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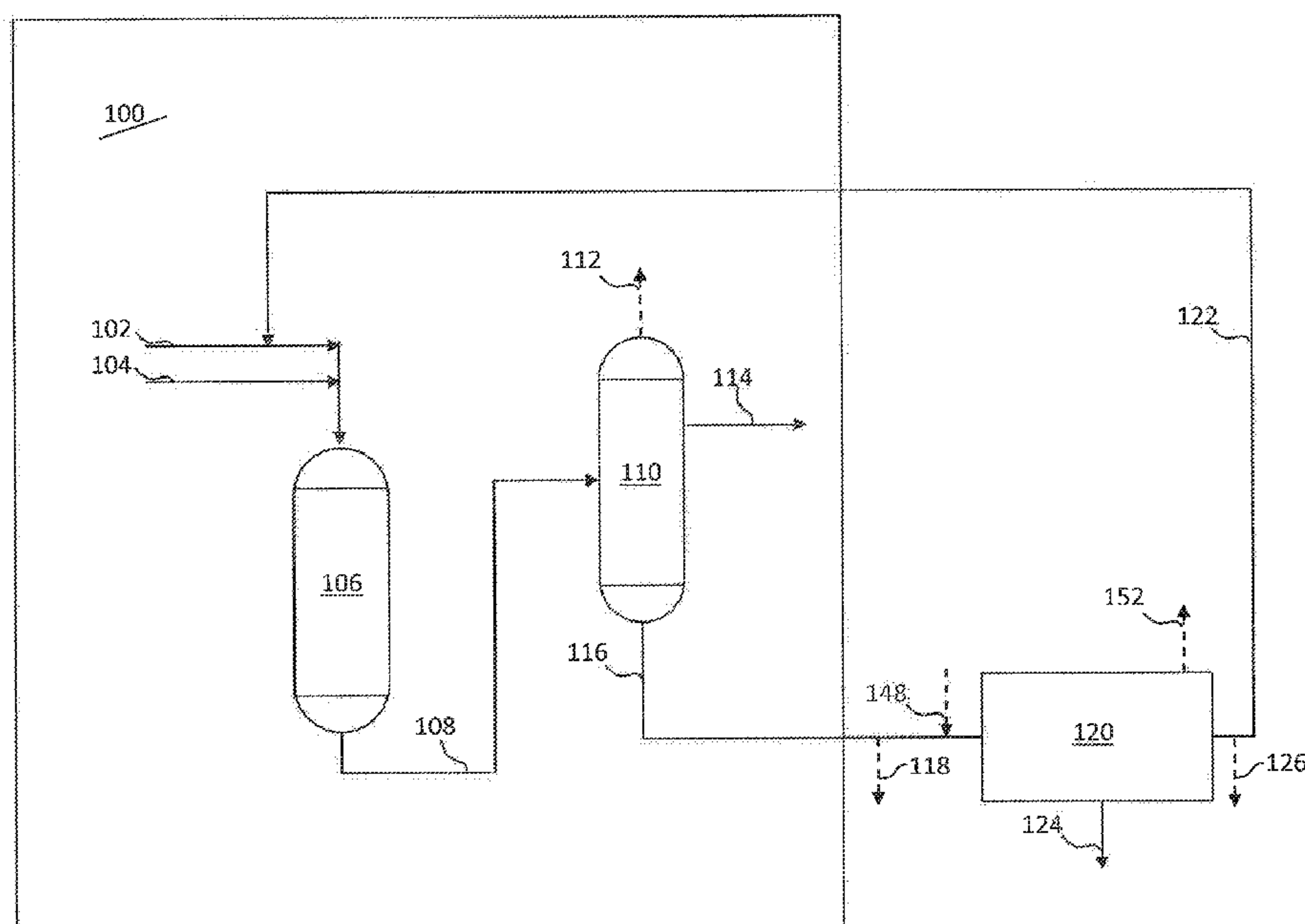


FIG. 1

(57) Abstract: Hydrocracker bottoms fractions are treated to remove HPNA compounds and/or HPNA precursor compounds and produce a reduced-HPNA stream effective for recycle, in a configuration of a single-stage hydrocracking reactor, series-flow once through hydrocracking operation, or two-stage hydrocracking operation. The hydrocracker bottoms fractions are subjected to thermal cracking and HPNA compounds are removed with the coke phase.

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HYDROCRACKING PROCESS AND SYSTEM INCLUDING REMOVAL OF HEAVY POLY NUCLEAR AROMATICS FROM HYDROCRACKER BOTTOMS BY COKING

RELATED APPLICATIONS

[01] This application claims priority to US Patent Application 16/727,431 filed December 26, 2019.

BACKGROUND OF THE INVENTION

Field of the Invention

[02] The present invention relates to hydrocracking processes, and in particular to hydrocracking processes including removal of heavy poly nuclear aromatics from recycle streams using thermal cracking.

Description of Related Art

[03] Hydrocracking processes are used commercially in a large number of petroleum refineries. They are used to process a variety of feeds boiling within the range of about 370-520°C in conventional hydrocracking units and boiling at 520°C and above in residue hydrocracking units. In general, hydrocracking processes split the molecules of the feed into smaller, i.e., lighter, molecules having higher average volatility and economic value. Additionally, hydrocracking processes typically improve the quality of the hydrocarbon feedstock by increasing the hydrogen-to-carbon ratio and by removing organosulfur and organonitrogen compounds. The significant economic benefit derived from hydrocracking processes has resulted in substantial development of process improvements and more active catalysts.

[04] In addition to sulfur-containing and nitrogen-containing compounds, a typical hydrocracking feedstream, such as vacuum gas oil (VGO), contains a small amount of poly nuclear aromatic (PNA) compounds, i.e., those containing less than seven fused aromatic rings. As the feedstream is subjected to hydroprocessing at elevated temperature and pressure, heavy poly nuclear aromatic (HPNA) compounds, i.e., those containing seven or more fused benzene rings, tend to form and are present in high concentration in the unconverted hydrocracker bottoms.

[05] Heavy feedstreams such as demetallized oil (DMO) or deasphalted oil (DAO) have much higher concentrations of N, S and PNA compounds than VGO feedstreams. These impurities can lower the overall efficiency of hydrocracking units by requiring higher operating temperature, higher hydrogen partial pressure or additional reactor/catalyst volume. In addition, high concentrations of impurities can accelerate catalyst deactivation.

[06] Three major hydrocracking process schemes include single-stage once through hydrocracking, series-flow hydrocracking with or without recycle, and two-stage recycle hydrocracking. Single-stage once through hydrocracking is the simplest of the hydrocracker configurations and typically occurs at operating conditions that are more severe than hydrotreating processes, and less severe than conventional full-pressure hydrocracking processes. It uses one or more reactors for both the treating steps and the cracking reaction, so the catalyst must be capable of both hydrotreating and hydrocracking. This configuration is cost effective, but typically results in relatively low product yields (for example, a maximum conversion rate of about 60%). Single-stage hydrocracking is often designed to maximize mid-distillate yield over single or dual catalyst systems. Dual catalyst systems can be used in a stacked-bed configuration or in two different reactors. The effluents are passed to a fractionator column to separate the H_2S , NH_3 , light gases ($\text{C}_1\text{-C}_4$), naphtha and diesel products boiling in the temperature range of 36-370°C. The hydrocarbons boiling above 370°C are typically unconverted bottoms that, in single stage systems, are passed to other refinery operations.

[07] Series-flow hydrocracking with or without recycle is one of the most commonly used configurations. It uses one reactor (containing both treating and cracking catalysts) or two or more reactors for both treating and cracking reaction steps. In a series-flow configuration the entire hydrocracked product stream from the first reaction zone, including light gases (typically $\text{C}_1\text{-C}_4$, H_2S , NH_3) and all remaining hydrocarbons, are sent to the second reaction zone. Unconverted bottoms from the fractionator column are recycled back into the first reactor for further cracking. This configuration converts heavy crude oil fractions, i.e., vacuum gas oil, into light products and has the potential to maximize the yield of naphtha, jet fuel, or diesel, depending on the recycle cut point used in the distillation section.

[08] Two-stage recycle hydrocracking uses two reactors and unconverted bottoms from the fractionation column are passed to the second reactor for further cracking. Since the first reactor accomplishes both hydrotreating and hydrocracking, the feed to second reactor is virtually free of ammonia and hydrogen sulfide. This permits the use of high-performance zeolite catalysts which are susceptible to poisoning by S or N compounds.

[09] Typical hydrocracking feedstocks are vacuum gas oils boiling in the nominal range of 370-565°C. Heavier oil feedstreams such as DMO or DAO, alone or blended with vacuum gas oil, can be processed in a hydrocracking unit. For instance, a typical hydrocracking unit processes vacuum

gas oils that contain from 10-25V% of DMO or DAO for optimum operation. A 100V% DMO or DAO feed can also be processed, typically under more severe conditions, since the DMO or DAO stream contains significantly more N compounds (2,000 ppmw vs. 1,000 ppmw) and a higher micro carbon residue (MCR) content than the VGO stream (10W% vs. <1W%).

[10] DMO or DAO content in blended feedstocks to a hydrocracking unit can lower the overall efficiency of the unit by increasing operating temperature or reactor/catalyst volume for existing units, or by increasing hydrogen partial pressure requirements or reactor/catalyst volume for grass-roots units. These impurities can also reduce the quality of the desired intermediate hydrocarbon products in the hydrocracking effluent. When DMO or DAO are processed in a hydrocracker, further processing of hydrocracking reactor effluents may be required to meet the refinery fuel specifications, depending upon the refinery configuration. When the hydrocracking unit is operating in its desired mode, that is to say, discharging a high quality effluent product stream, its effluent can be utilized in blending and to produce gasoline, kerosene and diesel fuel to meet established fuel specifications.

[11] In addition, formation of HPNA compounds is an undesirable side reaction that occurs in recycle hydrocrackers. The HPNA molecules form by dehydrogenation of larger hydro-aromatic molecules or cyclization of side chains onto existing HPNA molecules followed by dehydrogenation, which is favored as the reaction temperature increases. HPNA formation depends on many known factors including the type of feedstock, catalyst selection, process configuration, and operating conditions. Since HPNA molecules accumulate in the recycle system and lead to equipment fouling, HPNA formation must be controlled in the hydrocracking process.

[12] The rate of formation of the various HPNA compounds increases with higher conversion and heavier feedstocks. The fouling of equipment may not be apparent until large amounts of HPNA accumulate in the recycle liquid loop. The problem of HPNA formation is of universal concern to refiners and various removal methods have been developed by refinery operators to reduce its impact.

[13] Conventional methods to separate or treat heavy poly-nuclear aromatics formed in the hydrocracking process include adsorption, hydrogenation, extraction, solvent deasphalting and purging, or “bleeding” a portion of the recycle stream from the system to reduce the build-up of HPNA compounds and cracking or utilizing the bleed stream elsewhere in the refinery. The

hydrocracker bottoms are sometimes treated in separate units to eliminate the HPNA molecules and recycle HPNA-free bottoms back to the hydrocracking reactor.

[14] As noted above, one alternative when operating the hydrocracking unit in the recycle mode is to purge a certain amount of the recycle liquid to reduce the concentration of HPNA that is introduced with the fresh feed, although purging reduces the conversion rate to below 100%. Another solution to the build-up problem is to eliminate the HPNAs by passing them to a special purpose vacuum column which effectively fractionates 98-99% of the recycle stream leaving most of the HPNAs at the bottom of the column for rejection from the system as fractionator bottoms. This alternative incurs the additional capital cost and operating expenses of a dedicated fractionation column.

[15] The problem therefore exists of providing a process for removing HPNA compounds from the hydrocracker bottoms fraction from a hydrocracking zone fractionator that is more efficient and cost effective than the known processes.

SUMMARY OF THE INVENTION

[16] Hydrocracker bottoms fractions are treated by coking operations to reduce or eliminate HPNA compounds and/or HPNA precursor compounds, and produce a reduced-HPNA thermally cracked hydrocarbon products fraction effective for recycle, in a configuration of a single-stage hydrocracking reactor, series-flow once through hydrocracking operation, or two-stage hydrocracking operation. Hydrocracker bottoms, alone or in a combination with an additional feedstock, are subjected to thermal cracking in a coking zone. All or a portion of the thermally cracked hydrocarbon products obtained from the coking zone are recycled within the integrated hydrocracking operation. The resulting coke contains HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms fraction.

[17] The above methods for separation of HPNA and/or HPNA precursor compounds by thermal cracking can be integrated in a hydrocracking operation using a single reactor or plural reactors in a “once-through” configuration. Accordingly, in certain embodiments a hydrocracking process for treating a heavy hydrocarbon feedstream which contains undesired nitrogen-containing compounds and poly-nuclear aromatic compounds is provided that comprises subjecting the hydrocarbon feedstream to one or more hydrocracking stages to produce a hydrocracked effluent. The hydrocracked effluent is fractionated to recover hydrocracked products and a hydrocracked bottoms fraction containing HPNA and/or HPNA precursor compounds. The hydrocracked

bottoms fraction is subjected to thermal cracking in a coking zone, and all or a portion of the thermally cracked hydrocarbon products obtained from the coking zone is recycled.

