side reactor, where the side reactor may be operated as a liquid phase reactor or a boiling point reactor. While both catalytic distillation reactor systems described may be preferred over conventional liquid phase reaction followed by separations, a catalytic distillation column reactor may have the advantages of decreased piece count, reduced capital cost, increased

catalyst productivity per pound of catalyst, efficient heat removal (heat of reaction may be absorbed into the heat of vaporization of the mixture), and a potential for shifting equilibrium. Divided wall distillation columns, where at least one section of the divided wall column contains a catalytic distillation structure, may also be used, and are considered “catalytic distillation reactor systems” herein.

[0023] The hydrocarbon feed to the processes disclosed herein may be a sulfur-containing petroleum fraction which boils in the gasoline boiling range, including FCC gasoline, coker pentane/hexane, coker naphtha, FCC naphtha, straight run gasoline, pyrolysis gasoline, and mixtures containing two or more of these streams. Such gasoline blending streams typically have a normal boiling point within the range of 0°F and 470°F, as determined by an ASTM D86 distillation. Feeds of this type include light naphthas typically having a boiling range of about C₆ to 330°F; full range naphthas, typically having a boiling range of about C₅ to 420°F, heavier naphtha fractions boiling in the range of about 260°F to 412°F, or heavy gasoline fractions with high end points boiling in the range of about 330°F to 470°F or higher.

[0024] Processes disclosed herein are additionally suitable for the desulfurization of “high end point” petroleum fractions, which is herein defined as a naphtha fraction having an ASTM D86 end point of at least 450°F. Increasing the end point of the naphtha changes the behavior of the gasoline toward hydrodesulfurization, as the sulfur content of the gasoline increases dramatically with an increase in end point, rendering a significant number of prior processes unsuitable. Further, higher end point fractions typically include multi-substituted sulfur compounds, as described above, including multi-substituted benzothiophenes. These high end point sulfur-containing compounds are referred to herein as “hindered sulfur compounds” as these compounds are much less reactive during hydrodesulfurization processes. In some embodiments, high end point gasoline fractions that may be processed according to processes disclosed herein may have an ASTM D86 end point of at least 450°F, at least 470°F in other embodiments; at least 500°F in other embodiments; at least 510°F in other embodiments; at least 520°F in other embodiments; at least 525°F in other embodiments; and at least 550°F in yet other embodiments. In other embodiments, high end point gasoline fractions that may be processed according to embodiments disclosed herein may have an ASTM D86 end point in the range from about 450°F to

about 550°F; from about 470°F to about 550°F in other embodiments; and from about 500°F to about 520°F in yet other embodiments.

[0025] Organic sulfur compounds present in these gasoline fractions occur principally as mercaptans, aromatic heterocyclic compounds, and disulfides. Relative amounts of each depend on a number of factors, many of which are refinery, process and feed specific. In general, heavier fractions contain a larger amount of sulfur compounds, and a larger fraction of these sulfur compounds are in the form of aromatic heterocyclic compounds. In addition, certain streams commonly blended for gasoline, such as FCC naphthas, contain high amounts of the heterocyclic compounds. Gasoline streams containing significant amounts of these heterocyclic compounds are often difficult to process using many of the prior art processes. Very severe operating conditions have been conventionally specified for hydrotreating processes to desulfurize gasoline streams, resulting in loss of olefinic content and a large octane penalty. Prior methods of catalytic distillation for high-end point gasolines have not been successful in removing the required amount of sulfur due to the difficulty of breaking the hindered sulfur bonds in high-end point naphtha. Adsorption processes, used as an alternative to hydrogen processing, have very low removal efficiencies, as the aromatic heterocyclic sulfur compounds have adsorptive properties similar to the aromatic compounds in the hydrocarbon matrix.

[0026] Aromatic heterocyclic compounds that may be removed by the processes disclosed herein include alkyl substituted thiophene, thiophenol, alkylthiophene, benzothiophene, and multi-substituted benzothiophenes. Among the aromatic heterocyclic compounds of particular interest are thiophene, 2-methylthiophene, 3-methylthiophene, 2-ethylthiophene, benzothiophene and dimethylbenzothiophene. Mercaptans that may be removed by the processes described herein often contain from 2-10 carbon atoms, and are illustrated by materials such as 1-ethanethiol, 2-propanethiol, 2-butanethiol, 2-methyl-2-propanethiol, pentanethiol, hexanethiol, heptanethiol, octanethiol, nonanethiol, and thiophenol.

[0027] Sulfur in these gasoline streams may be in one of several molecular forms, including thiophenes, mercaptans and disulfides. For a given gasoline stream, the sulfur compounds tend to be concentrated in the higher boiling portions of the stream (*i.e.*, the heavier fractions of the stream), with hindered sulfur compounds being

present in higher concentrations at elevated boiling points, such as above about 350°F, and especially above about 450°F, and even more especially above about 500°F. The sulfur within the higher boiling portions of the stream may be more difficult to remove due to increased concentration of multi-substituted benzothiophenes. High end point naphtha streams that are particularly rich in hindered sulfur compounds may be suitably treated according to embodiments disclosed herein to produce a gasoline range product meeting desired sulfur specifications.

[0028] The total sulfur content of gasoline streams to be treated using the processes disclosed herein will generally exceed 50 ppm by weight, and typically range from about 150 ppm to as much as several thousand ppm sulfur. For fractions containing at least 5 volume percent boiling over about 520°F, the sulfur content may exceed about 1000 ppm by weight, and may be as high as 5000 to 10000 ppm by weight or even higher.

[0029] In addition to the sulfur compounds, naphtha feeds, including FCC naphtha, may include paraffins, naphthenes, and aromatics, as well as open-chain and cyclic olefins, dienes, and cyclic hydrocarbons with olefinic side chains. A cracked naphtha feed useful in the processes described herein may have an overall olefins concentration ranging from about 5 to 60 weight percent in some embodiments; from about 25 to 50 weight percent in other embodiments.

[0030] In general, processes described herein may treat a naphtha or gasoline fraction in one or more catalytic distillation reactor systems. Each catalytic distillation reactor system may have one or more reaction zones containing one or more of a hydrogenation catalyst, a thioetherification catalyst, and/or a hydrodesulfurization catalyst. For example, reactive distillation zones may be contained within the stripping section, hydrodesulfurizing the heavier compounds in the feed, or within the rectification section, hydrodesulfurizing the lighter compounds in the feed, or both. Hydrogen may also be fed to the catalytic distillation reactor system, and in some embodiments, a portion of the hydrogen may be fed below each respective reaction zone.

