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(54) Title: MERCAPTAN MANAGEMENT IN SELECTIVE HYDRODESULFURIZATION OF FCC NAPHTHA

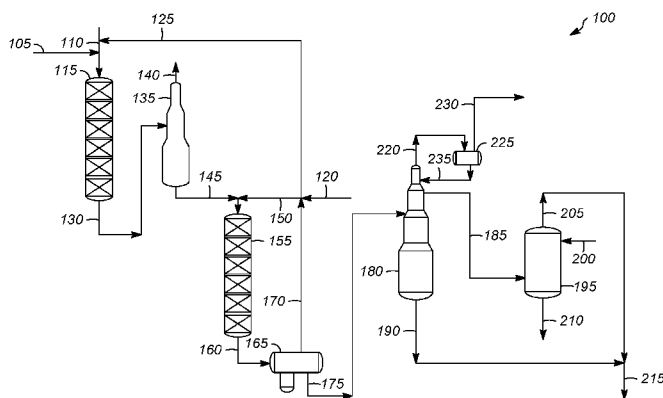


FIG. 1

(S7) Abstract: A process for reducing the sulfur content of FCC naphtha is described. The process includes introducing a FCC naphtha feed to a selective hydrogenation zone to form a hydrogenated feed. The hydrogenated feed is separated into light fraction and a heavy fraction. The heavy fraction is introduced into a selective hydrodesulfurization zone to form a desulfurized stream which contains mercaptans. The desulfurized stream is separated into a mercaptan rich stream and a mercaptan lean stream. The mercaptan rich stream is treated with a caustic extraction process, a hydrodesulfurization reaction zone, a selective hydrogenation process, an adsorption process, or an ionic liquid extraction process to remove at least a portion of the mercaptan compounds to form a second mercaptan lean stream.

(57) Abstract: A process for reducing the sulfur content of FCC naphtha is described. The process includes introducing a FCC naphtha feed to a selective hydrogenation zone to form a hydrogenated feed. The hydrogenated feed is separated into light fraction and a heavy fraction. The heavy fraction is introduced into a selective hydrodesulfurization zone to form a desulfurized stream which contains mercaptans. The desulfurized stream is separated into a mercaptan rich stream and a mercaptan lean stream. The mercaptan rich stream is treated with a caustic extraction process, a hydrodesulfurization reaction zone, a selective hydrogenation process, an adsorption process, or an ionic liquid extraction process to remove at least a portion of the mercaptan compounds to form a second mercaptan lean stream.



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MERCAPTAN MANAGEMENT IN SELECTIVE
HYDRODESULFURIZATION OF FCC NAPHTHA

STATEMENT OF PRIORITY

5 This application claims priority to U.S. Provisional Application No. 62/204534 which was filed August 13, 2015, the contents of which are hereby incorporated by reference in its entirety.

BACKGROUND OF THE INVENTION

10 The current Tier 2 Vehicle and Gasoline Sulfur Program of the US Environmental Protection Agency (EPA) requires new passenger vehicles to meet stringent emissions standards including a limit of 30 wt ppm sulfur. Beginning in 2017, the Tier 3 Vehicle Emission and Fuel Standards Program will establish even stricter standards with a limit of 10 wt ppm sulfur. Special processing is needed to obtain these sulfur levels.

15 Gasoline from fluid catalytic cracking (FCC) processes comprises up to 50 vol% of a refinery's motor gasoline pool, and up to 90% of the motor gasoline pool's sulfur content. Consequently, it is important that the treatment of this stream not significantly reduce its octane contribution to the pool.

20 In order to obtain the needed sulfur levels, the majority of gasoline worldwide obtained from fluid catalytic cracking (FCC) processes is selectively hydrodesulfurized which generally preserves the alkenes and aromatics. Typical processing conditions for hydrodesulfurization include a temperature of 250°C to 315°C and a pressure of 1.7 MPa (g) to 17-26 bar (g) with a supported CoMo catalyst.

25 However, selective hydrodesulfurization cannot bring down the sulfur level down sufficiently to meet the 10 wt ppm due to formation of recombinant mercaptans. The H_2S produced during the selective hydrodesulfurization reaction stage reacts with olefins present in the effluent to form mercaptans, predominantly butyl mercaptans. In addition, the current selective hydrodesulfurization catalytic system and the operating conditions are not optimized to target the reduction of there combinant mercaptans in the selective hydrodesulfurization reaction stage.

Consequently, in order meet this limit, some refiners have added a polishing reactor downstream of the selective hydrodesulfurization reactor. Typically, the polishing reactor uses a Ni based catalyst with LHSV of 1hr^{-1} and a temperature of 280°C to 380°C . The polishing reactor reduces the mercaptans especially by saturating the olefins and thereby
5 reducing the equilibrium mercaptans in the reactor effluent along with hydrodesulfurization of the recombinant mercaptans. However, saturating the olefins reduces the octane content.

Therefore, there is a need for improved processes for desulfurizing FCC gasoline.

SUMMARY OF THE INVENTION

One aspect of the invention is a process for reducing the sulfur content of full range fluidized catalytic cracker (FCC) naphtha. In one embodiment, the process includes introducing a FCC naphtha feed to a selective hydrogenation zone in the presence of hydrogen and a hydrogenation catalyst under selective hydrogenation conditions to form a hydrogenated feed. The hydrogenated feed is separated into at least two fractions, a light
10 fraction and a heavy fraction. The heavy fraction is introduced into a selective hydrodesulfurization zone in the presence of hydrogen and a hydrodesulfurization catalyst under selective hydrodesulfurization conditions to form a desulfurized stream, the desulfurized stream containing mercaptans. At least a portion of the desulfurized stream is separated into at least two streams, a mercaptan rich stream and a first mercaptan lean stream.
15 At least a portion of the mercaptan rich stream is treated to remove at least a portion of the mercaptan compounds to form a second mercaptan lean stream. A variety of processes can be used to treat the mercaptan rich stream including, but not limited to, a caustic extraction process, a hydrodesulfurization reaction zone, a selective hydrogenation process, an adsorption process, and an ionic liquid extraction process.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an illustration of one embodiment of the process of the present invention.

Fig. 2 is an illustration of another embodiment of the process of the present invention.

Fig. 3 is an illustration of still another embodiment of the process of the present invention.

Fig. 4 is an illustration of yet another embodiment of the process of the present invention.

5 Fig. 5 is an illustration of another embodiment of the process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The sulfur characterization of the selective hydrodesulfurization (HDS) reactor effluent points to the presence of an abundance of butyl mercaptans. There are a number of
10 different pathways through which thiophenes and substituted thiophenes undergo desulfurization. Typically, thiophene desulfurization proceeds along two parallel pathways. The thiophene hydrogenation and hydrogenolysis reactions occur simultaneously to generate cyclic sulfide and cis and trans-2-butene and then proceed further to 1-butene and butane. This reaction network also includes olefin saturation reactions. Hydrogenolysis and
15 hydrogenation reactions take place on different sites of the catalyst simultaneously. In general, the hydrogenolysis reaction is represented as occurring at the sigma site, and hydrogenation at the pi site. All the above postulates are reflected in experimental selective HDS runs where equilibrium mercaptans are present due to the recombination of butenes with the H₂S.

20 Several approaches have been developed to manage the mercaptans from the selective HDS reactor. They all rely of the fact that butyl mercaptans are rich in the naphtha fraction having a boiling point range of 60°C to 120°C of the selectively hydrotreated naphtha. This fraction, or a portion of it, is then treated to remove the mercaptans. Sulfur speciation measured by ASTM D-5623 method of the HDS reactor effluent stream and 100°C minus
25 and 100°C plus splits from this stream is mentioned in Table 1, and supports the above concept.

Attribute	Unit	Selective HD S Rx Effluent ¹	100°C– Cut	100°C+ Cut
SPLIT FRACTION	Wt%	100	65	35
Sulfur by XRF ²	Wppm	21	13	52
Sulfur by CdCl ₂ /Hg Wash ³	Wppm	16	8.7	31
ASTM D-5623 – Sulfur Speciation				
Sec-Butyl mercaptan	Wppm	10.6	5.7	0
n-Butyl mercaptan	Wppm	3.4	1.5	0
2-Methylthiophene	Wppm	3.9	1.0	5.9
3-Methylthiophene	Wppm	0	0.6	0
2-Ethyl thiophene	Wppm	3.2	0	5.1
Thiophene – BT unknowns	Wppm	0	4.1	39.9
Heavies	Wppm	0	0	1.1

Table 1

¹Selective hydrodesulfurization reactor effluent stream

² Sulfur analysis of stream using x-ray fluorescence

5 ³ Sulfur analysis of stream using x-ray fluorescence after washing stream with CdCl₂ followed by Hg wash

10 All of the processes begin with the treatment of the FCC naphtha feed in a selective hydrogenation zone to hydrogenate the diolefins in the feed. The hydrogenated feed is then separated in a splitter column into at least two fractions, a light fraction and a heavy fraction. In some embodiments, the light fraction has a boiling point in the range of less than 60°C, and the heavy fraction has a boiling point in the range of greater than 60°C. In other embodiments, the light fraction has a boiling point in the range of less than 65°C, and the heavy fraction typically has a boiling point in the range of greater than 65°C.

The heavy fraction is sent to the selective hydrodesulfurization zone where the sulfur in the feed is converted to hydrogen sulfide, and some of the hydrogen sulfide further reacts with olefins in the feed to form mercaptides.

The effluent from the selective hydrodesulfurization zone is separated into a least two streams, a mercaptan rich stream and a mercaptan lean stream. In some embodiments, there are two mercaptan lean streams, a low boiling mercaptan lean stream with a boiling point range lower than that of the mercaptan rich stream and a high boiling lean mercaptan stream with a boiling point range greater than that of the mercaptan rich stream.

The mercaptan rich stream is then treated to remove the mercaptans. In one embodiment, a mercaptan rich stream is sent to a caustic extraction zone to remove the mercaptans. The mercaptan free effluent stream from the caustic extraction zone can be sent to the gasoline pool. In another embodiment, the mercaptan rich stream is treated in a polishing reactor to reduce the level of mercaptans. By sending a concentrated mercaptan rich feed to the polishing reactor, the size of the polishing reactor can be reduced by a significant amount, in some cases as much as 75-80%. Another embodiment involves sending the mercaptan rich stream to the upstream selective hydrogenation reactor which converts the mercaptans into heavy disulfides. In this way, a separate polishing zone is avoided. In another embodiment, the mercaptan rich stream is treated in an adsorbent zone to reduce the mercaptans. Another possibility is to treat the mercaptan rich stream in an ionic liquid extraction zone. The ionic liquid can be regenerated as needed and recycled to the extraction zone.