[18] In additional embodiments, the above methods for separation of HPNA and/or HPNA precursor compounds by thermal cracking can be integrated in a two-stage hydrocracking configuration. Accordingly, in certain embodiments, a hydrocracking process for treating a heavy hydrocarbon feedstream which contains undesired nitrogen-containing compounds and polynuclear aromatic compounds is provided that comprises subjecting the hydrocarbon feedstream to one or more first hydrocracking stages to produce a first stage effluent. The first stage effluent is fractionated to recover hydrocracked products and a hydrocracked bottoms fraction containing HPNA and/or HPNA precursor compounds. The hydrocracked bottoms fraction is subjected to thermal cracking in a coking zone, and all or a portion of the thermally cracked hydrocarbon products obtained from the coking zone is passed to a second hydrocracking stage.

[19] In certain embodiments, a process for removal of HPNA compounds and/or HPNA precursor compounds from a hydrocracked bottoms fraction prior to recycling within a hydrocracking operation comprises: subjecting the hydrocracked bottoms fraction to thermal cracking to shift HPNA and/or HPNA precursor compounds to a coke phase and to produce thermally cracked hydrocarbon products, and recycling all or a portion of the thermally cracked hydrocarbon products within the hydrocracking operation. In certain embodiments, two stage hydrocracking process comprises subjecting a hydrocarbon stream to a first hydrocracking stage to produce a first hydrocracked effluent; fractionating the first hydrocracked effluent to recover one or more hydrocracked product fractions and a bottoms fraction corresponding to the hydrocracked bottoms fraction of in the above process for removal of HPNA; wherein recycling all or a portion of the thermally cracked hydrocarbon products comprises passing all or a portion of the thermally cracked hydrocarbon products to a second hydrocracking stage to produce a second hydrocracked effluent; and optionally wherein the second hydrocracked effluent is fractionated with the first hydrocracked effluent. In certain embodiments, a hydrocracking process comprising subjecting a hydrocarbon stream to one or more hydrocracking stages to produce a hydrocracked effluent; fractionating the hydrocracked effluent to recover one or more hydrocracked product fractions and a hydrocracked bottoms fraction corresponding to the hydrocracked bottoms fraction of in the above process for removal of HPNA; and wherein recycling all or a portion of the thermally cracked hydrocarbon products within the hydrocracking

operation comprises recycling all or a portion of the thermally cracked hydrocarbon products to at least one of the one or more hydrocracking stages. In certain embodiments, the thermal cracking process is delayed coking. In certain embodiments, the thermal cracking process is fluid coking. In certain embodiments, the coking process integrates adsorbent material and/or heterogeneous catalyst to enhance removal of HPNA and/or HPNA precursor compounds. In certain embodiments the process further passing an additional feed to the same thermal cracking process as the hydrocracked bottoms fraction.

[20] In certain embodiments, a system for removal of HPNA compounds and/or HPNA precursor compounds from a hydrocracked bottoms fraction is provided comprising a coking zone having one or more inlets in fluid communication with a hydrocracked bottoms outlet of a hydrocracking fractionating zone, and one or more outlets for discharging thermally cracked hydrocarbon products. The one or more outlets for discharging thermally cracked hydrocarbon products are in fluid communication with a hydrocracking operation as a bottoms recycle stream. The coking zone typically further comprised apparatus or sub-systems for recovery and handling of coke from the coking zone. In certain embodiments, a two stage hydrocracking system comprises a first hydrocracking reaction zone having one or more inlets in fluid communication with a source of an initial feedstock, and one or more outlets for discharging a first hydrocracked effluent stream; a fractionating zone having one or more inlets in fluid communication with the outlet(s) for discharging the first hydrocracked effluent stream, one or more outlets discharging a hydrocracked product fractions, and one or more outlets discharging a hydrocracked bottoms fraction in fluid communication with the HPNA separation zone as above; a second hydrocracking reaction zone having one or more inlets in fluid communication with the outlet(s) for discharging the HPNA-reduced hydrocracked bottoms portion of the HPNA separation zone as above, and one or more outlets discharging a second hydrocracked effluent stream; and optionally wherein the outlet(s) for discharging the second hydrocracked effluent is in fluid communication with the fractionating zone. In certain embodiments, a hydrocracking system comprises a hydrocracking reaction zone having one or more inlets in fluid communication with a source of an initial feedstock and is in fluid communication with the HPNA-reduced hydrocracked bottoms portion from the outlet(s) of the HPNA separation zone as above, and one or more outlets discharging an effluent stream; and a fractionating zone having one or more inlets in fluid communication with the outlet(s)for discharging the effluent stream, one or more outlets discharging a hydrocracked

product fractions, and one or more outlets discharging a hydrocracked bottoms fraction in fluid communication with the inlet(s) of the HPNA separation zone as above. In certain embodiments, the HPNA separation zone includes a contacting and/or mixing zone upstream of the sulfonation reaction zone. In certain embodiments, the HPNA separation zone is also in fluid communication with a source of additional feed.

[21] Still other aspects, embodiments, and advantages of these exemplary aspects and embodiments, are discussed in detail below. Moreover, it is to be understood that both the foregoing information and the following detailed description are merely illustrative examples of various aspects and embodiments, and are intended to provide an overview or framework for understanding the nature and character of the claimed aspects and embodiments. The accompanying drawings are included to provide illustration and a further understanding of the various aspects and embodiments, and are incorporated in and constitute a part of this specification. The drawings, together with the remainder of the specification, serve to explain principles and operations of the described and claimed aspects and embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[22] The invention will be described in further detail below and with reference to the attached drawings in which the same or similar elements are referred to by the same number, and where:

FIG. 1 is a process flow diagram of an embodiment of an integrated hydrocracking unit operation;

FIG. 2 is a process flow diagram of an integrated series-flow hydrocracking system;

FIG. 3 is a process flow diagram of an integrated two-stage hydrocracking system with recycle;

FIG. 4 is a process flow diagram of a hydrocracking operation integrated with a coking reaction and separation zone operating as a delayed coker;

FIG. 5 is a process flow diagram of a hydrocracking operation integrated with a coking reaction and separation zone operating as a fluid coker;

FIG. 6 is a process flow diagram of a hydrocracking operation integrated with a coking reaction and separation zone operating with additional material to assist coking; and

FIG. 7 is a plot of hydrocracker bottoms content in a delayed coker against the coke yield.

DETAILED DESCRIPTION OF THE INVENTION

[23] Integrated processes and systems are provided for to improve efficiency of hydrocracking operations, by removing HPNA and/or HPNA precursor compounds prior to recycling within a hydrocracking operation. The processes and systems herein are effective for different types of hydrocracking operations, and are also effective for a wide range of initial hydrocracking feedstocks obtained from various sources, such as one or more of straight run vacuum gas oil, treated vacuum gas oil, demetallized oil from solvent demetallizing operations, deasphalted oil from solvent deasphalting operations, coker gas oils from coker operations separate from the integrated coking zone, cycle oils from fluid catalytic cracking operations (including heavy cycle oil), and visbroken oils from visbreaking operations. The initial hydrocracking feedstock generally has a boiling point range within about 350-800, 370-800, 350-700, 370-700, 350-600, 370-600, 350-565 or 370-565°C.

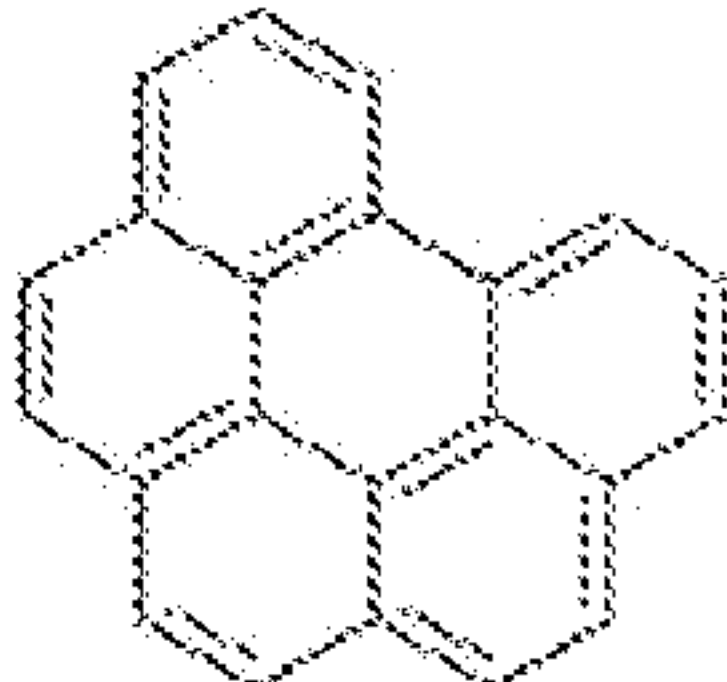
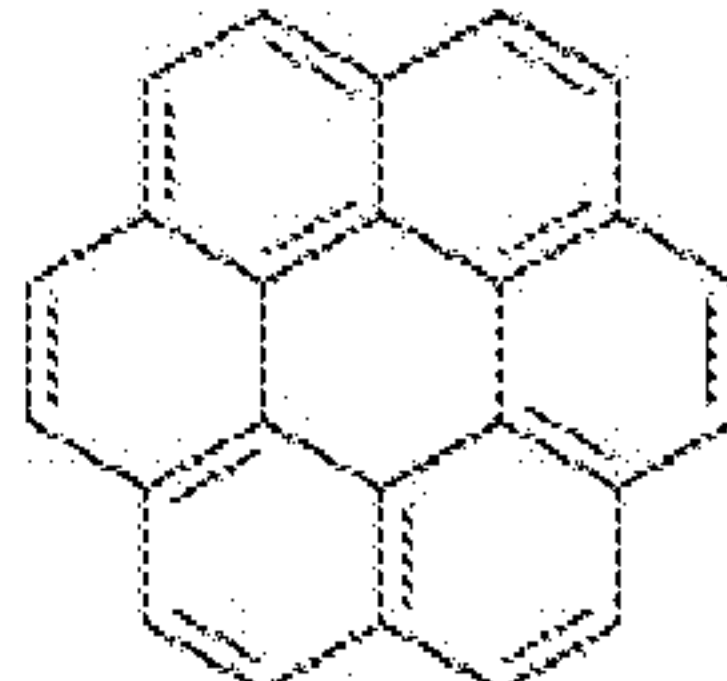
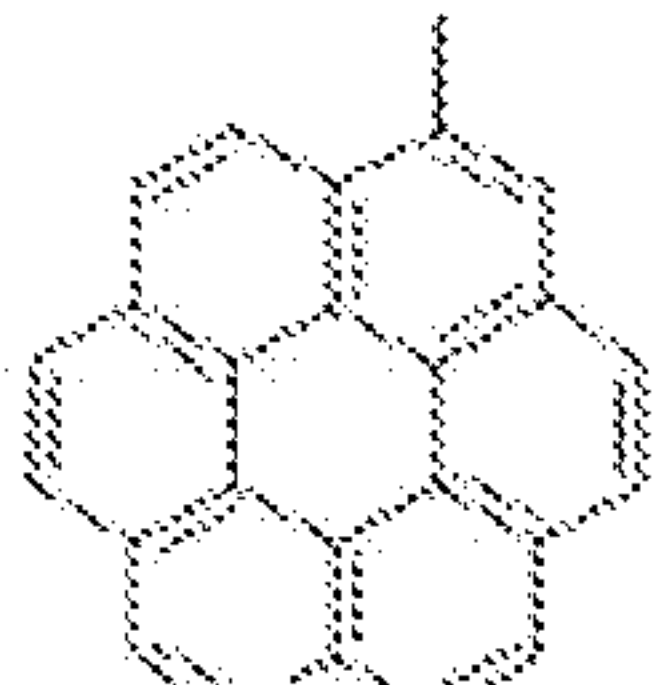
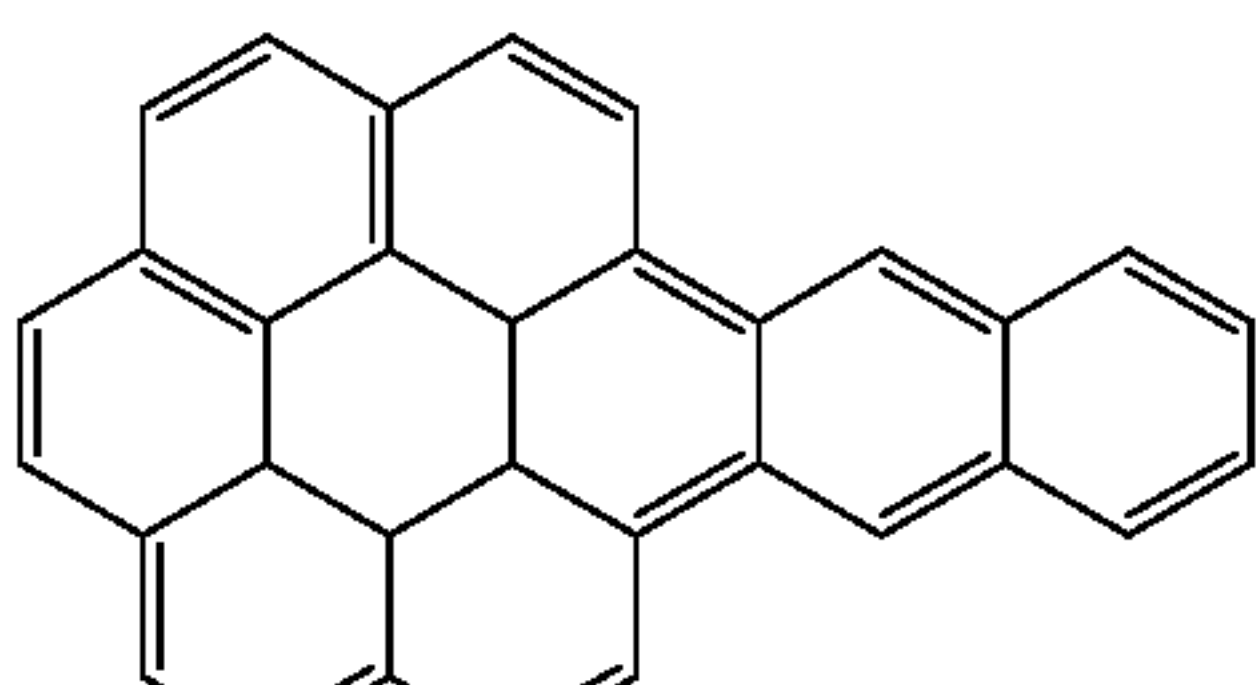
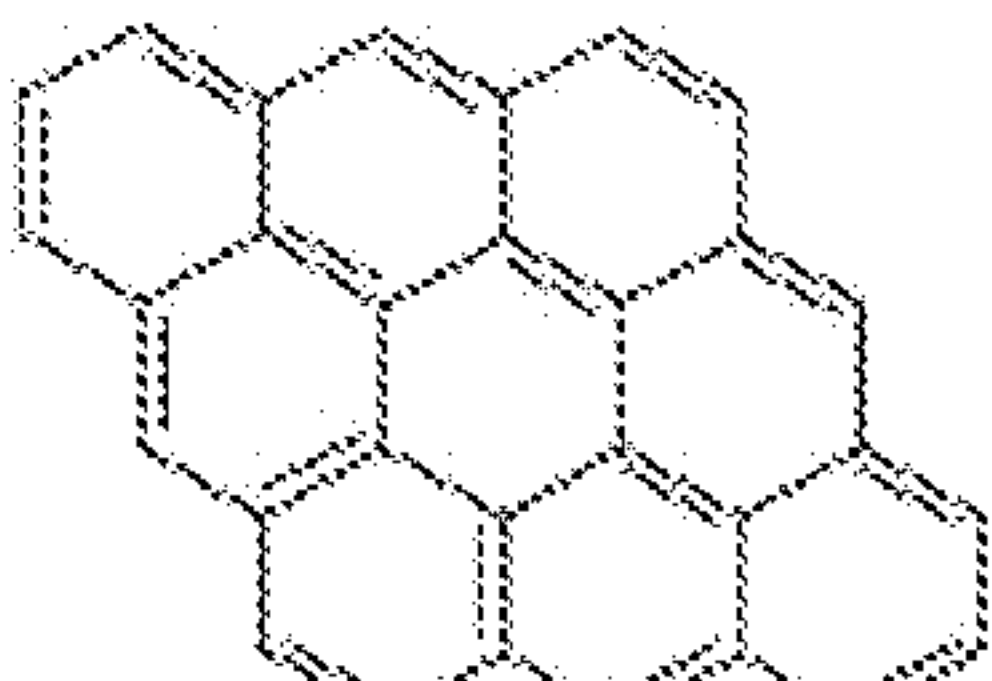
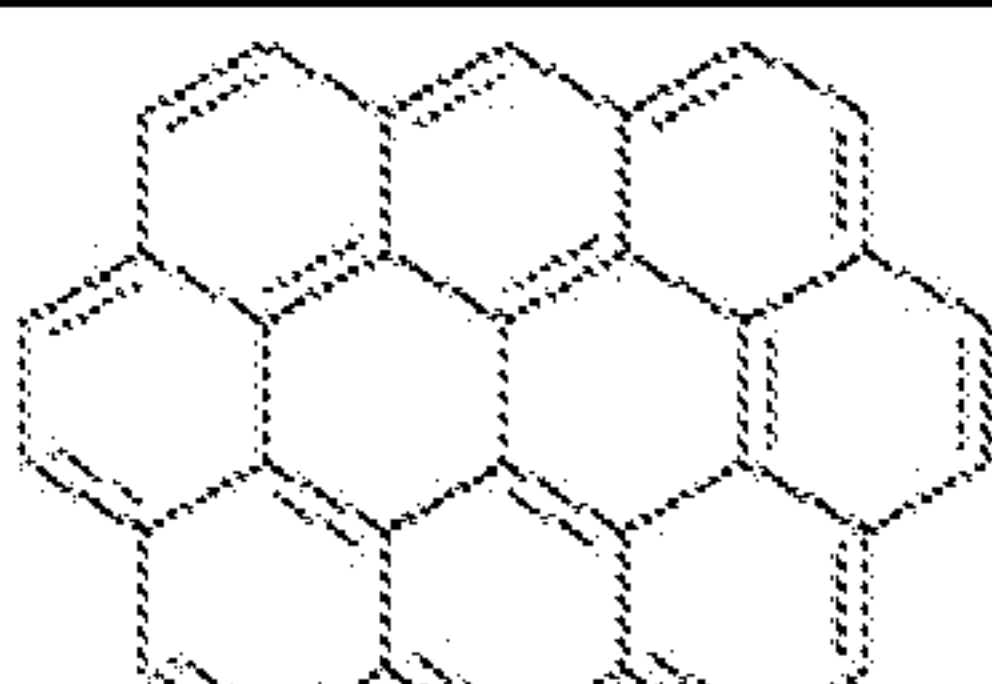
[24] As used herein, “HPNA compounds” and the shorthand expression “HPNA(s)” refers to fused polycyclic aromatic compounds having double bond equivalence (DBE) values of 19 and above, or having 7 or more rings, for example, including but not limited to coronenes ($C_{24}H_{12}$), benzocoronenes ($C_{28}H_{14}$), dibenzocorones ($C_{32}H_{16}$) and ovalenes ($C_{32}H_{14}$). The aromatic structure may have alkyl groups or naphthenic rings attached to it. For instance, coronene has 24 carbon atoms and 12 hydrogen atoms. Its double bond equivalency (DBE) is 19. DBE is calculated based on the sum of the number double bonds and number of rings. For example, the DBE value for coronene is 19 (7 rings+12 double bonds). Examples of HPNA compounds are shown in Table 1.