[0031] In each catalytic distillation reactor system, the steps to catalytically react the naphtha feed with hydrogen may be carried out at a temperature in the range of 100°F to 1000°F, at pressures in the range from about 0.1 to 500 psig, with hydrogen partial

pressures in the range from 0.01 to 100 psi at 2 to 2000 scf/bbl at weight hourly space velocities (WHSV) in the range of 0.1 to 10 hr⁻¹ based on feed rate and a particulate catalyst packaged in structures. If advanced specialty catalytic structures are used (where catalyst is one with the structure rather than a form of packaged pellets to be held in place by structure), the liquid hourly space velocity (LHSV) for such systems should be about in the same range as those of particulate or granular-based catalytic distillation catalyst systems as just referenced. In other embodiments, conditions in a reaction distillation zone of a naphtha hydrodesulfurization distillation column reactor system are: temperatures in the range from 450°F to 700°F, total pressure in the range from 75 to 300 psig, hydrogen partial pressure in the range from 6 to 75 psia, WHSV of naphtha in the range from about 1 to 5, and hydrogen feed rates in the range from 10-1000 scf/bbl.

[0032] The operation of a distillation column reactor results in both a liquid and a vapor phase within the distillation reaction zone. A considerable portion of the vapor is hydrogen, while a portion of the vapor is hydrocarbons from the hydrocarbon feed. In catalytic distillation it has been proposed that the mechanism that produces the effectiveness of the process is the condensation of a portion of the vapors in the reaction system, which occludes sufficient hydrogen in the condensed liquid to obtain the requisite intimate contact between the hydrogen and the sulfur compounds in the presence of the catalyst to result in their hydrogenation. In particular, sulfur species concentrate in the liquid while the olefins and H₂S concentrate in the vapor, allowing for high conversion of the sulfur compounds with low conversion of the olefin species.

[0033] As in any distillation, there is a temperature gradient within the catalytic distillation reactor system. The lower end of the column contains higher boiling material and thus is at a higher temperature than the upper end of the column. The lower boiling fraction, which contains more easily removable sulfur compounds, is subjected to lower temperatures at the top of the column, which may provide for greater selectivity, that is, no hydrocracking or less saturation of desirable olefinic compounds. The higher boiling portion is subjected to higher temperatures in the lower end of the distillation column reactor to crack open the sulfur containing ring compounds and hydrogenate the sulfur. The heat of reaction simply creates more boil up, but no increase in temperature at a given pressure. As a result, a great deal of

control over the rate of reaction and distribution of products can be achieved by regulating the system pressure.

[0034] Processes disclosed herein may additionally treat a naphtha or gasoline fraction, or a select portion thereof, in one or more fixed bed reactor systems. Each fixed bed reactor system may include one or more reactors in series or parallel, each reactor having one or more reaction zones containing one or more hydrodesulfurization catalysts. Such fixed bed reactors may be operated as a vapor phase reactor, a liquid phase reactor, or a mixed phase (V/L) reactor and may include traditional fixed bed reactors, trickle bed reactors, pulse flow reactors, and other reactor types known to those skilled in the art. The operating conditions used in the fixed bed reactor systems may depend upon the reaction phase(s), the boiling range of the naphtha fraction being treated, catalyst activity, selectivity, and age, and the desired sulfur removal per reaction stage, among other factors.

[0035] The flow of components through processes disclosed herein provides for efficient processing of high end point naphtha streams to reduce the total sulfur content of the streams to meet specifications and regulations. Further, the process flow schemes provide for the processing of high olefin-content portions of the naphtha at less severe conditions, maintaining a significant portion of the olefin content, and thus preserving high octane value components.

[0036] Referring now to Figure 1, a simplified process flow diagram of an embodiment of the hydrodesulfurization processes disclosed herein is illustrated. Hydrogen and a naphtha or other organic sulfur-containing hydrocarbon feed, which may include hindered sulfur compounds, may be fed via flow lines 6 and 8, respectively, to a first catalytic distillation reactor system 10 having one or more reactive distillation zones 12 for hydrotreating the hydrocarbon feed. As illustrated, catalytic distillation reactor system 10 includes at least one reactive distillation zone 12, located in an upper portion of the column, above the feed inlet, for treating the light hydrocarbon components in the feed.

[0037] Reaction zone 12 may include one or more catalysts for the hydrogenation of dienes, reaction of mercaptans and dienes (thioetherification), and/or hydrodesulfurization. For example, conditions in the first catalytic distillation reactor system 10 may provide for thioetherification and/or hydrogenation of dienes and

removal of mercaptan sulfur from the C₅/C₆ portion of the hydrocarbon feed. The C₅/C₆ portion of the naphtha, having a reduced sulfur content as compared to the C₅/C₆ portion of the feed, may be recovered from catalytic distillation reactor system 10 as a side draw product 16.

[0038] An overheads fraction may be recovered from catalytic distillation reactor system 10 via flow line 18, and may contain light hydrocarbons, unreacted hydrogen and hydrogen sulfide.. The first overheads 18 may be cooled, such as using a heat exchanger 14, and fed to a stripper 20. In stripper 20, hydrogen sulfide and unreacted hydrogen may be separated from the hydrocarbons contained in the overhead fraction, with unreacted hydrogen and hydrogen sulfide withdrawn from stripper 20 via flow line 22. Condensed hydrocarbons may be withdrawn from stripper 20 and fed to first catalytic distillation reactor system 10 as a total or partial reflux via flow line 24 and pump 26.

[0039] The C₅/C₆ side draw product withdrawn from catalytic distillation reactor system 10 via flow line 16 may contain many of the olefins present in the hydrocarbon feed. Additionally, dienes in the C₅/C₆ cut may be hydrogenated during treatment in catalytic distillation reactor system 10. This hydrogenated, desulfurized C₅/C₆ side draw product may thus be recovered for use in various processes. In various embodiments, the C₅/C₆ side draw product may be used as a gasoline blending fraction, hydrogenated and used as a gasoline blending feedstock, and as a feedstock for ethers production, among other possible uses. The particular processing or end use of the C₅/C₆ fraction may depend upon various factors, including availability of alcohols as a raw material, and the allowable olefin concentration in gasoline for a particular jurisdiction, among others

[0040] The heavy naphtha, e.g. C₇+ boiling range components, including any thioethers formed in reaction zone 12 and various other sulfur and hindered sulfur compounds in the hydrocarbon feed, may be recovered as a bottoms fraction from catalytic distillation reactor system 10 via flow line 20. Where catalytic distillation reactor system 10 includes a reaction zone in the stripping section of the column, or where boil-up of C₇+ components into reaction zone 12 occurs, the recovered bottoms fraction may be at least partially desulfurized.

[0041] The bottoms fraction recovered via flow line 20 is then fed to a second catalytic distillation reactor system 30 containing one or more reactions zones

containing one or more hydrodesulfurization catalysts. Hydrogen may be fed to catalytic distillation reactor system 30 via flow line 28.