The light fraction from the selective hydrodesulfurization zone can have a boiling point of less than 60°C, or less than 65°C. The light fraction typically has a T5 boiling point of 0°C to 25°C, a T95 boiling point of 50°C to 80°C, and a final boiling point of 85°C to 100°C. The heavy fraction from the selective hydrodesulfurization zone can have a boiling point in the range of 60°C to 220°C, 65°C to 220°C, 60°C to 200°C, or 65°C to 200°C, for example. The heavy fraction typically has a T5 boiling point of 50°C to 80°C, a T95 boiling point of 160°C to 220°C, and a final boiling point of greater than 220°C to 220°C.

This heavy fraction could be fractionated into a mercaptan rich stream with a boiling point in the range of 60°C to 120°C, or 60°C to 100°C, or 65°C to 120°C, or 65°C to 100°C, and a mercaptan lean stream with a boiling point in the range of 100°C to 220°C,

120°C to 220°C, or 100°C to 200°C, or 120°C to 200°C. In some embodiments, the mercaptan rich stream has a T5 boiling point of 60°C to 70°C, a T95 boiling point of 90°C to 100°C, and a final boiling point of 100°C to 120°C. In some embodiments, the mercaptan lean stream has a T5 boiling point of 120°C to 140°C, a T95 boiling point of 190°C to 210°C, and a final boiling point of 200°C to 220°C. In some embodiments, the mercaptan rich stream has a T5 boiling point of 60°C to 70°C, a T95 boiling point of 90°C to 100°C, and a final boiling point of 100°C.

Alternatively, the desulfurized stream could be divided into a low boiling mercaptan lean stream with a boiling point in the range of 60°C to 85°C, or 65°C to 85°C, a mercaptan rich stream with a boiling point in the range of 85°C to 120°C, or 85°C to 100°C, and a high boiling mercaptan lean stream with a boiling point in the range of 100°C to 220°C, or 120°C to 220°C, or 100°C to 200°C, or 120°C to 200°C. In some embodiments, the low boiling mercaptan lean stream has a T5 boiling point of 60°C to 65°C, a T95 boiling point of 75°C to 85°C, and a final boiling point of 80°C to 90°C. In some embodiments, the mercaptan rich stream has a T5 boiling point of 80°C to 90°C, a T95 boiling point of 90°C to 100°C, and a final boiling point of 100°C to 120°C. In some embodiments, the high boiling mercaptan lean stream has a T5 boiling point of 100°C to 120°C, a T95 boiling point of 180°C to 200°C, and a final boiling point of 200°C to 220°C. In some embodiments, the mercaptan rich stream has a T5 boiling point of 80°C to 90°C, a T95 boiling point of 90°C to 100°C, and a final boiling point of 100°C.

One embodiment of the process 100 is illustrated in Fig. 1. The full range fluidized catalytic cracker (FCC) naphtha feed 105 and hydrogen stream 110 are introduced into a selective hydrogenation zone 115. The hydrogen 110 can be a recycle hydrogen stream 125.

The selective hydrogenation zone 115 is normally operated at relatively mild hydrogenation conditions. These conditions will normally result in the hydrocarbons being present as liquid phase materials. The reactants will normally be maintained under the minimum pressure sufficient to maintain the reactants as liquid phase hydrocarbons. A broad range of suitable operating pressures therefore extends from 276 kPa (g) to 5516 kPa (g) (40 psig to 800 psig), or 345 kPa (g) to 2069 kPa (g) (50 and 300 psig). A relatively moderate temperature between 25°C and 350°C (77°F to 662°F), or 50°C and 200°C (122°F to 392°F) is typically employed. The liquid hourly space velocity of the reactants through

the selective hydrogenation catalyst should be above 1.0 hr^{-1} , or above 5.0 hr^{-1} , or between 5.01 hr^{-1} and 35.0 hr^{-1} . Another variable operating condition is the ratio of hydrogen to diolefinic hydrocarbons maintained within the selective hydrogenation zone 115. The amount of hydrogen required to achieve a certain conversion is believed dependent upon both reactor temperature and the molecular weight of the feed hydrocarbons. To avoid the undesired saturation of a significant amount mono olefinic hydrocarbons, there should be less than 2.0 times the stoichiometric amount of hydrogen required for the selective hydrogenation of the diolefinic hydrocarbons which are present in the liquid phase process stream to mono olefinic hydrocarbons. Preferably, the mole ratio of hydrogen to diolefinic hydrocarbons in the material entering the bed of selective hydrogenation catalyst is maintained between 1:1 and 1.8:1. In some instances, it may be desirable to operate with a less than stoichiometrically required amount of hydrogen, with mole ratios down to 0.75:1 being acceptable. The optimum set of conditions will of course vary depending on such factors as the composition of the feed stream and the degree of saturation of diolefinic hydrocarbons which it is desired to perform.

Any suitable catalyst which is capable of selectively hydrogenating diolefins in a naphtha stream may be used. Suitable catalysts include, but are not limited to, a catalyst comprising copper and at least one other metal such as titanium, vanadium, chrome, manganese, cobalt, nickel, zinc, molybdenum, and cadmium or mixtures thereof. The metals are preferably supported on inorganic oxide supports such as silica and alumina, for example.

In some embodiments, the catalyst is employed in a fixed bed reactor containing a cylindrical bed of catalyst through which the reactants move in a vertical direction. Other embodiments use trickle bed reactors. In some embodiments, the reactants flow upward through the reactor, while other embodiments use a downflow arrangement. The subject catalyst may be present within the reactor as pellets, spheres, extrudates, irregular shaped granules, etc. To employ the subject catalyst, the reactants would be preferably brought up to the desired inlet temperature of the reaction zone, admixed with hydrogen and then passed into and through the reactor. Alternatively, the reactants may be admixed with the desired amount of hydrogen and then heated to the desired inlet temperature. In either case, the effluent of the reaction zone may be passed into a product recovery facility for the removal of residual hydrogen or may be passed directly into downstream product utilization zones if the presence of the residual hydrogen is acceptable. Hydrogen may be removed by

flashing the effluent stream to a lower pressure or by passing the effluent stream into a stripping column.

The hydrogenated effluent 130 is sent to a splitter column 135 where it is separated into a light fraction 140 and a heavy fraction 145. The light fraction 140 typically has a boiling point in the range of less than 65°C, and the heavy fraction 145 typically has a boiling point in the range of greater than 65°C.

The heavy fraction 145 is combined with a hydrogen-rich stream 150 and introduced into a selective hydrodesulfurization zone 155 to selectively remove sulfur. The selective hydrodesulfurization zone 155 contains a hydrotreating catalyst (or a combination of hydrotreating catalysts) and operated at selected hydrotreating conditions effective to convert a majority of the sulfur in the feed to hydrogen sulfide and minimize saturation of olefins at the same time. In general, such selective conditions include a temperature from 260°C(500°F) to 315°C (600°F), a pressure from 0.69 MPa (100 psig) to 3.45 MPa (500 psig), a liquid hourly space velocity of the fresh hydrocarbonaceous feedstock from 0.5 hr⁻¹ to 10 hr⁻¹. Other hydrotreating conditions are also possible depending on the particular feed stocks being treated. The selective hydrodesulfurization zone 155 may contain a single reactor or multiple reactors and each reactor may contain one or more reaction zones with the same or different catalysts to convert sulfur and nitrogen to hydrogen sulfide and ammonia.

Suitable hydrodesulfurization catalysts are any known conventional hydrotreating catalysts and include those which are comprised of at least one Group VIII metal (preferably iron, cobalt and nickel, more preferably cobalt and/or nickel) and at least one Group VI metal (preferably molybdenum and tungsten) on a high surface area support material, preferably alumina. Other suitable hydrotreating catalysts include zeolitic catalysts, as well as noble metal catalysts where the noble metal is selected from palladium and platinum. It is within the scope of the processes herein that more than one type of hydrotreating catalyst be used in the same reaction vessel. The Group VIII metal is typically present in an amount ranging from 0.5 to 20 weight percent, preferably from 0.5 to 10 weight percent. The Group VI metal will typically be present in an amount ranging from 1 to 25 weight percent, and preferably from 1 to 12 weight percent. While the above describes some exemplary catalysts for hydrotreating, other hydrotreating and/or hydrodesulfurization catalysts may also be used depending on the particular feedstock and the desired effluent quality.

The conditions in the selective hydrodesulfurization zone 155 are effective to convert greater than 50 percent of the sulfur in the heavy fraction 145 to hydrogen sulfide and, preferably, 60 to 80 percent of the sulfur to hydrogen sulfide. At the same time, the selected conditions disfavor olefin saturation to generally maintain the octane level.

5 However, at these conditions, some of the hydrogen sulfide produced reacts to form mercaptans. These reactions are often called reversion or recombination reactions.

The effluent 160 from the selective hydrodesulfurization zone 155 can have a boiling point in the range of 60°C to 220°C, or 65°C to 220°C, or 60°C to 200°C, or 65°C to 200°C, for example. In some embodiments, the effluent 160 can have a T5 boiling point of
10 60°C to 70°C, a T95 boiling point of 160°C to 200°C, and a final boiling point of 200°C to 220°C or greater.

The effluent 160 from the selective hydrodesulfurization zone 155 is sent to a separator 165 where it is separated into the hydrogen rich stream 170 and a liquid stream 175.

In some embodiments, one portion of hydrogen rich stream 170 comprises
15 hydrogen-rich stream 150 and the remainder comprises recycle hydrogen stream 125. Make-up hydrogen 120 can be added to hydrogen rich stream 170 as needed.