[25] As used herein, “HPNA precursors” are poly nuclear compounds having less than 7 aromatic rings, for instance 2-7 or 3-7 aromatic rings.

[26] As used herein, the term “hydrocracking recycle stream” is synonymous with the terms “hydrocracker bottoms,” “hydrocracked bottoms,” “hydrocracker unconverted material” and “fractionator bottoms.”

[27] As used herein, the shorthand expressions “HPNAs/HPNA precursors,” “HPNA compounds and HPNA precursor compounds,” “HPNAs and HPNA precursors,” and “HPNA compounds and/or HPNA precursor compounds” are used interchangeably and refer to a combination of HPNA compounds and HPNA precursor compounds unless more narrowly defined in context.

Table 1

HPNAs	Ring #	Structure
benzoperylene	6	
coronene	7	
methylcoronene	7	
naphthenocoronene	9	
dibenzocoronene	9	
ovalene	10	

[28] Volume percent or “V%” refers to a relative at conditions of 1 atmosphere pressure and 15°C.

[29] The phrase “a major portion” with respect to a particular stream or plural streams, or content within a particular stream, means at least about 50 wt% and up to 100 wt%, or the same values of another specified unit.

[30] The phrase “a significant portion” with respect to a particular stream or plural streams, or content within a particular stream, means at least about 75 wt% and up to 100 wt%, or the same values of another specified unit.

[31] The phrase “a substantial portion” with respect to a particular stream or plural streams, or content within a particular stream, means at least about 90, 95, 98 or 99 wt% and up to 100 wt%, or the same values of another specified unit.

[32] The phrase “a minor portion” with respect to a particular stream or plural streams, or content within a particular stream, means from about 1, 2, 4 or 10 wt%, up to about 20, 30, 40 or 50 wt%, or the same values of another specified unit.

[33] The term "naphtha" as used herein refers to hydrocarbons boiling in the range of about 20-220, 20-210, 20-200, 20-190, 20-180, 20-170, 32-220, 32-210, 32-200, 32-190, 32-180, 32-170, 36-220, 36-210, 36-200, 36-190, 36-180 or 36-170°C.

[34] The term “light naphtha” as used herein refers to hydrocarbons boiling in the range of about 20-110, 20-100, 20-90, 20-88, 32-110, 32-100, 32-90, 32-88, 36-110, 36-100, 36-90 or 36-88°C.

[35] The term “heavy naphtha” as used herein refers to hydrocarbons boiling in the range of about 90-220, 90-210, 90-200, 90-190, 90-180, 90-170, 93-220, 93-210, 93-200, 93-190, 93-180, 93-170, 100-220, 100-210, 100-200, 100-190, 100-180, 100-170, 110-220, 110-210, 110-200, 110-190, 110-180 or 110-170°C.

[36] The term "middle distillate" as used herein relative to effluents from the atmospheric distillation unit or flash zone refers to hydrocarbons boiling in the range between an initial boiling point from about 170°C to 220°C and final boiling point from about 320°C to 370°C, for instance in the range of about 170-370, 170-360, 170-350, 170-340, 170-320, 180-370, 180-360, 180-350, 180-340, 180-320, 190-370, 190-360, 190-350, 190-340, 190-320, 200-370, 200-360, 200-350, 200-340, 200-320, 210-370, 210-210, 210-350, 210-340, 210-320, 220-370, 220-220, 220-350, 220-340 or 220-320°C.

[37] The term “unconverted oil,” and its acronym “UCO,” also known as hydrocracker bottoms, hydrocracked bottoms, hydrocracker unconverted material and fractionator bottoms, is used herein having its known meaning, and refers to a highly paraffinic fraction obtained from a separation zone associated with a hydroprocessing reactor, and contains reduced N, S and Ni content relative to the reactor feed, and includes in certain embodiments hydrocarbons having an initial boiling point in the range of about 340-370°C, for instance about 340, 360 or 370°C, and an

end point in the range of about 510-560°C, for instance about 540, 550, 560°C or higher depending on the characteristics of the feed to the hydroprocessing reactor, and hydroprocessing reactor design and conditions, for instance hydrocarbons boiling in the range of about 340-560, 340-550, 340-540, 360-560, 360-550, 360-540, 370-560, 370-550, or 370-540°C. UCO is also known in the industry by other synonyms including “hydrowax.”

[38] The term “atmospheric residue” as used herein refers to the bottom hydrocarbons obtained from atmospheric distillation and having an initial boiling point corresponding to the end point of the middle distillate range hydrocarbons, and having an end point based on the characteristics of the crude oil feed.

[39] The term “vacuum gas oil” and its acronym “VGO” as used herein refer to hydrocarbons obtained from vacuum distillation, typically of atmospheric residue, and having an initial boiling point in the range of about 350-420°C and an end boiling point in the range of about 510-565°C, for instance hydrocarbons boiling in the range of about 350-565, 350-540, 350-530, 350-510, 370-565, 370-550, 370-540, 370-530, 370-510, 400-565, 400-550, 400-540, 400-530, 400-510, 420-565, 420-550, 420-540, 420-530 or 420-510°C.

[40] The term “vacuum residue” as used herein refers to the bottom hydrocarbons obtained from vacuum distillation and having an initial boiling point corresponding to the end point of the VGO range hydrocarbons, and having an end point based on the characteristics of the crude oil feed.

[41] The modifying term “straight run” is used herein having its well-known meaning, that is, describing fractions that are conventionally derived directly from the distillation unit, optionally subjected to steam stripping, rather than being from another refinery treatment such as coking, hydroprocessing, fluid catalytic cracking or steam cracking.

[42] The term “coker gas oil” and its acronym “CGO” as used herein refer to hydrocarbons boiling above an end point of the middle distillate range, for instance having an initial boiling point in the range of about 320-370°C, and an end boiling point in the range of about 510-565°C, which are derived from thermal cracking operations in a coker unit, for instance hydrocarbons boiling in the range of about 320-565, 320-540, 320-510, 340-565, 340-540, 340-510, 370-565, 370-540, or 370-510°C.

[43] The term “heavy coker gas oil” is used herein to refer to coker gas oil in the heavy range, for instance having an initial boiling point from about 375-425°C, for instance hydrocarbons

boiling in the range of about 375-565, 375-540, 375-510, 400-565, 400-540, 400-510, 425-565, 425-540, or 425-510°C.

[44] The term “light coker gas oil” is used herein to refer to coker gas oil in the light range, for instance having an end boiling point from about 375-425°C, for instance hydrocarbons boiling in the range of about 320-425, 320-400, 320-375, 340-425, 340-375, 340-375, 370-425, 370-400, or 370-375°C.

[45] The term “coker naphtha” is used herein to refer to hydrocarbons boiling in the naphtha range derived from thermal cracking operations in a coker unit.

[46] The term “coker middle distillates” is used herein to refer to hydrocarbons boiling in the middle distillate range derived from thermal cracking operations in a coker unit.

[47] Hydrocracker bottoms fractions from a hydrocracking operation containing HPNA compounds and/or HPNA precursor compounds are subjected to thermal cracking, alone or in combination with an additional feedstock. The hydrocracking operation can be in the configuration of a single reactor with recycle, plural reactors in series flow with recycle, or two stages of reactor with recycle. Thermally cracked hydrocarbon products having reduced HPNA content relative to the hydrocracker bottoms fractions is used as a hydrocracking recycle stream in the hydrocracking operation. Resulting coke from the thermal cracking contains HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms fraction.

[48] The thermally cracked hydrocarbon products can include coker gas oil, coker middle distillates and coker naphtha; coker gas oil, coker middle distillates and coker heavy naphtha; coker gas oil and coker middle distillates; coker gas oil and heavy coker middle distillates; coker gas oil; or heavy coker gas oil. In certain embodiments, one or more coker distillate streams are also provided which contains coker distillate products outside of the range of the thermally cracked hydrocarbon products that are recycled to the hydrocracking operation.