[0042] In some embodiments, catalytic distillation reactor system 30 may contain a reaction zone 32 in the rectification section reacting at least a portion of the organic sulfur compounds in the hydrocarbon feed with hydrogen, converting at least a portion of the organic sulfur compounds to hydrogen sulfide. Catalytic distillation reactor system 30 may be operated at conditions to facilitate the aforementioned reaction and to concurrently separate the hydrocarbon feed into a first intermediate naphtha fraction having an ASTM D86 end point in the range from about 270°F to about 400°F, recovered as an overheads via flow line 36, and a heavy naphtha fraction, recovered as a bottoms fraction via flow line 54.

[0043] If desired, catalytic distillation reactor system 30 may include distillation reaction zones 32, 34, in each of the rectification and stripping sections of the column, such that the heavy fraction may be at least partially hydrodesulfurized as it traverses downward through catalytic distillation reactor system 30. In such a case, hydrogen may be fed below the lowermost reaction zone via flow line 28b, or alternatively may be fed below each reactive distillation zone 32 and 34, such as via flow lines 28a and 28b, respectively.

[0044] The overheads product recovered from catalytic distillation reactor system 30 via flow line 36 may contain the intermediate fraction hydrocarbons as well as hydrogen sulfide and unreacted hydrogen. The overheads fraction may then be processed to separate the hydrogen and hydrogen sulfide. For example, the overheads fraction may be partially condensed via indirect heat exchange using a heat exchanger 40 and fed to a “hot drum” 42 for separation of the condensate from the uncondensed vapors, which include hydrocarbons, hydrogen sulfide, and hydrogen. The condensate may be recovered from drum 42 via flow line 48, a portion of which may be fed as reflux to catalytic distillation reactor 30 via pump 46 and flow line 38. The remainder of the condensate may be fed via flow line 51, and the uncondensed vapors may be fed via flow line 44, to “cold drum” 50. Cold drum 50 may then separate hydrogen and hydrogen sulfide, recovered via flow line 52, from the intermediate and heavy hydrocarbon components, recovered via flow line 68.

[0045] The bottoms product recovered via flow line 54 may have a fairly high concentration of sulfur. However, it is actually beneficial to the process to have a

minimal amount of catalyst in reaction zone 34, leaving a high concentration of sulfur in the bottoms product, as this minimizes the concentration of hydrogen sulfide available for recombinant mercaptan formation in the upper portion of catalytic distillation column reactor 30 and the associated overheads recovery system.

[0046] The bottoms fraction recovered via flow line 54 from catalytic distillation reactor system 30 is hot (at reboil temperature) and does not contain a significant amount of hydrogen sulfide due to the counter-current flow pattern of the reactive distillation process. The bottoms fraction recovered via flow line 54 is then fed to a fixed bed reactor 60 for additional hydrotreating. Additional hydrogen, over that dissolved in the bottoms, may be fed to fixed bed reactor 60 via flow line 58, if necessary or desired. The partial pressure of hydrogen in the fixed bed unit is typically greater than about 20 psi, such as between about 25 psi and about 350 psi, providing additional driving force for the removal of sulfur from any hindered sulfur compounds in the heavy end of the hydrocarbon feed 8. High hydrogen concentrations may be used in the fixed bed reactor 60 as most olefins have been separated and recovered via flow lines 16 and 36. Additionally, use of select hydrodesulfurization catalysts, such as Co / Mo catalysts, in fixed bed reactor 60 may prevent saturation of aromatic compounds, thus avoiding the accompanying octane loss. Fixed bed reactor 60 and the resulting hydrodesulfurization of hindered sulfur compounds allows for the processing of very high endpoint feedstocks, even those having an endpoint in excess of 550°F in some embodiments.

[0047] The heavy gasoline effluent from fixed bed reactor 60 may be recovered via flow line 62. The effluent may then be fed via flow line 62 to drum 64, separating hydrogen sulfide and unreacted hydrogen from the liquid hydrocarbon effluent. The hydrogen and hydrogen sulfide may be withdrawn from drum 64 via flow line 66. The hydrocarbon effluent, having a reduced sulfur concentration, may be recovered via flow line 82.

[0048] In some embodiments, the hydrocarbon effluent recovered via flow line 82 may be combined with one or more of the lighter fractions, recovered via flow lines 16 and 68, for use as a gasoline blend stock or for further processing, as will be described below. In other embodiments, the heavy hydrocarbon fraction may be processed along with a heavy hydrocarbon fraction, such as a diesel hydrocarbon

fraction, fed via flow line 70, for further reducing the sulfur content of the heavy fraction and the diesel fraction.

[0049] Referring now to Figures 2 and 3, simplified process flow diagrams of embodiments of the hydrodesulfurization processes disclosed herein is illustrated, where like numerals represent like parts. Hydrogen and a naphtha or other organic sulfur-containing hydrocarbon feed, which may include hindered sulfur compounds, may be fed via flow lines 6 and 8, respectively, to a first catalytic distillation reactor system 10 having one or more reactive distillation zones 12 for hydrotreating the hydrocarbon feed. As illustrated, catalytic distillation reactor system 10 includes at least one reactive distillation zone 12, located in an upper portion of the column, above the feed inlet, for treating the light hydrocarbon components in the feed.

[0050] Reaction zone 12 may include one or more catalysts for the hydrogenation of dienes, reaction of mercaptans and dienes (thioetherification), and/or hydrodesulfurization. For example, conditions in the first catalytic distillation reactor system 10 may provide for thioetherification and/or hydrogenation of dienes and removal of mercaptan sulfur from the C₅/C₆ portion of the hydrocarbon feed. The C₅/C₆ portion of the naphtha, having a reduced sulfur content as compared to the C₅/C₆ portion of the feed, may be recovered from catalytic distillation reactor system 10 as a side draw product 16.

[0051] An overheads fraction may be recovered from catalytic distillation reactor system 10 via flow line 18, and may contain light hydrocarbons, unreacted hydrogen and hydrogen sulfide.. The first overheads 18 may be cooled, such as using a heat exchanger 14, and fed to a stripper 20. In stripper 20, hydrogen sulfide and unreacted hydrogen may be separated from the hydrocarbons contained in the overhead fraction, with unreacted hydrogen and hydrogen sulfide withdrawn from stripper 20 via flow line 22. Condensed hydrocarbons may be withdrawn from stripper 20 and fed to first catalytic distillation reactor system 10 as a total or partial reflux via flow line 24 and pump 26.