Liquid stream 175 is sent to a fractionation zone 180 where it is separated into at least two streams. As illustrated in Fig. 1, liquid stream 175 is separated into a mercaptan rich stream 185 taken as a side cut stream and a first mercaptan lean stream 190 taken from a
20 bottoms of the fractionation zone 180. In this embodiment, the mercaptan rich stream 185 has a boiling point in the range of 60°C to 120°C, or 60°C to 100°C, or 65°C to 120°C, or 65°C to 100°C. The first mercaptan lean stream 190 has a boiling point in the range of 100°C to 220°C, or 120°C to 220°C, or 100°C to 200°C, or 120°C to 200°C. In some embodiments, the mercaptan rich stream 185 has a T5 boiling point of 60°C to 70°C, a T95 boiling point of
25 90°C to 100°C, and a final boiling point of 100°C to 120°C. In some embodiments, the mercaptan lean stream 190 has a T5 boiling point of 120°C to 140°C, a T95 boiling point of 190°C to 210°C, and a final boiling point of 200°C to 220°C.

The mercaptan rich stream 185 is sent to a caustic extraction zone 195 to remove the mercaptans. A sulfur lean caustic stream 200 enters the caustic extraction zone
30 195 and contacts the mercaptan rich stream 185. The caustic extraction process may utilize any alkaline reagent which is capable of extracting mercaptans from the feed stream at practical operating conditions and which may be regenerated in the manner described. A

preferred alkaline reagent comprises an aqueous solution of an alkaline metal hydroxide, such as sodium hydroxide or potassium hydroxide. Sodium hydroxide, commonly referred to as caustic, may be used in concentrations of from 1 to 50 wt.%, with a preferred concentration range being from 5 to 25 wt.%. Optionally, there may be added an agent to increase the solubility of the mercaptans in the solution, typically methanol or ethanol although others such as a phenol, cresol or butyric acid may be used.

The conditions employed in the caustic extraction zone 195 may vary greatly depending on such factors as the nature of the hydrocarbon stream being treated and its mercaptan content, etc. In general, the extraction may be performed at an ambient temperature above 15.6°C(60°F) and at a pressure sufficient to ensure liquid state operation. The pressure may range from atmospheric up to 6.9 MPa (g) (1000 psig) or more, but a pressure in the range of from 345 kPa(g) to 1034 kPa(g) (50 psig to 150 psig) is preferred.

A second consideration is that the pressure chosen should ensure an adequate amount of oxygen is dissolved in the alkaline stream in the downstream oxidation step (not shown), which if practical is preferably operated at substantially the same pressure as the caustic extraction zone 195 after normal process flow pressure drops are taken into consideration. The temperature in the caustic extraction zone 195 is desirably in the range of 10°C to 121°C (50°F to 250°F), or 26.7°C to 48.9°C (80°F to 120°F). The ratio of the volume of the alkaline solution required per volume of the feed stream will vary depending on the mercaptan content of the feed stream. Normally this ratio will be between 0.01:1 and 1:1, although other ratios may be desirable. Optimum extraction in this liquid system is obtained with a velocity through the perforations of from 5 to 10 feet per second. Essentially all of the extractable mercaptans should be transferred to the alkaline solution from the feed stream. As used herein, the term "essentially all" is intended to refer to at least 95% and preferably 98% of all the material referred to.

The mercaptans are transferred from the mercaptan rich stream 185 to the sulfur lean caustic stream 200, resulting in a second mercaptan lean stream 205 and a sulfur rich caustic stream 210.

The sulfur rich caustic stream 210 can be sent for treatment to remove the sulfur (not shown) and recycled to the caustic extraction zone 195, if desired.

The second mercaptan lean stream 205 can be combined with the first mercaptan lean stream 190 to form a combined mercaptan lean stream 215. In some

embodiment, light fraction 140 can be combined with the first mercaptan lean stream 190, the second mercaptan lean stream 205, or both.

The combined mercaptan lean stream 215 can be sent to the gasoline pool.

5 There is also an overhead stream 220, which is condensed and separated in a separator 225 into a gas stream 230 and a liquid stream 235 which is refluxed to the fractionation zone 180.

In this approach, the olefins present in the naphtha fraction having a boiling point in the range of 60°C to 120°C in the mercaptan rich stream 185 taken from the side of the fractionation zone 180 are retained.

10 Alternatively, the liquid stream 175 from the separator 165 could be separated into a mercaptan rich stream and a low boiling first mercaptan lean stream, and a high boiling first mercaptan lean stream, as discussed below in regard to Fig. 2.

In the process 300 shown in Fig. 2, the mercaptan rich stream is treated in a polishing reactor to reduce the mercaptans.

15 The FCC naphtha feed 105 is hydrogenated in the selective hydrogenation zone 115, separated into a light fraction 140 and a heavy fraction 145 in splitter column 135, and desulfurized in selective hydrodesulfurization zone 155 in the same way as described above with respect to Fig. 1.

20 The effluent 160 from the selective hydrodesulfurization zone 155 is sent to separator 165, which is a divided wall separator. The divided wall separator 165 has a wall 305 dividing it in two sections 310, 315. The effluent 160 enters section 310 where it is separated into hydrogen-rich stream 170 and liquid stream 175.

25 Liquid stream 175 is sent to fractionation zone 180 where it is separated into a low boiling first mercaptan lean stream 320, a mercaptan rich stream 325, and a high boiling first mercaptan lean stream 330. The low boiling first mercaptan lean stream 320 has a boiling point range lower than the boiling point range of the mercaptan rich stream 325, while the high boiling first mercaptan lean stream 330 has a boiling point range greater than the mercaptan rich stream 325. For example, the low boiling mercaptan lean stream 320 could have a boiling point in the range of 60°C to 85°C, or 65°C to 85°C, the mercaptan rich stream 30 325 could have a boiling point in the range of 85°C to 120°C, or 85°C to 100°C, and the high boiling mercaptan lean stream 330 could have a boiling point in the range of 100°C to 220°C, or 120°C to 220°C, or 100°C to 200°C, or 120°C to 200°C. In some embodiments, the low

boiling mercaptan lean stream 320 has a T5 boiling point of 60°C to 65°C, a T95 boiling point of 75°C to 85°C, and a final boiling point of 80°C to 90°C). In some embodiments, the mercaptan rich stream 325 has a T5 boiling point of 80°C to 90°C, a T95 boiling point of 90°C to 100°C, and a final boiling point of 100°C to 120°C. In some embodiments, the high boiling mercaptan lean stream 330 has a T5 boiling point of 100°C to 120°C, a T95 boiling point of 180°C to 200°C, and a final boiling point of 200°C to 220°C.

The mercaptan rich stream 325 and a hydrogen rich stream 335 are sent to a polishing reactor (e.g., a hydrodesulfurization reactor) 340. The hydrogen rich stream 335 can be a portion of the hydrogen rich stream 170 from the divided wall separator 165.

The polishing reactor 340 contains a desulfurization catalyst. Suitable catalysts include, but are not limited to nickel, nickel and molybdenum, zeolitic catalysts, and noble metal catalysts, e.g. platinum or palladium. In general, the polishing reactor 340 is operated at a temperature in the range of 280°C to 380°C, and a pressure in the range of 350 kPa(g) to 3450 kPa(g).

The desulfurized effluent 345 from the polishing reactor 340 is sent to section 315 of the divided wall separator 165 where it is separated into the hydrogen rich stream 170 and liquid stream 350.

Liquid stream 350 is sent to a stripping zone 355 to remove gases 360 forming a third mercaptan lean stream 365. The third mercaptan lean stream 365 can be combined with one or more of the low boiling first mercaptan lean stream 320, the high boiling mercaptan lean stream 330, and the light fraction 140 from the splitter column 135 to form a combined mercaptan lean stream 370.

By sending a concentrated mercaptan rich stream 325 to the polishing reactor 340, the size of the polishing reactor 340 can be reduced by a significant amount, in some cases as much as 75-80%. In this embodiment, the low boiling mercaptan lean stream 320 which has a boiling point range of 60°C to 85°C is not sent to polishing reactor 340 which results in the olefins present in this fraction being retained.

Alternatively, the liquid stream 175 can be separated into a mercaptan rich stream and a mercaptan lean stream as described above in Fig. 1, rather than a mercaptan rich stream and at least two mercaptan lean streams.

In the process 400 shown in Fig. 3, the mercaptan rich stream is treated by recycling it to the selective hydrogenation zone 115 which converts the mercaptans into heavy disulfides. In this way, a separate polishing zone is avoided.

The FCC naphtha feed 105 is hydrogenated in the selective hydrogenation zone 115, separated into a light fraction 140 and a heavy fraction 145 in splitter column 135, desulfurized in selective hydrodesulfurization zone 155, separated into hydrogen-rich stream 170 and liquid stream 175 in the same way as described above with respect to Fig. 1.

The liquid stream 175 is sent to the fractionation zone 180 where it is separated into a low boiling first mercaptan lean stream 405, a mercaptan rich stream 410, and a high boiling first mercaptan lean stream 415.

The mercaptan rich stream 410 is sent to the selective hydrogenation zone 115 to be reprocessed.

The flow rates of the mercaptan rich stream 410 and the high boiling first mercaptan lean stream 415 can be controlled with a ratio controller 420.

The low boiling first mercaptan lean stream 405 can be combined with one or more of the high boiling first mercaptan lean stream 415 and the light fraction 140 from the splitter column 135 to form a combined mercaptan lean stream 425.

Alternatively, the liquid stream 175 can be separated into a mercaptan rich stream and a mercaptan lean stream as described above in Fig. 1, rather than a mercaptan rich stream and at least two mercaptan lean streams.

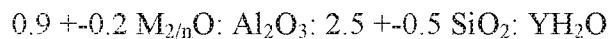
In the process 500 shown in Fig. 4, the mercaptan rich stream is treated by passing it on the adsorption zone 520.

The FCC naphtha feed 105 is hydrogenated in the selective hydrogenation zone 115, separated into a light fraction 140 and a heavy fraction 145 in splitter column 135, desulfurized in selective hydrodesulfurization zone 155, separated into hydrogen-rich stream 170 and liquid stream 175 in the same way as described above with respect to Fig. 1.

The liquid stream 175 is sent to the fractionation zone 180 where it is separated into a low boiling first mercaptan lean stream 505, a mercaptan rich stream 510, and a high boiling first mercaptan lean stream 515.

The mercaptan rich stream 510 is sent to an adsorption zone 520. The adsorption zone 520 contains one or more adsorbent beds containing an adsorbent. The adsorbent can be regenerable or non-regenerable.