[49] Operation of the integrated system and process herein overcomes conventional problems associated with upgrading of hydrocracker bottom containing HPNA compounds and/or HPNA precursor compounds that were formed in the reaction zones, since they are substantially removed from the system through the coking zone by cracking and forming additional distillate products. Those HPNA compounds and/or HPNA precursor compounds that are not cracked form part of the coke by-product. For instance, in the coking zone, 90W%, 95 W%, 99 W%, 99.9 W% of

HPNA compounds and/or 50W%, 75 W%, 90 W%, 95.0 W% HPNA precursor compounds is removed and passed to the coke phase.

[50] FIG. 1 is a process flow diagram of an embodiment of a hydrocracking unit operation integrated with a coking reaction and separation zone. A hydrocracking system **100** operates as single stage hydrocracking unit with recycle. In general, the hydrocracking system **100** includes a hydrocracking reaction zone **106** and a fractionating zone **110**, which are integrated with a coking reaction and separation zone **120**. Reaction zone **106** generally includes one or more inlets in fluid communication with a source of initial hydrocracking feedstock **102**, a source of hydrogen gas **104**, and the coking reaction and separation zone **120** to receive a recycle stream comprising all or a portion of a thermally cracked hydrocarbon products stream **122**. Reaction zone **106** includes an effective reactor configuration with the requisite reaction vessel(s), feed heaters, heat exchangers, hot and/or cold separators, product fractionators, strippers, and/or other units to process, and operates with effective catalyst(s) and under effective operating conditions to carry out the desired degree of treatment and conversion of the feed. One or more outlets of reaction zone **106** that discharge effluent stream **108** are in fluid communication with one or more inlets of the fractionating zone **110**. In certain embodiments (not shown), effluents from the hydrocracking reaction vessels are cooled in an exchanger and sent to a high pressure hot and/or cold separator. The fractionating zone **110** generally includes one or more outlets for discharging a distillate fraction **114** containing cracked naphtha and cracked middle distillate/diesel products; and one or more outlets for discharging a hydrocracker bottoms fraction **116** containing unconverted oil. In certain embodiments, the fractionation zone **110** includes one or more outlets for discharging gases, stream **112**, typically H₂, H₂S, NH₃, and light hydrocarbons (C₁-C₄).

[51] The hydrocracker bottoms fraction **116** outlet is in fluid communication with one or more inlets of the coking reaction and separation zone **120**. In certain embodiments one or more optional additional feeds, stream **148**, are in fluid communication with one or more inlets of the coking reaction and separation zone **120**. As shown in the integration with system **100**, the coking reaction and separation zone **120** generally includes one or more outlets for discharging the thermally cracked hydrocarbon products stream **122**, and a coke discharge, schematically shown as line **124**, within which HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms are contained. In certain embodiments the coking reaction and separation zone **120** contains one or more outlets for discharging thermally cracked distillates stream **152** (shown in

dashed lines) which can include coker naphtha, coker middle distillates and/or light coker gas oil. The outlet discharging the thermally cracked hydrocarbon products stream **122** is in fluid communication with one or more inlets of reaction zone **106** for recycle of all or a portion of the stream. In certain embodiments, a bleed stream **118** is drawn from bottoms **116** upstream of the coking reaction and separation zone **120**. In additional embodiments, a bleed stream **126** is drawn from the thermally cracked hydrocarbon products stream **122** downstream of the coking reaction and separation zone **120**, in addition to or instead of bleed stream **118**. Either or both of these bleed streams contain unconverted oil that is hydrogen-rich and therefore can be effectively integrated with certain fuel oil pools, or serve as feed to fluidized catalytic cracking or steam cracking processes (not shown).

[52] In operation of the system **100/120**, the initial feedstock stream **102** and a hydrogen stream **104** are charged to the reaction zone **106**. Hydrogen stream **104** contains an effective quantity of hydrogen to support the requisite degree of hydrocracking, feed type, and other factors, and can be any combination including make-up hydrogen, recycle hydrogen from optional gas separation subsystems (not shown) between reaction zone **106** and fractionating zone **110**, derived from fractionator gas stream **112**, and/or derived from coker gas products from coking reaction and separation zone **120**. Reaction zone **106** operates under effective conditions for production of a reaction effluent stream **108** which contains converted, partially converted and unconverted hydrocarbons, including HPNA and/or HPNA precursor compounds formed in the reaction zone **106**. One or more high pressure and low pressure separation stages can be integrated as is known to recover recycle hydrogen between the reaction zone **106** and fractionating zone **110**. For example, effluents from the hydrocracking reaction vessel are cooled in an exchanger and sent to a high pressure hot and/or cold separator. Separator tops are cleaned in an amine unit and the resulting hydrogen rich gas stream is passed to a recycling compressor to be used as a recycle gas in the hydrocracking reaction vessel. Separator bottoms from the high pressure separator, which are in a substantially liquid phase, are cooled and then introduced to a low pressure cold separator. Remaining gases including hydrogen, H_2S , NH_3 and any light hydrocarbons, which can include C_1 - C_4 hydrocarbons, can be conventionally purged from the low pressure cold separator and sent for further processing, such as flare processing or fuel gas processing. The liquid stream from the low pressure cold separator is passed to the fractionating zone **110**.

[53] The reaction effluent stream **108** is passed to fractionating zone **110**, generally to recover gas stream **112** and liquid products **114** and to separate a bottoms fraction **116** containing HPNA compounds. Gas stream **112**, typically containing H₂, H₂S, NH₃, and light hydrocarbons (C₁-C₄), is discharged and recovered and can be further processed as is known in the art, including for recovery of recycle hydrogen. In certain embodiments one or more gas streams are discharged from one or more separators between the reactor and the fractionator (not shown), and gas stream **112** can be optional from the fractionator. One or more cracked product streams **114** are discharged from appropriate outlets of the fractionator and can be further processed and/or blended in downstream refinery operations as gasoline, kerosene and/or diesel fuel products or intermediates, and/or other hydrocarbon mixtures that can be used to produce petrochemical products. In certain embodiments (not shown), fractionating zone **110** can operate as one or more flash vessels to separate heavy components at a suitable cut point, for example, a range corresponding to the upper temperature range of the desired product stream **114**.

[54] In certain embodiments, all, a major portion, a significant portion, or a substantial portion of the fractionator bottoms stream **116** derived from the reaction effluent, containing HPNA compounds and/or HPNA precursors formed in the reaction zone **106**, is passed to the coking reaction and separation zone **120** for thermal cracking. In certain embodiments a portion of the fractionator bottoms from the reaction effluent is removed from the recycle loop as bleed stream **118**. Bleed stream **118** can contain a suitable portion (V%) of the fractionator bottoms **116**, in certain embodiments about 0-10, 0-5, 0-3, 1-10, 1-5 or 1-3. HPNA compounds and/or HPNA precursors in the hydrocracking effluent fractionator bottoms are retained in the coke phase in the coking reaction and separation zone **120**, and all or a portion of the thermally cracked hydrocarbon products stream **122** is recycled. In certain embodiments, instead of or in conjunction with bleed stream **118**, a portion of the thermally cracked hydrocarbon products stream **122** is removed from the recycle loop as bleed stream **126**. Bleed stream **126** can contain a suitable portion (V%) of the thermally cracked hydrocarbon products stream **122**, in certain embodiments about 0-10, 0-5, 0-3, 1-10, 1-5 or 1-3. A coke discharge **124** containing HPNA compounds is removed from the system. The coke contains solvent insoluble compounds, and in the process herein HPNA and/or HPNA precursor compounds react with one another and dimerize or polymerize, forming HPNA compounds and/or larger HPNA compounds with a greater number of rings. These will become insoluble become coke material. In certain embodiments, all, a major portion, a significant portion,

or a substantial portion of the thermally cracked hydrocarbon products stream **122** is recycled to the reaction zone **106**. The stream **122** is obtained from the coking reaction and separation zone **120** and has a reduced concentration of HPNA compounds relative to the hydrocracker bottoms fraction. In certain embodiments, a thermally cracked distillates stream **152** (shown in dashed lines) is discharged from the coking reaction and separation zone **120** which can include coker naphtha, coker middle distillates and/or light coker gas oil.

[55] In additional embodiments, one or more optional additional feeds, stream **148** can be routed to the coking reaction and separation zone **120**. In certain embodiments the only feed to the coking reaction and separation zone **120** are derived from the fractionator bottoms **116**.

[56] Reaction zone **106** can contain one or more fixed-bed, ebullated-bed, slurry-bed, moving bed, continuous stirred tank (CSTR), or tubular reactors, in series and/or parallel arrangement. The reactor(s) are generally operated under conditions effective for the desired level of treatment, degree of conversion, type of reactor, the feed characteristics, and the desired product slate. In certain embodiments the reactors operate at conversion levels (V% of feed that is recovered above the unconverted oil range) in the range of 30-90, 50-90, 60-90 or 70-90. For instance, these conditions can include a reaction temperature (°C) in the range of from about 300-500, 300-475, 300-450, 330-500, 330-475 or 330-450; a reaction pressure (bars) in the range of from about 60-300, 60-200, 60-180, 100-300, 100-200, 100-180, 130-300, 130-200 or 130-180; a hydrogen feed rate (standard liter per liter of hydrocarbon feed (SL/L)) of up to about 2500, 2000 or 1500, in certain embodiments from about 800-2500, 800-2000, 800-1500, 1000-2500, 1000-2000 or 1000-1500; and a feed rate liquid hourly space velocity (h^{-1}) in the range of from about 0.1-10, 0.1-5, 0.1-2, 0.25-10, 0.25-5, 0.25-2, 0.5-10, 0.5-5 or 0.5-2. Effective catalysts used in reaction zone **106** possess hydrotreating functionality (hydrodesulfurization, hydrodenitrification and/or hydrodemetallization) and hydrocracking functionality. Hydrodesulfurization, hydrodenitrification and/or hydrodemetallization is carried out to remove S, N and other contaminants, and conversion of feedstocks occurs by cracking into lighter fractions, for instance, in certain embodiments at least about 30 V% conversion.

[57] FIG. 2 is a process flow diagram of another embodiment of a hydrocracking unit operation integrated with a coking reaction and separation zone. A hydrocracking system **200** operates as series-flow hydrocracking system with recycle to the first reactor zone, the second reactor zone, or both the first and second reactor zones. In general, the hydrocracking system **200** includes a first

reaction zone **228**, a second reaction zone **232** and a fractionating zone **210**, which are integrated with a coking reaction and separation zone **220**. The first reaction zone **228** generally includes one or more inlets in fluid communication with a source of initial hydrocracking feedstock **202**, a source of hydrogen gas **204**, and optionally the coking reaction and separation zone **220** to receive a recycle stream comprising all or a portion of a thermally cracked hydrocarbon products stream **222**, shown in dashed lines as stream **222b**. The first reaction zone **228** includes an effective reactor configuration with the requisite reaction vessel(s), feed heaters, heat exchangers, hot and/or cold separators, product fractionators, strippers, and/or other units to process, and operates with effective catalyst(s) and under effective operating conditions to carry out the desired degree of treatment and conversion of the feed. One or more outlets of the first reaction zone **228** that discharge effluent stream **230** is in fluid communication with one or more inlets of the second reaction zone **232**. In certain embodiments, the effluents **230** are passed to the second reaction zone **232** without separation of any excess hydrogen and light gases. In optional embodiments, one or more high pressure and low pressure separation stages are provided between the first and second reaction zones **228**, **232** for recovery of recycle hydrogen (not shown). The second reaction zone **232** generally includes one or more inlets in fluid communication with one or more outlets of the first reaction zone **228**, optionally a source of additional hydrogen gas **205** and optionally the coking reaction and separation zone **220** to receive a recycle stream comprising all or a portion of the thermally cracked hydrocarbon products stream **222**, shown in dashed lines as stream **222a**. The second reaction zone **232** includes an effective reactor configuration with the requisite reaction vessel(s), feed heaters, heat exchangers, hot and/or cold separators, product fractionators, strippers, and/or other units to process, and operates with effective catalyst(s) and under effective operating conditions to carry out the desired degree of additional conversion of the feed. One or more outlets of the second reaction zone **232** that discharge effluent stream **234** is in fluid communication with one or more inlets of the fractionating zone **210** (optionally having one or more high pressure and low pressure separation stages therebetween for recovery of recycle hydrogen, not shown). The fractionating zone **210** generally includes one or more outlets for discharging a distillate fraction **214** containing cracked naphtha and cracked middle distillate/diesel products and one or more outlets for discharging a bottoms fraction **216** containing unconverted oil. In certain embodiments, the fractionation zone **210** includes one or more outlets for discharging gases, stream **212**, typically H₂, H₂S, NH₃, and light hydrocarbons (C₁-C₄).