[0052] The C₅/C₆ side draw product withdrawn from catalytic distillation reactor system 10 via flow line 16 may contain many of the olefins present in the hydrocarbon feed. Additionally, dienes in the C₅/C₆ cut may be hydrogenated during treatment in catalytic distillation reactor system 10. This hydrogenated, desulfurized C₅/C₆ side draw product may thus be recovered for use in various processes. In

various embodiments, the C5/C6 side draw product may be used as a gasoline blending fraction, hydrogenated and used as a gasoline blending feedstock, and as a feedstock for ethers production, among other possible uses. The particular processing or end use of the C5/C6 fraction may depend upon various factors, including availability of alcohols as a raw material, and the allowable olefin concentration in gasoline for a particular jurisdiction, among others

[0053] The heavy naphtha, e.g. C7+ boiling range components, including any thioethers formed in reaction zone 12 and various other sulfur and hindered sulfur compounds in the hydrocarbon feed, may be recovered as a bottoms fraction from catalytic distillation reactor system 10 via flow line 20. Where catalytic distillation reactor system 10 includes a reaction zone in the stripping section of the column, or where boil-up of C7+ components into reaction zone 12 occurs, the recovered bottoms fraction may be at least partially desulfurized.

[0054] The bottoms fraction recovered via flow line 20 is then fed to a second catalytic distillation reactor system 30 containing one or more reactions zones containing one or more hydrodesulfurization catalysts. Hydrogen may be fed to catalytic distillation reactor system 30 via flow line 28.

[0055] In some embodiments, catalytic distillation reactor system 30 may contain a reaction zone 32 in the rectification section reacting at least a portion of the organic sulfur compounds in the hydrocarbon feed with hydrogen, converting at least a portion of the organic sulfur compounds to hydrogen sulfide. Catalytic distillation reactor system 30 may be operated at conditions to facilitate the aforementioned reaction and to concurrently separate the hydrocarbon feed into a first intermediate naphtha fraction having an ASTM D86 end point in the range from about 270°F to about 400°F, recovered as an overheads via flow line 36, and a heavy naphtha fraction, recovered as a bottoms fraction via flow line 54.

[0056] If desired, catalytic distillation reactor system 30 may include distillation reaction zones 32, 34, in each of the rectification and stripping sections of the column, such that the heavy fraction may be at least partially hydrodesulfurized as it traverses downward through catalytic distillation reactor system 30. In such a case, hydrogen may be fed below the lowermost reaction zone via flow line 28b, or alternatively may be fed below each reactive distillation zone 32 and 34, such as via flow lines 28a and 28b, respectively.

[0057] The bottoms product recovered via flow line 54 may have a fairly high concentration of sulfur. However, it is actually beneficial to the process to have a minimal amount of catalyst in reaction zone 34, leaving a high concentration of sulfur in the bottoms product, as this minimizes the concentration of hydrogen sulfide available for recombinant mercaptan formation in the upper portion of catalytic distillation column reactor 30 and the associated overheads recovery system.

[0058] The bottoms fraction recovered via flow line 54 from catalytic distillation reactor system 30 is hot (at reboil temperature) and does not contain a significant amount of hydrogen sulfide due to the counter-current flow pattern of the reactive distillation process. The bottoms fraction recovered via flow line 54 is then fed to a fixed bed reactor 60 for additional hydrotreating. Additional hydrogen, over that dissolved in the bottoms, may be fed to fixed bed reactor 60 via flow line 58. The partial pressure of hydrogen in the fixed bed unit is greater than about 20 psi, such as between about 25 psi and about 350 psi, providing additional driving force for the removal of sulfur from any hindered sulfur compounds in the heavy end of the hydrocarbon feed 8. High hydrogen concentrations may be used in the fixed bed reactor 60 as most olefins have been separated and recovered via flow lines 16 and 36. Additionally, use of select hydrodesulfurization catalysts, such as Co / Mo catalysts, in fixed bed reactor 60 may prevent saturation of aromatic compounds, thus avoiding the accompanying octane loss. Fixed bed reactor 60 and the resulting hydrodesulfurization of hindered sulfur compounds allows for the processing of very high endpoint feedstocks, even those having an endpoint in excess of 550°F in some embodiments.

[0059] The heavy gasoline effluent from fixed bed reactor 60 may be recovered via flow line 62. In some embodiments, a portion of the effluent in flow line 62 may be recycled to the inlet of reactor 60, such as via flow line 61. The effluent may then be fed via flow line 62 to drum 64, separating hydrogen sulfide and unreacted hydrogen from the liquid hydrocarbon effluent. The hydrogen and hydrogen sulfide may be withdrawn from drum 64 via flow line 66. The hydrocarbon effluent, having a reduced sulfur concentration, may be recovered via flow line 82.

[0060] The overheads product recovered from catalytic distillation reactor system 30 via flow line 36 may contain the intermediate fraction hydrocarbons as well as hydrogen sulfide and unreacted hydrogen. The overheads fraction may then be

processed to separate the hydrogen and hydrogen sulfide. For example, the overheads fraction may be partially condensed via indirect heat exchange using a heat exchanger 40 and fed to a “hot drum” 42 for separation of the condensate from the uncondensed vapors, which include hydrocarbons, hydrogen sulfide, and hydrogen. The condensate may be recovered from drum 42 via flow line 48, a portion of which may be fed as reflux to catalytic distillation reactor 30 via pump 46 and flow line 38. The remainder of the condensate may be fed via flow line 51, and the uncondensed vapors may be fed via flow line 44, to “cold drum” 50. Cold drum 50 may then separate hydrogen and hydrogen sulfide, recovered via flow line 52, from the intermediate and heavy hydrocarbon components, recovered via flow line 68.

[0061] In some embodiments of the hydrodesulfurization processes disclosed herein, it may be desired to recover a desulfurized hydrocarbon stream inclusive of both the intermediate fraction and the heavy fraction. Referring now to Figure 1, the separated heavy gasoline effluent recovered from drum 64 via flow line 82 may be fed to cold drum 50 for additional removal of hydrogen and hydrogen sulfide, if necessary, and recovered for further processing along with the intermediate fraction via flow line 68. The heavy gasoline effluent may alternatively be combined with the intermediate fraction downstream of drum 50.

[0062] The combined heavy and intermediate fractions may then be fed via flow line 68 and hydrogen via flow line 72 to a second fixed bed reactor 74 containing a hydrodesulfurization catalyst. The desulfurized heavy gasoline fraction may thus act as a heavy, inert diluent for the hydrodesulfurization of the intermediate fraction in second fixed bed reactor 74. Second fixed bed reactor 74 may be especially useful for removing mercaptan and recombinant mercaptan sulfur formed in the overhead system and present in the intermediate fraction. The effluent from second fixed bed reactor 74 may then be fed via flow line 76 to stripper 80 for the separation of hydrogen and hydrogen sulfide, recovered via flow line 78, from the hydrodesulfurized intermediate and heavy gasoline fractions, recovered via flow line 84.

[0063] In some embodiments, processes disclosed herein may provide control over the end point of the intermediate gasoline fractions recovered as a product. Referring now to Figure 2, the intermediate fraction may be fed via flow line 68 and hydrogen via flow line 72 to a second fixed bed reactor 74 containing a hydrodesulfurization

catalyst. The effluent from second fixed bed reactor 74 may then be fed via flow line 76 to stripper 80 for the separation of hydrogen and hydrogen sulfide, recovered via flow line 78, from the hydrodesulfurized intermediate gasoline fraction, recovered via flow line 84.