Suitable adsorbents include, but are not limited to nickel zeolite Y, nickel exchanged zeolite X, molybdenum exchanged zeolite X, a smectite clay having a surface area of at least 150 m²/g, and mixtures thereof. Zeolite X belongs to the faujasite family of zeolites. Its synthesis was first reported in U.S. Pat. No. 2,882,244 which is incorporated by
 5 reference. Zeolite X has the empirical formula:



where M is an alkali or alkaline earth metal, "n" is the valence of M and "Y" has a value up to
 10 8. Briefly, zeolite X is prepared by forming a reaction mixture containing reactive sources of the components, reacting the mixture at a temperature of 21°C to 120°C for a time of 1 hours to 100 hours. Zeolite X is usually synthesized in the sodium form. That is, sodium is the counter ion present in the pores of the zeolite.

The synthesis of zeolite Y is described in U.S. Pat. No. 3,130,007 which is
 15 incorporated by reference. Zeolite Y has an empirical formula expressed in terms of moles of oxides of:



where "w" has a value of greater than 3 up to 6 and "x" has a value up to 9. As with zeolite X,
 20 a reaction mixture containing the appropriate ratio of materials is prepared, and then reacted at a temperature of 20°C to 125°C for a time of 16 hours to 8 days.

The nickel or molybdenum forms of zeolites X and Y can be prepared by ion exchange methods well known in the art. Ion exchange can be carried out in a batch or continuous process with a continuous process preferred. The metal salts which can be used to
 25 carry out the exchange include nickel chloride, nickel nitrate, and sodium molybdate.

Yet another set of adsorbents is the group of clays which make up the smectite family of clays and which have a surface area of at least 150 m²/g. Clays are composed of infinite layers (lamellae) of metal oxides and hydroxides stacked one on top of the other. These layers or sheets are composed of tetrahedrally coordinated cations which are linked
 30 through shared oxygens to sheets of cations octahedrally coordinated to oxygens and hydroxyls. When one octahedral sheet is linked to one tetrahedral sheet a 1:1 layered structure is formed as in kaolinite, whereas when one octahedral sheet is linked to two

tetrahedral sheets, a 2:1 layered structure is produced as in beidellite. Anionic charges on the tetrahedral layers (usually siliceous layers) are neutralized by cations such as Na^+ or Ca^{+2} in the interlamellar spaces. These cations can be exchanged with other cations.

The smectite clays are 2:1 layered swellable clays. By swellable is meant that the clays swell or expand when placed in water or other solvents. Specific smectite clays are montmorillonite, beidellite, nontronite, hectorite, saponite and sauconite.

Contacting of the liquid hydrocarbon stream with any of the adsorbents described above can be carried out by means well known in the art. For example, the contacting can be carried out in a batch mode or in a continuous mode. In a batch mode, the stream to be treated is mixed with a sufficient amount of adsorbent in an appropriate size reaction vessel. The resultant mixture can be stirred or agitated to ensure complete contact of the stream with the adsorbent. In order to ensure that the sulfur compounds are completely adsorbed onto the support, it is necessary that the hydrocarbon stream be contacted with the solid solution for a time of 10 minutes to 10 hours. If a continuous process is used, the adsorbent is placed in a vertical column and the stream to be treated is upflowed through the column. The stream is flowed at a liquid hourly space velocity of 0.1 hr^{-1} to 10 hr^{-1} .

Whether the process is carried out in a batch or continuous manner, the adsorbent can be used in the form of extrudates, pills, beads, spheres, etc. Usually, the adsorbent is mixed with a binder such as atapulgite clay, minugel clay and bentonite clay and then formed into the desired shape. The amount of binder which is used varies from 8 to 20 wt. %. Processes for forming the various shapes are well known in the art.

Finally, the contacting can be carried out over a broad temperature range. Generally the temperature range is from 10°C to 100°C , or 20°C to 70°C . The process is conducted at atmospheric pressure or pressures up to 1379 kPa (g) (200 psig).

The second mercaptan lean stream 525 from the adsorption zone 520 can be combined with the low boiling first mercaptan lean stream 505, and/or the high boiling first mercaptan lean stream 515 to form a combined mercaptan lean stream 530. In some embodiments, the light fraction 140 can be combined with one or more of these streams as well.

Alternatively, the liquid stream 175 can be separated into a mercaptan rich stream and a mercaptan lean stream as described above in Fig. 1, rather than a mercaptan rich stream and at least two mercaptan lean streams.

In the embodiment shown in Fig. 5, the mercaptan rich stream is treated using an ionic liquid.

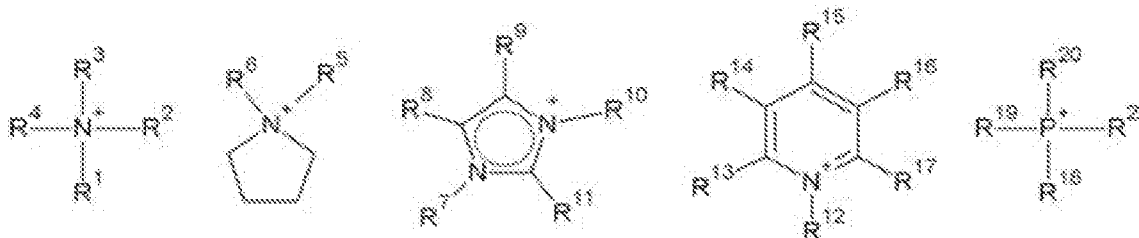
The FCC naphtha feed 105 is hydrogenated in the selective hydrogenation zone 115, separated into a light fraction 140 and a heavy fraction 145 in splitter column 135, desulfurized in selective hydrodesulfurization zone 155, separated into hydrogen-rich stream 170 and liquid stream 175 in the same way as described above with respect to Fig. 1.

The liquid stream 175 is sent to the fractionation zone 180 where it is separated into a low boiling first mercaptan lean stream 605, a mercaptan rich stream 610, and a high boiling first mercaptan lean stream 615.

The mercaptan rich stream 610 is sent to an ionic liquid extraction zone 620 along with lean ionic liquid stream 625. The lean ionic liquid stream 625 can include fresh ionic liquid and/or regenerated ionic liquid.

Ionic liquids suitable for use in the instant invention are naphtha-immiscible ionic liquids. As used herein the term “naphtha-immiscible ionic liquid” means the ionic liquid is capable of forming a separate phase from naphtha under the operating conditions of the process. Ionic liquids that are miscible with naphtha at the process conditions will be completely soluble with the naphtha; therefore, no phase separation will be feasible. Thus, naphtha-immiscible ionic liquids may be insoluble with or partially soluble with the hydrocarbon feed under the operating conditions. An ionic liquid capable of forming a separate phase from the naphtha under the operating conditions is considered to be naphtha-immiscible. Ionic liquids according to the invention may be insoluble, partially soluble, or completely soluble (miscible) with water.

The ionic liquid can be any acidic ionic liquid. There can be one or more ionic liquids. The ionic liquid comprises an organic cation and an anion. Suitable cations include, but are not limited to, nitrogen-containing cations and phosphorus-containing cations. Suitable organic cations include, but are not limited to:



where R^1 - R^{21} are independently selected from C_1 - C_{20} hydrocarbons, C_1 - C_{20} hydrocarbon derivatives, halogens, and H. Suitable hydrocarbons and hydrocarbon derivatives include saturated and unsaturated hydrocarbons, halogen substituted and partially substituted hydrocarbons and mixtures thereof. C_1 - C_8 hydrocarbons are particularly suitable.

The anion can be derived from halides, typically halometallates, and combinations thereof. The anion is typically derived from metal and nonmetal halides, such as metal and nonmetal chlorides, bromides, iodides, fluorides, or combinations thereof. Combinations of halides include, but are not limited to, mixtures of two or more metal or nonmetal halides (e.g., $AlCl_4^-$ and BF_4^-), and mixtures of two or more halides with a single metal or nonmetal (e.g., $AlCl_3Br^-$). In some embodiments, the metal is aluminum, with the mole fraction of aluminum ranging from $0 < Al < 0.25$ in the anion. Suitable anions include, but are not limited to, $AlCl_4^-$, $Al_2Cl_7^-$, $Al_3Cl_{10}^-$, $AlCl_3Br^-$, $Al_2Cl_6Br^-$, $Al_3Cl_9Br^-$, $AlBr_4^-$, $Al_2Br_7^-$, $Al_3Br_{10}^-$, $GaCl_4^-$, $Ga_2Cl_7^-$, $Ga_3Cl_{10}^-$, $GaCl_3Br^-$, $Ga_2Cl_6Br^-$, $Ga_3Cl_9Br^-$, $CuCl_2^-$, $Cu_2Cl_3^-$, $Cu_3Cl_4^-$, $ZnCl_3^-$, $FeCl_3^-$, $FeCl_4^-$, $Fe_3Cl_7^-$, PF_6^- , and BF_4^- .

The mercaptan removal step may be conducted under mercaptan removal conditions including temperatures and pressures sufficient to keep the ionic liquid and naphtha feeds and effluents as liquids. For example, the mercaptan removal step temperature may range between $10^\circ C$ and less than the decomposition temperature of the ionic liquid, and the pressure may range between atmospheric pressure and 700 kPa (g). When the ionic liquid comprises more than one ionic liquid component, the decomposition temperature of the ionic liquid is the lowest temperature at which any of the ionic liquid components decompose. The mercaptan removal step may be conducted at a uniform temperature and pressure or the contacting and separating steps of the mercaptan removal step may be operated at different temperatures and/or pressures. In an embodiment, the contacting step is conducted at a first temperature, and the separating step is conducted at a temperature at least $5^\circ C$ lower than the first temperature. Such temperature differences may facilitate separation of the naphtha and ionic liquid phases.