[58] The bottoms fraction **216** outlet is in fluid communication with one or more inlets of the coking reaction and separation zone **220**. In certain embodiments one or more optional additional feeds, stream **248**, are in fluid communication with one or more inlets of the coking reaction and separation zone **220**. As shown in the integration with system **200**, the coking reaction and separation zone **220** generally includes one or more outlets for discharging the thermally cracked hydrocarbon products stream **222**, and a coke discharge, schematically shown as line **224**, within which HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms are contained. In certain embodiments the coking reaction and separation zone **220** contains one or more outlets for discharging thermally cracked distillates stream **252** (shown in dashed lines) which can include coker naphtha, coker middle distillates and/or light coker gas oil. The outlet discharging the thermally cracked hydrocarbon products stream **222** is in fluid communication with one or more inlets of reaction zone **228** and/or **232** for recycle of all or a portion of the stream. In certain embodiments, a bleed stream **218** is drawn from bottoms **216** upstream of the coking reaction and separation zone **220**. In additional embodiments, a bleed stream **226** is drawn from the thermally cracked hydrocarbon products stream **222** downstream of the coking reaction and separation zone **220**, in addition to or instead of bleed stream **218**. Either or both of these bleed streams contain unconverted oil that is hydrogen-rich and therefore can be effectively integrated with certain fuel oil pools, or serve as feed to fluidized catalytic cracking or steam cracking processes (not shown).

[59] In operation of the system **200/220**, the initial feedstock stream **202** and a hydrogen stream **204** are charged to the first reaction zone **228**. Hydrogen stream **204** includes an effective quantity of hydrogen to support the requisite degree of hydrocracking, feed type, and other factors, and can be any combination including make-up hydrogen, recycle hydrogen from optional gas separation subsystems (not shown) between reaction zones **228** and **232**, recycle hydrogen from optional gas separation subsystems (not shown) between reaction zone **232** and fractionator **210**, , derived from fractionator gas stream **212**, and/or derived from coker gas products from coking reaction and separation zone **220**. The first reaction zone **228** operates under effective conditions for production of a reaction effluent stream **230** (optionally after one or more high pressure and low pressure separation stages to recover recycle hydrogen) which is passed to the second reaction zone **232**, optionally along with an additional hydrogen stream **205**. The second reaction zone **232** operates under conditions effective for production of the reaction effluent stream **234**, which contains

converted, partially converted and unconverted hydrocarbons. The reaction effluent stream further includes HPNA compounds that were formed in the reaction zones **228** and/or **232**. One or more high pressure and low pressure separation stages can be integrated as is known to recover recycle hydrogen between the reaction zone **228** and the reaction zone **232**, and/or between the reaction zone **232** and fractionating zone **210**. For example, effluents from the hydrocracking reaction zones **228** and/or **232** are cooled in an exchanger and sent to a high pressure hot and/or cold separator. Separator tops are cleaned in an amine unit and the resulting hydrogen rich gas stream is passed to a recycling compressor to be used as a recycle gas in the hydrocracking reaction vessel. Separator bottoms from the high pressure separator, which are in a substantially liquid phase, are cooled and then introduced to a low pressure cold separator. Remaining gases including hydrogen, H₂S, NH₃ and any light hydrocarbons, which can include C₁-C₄ hydrocarbons, can be conventionally purged from the low pressure cold separator and sent for further processing, such as flare processing or fuel gas processing. The liquid stream from the low pressure cold separator is passed to the next stage, that is, the second reactor **232** or the fractionating zone **210**.

[60] The reaction effluent stream **234** is passed to the fractionation zone **210**, generally to recover gas stream **212** and liquid products **214** and to separate a bottoms fraction **216** containing HPNA compounds. Gas stream **212**, typically containing H₂, H₂S, NH₃, and light hydrocarbons (C₁-C₄), is discharged and recovered and can be further processed as is known in the art, including for recovery of recycle hydrogen. In certain embodiments one or more gas streams are discharged from one or more separators between the reactors, or between the reactor and the fractionator (not shown), and gas stream **212** can be optional from the fractionator. One or more cracked product streams **214** are discharged from appropriate outlets of the fractionator and can be further processed and/or blended in downstream refinery operations as gasoline, kerosene and/or diesel fuel products or intermediates, and/or other hydrocarbon mixtures that can be used to produce petrochemical products. In certain embodiments (not shown), fractionating zone **210** can operate as one or more flash vessels to separate heavy components at a suitable cut point, for example, a range corresponding to the upper temperature range of the desired product stream **214**.

[61] In certain embodiments, all, a major portion, a significant portion, or a substantial portion of the fractionator bottoms stream **216**, containing HPNA compounds and/or HPNA precursors formed in the reaction zones, is passed to the coking reaction and separation zone **220** for thermal cracking. In certain embodiments a portion of the fractionator bottoms from the reaction effluent

is removed from the recycle loop as bleed stream **218**. Bleed stream **218** can contain a suitable portion (V%) of the fractionator bottoms **216**, in certain embodiments about 0-10, 0-5, 0-3, 1-10, 1-5 or 1-3. HPNA compounds and/or HPNA precursors in the hydrocracking effluent fractionator bottoms are retained in the coke phase in the coking reaction and separation zone **220**, and all or a portion of the thermally cracked hydrocarbon products stream **222** is recycled. A coke discharge **224** containing HPNA compounds is removed from the system. In certain embodiments, instead of or in conjunction with bleed stream **218**, a portion of the thermally cracked hydrocarbon products stream **222** is removed from the recycle loop as bleed stream **226**. Bleed stream **226** can contain a suitable portion (V%) of the thermally cracked hydrocarbon products stream **222**, in certain embodiments about 0-10, 0-5, 0-3, 1-10, 1-5 or 1-3. In certain embodiments, all or a portion of the thermally cracked hydrocarbon products stream **222** is recycled to the second reaction zone **232** as stream **222a**, the first reaction zone **228** as stream **222b**, or both the first and second reaction zones **228** and **232**. For instance, stream **222b** comprises (V%) 0-100, 0-80 or 0-50 relative to stream **222** that is recycled to zone **228**, and stream **222a** comprises 0-100, 0-80 or 0-50 relative to stream **222** that is recycled to zone **232**. In certain embodiments, all, a major portion, a significant portion, or a substantial portion of the thermally cracked hydrocarbon products stream **222** is recycled to the first reaction zone **228** as stream **222b**. The stream **222** is obtained from the coking reaction and separation zone **220** and has a reduced concentration of HPNA compounds relative to the hydrocracker bottoms fraction. In certain embodiments, a thermally cracked distillates stream **252** (shown in dashed lines) is discharged from the coking reaction and separation zone **220** which can include coker naphtha, coker middle distillates and/or light coker gas oil.

[62] In additional embodiments, one or more optional additional feeds, stream **248** can be routed to the coking reaction and separation zone **220**. In certain embodiments the only feed to the coking reaction and separation zone **220** are derived from the fractionator bottoms **216**.

[63] The first reaction zone **228** can contain one or more fixed-bed, ebullated-bed, slurry-bed, moving bed, CSTR, or tubular reactors, in series and/or parallel arrangement. The reactor(s) are generally operated under conditions effective for the desired level of treatment and degree of conversion in the first reaction zone **228**, the particular type of reactor, the feed characteristics, and the desired product slate. For instance, these conditions can include a reaction temperature (°C) in the range of from about 300-500, 300-475, 300-450, 330-500, 330-475 or 330-450; a

reaction pressure (bars) in the range of from about 60-300, 60-200, 60-180, 100-300, 100-200, 100-180, 130-300, 130-200 or 130-180; a hydrogen feed rate (SL/L) of up to about 2500, 2000 or 1500, in certain embodiments from about 800-2500, 800-2000, 800-1500, 1000-2500, 1000-2000 or 1000-1500; and a feed rate liquid hourly space velocity (h^{-1}) in the range of from about 0.1-10, 0.1-5, 0.1-2, 0.25-10, 0.25-5, 0.25-2, 0.5-10, 0.5-5 or 0.5-2. The catalyst used in the first reaction zone **228** can comprise those having hydrotreating functionality, and in certain embodiments those having hydrotreating and hydrocracking functionality. In embodiments in which catalysts used in first reaction zone **228** possess hydrotreating functionality, including hydrodesulfurization, hydrodenitrification and/or hydrodemetallization, the focus is removal of S, N and other contaminants, with a limited degree of conversion (for instance in the range of 10-30 V%). In embodiments in which catalysts used in first reaction zone **228** possess hydrotreating and hydrocracking functionality, a higher degree of conversion, generally above about 20 V%, occurs.

[64] The second reaction zone **232** can contain one or more fixed-bed, ebullated-bed, slurry-bed, moving bed, CSTR, or tubular reactors, in series and/or parallel arrangement. The reactor(s) are generally operated under conditions effective for the desired degree of conversion, particular type of reactor, the feed characteristics, and the desired product slate. For instance, these conditions can include a reaction temperature ($^{\circ}\text{C}$) in the range of from about 300-500; a reaction pressure (bars) in the range of from about 60-300, 60-200, 60-180, 100-300, 100-200, 100-180, 130-300, 130-200 or 130-180; a hydrogen feed rate (SL/L) of up to about 2500, 2000 or 1500, in certain embodiments from about 800-2500, 800-2000, 800-1500, 1000-2500, 1000-2000 or 1000-1500; and a feed rate liquid hourly space velocity (h^{-1}) in the range of from about 0.1-10, 0.1-5, 0.1-2, 0.25-10, 0.25-5, 0.25-2, 0.5-10, 0.5-5 or 0.5-2. The catalyst used in the second reaction zone **232** can comprise those having hydrocracking hydrodesulfurization and hydrodenitrogenation functionality, and in certain embodiments those having hydrocracking and hydrogenation functionality.

[65] FIG. 3 is a process flow diagram of another embodiment of a hydrocracking unit operation integrated with a coking reaction and separation zone. A hydrocracking system **300** operates as two-stage hydrocracking system with recycle. In general, the hydrocracking system **300** includes a first reaction zone **336**, a second reaction zone **340** and a fractionating zone **310**, which are integrated with a coking reaction and separation zone **320**. The first reaction zone **336** generally includes one or more inlets in fluid communication with a source of initial hydrocracking feedstock

302 and a source of hydrogen gas **304**. The first reaction zone **336** includes an effective reactor configuration with the requisite reaction vessel(s), feed heaters, heat exchangers, hot and/or cold separators, product fractionators, strippers, and/or other units to process, and operates with effective catalyst(s) and under effective operating conditions to carry out the desired degree of treatment and conversion of the feed. One or more outlets of the first reaction zone **336** that discharge effluent stream **338** is in fluid communication with one or more inlets of the fractionating zone **310** (optionally having one or more high pressure and low pressure separation stages therebetween for recovery of recycle hydrogen, not shown). The fractionating zone **310** generally includes one or more outlets for discharging a distillate fraction **314** containing cracked naphtha and cracked middle distillate/diesel products; and one or more outlets for discharging a bottoms fraction **316** containing unconverted oil. In certain embodiments, the fractionation zone **310** includes one or more outlets for discharging gases, stream **312**, typically H₂, H₂S, NH₃, and light hydrocarbons (C₁-C₄). The second reaction zone **340** generally includes one or more inlets in fluid communication with one or more outlets of the coking reaction and separation zone **320** to receive a recycle stream comprising all or a portion of a thermally cracked hydrocarbon products stream **322**, shown as stream **322a**, and a source of hydrogen gas **306**. The second reaction zone **340** includes an effective reactor configuration with the requisite reaction vessel(s), feed heaters, heat exchangers, hot and/or cold separators, product fractionators, strippers, and/or other units to process, and operates with effective catalyst(s) and under effective operating conditions to carry out the desired degree of additional conversion of the feed. One or more outlets of the second reaction zone **340** that discharge effluent stream **342** are in fluid communication with one or more inlets of the fractionating zone **310** (optionally having one or more high pressure and low pressure separation stages for recovery of recycle hydrogen, not shown).

[66] The bottoms fraction **316** outlet is in fluid communication with one or more inlets of the coking reaction and separation zone **320**. In certain embodiments one or more optional additional feeds, stream **348**, are in fluid communication with one or more inlets of the coking reaction and separation zone **320**. As shown in the integration with system **300**, the coking reaction and separation zone **320** generally includes one or more outlets for discharging the thermally cracked hydrocarbon products stream **322**, and a coke discharge, schematically shown as line **324**, within which HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms are contained. In certain embodiments the coking reaction and separation zone **320** contains one or

more outlets for discharging thermally cracked distillates stream **352** (shown in dashed lines) which can include coker naphtha, coker middle distillates and/or light coker gas oil. The outlet discharging the thermally cracked hydrocarbon products stream **322** is in fluid communication with one or more inlets of the second reaction zone **340** for recycle of all or a portion **322a** of the recycle stream **322**. In certain optional embodiments, a portion **322b**, shown in dashed lines, is in fluid communication with one or more inlets of the first reaction zone **336**. In certain embodiments, a bleed stream **318** is drawn from bottoms **316** upstream of the coking reaction and separation zone **320**. In additional embodiments, a bleed stream **326** is drawn from the thermally cracked hydrocarbon products stream **322** downstream of the coking reaction and separation zone **320**, in addition to or instead of bleed stream **318**. Either or both of these bleed streams contain unconverted oil that is hydrogen-rich and therefore can be effectively integrated with certain fuel oil pools, or serve as feed to fluidized catalytic cracking or steam cracking processes (not shown).