[0064] The intermediate gasoline fraction may then be fed to separator 92 for fractionation of the hydrodesulfurized intermediate gasoline fraction to recover a light intermediate naphtha fraction via flow line 94 and a heavy naphtha fraction via flow line 86. Control of the end point of the intermediate naphtha fraction may be controlled by the operating conditions used in separator 92. An intermediate naphtha fraction having a higher end point may be achieved using higher temperatures and/or lower pressures in separator 92.

[0065] In some embodiments, the heavy naphtha fraction recovered via flow line 86 may be recycled to fixed bed reactor 74 to act as a heavy, inert diluent, as described above. A portion of the heavy gasoline recovered from drum 64 via flow line 82 may also be fed via flow line 90 to second fixed bed reactor 74 to act as a diluent, to provide heavy hydrocarbons for additional control of the end point of the intermediate naphtha recovered via flow line 94, and to provide heavy material for control of reboil temperature in separator 92. As necessary, heavy hydrocarbons recirculating from separator 92 to fixed bed reactor 74 may be withdrawn via flow line 98 and recovered with the heavy gasoline fraction in flow line 82.

[0066] In the configuration as illustrated in Figure 2, the heavy fraction recovered via flow line 82 may be useful as a diesel gasoline fraction. In such instances, it may be desired to saturate aromatics in the heavy gasoline fraction. Thus, a refiner may opt to load a Ni/Mo catalyst, a Co/Mo catalyst, a Ni/W catalyst, or a mixture thereof in fixed bed reactor 60 to meet the local diesel specifications.

[0067] To result in high end point gasoline products having a low sulfur content, such as less than 50 ppm sulfur, by weight, in some embodiments, and less than 20 ppm or 10 ppm sulfur in other embodiments, the hydrocarbons recovered from drum 50 via flow line 68 may have a target sulfur concentration of less than about 150 ppm sulfur, by weight. In some embodiments, the target sulfur concentration of the hydrocarbons recovered via flow line 68 may be less than 125 ppm sulfur, by weight; less than 100 ppm sulfur, by weight in other embodiments; and from 50 ppm to 100 ppm sulfur, by weight, in yet other embodiments.

[0068] Operating conditions useful in each of catalytic distillation reactor systems 10, 30 and fixed bed reactor systems 60, 74 are provided in Table 1 below. Such conditions are useful in attaining the target product sulfur concentrations as detailed above.

Table 1

Reactor / Reaction Zone	10	30	60	74
Temperature (°F)	260-400	300-700	500-700	400-600
Pressure (psig)	75-300	75-300	50-500	50-350
WHSV	1-5	1-5	0.5-10	5-10
Hydrogen partial pressure (psi)	5-75	5-75	20-400	
Hydrogen feed rates (scf/bbl)	10-1000	10-1000		

[0069] Catalysts useful in the first catalytic distillation reactor column may be characterized as thioetherification catalysts or alternatively hydrogenation catalysts. In the first catalytic distillation reactor column, reaction of the diolefins with the sulfur compounds is selective over the reaction of hydrogen with olefinic bonds. The preferred catalysts are palladium and/or nickel or a Ni / Pd dual bed as shown in U.S. Pat. No. 5,595,643, since in the first catalytic distillation reactor column the sulfur removal is carried out with the intention to preserve the olefins. Although the metals are normally deposited as oxides, other forms may be used. The nickel is believed to be in the sulfide form during the hydrogenation.

[0070] Another suitable catalyst for the thioetherification reaction may be 0.34 wt % Pd on 7 to 14 mesh alumina spheres, supplied by Sud-Chemie, designated as G-68C. The catalyst also may be in the form of spheres having similar diameters. They may be directly loaded into standard single pass fixed bed reactors which include supports and reactant distribution structures. However, in their regular form they form too compact a mass for operation in a catalytic distillation reactor system column and must then be prepared in the form of a catalytic distillation structure. The catalytic distillation structure must be able to function as catalyst and as mass transfer medium. The catalyst must be suitably supported and spaced within the column to act as a catalytic distillation structure.

[0071] Without being bound to any specific theory, the catalyst is believed to be the hydride of palladium which is produced during operation. The hydrogen rate to the

catalytic reactor must be sufficient to maintain the catalyst in the active form because hydrogen is lost from the catalyst by hydrogenation, but kept below that which would cause flooding of the column which is understood to be the "effectuating amount of hydrogen" as that term is used herein. Generally the mole ratio of hydrogen to diolefins and acetylenes in the feed is at least 1.0 to 1.0 and preferably 2.0 to 1.0.

[0072] In second and subsequent catalytic distillation reactor columns and catalytic fixed bed reaction zones used in embodiments disclosed herein, it may be the purpose of the catalyst to destroy the sulfur compounds to produce a hydrocarbon stream containing hydrogen sulfide, which is easily separated from the heavier components therein. Hydrogen and hydrogen sulfide may be separated from heavy hydrocarbon components in a stripping column, as described above. The focus of these catalytic reactions that occur after the first catalytic distillation reactor column is to carry out destructive hydrogenation of the sulfides and other organic sulfur compounds.

[0073] Catalysts useful as the hydrodesulfurization catalyst in the reaction zones of the catalytic distillation reactor systems may include Group VIII metals, such as cobalt, nickel, palladium, alone or in combination with other metals, such as molybdenum or tungsten, on a suitable support, which may be alumina, silica-alumina, titania-zirconia or the like. Normally the metals are provided as the oxides of the metals supported on extrudates or spheres and as such are not generally useful as distillation structures. Alternatively, catalyst may be packaged in a suitable catalytic distillation structure, which characteristically can accommodate a wide range of typically manufactured fixed-bed catalyst sizes.

[0074] The catalysts may contain components from Group V, VIB, VIII metals of the Periodic Table or mixtures thereof. The incorporation of the distillation column reactor systems may reduce the deactivation of catalysts and may provide for longer runs than the fixed bed hydrogenation reactors of the prior art. The Group VIII metal may also provide increased overall average activity. Catalysts containing a Group VIB metal, such as molybdenum, and a Group VIII metal, such as cobalt or nickel, are preferred. Catalysts suitable for the hydrodesulfurization reaction include cobalt-molybdenum, nickel-molybdenum and nickel-tungsten. The metals are generally present as oxides supported on a neutral base such as alumina, silica-alumina or the

like. The metals are converted to the sulfide either in use or prior to use by exposure to sulfur compound containing streams and hydrogen.

[0075] The catalyst may also catalyze the hydrogenation of the olefins and dienes contained within the light cracked naphtha and to a lesser degree the isomerization of some of the mono-olefins. The hydrogenation, especially of the mono-olefins in the lighter fraction, may not be desirable.