The mercaptan removal step conditions such as the contacting or mixing time, the separation or settling time, and the ratio of the mercaptan rich stream 610 to the lean ionic liquid stream 625 may vary greatly based, for example, on the specific ionic liquid or liquids

employed, the nature of the naphtha feed (straight run or previously processed), the sulfur content of the naphtha feed, the degree of sulfur removal required, the number of sulfur removal steps employed, and the specific equipment used. In general it is expected that contacting time may range from less than one minute to two hours; settling time may range from one minute to eight hours; and the weight ratio of naphtha feed to lean ionic liquid introduced to the sulfur removal step may range from 1:10,000 to 10,000:1. In an embodiment, the weight ratio of naphtha feed to lean ionic liquid may range from 1:1,000 to 1,000:1; and the weight ratio of naphtha feed to lean ionic liquid may range from 1:100 to 100:1. In an embodiment the weight of naphtha feed is greater than the weight of ionic liquid introduced to the sulfur removal step.

The mercaptan rich stream 610 and the lean ionic liquid stream 625 are contacted forming the second mercaptan lean stream 630, and a mercaptan rich ionic liquid stream 635 containing mercaptan compounds.

In one embodiment, the ionic liquid extraction zone 620 includes a contacting zone with a mixer/settler in which the mercaptan rich stream 610 and the lean ionic liquid stream 625 are mixed and then allowed settle, forming two phases: an ionic liquid phase and a naphtha phase.

In another embodiment, the ionic liquid extraction zone 620 includes a countercurrent extraction column. The mercaptan rich stream 610 and the lean ionic liquid stream 625 flow counter currently and the mercaptan compounds are transferred from the mercaptan rich stream to the ionic liquid.

The ionic liquid extraction zone 620 can include an optional water washing zone to recover ionic liquid that is entrained or otherwise remains in the naphtha. The water washing step can be performed using any suitable equipment and conditions used to conduct other liquid-liquid wash and extraction operations.

If desired, the mercaptan rich ionic liquid stream 635 can be sent to an optional regeneration zone to regenerate the rich ionic liquid by removing the mercaptan compounds from the ionic liquid. The rich ionic liquid can be regenerated in any suitable manner. A variety of methods for regenerating ionic liquids have been developed. For example, US 7,651,970; US 7,825,055; US 7,956,002; US 7,732,363, each of which is incorporated herein by

reference, describe contacting ionic liquid containing the conjunct polymer with a reducing metal (e.g., Al), an inert hydrocarbon (e.g., hexane), and hydrogen and heating to 100°C to transfer the conjunct polymer to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. Another method involves contacting ionic liquid containing conjunct polymer with a reducing metal (e.g., Al) in the presence of an inert hydrocarbon (e.g. hexane) and heating to 100°C to transfer the conjunct polymer to the hydrocarbon phase, allowing for the conjunct polymer to be removed from the ionic liquid phase. See e.g., US 7,674,739 B2; which is incorporated herein by reference. Still another method of regenerating the ionic liquid involves contacting the ionic liquid containing the conjunct polymer with a reducing metal (e.g., Al), HCl, and an inert hydrocarbon (e.g. hexane), and heating to 100°C to transfer the conjunct polymer to the hydrocarbon phase. See e.g., US 7,727,925, which is incorporated herein by reference. The ionic liquid can be regenerated by adding a homogeneous metal hydrogenation catalyst (e.g., $(PPh_3)_3RhCl$) to ionic liquid containing conjunct polymer and an inert hydrocarbon (e.g. hexane), and introducing hydrogen. The conjunct polymer is reduced and transferred to the hydrocarbon layer. See e.g., US 7,678,727, which is incorporated herein by reference. Another method for regenerating the ionic liquid involves adding HCl, isobutane, and an inert hydrocarbon to the ionic liquid containing the conjunct polymer and heating to 100°C. The conjunct polymer reacts to form an uncharged complex, which transfers to the hydrocarbon phase. See e.g., US 7,674,740, which is incorporated herein by reference. The ionic liquid could also be regenerated by adding a supported metal hydrogenation catalyst (e.g. Pd/C) to the ionic liquid containing the conjunct polymer and an inert hydrocarbon (e.g. hexane). Hydrogen is introduced and the conjunct polymer is reduced and transferred to the hydrocarbon layer. See e.g., US 7,691,771, which is incorporated herein by reference. Still another method involves adding a suitable substrate (e.g. pyridine) to the ionic liquid containing the conjunct polymer. After a period of time, an inert hydrocarbon is added to wash away the liberated conjunct polymer. The ionic liquid precursor [butylpyridinium] [Cl] is added to the ionic liquid (e.g. [butylpyridinium] $[Al_2Cl_7]$) containing the conjunct polymer followed by an inert hydrocarbon. After mixing, the hydrocarbon layer is separated, resulting in a regenerated ionic liquid. See, e.g., US 7,737,067, which is incorporated herein by reference. Another method involves adding ionic liquid containing conjunct polymer to a suitable substrate (e.g. pyridine) and an electrochemical cell containing two aluminum electrodes and an inert hydrocarbon. A voltage is applied, and the current measured to determine

the extent of reduction. After a given time, the inert hydrocarbon is separated, resulting in a regenerated ionic liquid. See, e.g., US 8,524,623, which is incorporated herein by reference. Ionic liquids can also be regenerated by contacting with silane compounds (U.S. Application Serial No. 14/269,943), borane compounds (US. Application Serial No. 14/269,978), Brønsted acids, (US Application Serial No. 14/229,329), or C₁ to C₁₀ Paraffins (US Application Serial No. 14/229,403), each of which is incorporated herein by reference.

The second mercaptan lean stream 630 can be combined with the low boiling first mercaptan lean stream 605, and/or the high boiling first mercaptan lean stream 615 to form a combined mercaptan lean stream 640. In some embodiments, the light fraction 140 can be combined with one or more of these streams as well.

Alternatively, the liquid stream 175 can be separated into a mercaptan rich stream and a mercaptan lean stream as described above in Fig. 1, rather than a mercaptan rich stream and at least two mercaptan lean streams.

SPECIFIC EMBODIMENTS

While the following is described in conjunction with specific embodiments, it will be understood that this description is intended to illustrate and not limit the scope of the preceding description and the appended claims.

A first embodiment of the invention is a process for reducing the sulfur content of full range naphtha comprising introducing a naphtha feed into a selective hydrogenation zone in the presence of hydrogen and a hydrogenation catalyst under selective hydrogenation conditions to form a hydrogenated feed; separating the hydrogenated feed into at least two fractions, a light fraction and a heavy fraction; introducing the heavy fraction to a selective hydrodesulfurization zone in the presence of hydrogen and a hydrodesulfurization catalyst under selective hydrodesulfurization conditions to form a desulfurized stream, the desulfurized stream containing mercaptans; separating at least a portion of the desulfurized stream into at least two streams, a mercaptan rich stream and a first mercaptan lean stream; and treating at least a portion of the mercaptan rich stream to remove at least a portion of the mercaptan compounds to form a second mercaptan lean stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein treating the at least the portion of the mercaptan rich stream comprises introducing the mercaptan rich stream into at least one of a caustic

extraction zone, a hydrodesulfurization reaction zone, the selective hydrogenation zone, an adsorption zone, and an ionic liquid extraction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph further comprising combining the first mercaptan lean stream with the second mercaptan lean stream. An embodiment of the invention is one, any or all of prior
5 embodiments in this paragraph up through the first embodiment in this paragraph further comprising combining the light fraction with at least one of the first mercaptan lean stream and the second mercaptan lean stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph
10 wherein separating the at least the portion of the desulfurized stream into at least two streams comprises separating the at least the portion of the desulfurized stream into the mercaptan rich stream and the first mercaptan lean stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the mercaptan rich stream has a boiling point in a range of 60°C to 100°C,
15 and the first mercaptan lean stream has a boiling point in a range of 100°C to 220°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein separating the at least the portion of the desulfurized stream into at least two streams comprises separating the at least the portion of the desulfurized stream into the mercaptan rich stream and at least two first mercaptan lean
20 streams, a low boiling first mercaptan lean stream having a boiling point range lower than a boiling point range of the mercaptan rich stream and a high boiling first mercaptan stream having a boiling point range greater than the boiling point range of the mercaptan rich stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the mercaptan rich stream has a
25 boiling point in a range of 85°C to 100°C, and the low boiling first mercaptan lean stream has a boiling point in a range of 60°C to 85°C, and the high boiling first mercaptan lean stream has a boiling point in a range of 100°C to 220°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein the mercaptan rich stream has a boiling point in a range of 60°C to 100°C
30 and the first mercaptan lean stream has a boiling point in a range of 100°C to 220°C, and wherein treating the mercaptan rich stream comprises introducing the mercaptan rich stream into a caustic extraction zone. An embodiment of the invention is one, any or all of prior

embodiments in this paragraph up through the first embodiment in this paragraph and further comprising separating the desulfurized stream into a gas stream and a liquid stream in a first side of a divided wall separator and wherein separating the at least the portion of the desulfurized stream into the at least two streams comprises separating the liquid stream into

5 at least the mercaptan rich stream and at least two first mercaptan lean streams, wherein the mercaptan rich stream has a boiling point in a range of 85°C to 100°C, and the at least two first mercaptan lean streams comprise a low boiling first mercaptan lean stream having a boiling point in a range of 60°C to 85°C, and a high boiling mercaptan lean stream having a boiling point in a range of 100°C to 220°C, and wherein treating the at least the portion of

10 the mercaptan rich stream comprises introducing at least the portion of the mercaptan rich stream into a hydrodesulfurization reaction zone forming a hydrodesulfurization reaction zone effluent; and further comprising separating the hydrodesulfurization reaction zone effluent into a gas stream and a liquid stream in the second side of the divided wall separator; stripping the liquid stream in a stripping zone to form a third mercaptan lean stream. An

15 embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein separating the at least the portion of the desulfurized stream into at least two streams comprises separating the at least the portion of the desulfurized stream into at least the mercaptan rich stream and at least two mercaptan lean streams, wherein the mercaptan rich stream has a boiling point in a range of 85°C to

20 100°C, and the at least two first mercaptan lean streams comprise a low boiling first mercaptan lean stream having a boiling point in a range of 60°C to 85°C, and a high boiling mercaptan lean stream having a boiling point in a range of 100°C to 220°C, and wherein treating the at least the portion of the mercaptan rich stream comprises introducing the at least the portion of the mercaptan rich stream into the selective hydrogenation zone. An

25 embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein separating at least the portion of the desulfurized stream into at least two streams comprises separating at least the portion of the desulfurized stream into at least the mercaptan rich stream and at least two mercaptan lean streams, wherein the mercaptan rich stream has a boiling point in a range of 85°C to 100°C,

30 and the at least two first mercaptan lean streams comprise a low boiling first mercaptan lean stream having a boiling point in a range of 60°C to 85°C, and a high boiling mercaptan lean stream having a boiling point in a range of 100°C to 220°C, and wherein treating the at least

the portion of the mercaptan rich stream comprises introducing the at least the portion of the mercaptan rich stream into an adsorption zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the first embodiment in this paragraph wherein separating at least the portion of the desulfurized stream into at least two streams comprises separating at least the portion of the desulfurized stream into at least the mercaptan rich stream and at least two mercaptan lean streams, wherein the mercaptan rich stream has a boiling point in a range of 85°C to 100°C, and the at least two first mercaptan lean streams comprise a low boiling first mercaptan lean stream having a boiling point in a range of 60°C to 85°C, and a high boiling mercaptan lean stream having a boiling point in a range of 100°C to 220°C, and wherein treating the at least the portion of the mercaptan rich stream comprising introducing the at least the portion of the mercaptan rich stream into an ionic liquid extraction zone.