[67] In operation of the system **300/320**, the initial feedstock stream **302** and a hydrogen stream **304** are charged to the first reaction zone **336**. Hydrogen stream **304** includes an effective quantity of hydrogen to support the requisite degree of hydrocracking, feed type, and other factors, and can be any combination including make-up hydrogen, recycle hydrogen from optional gas separation subsystems (not shown) between first reaction zone **336** and fractionating zone **310**, recycle hydrogen from optional gas separation subsystems (not shown) between second reaction zone **340** and fractionating zone **310**, derived from fractionator gas stream **312**, and/or derived from coker gas products from coking reaction and separation zone **320**. The first reaction zone **336** operates under effective conditions for production of reaction effluent stream **338**. The reaction effluent stream further includes HPNA compounds that were formed in the reaction zone **336**. One or more high pressure and low pressure separation stages can be integrated as is known to recover recycle hydrogen between the reaction zone **336** and the fractionating zone **310**. For example, effluents from the hydrocracking reaction vessel are cooled in an exchanger and sent to a high pressure hot and/or cold. Separator tops are cleaned in an amine unit and the resulting hydrogen rich gas stream is passed to a recycling compressor to be used as a recycle gas in the hydrocracking reaction vessel. Separator bottoms from the high pressure separator, which are in a substantially liquid phase, are cooled and then introduced to a low pressure cold separator. Remaining gases including hydrogen, H_2S , NH_3 and any light hydrocarbons, which can include C_1 - C_4 hydrocarbons, can be conventionally purged from the low pressure cold separator and sent for further processing, such

as flare processing or fuel gas processing. The liquid stream from the low pressure cold separator is passed to the fractionating zone **310**.

[68] The reaction effluent stream **338** is passed to the fractionation zone **310**, generally to recover gas stream **312** and liquid products **314** and to separate a bottoms fraction **316** containing HPNA compounds. Gas stream **312**, typically containing H₂, H₂S, NH₃, and light hydrocarbons (C₁-C₄), is discharged and recovered and can be further processed as is known in the art, including for recovery of recycle hydrogen. In certain embodiments one or more gas streams are discharged from one or more separators between the reactors (not shown), or between the reactor and the fractionator, and gas stream **312** can be optional from the fractionator. One or more cracked product streams **314** are discharged from appropriate outlets of the fractionator and can be further processed and/or blended in downstream refinery operations as gasoline, kerosene and/or diesel fuel products or intermediates, and/or other hydrocarbon mixtures that can be used to produce petrochemical products. In certain embodiments (not shown), fractionating zone **310** can operate as one or more flash vessels to separate heavy components at a suitable cut point, for example, a range corresponding to the upper temperature range of the desired product stream **314**.

[69] In certain embodiments, all, a major portion, a significant portion, or a substantial portion of the fractionator bottoms stream **316** containing HPNA compounds and/or HPNA precursors formed in the reaction zones is passed to the coking reaction and separation zone **320** for treatment. In certain embodiments a portion of the fractionator bottoms from the reaction effluent is removed as bleed stream **318**. Bleed stream **318** can contain a suitable portion (V%) of the fractionator bottoms **316**, in certain embodiments about 0-10, 0-5, 0-3, 1-10, 1-5 or 1-3. HPNA compounds and/or HPNA precursors in the hydrocracking effluent fractionator bottoms are retained in the coke phase in the coking reaction and separation zone **320**, and all or a portion of the thermally cracked hydrocarbon products stream **322** is recycled. A coke discharge **324** containing HPNA compounds is removed from the system. In certain embodiments, instead of or in conjunction with bleed stream **318**, a portion of the thermally cracked hydrocarbon products stream **322** is removed from the recycle loop as bleed stream **326**. Bleed stream **326** can contain a suitable portion (V%) of the thermally cracked hydrocarbon products stream **322**, in certain embodiments about 0-10, 0-5, 0-3, 1-10, 1-5 or 1-3. In certain embodiments, all or a portion of the thermally cracked hydrocarbon products stream **322** is passed to the second reaction zone **340** as stream **322a**. In certain embodiments, all or a portion of the thermally cracked hydrocarbon products stream **322**

is recycled to the second reaction zone **340** as stream **322a**, the first reaction zone **336** as stream **322b**, or both the first and second reaction zones **336** and **340**. For instance, stream **322a** comprises (V%) 0-100, 0-80 or 0-50 relative to stream **322** that is recycled to zone **340**, and stream **322b** comprises 0-100, 0-80 or 0-50 relative to stream **322** that is recycled to zone **336**. In certain embodiments, all, a major portion, a significant portion, or a substantial portion of the thermally cracked hydrocarbon products stream **322** is passed to the second reaction zone **340** as stream **322a**. The stream **322** is obtained from the coking reaction and separation zone **320** and has a reduced concentration of HPNA compounds relative to the hydrocracker bottoms fraction. In certain embodiments, a thermally cracked distillates stream **352** (shown in dashed lines) is discharged from the coking reaction and separation zone **320** which can include coker naphtha, coker middle distillates and/or light coker gas oil. The second reaction zone **340** operates under conditions effective for production of the reaction effluent stream **342**, which contains converted, partially converted and unconverted hydrocarbons. The second stage the reaction effluent stream **342** is passed to the fractionating zone **310**, optionally through one or more gas separators to recovery recycle hydrogen and remove certain light gases.

[70] In additional embodiments, one or more optional additional feeds, stream **348** can be routed to the coking reaction and separation zone **320**. In certain embodiments the only feed to the coking reaction and separation zone **320** are derived from the fractionator bottoms **316**.

[71] The first reaction zone **336** can contain one or more fixed-bed, ebullated-bed, slurry-bed, moving bed, CSTR, or tubular reactors, in series and/or parallel arrangement. The reactor(s) are generally operated under conditions effective for the desired level of treatment and degree of conversion in the first reaction zone **336**, the particular type of reactor, the feed characteristics, and the desired product slate. For instance, these conditions can include a reaction temperature (°C) in the range of from about 300-500, 300-475, 300-450, 330-500, 330-475 or 330-450; a reaction pressure (bars) in the range of from about 60-300, 60-200, 60-180, 100-300, 100-200, 100-180, 130-300, 130-200 or 130-180; a hydrogen feed rate (SL/L) of up to about 2500, 2000 or 1500, in certain embodiments from about 800-2500, 800-2000, 800-1500, 1000-2500, 1000-2000 or 1000-1500; and a feed rate liquid hourly space velocity (h^{-1}) in the range of from about 0.1-10, 0.1-5, 0.1-2, 0.25-10, 0.25-5, 0.25-2, 0.5-10, 0.5-5 or 0.5-2. The catalyst used in the first reaction zone **336** can comprise those having hydrotreating functionality, and in certain embodiments those having hydrotreating and hydrocracking functionality. In embodiments in which catalysts used in

first reaction zone **336** possess hydrotreating functionality, including hydrodesulfurization, hydrodenitrification and/or hydrodemetallization, the focus is removal of S, N and other contaminants, with a limited degree of conversion (for instance in the range of 10-30 V%). In embodiments in which catalysts used in first reaction zone **336** possess hydrotreating and hydrocracking functionality, a higher degree of conversion occurs, generally above about 30 V%, for instance in the range of about 30-60 V%.

[72] The second reaction zone **340** can contain one or more fixed-bed, ebullated-bed, slurry-bed, moving bed, CSTR, or tubular reactors, in series and/or parallel arrangement. The reactor(s) are generally operated under conditions effective for the desired degree of conversion, particular type of reactor, the feed characteristics, and the desired product slate. For instance, these conditions can include a reaction temperature (°C) in the range of from about 300-500, 300-475, 300-450, 330-500, 330-475 or 330-450; a reaction pressure (bars) in the range of from about 60-300, 60-200, 60-180, 100-300, 100-200, 100-180, 130-300, 130-200 or 130-180; a hydrogen feed rate (SL/L) of up to about 2500, 2000 or 1500, in certain embodiments from about 800-2500, 800-2000, 800-1500, 1000-2500, 1000-2000 or 1000-1500; and a feed rate liquid hourly space velocity (h^{-1}) in the range of from about 0.1-10, 0.1-5, 0.1-2, 0.25-10, 0.25-5, 0.25-2, 0.5-10, 0.5-5 or 0.5-2. The catalyst used in the second reaction zone **340** can comprise those having hydrodesulfurization, hydrodenitrification, and hydrocracking functionality for further conversion of refined and partially cracked components from the feedstock, and in certain embodiments those having hydrocracking and hydrogenation functionality.

[73] In certain embodiments, the feedstock to the reactor(s) within the hydrocracking zones (a single reactor with one bed, a single reactor with multiple beds, or multiple reactors) is mixed with an excess of hydrogen gas in a mixing zone. A portion of the hydrogen gas is mixed with the feedstock to produce a hydrogen-enriched liquid hydrocarbon feedstock. This hydrogen-enriched liquid hydrocarbon feedstock and undissolved hydrogen can be supplied to a flashing zone in which at least a portion of undissolved hydrogen is flashed, and the hydrogen is recovered and recycled. The hydrogen-enriched liquid hydrocarbon feedstock from the flashing zone is supplied as a feed stream to the reactor. The liquid product stream that is recovered from the reactor is further processed and/or recovered as provided here.

[74] Effective catalysts used in embodiments in which those possessing hydrotreating functionality required, for instance, in first reaction zone **228** or first reaction zone **336**, are known.

Such hydrotreating catalysts, sometimes referred to in the industry as “pretreat catalyst,” are effective for hydrotreating, and inherently a limited degree of conversion occurs (generally below about 30 V%). The catalysts generally contain one or more active metal components of metals or metal compounds (oxides or sulfides) selected from the Periodic Table of the Elements IUPAC Groups 6, 7, 8, 9 and 10. One or more active metal component(s) are typically deposited or otherwise incorporated on a support, which can be amorphous and/or structured, such as alumina, silica-alumina, silica, titania, titania-silica or titania-silicates. Combinations of active metal components can be composed of different particles/granules containing a single active metal species, or particles containing multiple active species. For example, effective hydrotreating catalysts include one or more of an active metal component selected from the group consisting of Co, Ni, W, Mo (oxides or sulfides), incorporated on an alumina support, typically with other additives. In certain embodiments in which an objective is hydrodenitritication and treatment of difficult feedstocks such as demetallized oil, the supports are acidic alumina, silica alumina or a combination thereof. In embodiments in which the objective is hydrodenitritication with increased hydrocarbon conversion, the supports are silica alumina, or a combination thereof. Silica alumina is useful for difficult feedstocks for stability and enhanced cracking. The catalyst particles are provided in particulate form of suitable dimension, such as granules, extrudates, tablets, or pellets, and may be formed into various shapes such as spheres, cylinders, trilobes, quadrilobes or natural shapes. In certain embodiments, the catalyst particles have a pore volume in the range of about (cc/gm) 0.15-1.70, 0.15-1.50, 0.30-1.50 or 0.30-1.70; a specific surface area in the range of about (m²/g) 100-400, 100-350, 100-300, 150-400, 150-350, 150-300, 200-400, 200-350 or 200-300; and an average pore diameter of at least about 10, 50, 100, 200, 500 or 1000 angstrom units. The active metal component(s) are incorporated in an effective concentration, for instance, in the range of (wt% based on the mass of the oxides, sulfides or metals relative to the total mass of the catalysts) 1-40, 1-30, 1-10, 1-5, 2-40, 2-30, 2-10, 3-40, 3-30 or 3-10. In certain embodiments, the active metal component(s) include one or more of Co, Ni, W and Mo, and effective concentrations are based on all the mass of active metal components on an oxide basis. In certain embodiments, hydrotreating catalysts are configured in one or more beds selected from Ni/W/Mo, Co/Mo, Ni/Mo, Ni/W, and Co/Ni/Mo. Combinations of one or more beds of Ni/W/Mo, Co/Mo, Ni/Mo, Ni/W and Co/Ni/Mo, are useful for difficult feedstocks such as demetallized oil, and to increase

hydrocracking functionality. In additional embodiments, the catalyst includes a bed of Co/Mo catalysts and a bed of Ni/Mo catalysts.

[75] Effective catalysts used in embodiments where those possessing hydrotreating and hydrocracking functionality are required, for instance, reaction zone **106**, first reaction zone **228** or first reaction zone **336**, are known. These catalysts, effective for hydrotreating and a degree of conversion generally in the range of about 30-60 V% contain one or more active metal components of metals or metal compounds (oxides or sulfides) selected from the Periodic Table of the Elements IUPAC Groups 6, 7, 8, 9 and 10. One or more active metal component(s) are typically deposited or otherwise incorporated on a support, which can be amorphous and/or structured, such as alumina, silica-alumina, silica, titania, titania-silica, titania-silicates, or zeolites. Combinations of active metal components can be composed of different particles/granules containing a single active metal species, or particles containing multiple active species. For example, effective hydrotreating/hydrocracking catalysts include one or more of an active metal component selected from the group consisting of Co, Ni, W, Mo (oxides or sulfides), incorporated on acidic alumina, silica alumina, zeolite or a combination thereof. In embodiments in which zeolites are used, they are conventionally formed with one or more binder components such as alumina, silica, silica-alumina and mixtures thereof. In certain embodiments in which an objective is hydrodenitrification and treatment of difficult feedstocks such as demetallized oil, the supports are acidic alumina, silica alumina or a combination thereof. In embodiments in which the objective is hydrodenitrification with increased hydrocarbon conversion, the supports are silica alumina, or a combination thereof. Silica alumina is useful for difficult feedstocks for stability and enhanced cracking. The catalyst particles are provided in particulate form of suitable dimension, such as granules, extrudates, tablets, or pellets, and may be formed into various shapes such as spheres, cylinders, trilobes, quadrilobes or natural shapes. In certain embodiments, the catalyst particles have a pore volume in the range of about (cc/gm) 0.15-1.70, 0.15-1.50, 0.30-1.50 or 0.30-1.70; a specific surface area in the range of about (m²/g) 100-900, 100-500, 100-450, 180-900, 180-500, 180-450, 200-900, 200-500 or 200-450; and an average pore diameter of at least about 45, 50, 100, 200, 500 or 1000 angstrom units. The active metal component(s) are incorporated in an effective concentration, for instance, in the range of (wt% based on the mass of the oxides, sulfides or metals relative to the total mass of the catalysts) 1-40, 1-30, 1-10, 1-5, 2-40, 2-30, 2-10, 3-40, 3-30 or 3-10. In certain embodiments, the active metal component(s) include one or more of Co, Ni, W and

Mo, and effective concentrations are based on all the mass of active metal components on an oxide basis. In certain embodiments, one or more beds are provided in series in a single reactor or in a series of reactors. For instance, a first catalyst bed containing active metals on silica alumina support is provided for hydrodenitrogenation, hydrodesulfurization and hydrocracking functionalities, followed by a catalyst bed containing active metals on zeolite support for hydrocracking functionality.