[0076] The catalyst typically is in the form of extrudates having a diameter of 1/8, 1/16 or 1/32 inches and an L/D of 1.5 to 10. The catalyst also may be in the form of spheres having similar diameters. They may be directly loaded into standard single pass fixed bed reactors which include supports and reactant distribution structures. However, in their regular form they form too compact a mass for operation in the catalytic distillation reactor system column and must then be prepared in the form of a catalytic distillation structure. As described above, the catalytic distillation structure must be able to function as catalyst and as mass transfer medium. The catalyst must be suitably supported and spaced within the column to act as a catalytic distillation structure.

[0077] In some embodiments, the catalyst is contained in a structure as disclosed in U.S. Patent No. 5,730,843. In other embodiments, catalyst is contained in a plurality of wire mesh tubes closed at either end and laid across a sheet of wire mesh fabric such as demister wire. The sheet and tubes are then rolled into a bale for loading into the distillation column reactor. This embodiment is described, for example, in U.S. Patent No. 5,431,890. Other useful catalytic distillation structures are disclosed in U.S. Patent Nos. 4,731,229, 5,073,236, 5,431,890 and 5,266,546.

[0078] Hydrodesulfurization catalysts described above with relation to the operation of the catalytic distillation reactor systems may also be used in the fixed bed reactors. In selected embodiments, catalysts used in the fixed bed reactors may include hydrodesulfurization catalysts that only promote the desulfurization of mercaptan species, which are among the easiest to convert to hydrogen sulfide. Conditions in the fixed bed reactors, including high temperature and high hydrogen mole fractions, are conducive to olefin saturation. For preservation of olefin content and conversion of

mercaptans to hydrogen sulfide at these conditions, suitable catalysts may include nickel catalysts with very low molybdenum promotion, or no promoters at all, and molybdenum catalysts with very low copper promotion, or no promoters at all. Such catalysts may have lower hydrogenation activity, promoting the desulfurization of the mercaptan species without significant loss of olefins.

[0079] The effluent streams from the catalytic distillation reactor systems may be condensed in one or more stages, separating the hydrocarbons from the hydrogen sulfide and the hydrogen. As described above, it may be advantageous to use a hot drum – cold drum system to limit the formation of recombinant mercaptans. The recovered hydrogen may be compressed and recycled to various portions of the hydrodesulfurization systems described herein.

[0080] As mentioned above, heavy hydrocarbons may act as a diluent in fixed bed reactor 74 in embodiments disclosed herein. Dilution may result in a decreased driving force for the reverse reaction (recombinant mercaptan formation) as well as aid in olefin preservation. The heavy gasoline fraction recycle may dilute the olefins and hydrogen sulfide in the overhead fraction fed to the fixed bed reactor. This may reduce the amount of hydrogen required to provide dilution in the fixed bed reactors, and may also reduce the pressure drop across the associated control valve. This non-hydrogen dilution of the fixed bed reactor feed may in turn reduce the power required to run compressors, due to decreased hydrogen traffic.

[0081] As described above, embodiments disclosed herein may provide for the production of a high end point gasoline, such as may be recovered by one or more of flow lines 94, 84, and 82, having a total sulfur content of less than 50, 20, or even 10 ppm by weight.

[0082] After treatment according to the processes described herein, the sulfur content of the C5/C6 side draw product recovered via flow line 16 may be less than about 50 ppm in some embodiments; less than 40 ppm in other embodiments; less than 30 ppm in other embodiments; less than 20 ppm in other embodiments; less than 10 ppm in other embodiments; less than 5 ppm in other embodiments; and less than 1 ppm in yet other embodiments, where each of the above are based on weight.

[0083] After treatment according to the processes described herein, the sulfur content of the hydrocarbon fraction recovered via flow line 82 may be less than about 50 ppm

in some embodiments; less than 40 ppm in other embodiments; less than 30 ppm in other embodiments; less than 20 ppm in other embodiments; less than 10 ppm in other embodiments; less than 5 ppm in other embodiments; and less than 1 ppm in yet other embodiments, where each of the above are based on weight.

[0084] After treatment according to the processes described herein, the sulfur content of the intermediate hydrocarbon fraction recovered via flow line 94 may be less than about 50 ppm in some embodiments; less than 40 ppm in other embodiments; less than 30 ppm in other embodiments; less than 20 ppm in other embodiments; less than 10 ppm in other embodiments; less than 5 ppm in other embodiments; and less than 1 ppm in yet other embodiments, where each of the above are based on weight.

[0085] After treatment according to the processes described herein, the sulfur content of the heavy hydrocarbon fraction recovered via flow line 82 may be less than about 50 ppm in some embodiments; less than 40 ppm in other embodiments; less than 30 ppm in other embodiments; less than 20 ppm in other embodiments; less than 10 ppm in other embodiments; less than 5 ppm in other embodiments; and less than 1 ppm in yet other embodiments, where each of the above are based on weight.

[0086] In contrast to typical hydrodesulfurization processes, which often use harsh operating conditions resulting in significant loss of olefins, desulfurized products resulting from the processes disclosed herein may retain a significant portion of the olefins, resulting in a higher value end product. In some embodiments, products resulting from the processes described herein may have an overall olefins concentration ranging from 5 to 55 weight percent; from about 10 to about 50 weight percent in other embodiments; and from about 20 to about 45 weight percent in other embodiments. As compared to the initial hydrocarbon feed (flow line 8) the overall product streams recovered from embodiments disclosed herein (including flow lines 16, 94, 82, and 84 as appropriate for the respective embodiments) may retain at least 25% of the olefins in the initial hydrocarbon feed; at least 30% of the olefins in the initial hydrocarbon feed in other embodiments; at least 35% of the olefins in the initial hydrocarbon feed in other embodiments; at least 40% of the olefins in the initial hydrocarbon feed in other embodiments; at least 45% of the olefins in the initial hydrocarbon feed in other embodiments; at least 50% of the olefins in the initial hydrocarbon feed in other embodiments; and at least 60% of the olefins in the initial hydrocarbon feed in other embodiments.

[0087] Advantageously, embodiments disclosed herein may provide for the production of a low sulfur content gasoline fraction (having <10 ppm S, by weight in some embodiments) from a hydrocarbon feedstock having an ASTM D-86 end point of at least 350°F, and even from a high end point hydrocarbon feedstock (e.g., having an end point of greater than 450°F, 470°F, 500°F, 525°F, or 550°F and containing hindered sulfur compounds). Additionally, due to the treatment at varying severities and selected operating conditions, including dilution with heavy hydrocarbons or use of appropriate catalysts, embodiments disclosed herein may provide for one or more a high retention of olefins, select saturation of olefins and/or aromatics, and reduced recombinant mercaptan formation. A further benefit of processes according to embodiments disclosed herein is the ability to control the end point of the intermediate gasoline fraction produced.