A second embodiment of the invention is a process for reducing the sulfur content of full range FCC naphtha comprising introducing a FCC naphtha feed into a selective hydrogenation zone in the presence of hydrogen and a hydrogenation catalyst under selective hydrogenation conditions to form a hydrogenated feed; separating the hydrogenated feed into at least two fractions, a lighter fraction and a heavier fraction; introducing the heavier fraction to a selective hydrodesulfurization zone in the presence of hydrogen and a hydrodesulfurization catalyst under selective hydrodesulfurization conditions to form a desulfurized stream, the desulfurized stream containing mercaptans; separating at least a portion of the desulfurized stream into at least two streams, a mercaptan rich stream and a first mercaptan lean stream; and treating at least a portion of the mercaptan rich stream to remove at least a portion of the mercaptan compounds to form a second mercaptan lean stream, wherein treating the at least the portion of the mercaptan rich stream comprises introducing the at least the portion of the mercaptan rich stream into at least one of a caustic extraction zone, a hydrodesulfurization reaction zone, the selective hydrogenation zone, an adsorption zone, and an ionic liquid extraction zone. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph further comprising at least one of combining the first mercaptan lean stream with the second mercaptan lean stream; and combining the lighter fraction with at least one of the first mercaptan lean stream and the second mercaptan lean stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second

embodiment in this paragraph wherein separating the at least the portion of the desulfurized stream into at least two streams comprises separating the at least the portion of the desulfurized stream into the mercaptan rich stream and the first mercaptan lean stream. The process of claim 16 wherein the mercaptan rich stream has a boiling point 60°C to 100°C and the first mercaptan lean stream has a boiling point in a range of 100°C to 220°C. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein separating the at least the portion of the desulfurized stream into at least two streams comprises separating the at least the portion of the desulfurized stream into the mercaptan rich stream and at least two first mercaptan lean streams, a low boiling first mercaptan lean stream having a boiling point range lower than a boiling point range of the mercaptan rich stream and a high boiling first mercaptan stream having a boiling point range greater than the boiling range of the mercaptan rich stream. An embodiment of the invention is one, any or all of prior embodiments in this paragraph up through the second embodiment in this paragraph wherein the boiling point range of the mercaptan rich stream is 85°C to 100°C, and the boiling point range of the low boiling first mercaptan lean stream is 60°C to 85°C, and the boiling point range of the high boiling first mercaptan lean stream is 100°C to 220°C.

A third embodiment of the invention is a process for reducing the sulfur content of full range FCC naphtha comprising introducing a FCC naphtha feed into a selective hydrogenation zone in the presence of hydrogen and a hydrogenation catalyst under selective hydrogenation conditions to form a hydrogenated feed; separating the hydrogenated feed into at least two fractions, a lighter fraction and a heavier fraction; introducing the heavier fraction to a selective hydrodesulfurization zone in the presence of hydrogen and a hydrodesulfurization catalyst under selective hydrodesulfurization conditions to form a desulfurized stream, the desulfurized stream containing mercaptans; separating at least a portion of the desulfurized stream into at least a mercaptan rich stream, a low boiling mercaptan lean stream having a boiling point range lower than a boiling point range of the mercaptan rich stream, and a high boiling first mercaptan stream having a boiling point range greater than the boiling range of the mercaptan rich stream; and treating at least a portion of the mercaptan rich stream to remove at least a portion of the mercaptan compounds to form a second mercaptan lean stream, wherein treating the at least the portion of the mercaptan rich stream comprises introducing the at least the portion of the mercaptan rich stream into at least

one of a caustic extraction zone, a hydrodesulfurization reaction zone, the selective hydrogenation zone, an adsorption zone, and an ionic liquid extraction zone.

Without further elaboration, it is believed that using the preceding description that one skilled in the art can utilize the present invention to its fullest extent and easily ascertain the essential characteristics of this invention, without departing from the spirit and scope thereof, to make various changes and modifications of the invention and to adapt it to various usages and conditions. The preceding preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limiting the remainder of the disclosure in any way whatsoever, and that it is intended to cover various modifications and equivalent arrangements included within the scope of the appended claims.

In the foregoing, all temperatures are set forth in degrees Celsius and, all parts and percentages are by weight, unless otherwise indicated.

What is claimed is:

1. A process for reducing the sulfur content of full range naphtha comprising:

5 introducing a naphtha feed into a selective hydrogenation zone in the presence of hydrogen and a hydrogenation catalyst under selective hydrogenation conditions to form a hydrogenated feed;

separating the hydrogenated feed into at least two fractions, a light fraction and a heavy fraction;

10 introducing the heavy fraction to a selective hydrodesulfurization zone in the presence of hydrogen and a hydrodesulfurization catalyst under selective hydrodesulfurization conditions to form a desulfurized stream, the desulfurized stream containing mercaptans;

15 separating at least a portion of the desulfurized stream into at least two streams, a mercaptan rich stream and a first mercaptan lean stream; and

treating at least a portion of the mercaptan rich stream to remove at least a portion of the mercaptan compounds to form a second mercaptan lean stream.

2. The process of claim 1 wherein treating the at least the portion of the mercaptan rich stream comprises introducing the mercaptan rich stream into at least one of a caustic extraction zone, a hydrodesulfurization reaction zone, the selective hydrogenation zone, an adsorption zone, and an ionic liquid extraction zone.

25 3. The process of any of claims 1-2 wherein separating the at least the portion of the desulfurized stream into at least two streams comprises separating the at least the portion of the desulfurized stream into the mercaptan rich stream and the first mercaptan lean stream.

30 4. The process of claim 3 wherein the mercaptan rich stream has a boiling point in a range of 60°C to 100°C, and the first mercaptan lean stream 190 a boiling point in a range of 100°C to 220°C.

5 5. The process of any of claims 1-2 wherein separating the at least the portion of the desulfurized stream into at least two streams comprises separating the at least the portion of the desulfurized stream into the mercaptan rich stream and at least two first mercaptan lean streams, a low boiling first mercaptan lean stream having a boiling point range lower than a boiling point range of the mercaptan rich stream and a high boiling first mercaptan stream having a boiling point range greater than the boiling point range of the mercaptan rich stream.

10 6. The process of claim 5 wherein the mercaptan rich stream has a boiling point in a range of 85°C to 100°C, and the low boiling first mercaptan lean stream has a boiling point in a range of 60°C to 85°C, and the high boiling first mercaptan lean stream has a boiling point in a range of 100°C to 220°C.

15 7. The process of any of claims 1-2 and further comprising:
separating the desulfurized stream into a gas stream and a liquid stream in a first side of a divided wall separator and wherein separating the at least the portion of the desulfurized stream into the at least two streams comprises separating the liquid stream into at least the mercaptan rich stream and at least two first mercaptan lean streams,

20 wherein the mercaptan rich stream has a boiling point in a range of 85°C to 100°C, and the at least two first mercaptan lean streams comprise a low boiling first mercaptan lean stream having a boiling point in a range of 60°C to 85°C, and a high boiling mercaptan lean stream having a boiling point in a range of 100°C to 220°C, and

25 wherein treating the at least the portion of the mercaptan rich stream comprises introducing at least the portion of the mercaptan rich stream into a hydrodesulfurization reaction zone forming a hydrodesulfurization reaction zone effluent;

and further comprising:

separating the hydrodesulfurization reaction zone effluent into a gas stream and a liquid stream in the second side of the divided wall separator;

30 stripping the liquid stream in a stripping zone to form a third mercaptan lean stream.

8. The process of any of claims 1-2 wherein separating the at least the portion of the desulfurized stream into at least two streams comprises separating the at least the portion of the desulfurized stream into at least the mercaptan rich stream and at least two mercaptan lean streams,

5 wherein the mercaptan rich stream has a boiling point in a range of 85°C to 100°C, and the at least two first mercaptan lean streams comprise a low boiling first mercaptan lean stream having a boiling point in a range of 60°C to 85°C, and a high boiling mercaptan lean stream having a boiling point in a range of 100°C to 220°C, and

10 wherein treating the at least the portion of the mercaptan rich stream comprises introducing the at least the portion of the mercaptan rich stream into the selective hydrogenation zone.

9. The process of any of claims 1-2 wherein separating at least the portion of the desulfurized stream into at least two streams comprises separating at least the portion of the desulfurized stream into at least the mercaptan rich stream and at least two mercaptan lean streams,

15 wherein the mercaptan rich stream has a boiling point in a range of 85°C to 100°C, and the at least two first mercaptan lean streams comprise a low boiling first mercaptan lean stream having a boiling point in a range of 60°C to 85°C, and a high boiling mercaptan lean stream having a boiling point in a range of 100°C to 220°C, and

20 wherein treating the at least the portion of the mercaptan rich stream comprises introducing the at least the portion of the mercaptan rich stream into an adsorption zone.

25 10. The process of any of claims 1-2 wherein separating at least the portion of the desulfurized stream into at least two streams comprises separating at least the portion of the desulfurized stream into at least the mercaptan rich stream and at least two mercaptan lean streams

30 wherein the mercaptan rich stream has a boiling point in a range of 85°C to 100°C, and the at least two first mercaptan lean streams comprise a low boiling first mercaptan lean stream having a boiling point in a range of 60°C to 85°C, and a high boiling mercaptan lean stream having a boiling point in a range of 100°C to 220°C, and

wherein treating the at least the portion of the mercaptan rich stream comprising introducing the at least the portion of the mercaptan rich stream into an ionic liquid extraction zone.