[76] Effective catalysts used in embodiments where those possessing hydrocracking functionality, for instance, second reaction zone **232** or second reaction zone **340**, are known. These catalysts, effective for further conversion of refined and partially cracked components from the feedstock, contain one or more active metal components of metals or metal compounds (oxides or sulfides) selected from the Periodic Table of the Elements IUPAC Groups 6, 7, 8, 9 and 10. One or more active metal component(s) are typically deposited or otherwise incorporated on a support, which can be amorphous and/or structured, such as silica-alumina, silica, titania, titania-silica, titania-silicates, or zeolites. Combinations of active metal components can be composed of different particles/granules containing a single active metal species, or particles containing multiple active species. In embodiments in which zeolites are used, they are conventionally formed with one or more binder components such as alumina, silica, silica-alumina and mixtures thereof. For example, effective hydrocracking catalysts include one or more of an active metal component selected from the group consisting of Ni, W, Mo (oxides or sulfides), incorporated on acidic alumina, silica alumina, zeolite or a combination thereof. The catalyst particles are provided in particulate form of suitable dimension, such as granules, extrudates, tablets, or pellets, and may be formed into various shapes such as spheres, cylinders, trilobes, quadrilobes or natural shapes. In certain embodiments, the catalyst particles have a pore volume in the range of about (cc/gm) 0.15-1.70, 0.15-1.50, 0.30-1.50 or 0.30-1.70; a specific surface area in the range of about (m²/g) 100-900, 100-500, 100-450, 180-900, 180-500, 180-450, 200-900, 200-500 or 200-450; and an average pore diameter of at least about 45, 50, 100, 200, 500 or 1000 angstrom units. The active metal component(s) are incorporated in an effective concentration, for instance, in the range of (wt% based on the mass of the oxides, sulfides or metals relative to the total mass of the catalysts) 1-40, 1-30, 1-10, 1-5, 2-40, 2-30, 2-10, 3-40, 3-30 or 3-10. In certain embodiments, the active metal component(s) include one or more of Co, Ni, W and Mo, and effective concentrations are based on all the mass of active metal components on an oxide basis. In a typical hydrocracking

reaction scheme, the main cracking catalyst bed or beds are followed by post treat catalyst to remove mercaptans formed during hydrocracking. Typical supports for post treat catalyst are silica-alumina, zeolites or combination thereof.

[77] Effective catalysts used in embodiments where those possessing hydrocracking and hydrogenation functionality, for instance, second reaction zone **232** or second reaction zone **340**, are known. These catalysts, effective for further conversion and also for hydrogenation of refined and partially cracked components from the feedstock, contain one or more active metal components of metals or metal compounds (oxides or sulfides) selected from the Periodic Table of the Elements IUPAC Groups 6, 7, 8, 9 and 10. One or more active metal component(s) are typically deposited or otherwise incorporated on a support, which can be amorphous and/or structured, such as alumina, silica-alumina, silica, titania, titania-silica, titania-silicates, or zeolites. Combinations of active metal components can be composed of different particles/granules containing a single active metal species, or particles containing multiple active species. For example, effective hydrocracking catalysts include one or more of an active metal component selected from the group consisting of Co, Ni, W, Mo (oxides), incorporated on acidic alumina, silica alumina, zeolite or a combination thereof. The catalyst particles are provided in particulate form of suitable dimension, such as granules, extrudates, tablets, or pellets, and may be formed into various shapes such as spheres, cylinders, trilobes, quadrilobes or natural shapes. In certain embodiments, the catalyst particles have a pore volume in the range of about (cc/gm) 0.15-1.70, 0.15-1.50, 0.30-1.50 or 0.30-1.70; a specific surface area in the range of about (m²/g) 100-900, 100-800, 100-500, 100-450, 180-900, 180-800, 180-500, 180-450, 200-900, 200-800, 200-500 or 200-450; and an average pore diameter of at least about 45, 50, 100, 200, 500 or 1000 angstrom units. The active metal component(s) are incorporated in an effective concentration, for instance, in the range of (wt% based on the mass of the oxides, sulfides or metals relative to the total mass of the catalyst) 0.01-40, 0.01-30, 0.01-10, 0.01-5, 1-40, 1-30, 1-10, 1-5, 2-40, 2-30, 2-10, 3-40, 3-30 or 3-10. In certain embodiments, the active metal component(s) include one or more of Co, Ni, W and Mo, and effective concentrations are based on all the mass of active metal components on an oxide basis. In embodiments in which one or more upstream reaction zone(s) reduces contaminants such as S and N, so that hydrogen sulfide and ammonia are minimized in the reaction zone, active metal components effective as hydrogenation catalysts can include one or more noble metals such as platinum, palladium or rhodium, alone or in combination with other active metals

such as Ni. Such noble metals can be provided in the range of (wt% based on the mass of the metal relative to the total mass of the catalyst) 0.01-5, 0.01-2, 0.05-5, 0.05-2, 0.1-5, 0.1-2, 0.5-5, or 0.5-2.

[78] In certain embodiments, the catalyst and/or the catalyst support is prepared in accordance with US Patent 9,221,036 and related US Patent 10,081,009 (jointly owned by the owner of the present application), which are incorporated herein by reference in their entireties, includes a modified USY zeolite support having one or more of Ti, Zr and/or Hf substituting the aluminum atoms constituting the zeolite framework thereof.

[79] In embodiments described herein using zeolite-based hydrocracking catalysts, HPNA compounds have relatively greater tendency to accumulate in the recycle stream due to the inability for these larger molecules to diffuse into the catalyst pore structure, particularly at relatively lower hydrogen partial pressure levels in the reactor. For instance, at hydrogen partial pressures less than about 100 bars, HPNA formation is known to reduce catalyst lifecycle to by 30-70% depending upon the feedstock processed and targeted conversion rate. However, according to the process herein, by removing HPNA compounds from the recycle stream, the lifecycle of such zeolite catalyst is increased.

[80] The coking reaction and separation zones **120**, **220** and **320** integrated in hydrocracking operations **100**, **200** and **300** described herein, and variations thereto apparent to a person having ordinary skill in the art, are effective for thermal cracking of a hydrocracker bottoms fraction of unconverted oil, and recycling all or a portion of thermally cracked hydrocarbon products within the hydrocracking operation. In this manner, HPNA compounds and/or HPNA precursor compounds that were formed in the hydrocracking reaction zone(s) (and are in the unconverted oil) are removed from circulation by remaining with the coke phase, and in certain embodiments by thermal cracking to form lighter hydrocarbons. Thermal treatment in the coking zone can dealkylate alkyl groups that are attached to the HPNA compounds or can crack any paraffinic or naphthenic bonds present in the HPNA compounds. HPNA compounds and HPNA precursor compounds that are not cracked remain in the coke phase or they tend to polymerize to form heavier HPNA compounds or coke and will not be recycled, thereby minimizing fouling or other detriments to the catalysts in the reaction zones. The hydrocracker bottom stream, which is rich in hydrogen due to its highly paraffinic nature, serves as a hydrogen donor and advantageously stabilizes radicals during thermal cracking and as a result minimizes coke formation.

[81] In addition, the hydrocracker bottoms fraction is low in S and N, and is free of metals or substantially free of metals. Accordingly, this stream serves to dilute other S rich coking feedstreams when used in combination and as a result, higher grade coke production from the delayed coking is facilitated as compared to coking operations without use of the hydrocracker bottoms fraction.

[82] The coking zone can operate in accordance with known cokers used in oil refineries, including more commonly known delayed coker units, and in certain arrangements a fluid coking process. In general, coking operations are carbon rejection processes that are used to convert lower value atmospheric or vacuum distillation residue streams to lighter products, thermally cracked hydrocarbon products. Typically these thermally cracked hydrocarbon products can be hydrotreated and/or subjected to other known treatment processes to produce transportation fuels such as gasoline and diesel, and increments of light products which can be further desulfurized, treated, and/or concentrated to produce petrochemicals. In the integrated processes and systems herein, all or a portion of the thermally cracked hydrocarbon products are recycled to the hydrocracking operation as stream **122**, **222** or **322**.

[83] The thermally cracked hydrocarbon products that are recycled to the hydrocracking operation, shown as streams **122**, **222** and **322** above and streams **422**, **522** and **622** below, can include coker gas oil, coker middle distillates and coker naphtha; coker gas oil, coker middle distillates and coker heavy naphtha; coker gas oil and coker middle distillates; coker gas oil and heavy coker middle distillates; coker gas oil; or heavy coker gas oil. In certain embodiments, one or more coker distillate streams are also provided, shown as shown as streams **152**, **252** and **352** above and streams **452**, **552** and **652** below, which can contain distillate products from the fractionating zone that are not passed with thermally cracked hydrocarbon products that are recycled to the hydrocracking operation. In certain embodiments, depending on the S and N content of the coker distillate stream **152**, **252**, **352** **452**, **552** or **652**, all or a portion can be combined with a hydrocracker distillate stream.

[84] Coking of residuum from heavy high sulfur, or sour, crude oils is typically carried out to convert part of the material to more valuable liquid and gas products. Typical coking processes include delayed coking and fluid coking. The treatment of coke varies depending on the type of coking process and the quality of the coke. In certain embodiments, for instance with delayed coking units, resulting coke is removed from drums, and is generally treated as a low value by-

product or recovered for various uses depending upon its quality. In a fluid coking unit, coke is removed as particles and a portion is recycled to provide hot surfaces for thermal cracking.

[85] A delayed coking unit and its general process description is shown and schematically illustrated below. The coker feedstream is mixed with steam and the mixture rapidly heated in a coking furnace to a coking temperature, and then fed to a coking drum. The hot mixed coker feedstream is maintained in the coke drum at coking conditions of temperature and pressure where the feed decomposes or cracks to form coke and volatile components. The volatile components are recovered as vapor and transferred to a coking product fractionator. One or more heavy fractions of the coke drum vapors can be condensed, for example by quenching or heat exchange. In certain embodiments the coke drum vapors are contacted with heavy gas oil in the coking unit product fractionator, and heavy fractions form all or part of a recycle oil stream having condensed coking unit product vapors and heavy gas oil. In certain embodiments, heavy gas oil from the coking feed fractionator is added to a flash zone of the fractionator to condense the heaviest components from the coking unit product vapors. Delayed coking units are typically configured with two or more parallel drums and operated in an alternating swing mode if there are two drums, or in a sequentially cyclic operating mode if there are three or more drums. Parallel coking drum trains, with two or more drums per train, are also possible. When the coke drum is full of coke, the feed is switched to another drum, and the full drum is cooled. Liquid and gas streams from the coke drum are passed to a coking product fractionator for recovery. Any hydrocarbon vapors remaining in the coke drum are removed, for instance by steam injection. The coke remaining in the drum is typically cooled with water and then removed from the coke drum by conventional methods, such as by hydraulic and/or mechanical techniques to remove green coke from the drum walls for recovery.

[86] Referring to FIG. 4, an embodiment of a coking reaction and separation zone **420**, including a coking zone operating as a delayed coker and an associated fractioning zone, is shown integrated with a hydrocracking system **400**, which can be any suitable hydrocracking unit, for instance similar to any of the systems **100**, **200** or **300** described herein, and that generally produces a hydrocracked bottoms fraction **416** and a distillate fraction **414**. In certain embodiments, the products are the thermally cracked hydrocarbon products stream **422** (all or a portion of which is in fluid communication with the hydrocracking system **400** as a recycle stream) and petroleum coke **424**. In additional embodiments, the coking reaction and separation zone **420** produces a first

thermally cracked hydrocarbon products stream **452**, a second thermally cracked hydrocarbon products stream **422** (all or a portion of which is in fluid communication with the hydrocracking system **400** as a recycle stream) and petroleum coke **424**.

[87] The coking reaction and separation zone **420** includes a coking furnace **454**, a coking reaction zone **450** (shown as parallel coking drum **450a** and **450b**) and a coking product fractionator **460**. A coker furnace feed **480** is in fluid communication with an inlet of the coking furnace **454**. The coker furnace feed **480** include one or more of a hydrocracker bottoms fraction **416** (corresponding to streams **116**, **216**, **316**), an additional feedstock **448** (corresponding to streams **148**, **248**, **348**), and/or a bottoms stream **446** from the coking product fractionator **460**. A heated feedstream from an outlet of the coking furnace **454** is in fluid communication with an inlet of the coking reaction zone **450**, and a coker liquid and gas stream **456** is discharged from an outlet of the coking reaction zone **450**. The outlet discharging the coker liquid and gas stream **456** is in fluid communication with an inlet of the coking product fractionator **460**. The coking zone **420** also includes associated apparatus or sub-systems for recovery and handling of coke **424**, for instance, hydraulic and/or mechanical cutters.