[0088] While the invention has been described with respect to a limited number of embodiments, those skilled in the art, having benefit of this disclosure, will appreciate that other embodiments can be devised which do not depart from the scope of the invention as disclosed herein. Accordingly, the scope of the invention should be limited only by the attached claims.

CLAIMS

1. A process for the desulfurization of a high end point sulfur-containing petroleum fraction comprising the steps of:
 - (a) feeding (1) a sulfur-containing petroleum fraction containing C5 hydrocarbons, olefins, diolefins, mercaptans, other organic sulfur compounds, and hindered sulfur compounds and having an ASTM D86 end boiling point of at least 450°F, and (2) hydrogen to a first distillation column reactor, wherein the hydrogen is fed to the first distillation column reactor at a rate of 10 to 1000 scf/bbl of the sulfur-containing petroleum fraction;
 - (b) concurrently in the first distillation column reactor,
 - (i) contacting the diolefins and the mercaptans in the presence of a Group VIII metal catalyst in the rectification section of the first distillation column reactor, at a temperature in the range of 260°F to 400°F, a pressure in the range of 75 to 300 psig, and a WHSV in the range of 1 to 5, thereby reacting:
 - (A) a portion of the mercaptans with a portion of the diolefins to form thioethers, and/or
 - (B) a portion of the dienes with a portion of the hydrogen to form olefins; and
 - (ii) fractionating the sulfur-containing petroleum fraction into (A) a distillate product containing C5 hydrocarbons having a total sulfur content of less than 10 ppm S, by weight and (B) a first heavy fraction containing C7+ hydrocarbons, sulfur compounds, and hindered sulfur compounds;
 - (c) recovering the first heavy fraction from the first distillation column reactor as a first bottoms;
 - (d) feeding the first bottoms and hydrogen to a second distillation column reactor, wherein the hydrogen is fed to the second distillation column reactor at a rate of 10 to 1000 scf/bbl of the sulfur-containing petroleum fraction;
 - (e) concurrently in the second distillation column reactor,

- (i) reacting at least a portion of the organic sulfur compounds in the first bottoms with hydrogen in the presence of a hydrodesulfurization catalyst in the rectification section of the second distillation column reactor at a temperature in the range of 300°F to 700°F, a pressure in the range of 75 to 300 psig, and a WHSV in the range of 1 to 5, to convert a portion of the other organic sulfur compounds to hydrogen sulfide, and
 - (ii) separating the first heavy fraction into a first intermediate fraction having an ASTM D86 end point in the range from 270°F to 400°F and a second heavy fraction;
- (f) recovering the first intermediate fraction, unreacted hydrogen, and hydrogen sulfide from the second distillation column reactor as a second overheads, where a total sulfur content in the first intermediate fraction is in the range from about 50 ppm S to about 100 ppm S, by weight;
- (g) recovering the second heavy fraction containing the hindered organic sulfur compounds from the second distillation column reactor as a second bottoms;
- (h) feeding the second bottoms and hydrogen to a first fixed bed reactor containing a hydrodesulfurization catalyst;
- (i) contacting the second bottoms and hydrogen with the hydrodesulfurization catalyst in the first fixed bed reactor at a temperature in the range of 500°F to 700°F, a pressure in the range of 50 to 500 psig, a hydrogen partial pressure in the range of 25 psi to about 350 psi, and a WHSV in the range of 0.5 to 10 to convert at least a portion of the hindered organic sulfur compounds to hydrogen sulfide;
- (j) recovering an effluent from the first fixed bed;
- (k) separating unreacted hydrogen and hydrogen sulfide from the effluent from the first fixed bed reactor to recover a desulfurized heavy fraction having a total sulfur content of less than 50 ppm S, by weight;
- (l) separating unreacted hydrogen and hydrogen sulfide from the second overheads;
- (m) feeding at least a portion of the second overheads and hydrogen to a second fixed bed reactor containing a hydrodesulfurization catalyst at a temperature in the range of 400°F to 600°F, a pressure in the range of 50 to 350 psig, and a

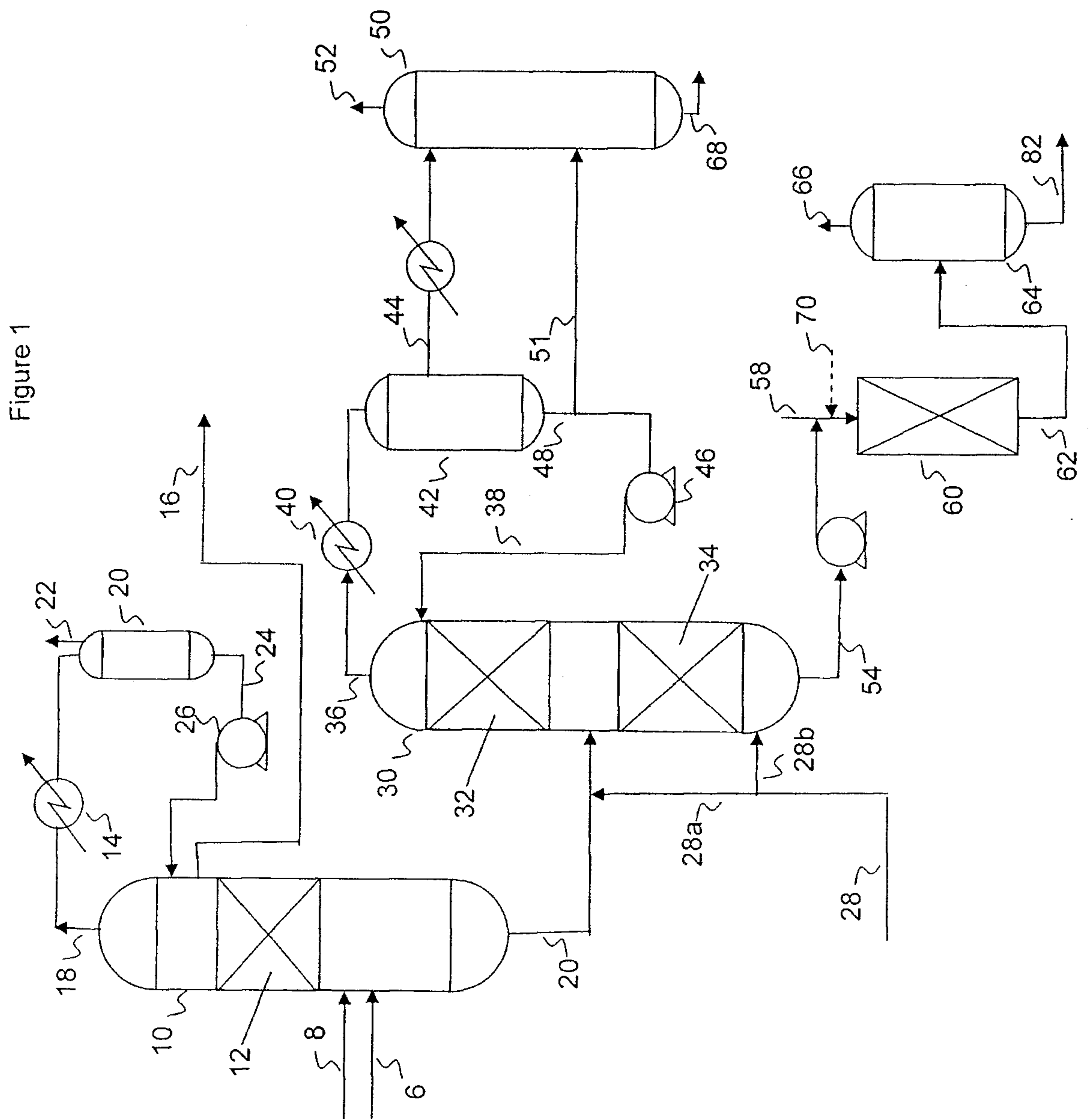
WHSV in the range of 5 to 10 to convert at least a portion of the sulfur compounds in the second overheads to hydrogen sulfide;