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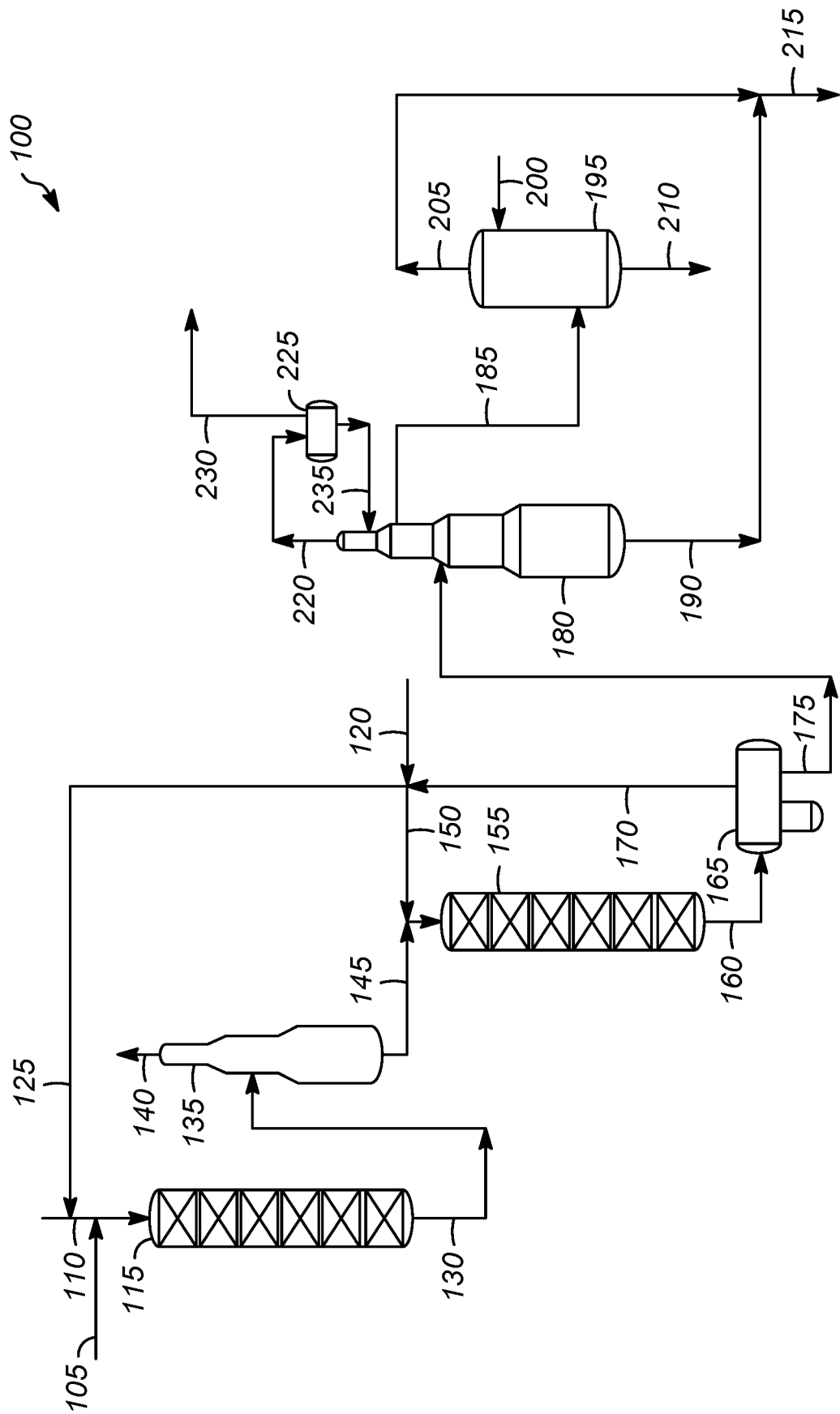