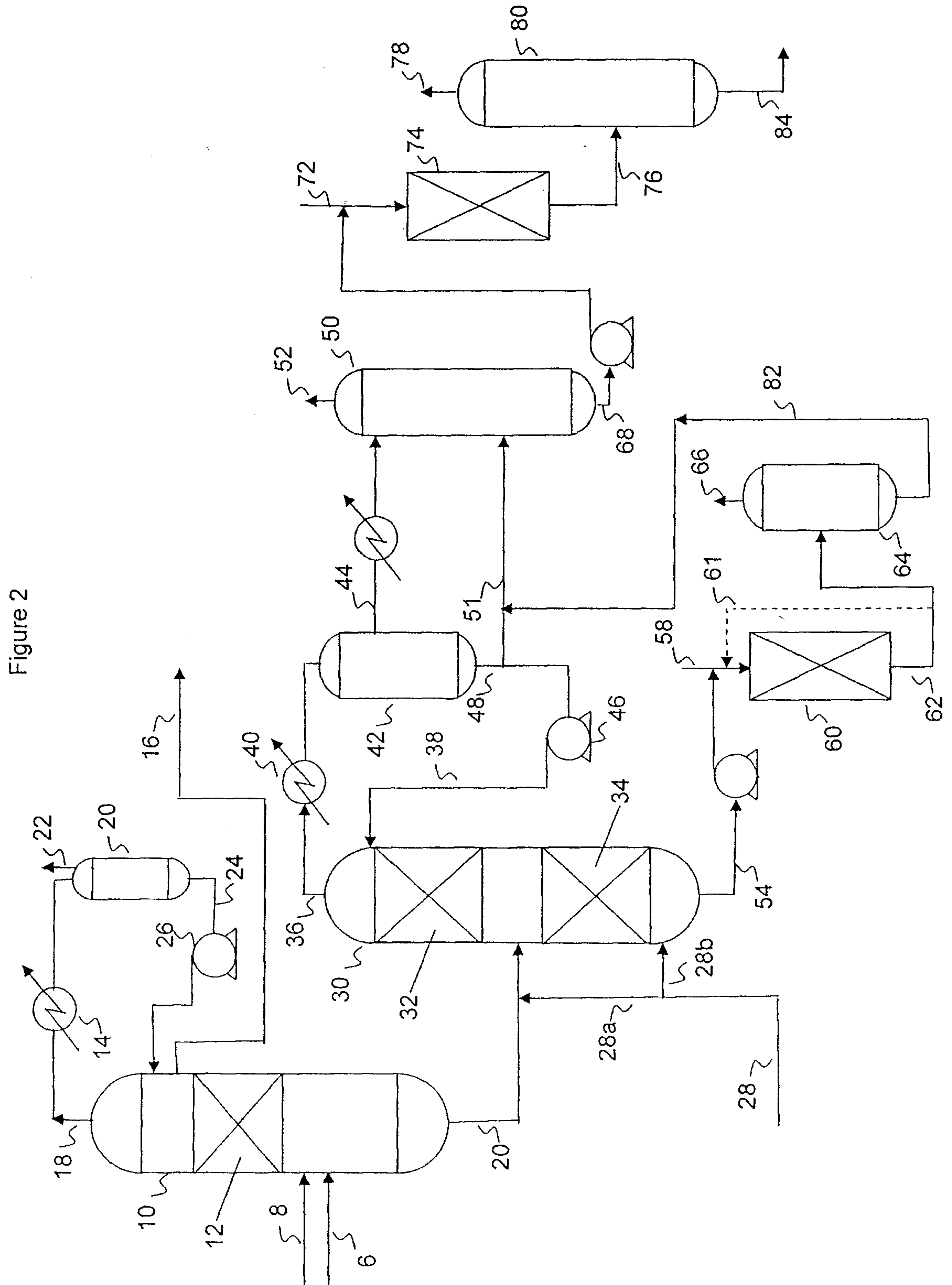
- (n) recovering an effluent from the second fixed bed reactor;
- (o) separating at least a portion of the hydrogen sulfide from the effluent from the second fixed bed reactor to form a desulfurized intermediate fraction having a total sulfur content of less than 50 ppm S, by weight;

wherein a combined olefin content of the distillate product, the desulfurized heavy fraction, and the desulfurized intermediate fraction is at least 60% of the olefin content of the sulfur-containing petroleum fraction.

2. The process of claim 1, wherein the sulfur-containing petroleum fraction has an ASTM D86 end boiling point of at least 500°F.
3. The process of claim 1, wherein the sulfur-containing petroleum fraction has an ASTM D86 end boiling point of at least 525°F.
4. The process of claim 1, wherein the sulfur-containing petroleum fraction has an ASTM D86 end boiling point of at least 550°F.
5. The process of claim 1, wherein the hindered sulfur compounds comprise multi-substituted benzothiophenes, and wherein the operating conditions in the first fixed bed reactor are sufficient to convert at least a portion of the multi-substituted benzothiophenes.
6. The process of claim 1, further comprising (p) forming a gasoline from two or more of (i) the distillate product, the desulfurized heavy fraction, and the desulfurized intermediate fraction, wherein the gasoline has a total sulfur content of less than 20 ppm S, by weight.
7. The process of claim 6, wherein the gasoline has a total sulfur content of less than about 10 ppm S, by weight.
8. The process of claim 1, wherein the distillate product has a total sulfur content of less than 1 ppm S, by weight.

9. The process of claim 1, wherein the desulfurized heavy fraction has a total sulfur content of less than 20 ppm S, by weight.
10. The process of claim 1, wherein the desulfurized intermediate fraction has a total sulfur content of less than 20 ppm S, by weight.
11. The process of claim 1, further comprising feeding at least a portion of the effluent in (k) to the second fixed bed reactor.





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Figure 3