FIG. 1

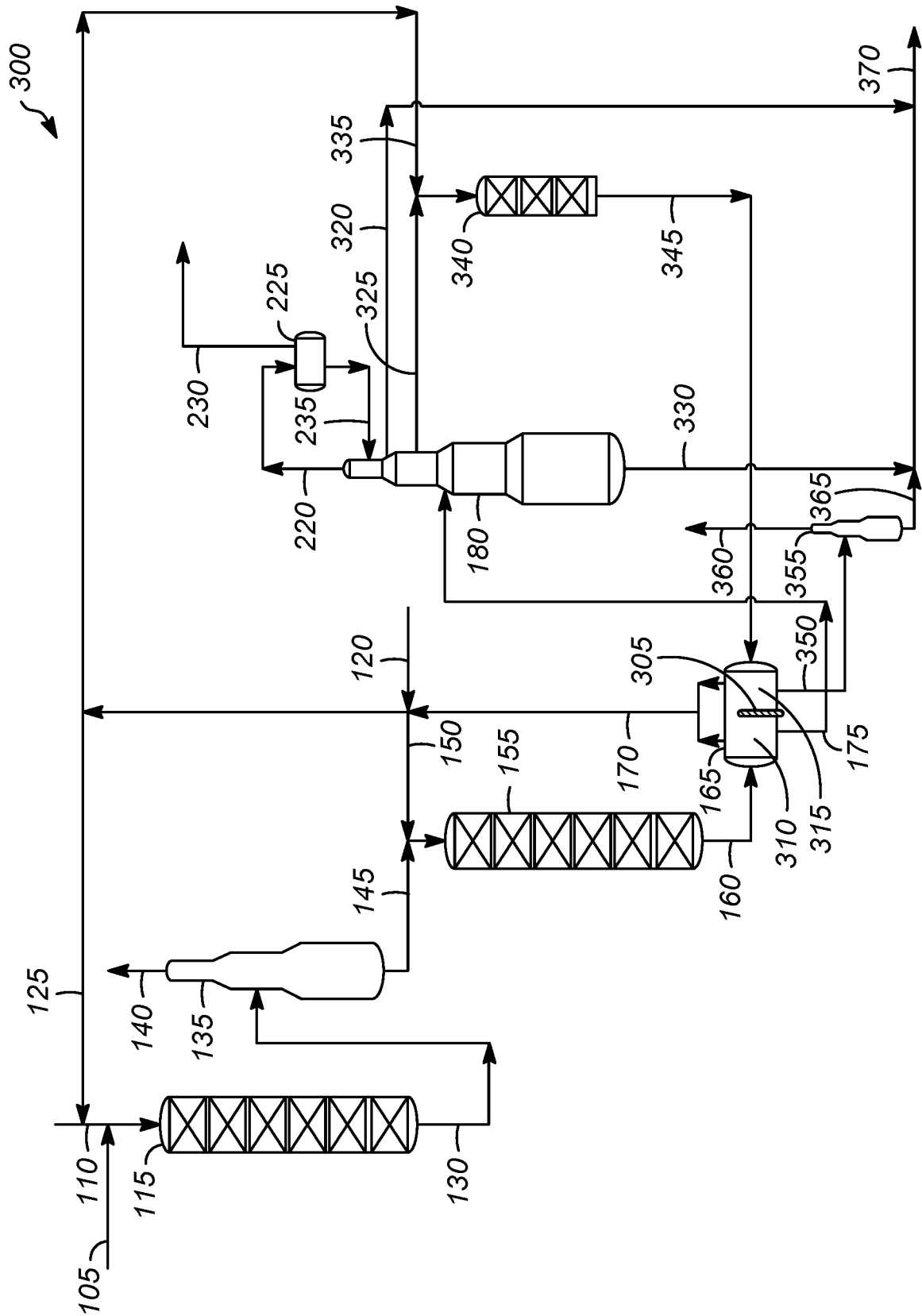


FIG. 2

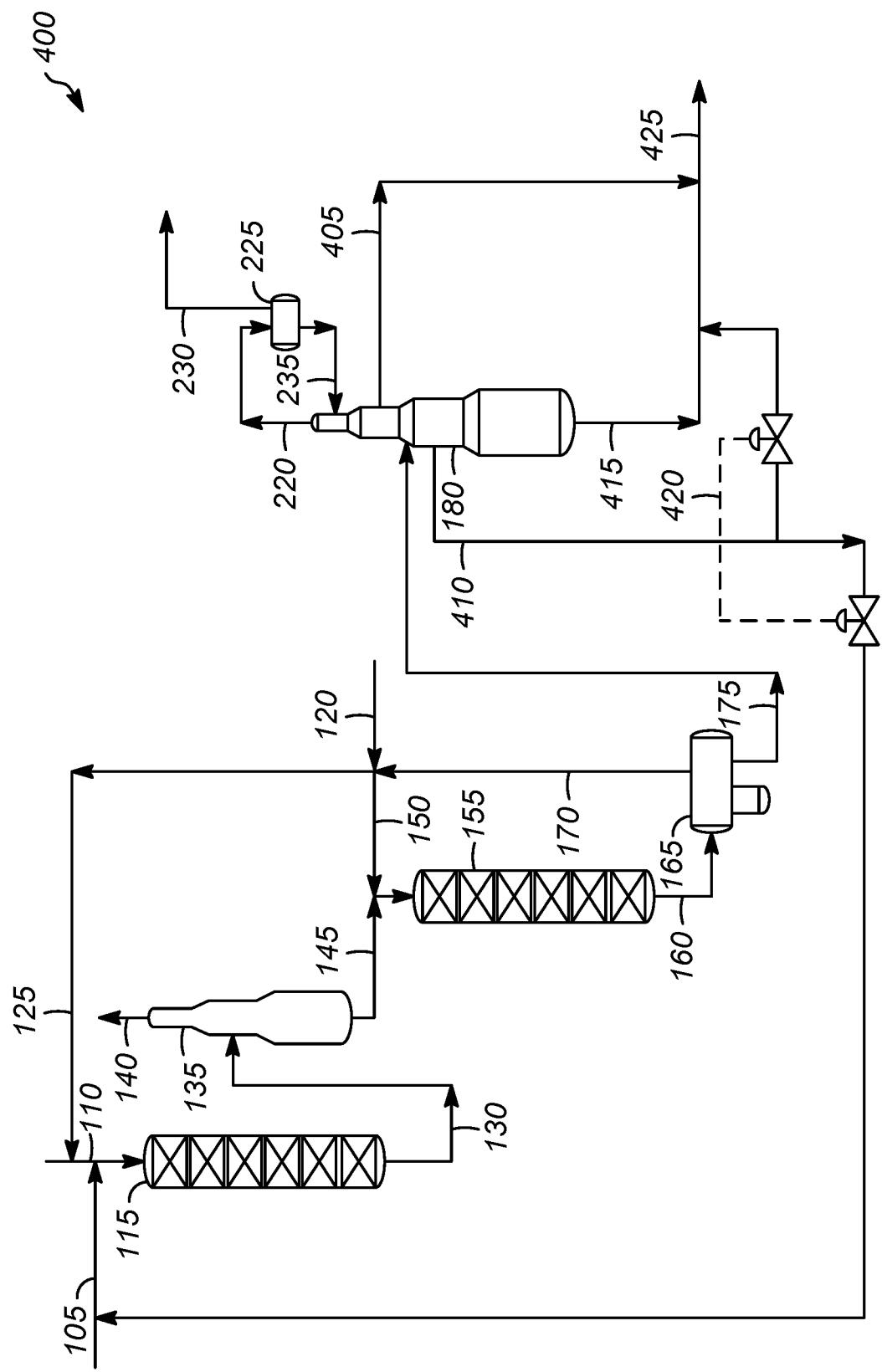


FIG. 3

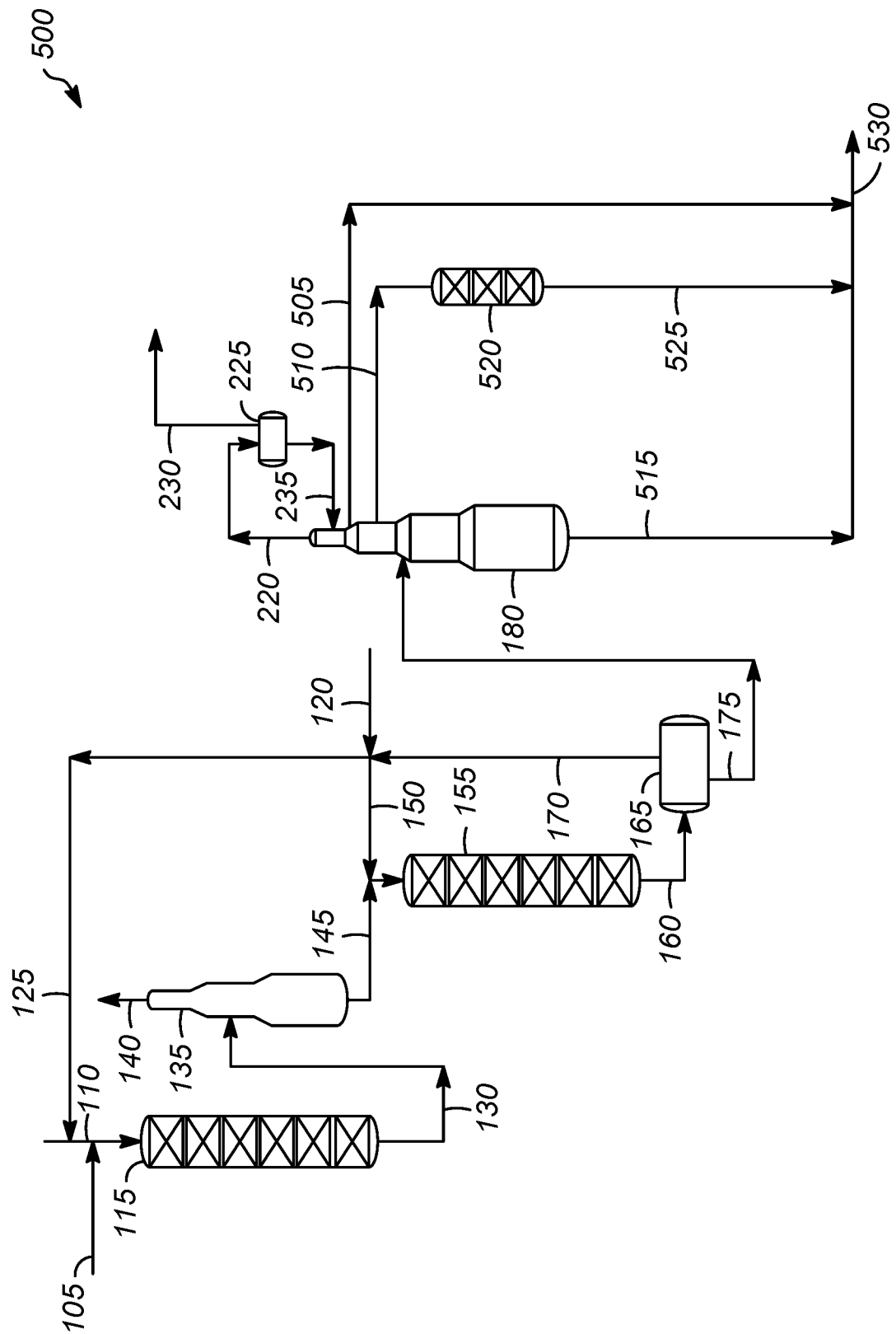


FIG. 4

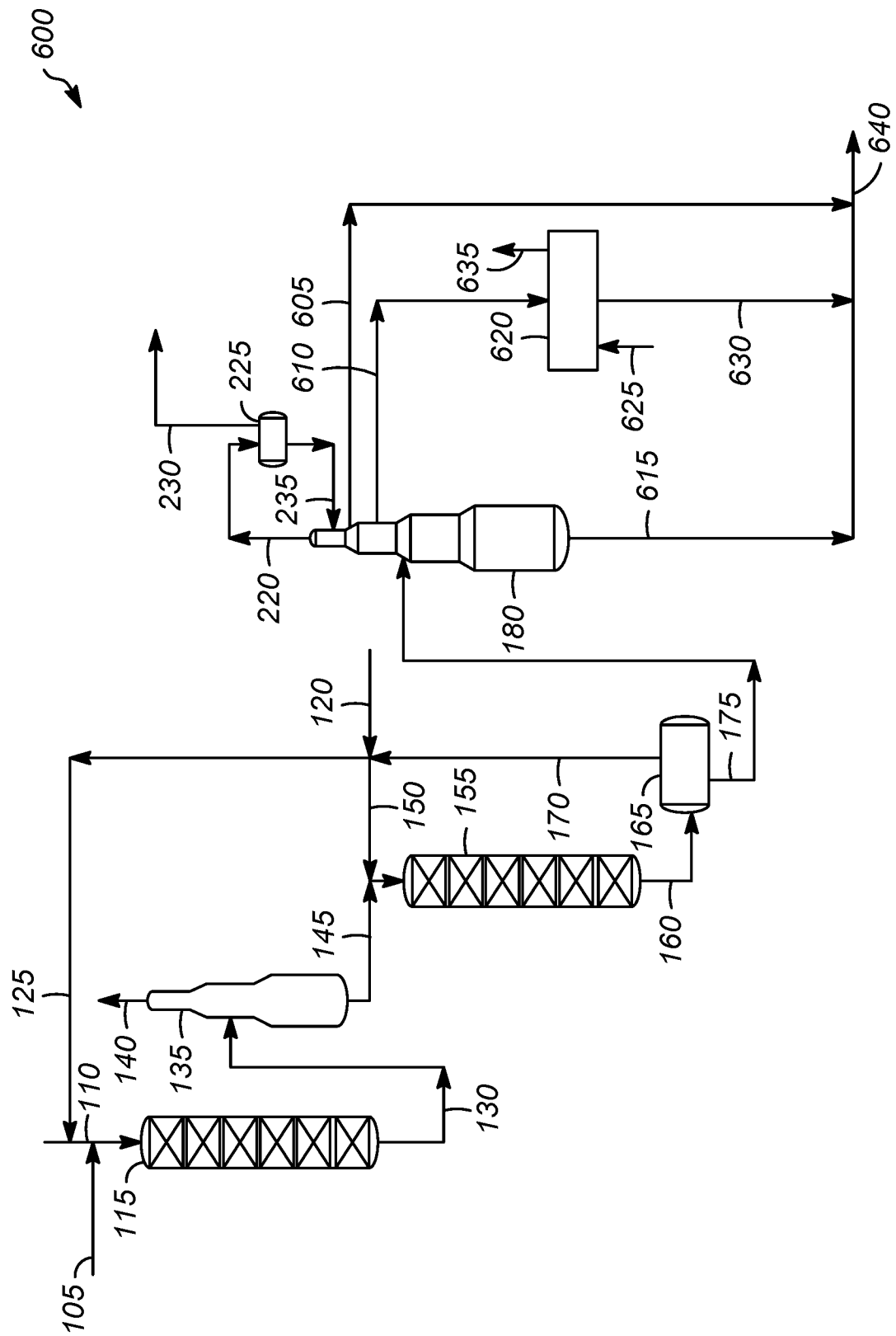


FIG. 5

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2016/046281

A. CLASSIFICATION OF SUBJECT MATTER

C10G 45/02 (2006.01)
C10G 65/04 (2006.01)
C10G 19/02 (2006.01)
C10G 67/10 (2006.01)
C10G 67/06 (2006.01)
C10G 67/02 (2006.01)
C10G 7/00 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10G 45/02, 65/04, 19/02, 67/10, 67/06, 67/02, 7/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6444118 B1 (CATALYTIC DISTILLATION TECHNOLOGIES) 03.09.2002, fig. 1, col. 6, lines 58-61	1-6, 8
Y		7, 9, 10
Y	US 7951290 B2 (UOP LLC) 31.05.2011, claim 5, col. 11, lines 20-25	7
Y	US 6454934 B2 (JGC CORPORATION) 24.09.2002, fig. 4	9
Y	US 2015/0090639 A1 (INSTITUTO MEXICANO DEL PETROLEO) 02.04.2015, abstract, par. [0008]	10



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:		"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

28 October 2016 (28.10.2016)

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