[88] The coker fractionating zone **460** includes one or more inlets in fluid communication with the coker liquid and gas stream **456**, and in certain embodiments also in fluid communication with the hydrocracker bottoms fraction **416** and/or the additional feedstock **448**. The coker fractionating zone **460** also includes one or more outlets discharging naphtha, middle distillate and gas oil range coker products. A thermally cracked hydrocarbon products stream **422**, or a first thermally cracked hydrocarbon products stream **452** and a second thermally cracked hydrocarbon products stream **422**, are discharged from outlets of the coking product fractionator **460**. One or more light outlets can also be provided (not shown), for instance, discharging gases H_2 , H_2S , NH_3 , and C_1 - C_4 hydrocarbons. One or more bottoms outlets **446** are provided, for instance, including hydrocarbon components having an initial boiling point corresponding to that of vacuum residue. This stream can be recycled to the furnace as all or a portion of stream **480**.

[89] In certain embodiments the fractionating zone **460** includes as outlets a first thermally cracked hydrocarbon products stream **452** and a second thermally cracked hydrocarbon products stream **422**. One or more light outlets can also be provided (not shown), for instance, discharging gases H_2 , H_2S , NH_3 , and C_1 - C_4 hydrocarbons. In certain embodiments these light products can be

included with a first thermally cracked hydrocarbon products stream **452** containing unstabilized naphtha (full or partial range naphtha, or light naphtha).

[90] The coker furnace feed **480** is charged to the coking furnace **454** where the contents are rapidly heated to a coking temperature and then fed to the coking drum **450a** or **450b**. The coking unit **420** can be configured with two or more parallel drums **450a** and **450b** and can be operated in a swing mode, such that when one of the drums is filled with coke, the feed is transferred to the empty parallel drum so that accumulated coke **424** can be recovered from the filled drum.

[91] The coker liquid and gas products are recovered as a the coker liquid and gas stream **456** from one or more outlets of the coker drum **450a** or **450b**. The coker liquid and gas stream **456** is passed to the coking product fractionator **460**, which produces the thermally cracked hydrocarbon products stream **422**. In certain embodiments the hydrocracker bottoms fraction **416** and/or an additional feed **448** is also charged to the coking product fractionator **460**. In certain embodiments, the coker liquid and gas stream **456** is fractionated to yield separate product streams that can include the first thermally cracked hydrocarbon products stream **452**, and the second thermally cracked hydrocarbon products stream **422**. In certain embodiments, all, a major portion, a significant portion, or a substantial portion of the thermally cracked hydrocarbon products stream **422** is used as a recycle stream within the hydrocracking system **400**. The coker fractionator bottoms stream **446** can be recycled as all or a portion of the coker furnace stream **480**. Any hydrocarbon vapors remaining in the coke drum are removed by steam injection. The coke is cooled with water and then removed from the coke drum using hydraulic and/or mechanical means.

[92] In operation of the delayed coker, the coker feed **480** and steam are introduced into the coking furnace **454** for heating to a predetermined temperature or temperature range that is similar to the coking temperature. In typical operations the temperature of the heated coker feedstream is closely monitored and controlled in the furnace utilizing appropriately positioned thermocouples, or other suitable temperature-indicating sensors to avoid or minimize the undesirable formation of coke in the tubes of the furnace. The sensors and control of the heat source, such as open flame heaters, can be automated as is known to those of skill of the art. For example, in known delayed cokers, a fired furnace or heater with horizontal tubes is used to reach thermal cracking temperatures, for instance, in the range of about 425-650, 425-530, 425-510, 425-505, 425-500, 450-650, 450-530, 450-510, 450-505, 450-500, 480-650, 480-530, 480-510, 480-505 or 480-500°C. With a short residence time in the furnace tubes of the coking furnace **454**, and with

addition of steam, coking of the feed material on the furnace tubes is minimized or obviated, and coking is thereby “delayed” until it is discharged into relatively larger coking drums in the coking reaction zone **450** downstream of the heater. In addition, the necessary heat for coking is provided in the coking furnace **454**.

[93] The flow of the heated coker feedstream from the coking furnace **454** is directed into one of the coking drums **450a** or **450b** via a feed line by adjustment of an inlet control valve, for instance, a three-way valve. The coking unit process can be conducted as a semi-continuous process by providing at least two vertical coking drums that are operated in swing mode. This allows the flow through the tube furnace to be continuous. The feedstream is switched from one to another of the at least two drums. In a coking unit with two drums, one drum is on-line filling with coke while the other drum is being steam-stripped, cooled, decoked, pressure checked and warmed up. The overhead vapors from the coke drums flow from the drum used for thermal cracking to the fractionating zone in a continuous manner.

[94] The coke drum is maintained at coking conditions of temperature and pressure where the feed decomposes or cracks to form coke and volatile components. The hydrocracker bottom stream, which is rich in hydrogen due to its highly paraffinic and naphthenic nature, serves as a hydrogen donor during these cracking reactions, and advantageously stabilizes radicals during thermal cracking and as a result minimizes coke formation. The volatile components are recovered as vapor and transferred to the coking unit product fractionator. In certain embodiments, heavy gas oil from the fractionator is added to the flash zone of the fractionator to condense the heaviest components from the coking unit product vapors. The heaviest fraction of the coke drum vapors can be condensed by other techniques, such as heat exchange. In certain embodiments, as in commercial operations, incoming vapors can be contacted with heavy gas oil in the coking unit product fractionator. Conventional heavy recycle oil includes condensed coking unit product vapors and unflashed heavy gas oil.

[95] When a drum **450a** or **450b** contains the predetermined maximum amount of coke, the inlet control valve is adjusted to direct the heated coker feedstream into the other drum **450b** or **450a**. Substantially at the same time, a coking drum outlet valve is adjusted so that the liquid and gas products are discharged through the appropriate line as the coker liquid and gas stream **456** that is passed to the fractionating zone **460**. Any hydrocarbon vapors remaining in the coke drum are typically removed by steam injection. Typically, the coking zone **420** includes associated

apparatus, for instance, hydraulic and/or mechanical cutters, whereby coke is cooled with water and then removed from the coke drum using hydraulic and/or mechanical cutters while that coking drum is temporarily decommissioned. Coke that is subsequently removed from a drum when it is out of service is schematically represented as lines **424**.

[96] The operating temperature (°C) in the coking drums **450** can range from about 425-650, 425-510, 425-505, 425-500, 450-650, 450-510, 450-505, 450-500, 485-650, 485-510, 485-505, 485-500, 470-650, 470-510, 470-505 or 470-500. The operating pressure (bars) in the coking drum can be in the range of about 1-20, 1-10 or 1-3, and in certain embodiments is mildly super-atmospheric. In certain embodiments of the process, steam is introduced or injected with the heated residue into the coking furnace, for instance with a steam introduction rate of about 0.1-3, 0.5-3 or 1-3 wt% relative to the heated residue, to increase the velocity in the tube furnace, and to reduce the partial pressure of the feedstock oil in the drum. The steam also serves to increase the amount of gas oil removed from the coke drums. Steam also assists in decoking of the tubes in the event of a brief interruption of the feed flow. The coking in each drum can occur in cycles, for instance, in the range of about 10-30, 10-24, 10-18, 12-30, 12-24, 12-18, 16-30, 16-24 or 16-18 hours.

[97] In certain embodiments, a fluid coking process is used, wherein circulated coke particles contact the feed and in which coking occurs on the surface of the coke particles, for instance similar to a Flexicoking™ process commercially available from ExxonMobil. Referring to FIG. 5, an embodiment of a coking reaction and separation zone **520**, including a coking zone operating as a fluid coker and an associated fractioning zone, is shown integrated with a hydrocracking system **500**, which can be any suitable hydrocracking unit, for instance similar to any of the systems **100**, **200** or **300** described herein, and that generally produces a hydrocracked bottoms fraction **516** and a distillate fraction **514**. In certain embodiments, the products are the thermally cracked hydrocarbon products stream **522** (all or a portion of which is in fluid communication with the hydrocracking system **500** as a recycle stream) and coke **568**. In additional embodiments, the coking reaction and separation zone **520** produces a first thermally cracked hydrocarbon products stream **552**, a second thermally cracked hydrocarbon products stream **522** (all or a portion of which is in fluid communication with the hydrocracking system **500** as a recycle stream) and coke **568**.

[98] The coking reaction and separation zone **520** includes a coking furnace **554**, a coking reaction zone **550** and a coking product fractionator **560**. In addition, suitable systems are provided

to facilitate circulation of coke particles including a coke combusting zone **562** and a fines separation zone **566**. A coker furnace feed **580** is in fluid communication with an inlet of the coking furnace **554**. The coker furnace feed **580** include one or more of a hydrocracker bottoms fraction **516** (corresponding to streams **116**, **216**, **316**), an additional feedstock **548** (corresponding to streams **148**, **248**, **348**), and/or a bottoms stream **546** from the coking product fractionator **560**. A heated feedstream from an outlet of the coking furnace **554** is in fluid communication with an inlet of the coking reaction zone **550**, and a coker liquid and gas stream **556** is discharged from an outlet of the coking reaction zone **550**. The outlet discharging the coker liquid and gas stream **556** is in fluid communication with an inlet of the coking product fractionator **560**.

[99] The coker fractionating zone **560** includes one or more inlets in fluid communication with the coker liquid and gas stream **556**, and in certain embodiments also in fluid communication with the hydrocracker bottoms fraction **516** and/or the additional feedstock **548**. The coker fractionating zone **560** also includes one or more outlets discharging naphtha, middle distillate and gas oil range coker products. A thermally cracked hydrocarbon products stream **522**, or a first thermally cracked hydrocarbon products stream **552** and a second thermally cracked hydrocarbon products stream **522**, are discharged from outlets of the coking product fractionator **560**. One or more light outlets can also be provided (not shown), for instance, discharging gases H_2 , H_2S , NH_3 , and C_1 - C_4 hydrocarbons. One or more bottoms outlets **546** are provided, for instance, including hydrocarbon components having an initial boiling point corresponding to that of vacuum residue. This stream can be recycled to before the furnace as all or a portion of stream **580**.

[100] In certain embodiments the fractionating zone **560** includes as outlets a first thermally cracked hydrocarbon products stream **552** and a second thermally cracked hydrocarbon products stream **522**. One or more light outlets can also be provided (not shown), for instance, discharging gases H_2 , H_2S , NH_3 , and C_1 - C_4 hydrocarbons. In certain embodiments these light products can be included with a first thermally cracked hydrocarbon products stream **552** containing unstabilized naphtha (full or partial range naphtha, or light naphtha).

[101] The coker furnace feed **580** is charged to a coking furnace **554** where the contents are rapidly heated to a coking temperature and then fed to a coking drum **550**. The coking reaction zone **550** includes a reactor having one or more inlets that receive a heated feedstream by spraying or other suitable means of injection. A portion of the coke effluent **524**, in particle form, is discharged via one or more outlets, and is in fluid or particulate communication with the coke

combusting zone **562**. Heated coke **564** is discharged from one or more outlets of the coke combusting zone **562** and is in fluid or particulate communication with one or more inlets of the coking drum **550**.

[102] The coker liquid and gas products are recovered as the coker liquid and gas stream **556** from one or more outlets of the coking drum **550**, generally through a fines separation zone **566** for recovery of fine coke particles. The coker liquid and gas stream **556** is passed to the coking product fractionator **560**, which produces the thermally cracked hydrocarbon products stream **522**. In certain embodiments the hydrocracker bottoms fraction **516** and/or an additional feed **548** is also charged to the coking product fractionator **560**. In certain embodiments, the coker liquid and gas stream **556** is fractionated to yield separate product streams that can include the first thermally cracked hydrocarbon products stream **552**, and the second thermally cracked hydrocarbon products stream **522**. In certain embodiments, all, a major portion, a significant portion, or a substantial portion of the thermally cracked hydrocarbon products stream **522** is used as a recycle stream within the hydrocracking system **500**. The coker fractionator bottoms stream **546** can be recycled as all or a portion of the coker furnace stream **580**.

[103] In operation of the fluid coking unit, the coker feed **580** and steam are introduced into the coking furnace **554** for heating to a predetermined temperature or temperature range, for instance, typically at about the coking temperature. For example, a fired furnace or heater with horizontal tubes is used to reach temperature levels that are at or below thermal cracking temperatures, for instance, in the range (°C) of about 425-650, 425-570, 425-525, 450-650, 450-570, 450-525, 485-650, 485-570 or 485-525. With a short residence time in the furnace tubes of the coking furnace **554**, and with addition of steam, coking of the feed material on the furnace tubes is minimized or obviated. In the fluid coking unit, coking occurs on coke particles in the coker reactor **550**. Further, additional heat for coking is provided by recirculating combusted heated coke particles **564** in the coking drum **550**.

[104] All or a portion of the coke product **524** is burned to provide additional heat for coking reactions to the feed into gases, distillate liquids, and coke. Coking occurs on the surface of circulating coke particles of coke. Coke is heated by burning the surface layers of accumulated coke in the coke combustion zone **562**, by partial combustion of coke produced. The products of coking are sent to the fractionating zone after recovery of fine coke particles in the separation zone **566**. Steam can also be added at the bottom of the reactor (not shown), for instance, in a scrubber

to add fluidization and to strip heavy liquids sticking to the surface of coke particles before they are sent to the burner. Coke is deposited in layers on the fluidized coke particles in the reactor. Air is injected into the burner for combustion to burn a portion of the coke produced in the reactor. A portion of the combusted particles are returned to the reactor, heated coke **564**, and the remainder is drawn out as coke **568**.

[105] The operating temperature (°C) in the coking drum **550** can range from about 450-760, 450-650, 450-570, 470-760, 470-650, 470-570, 510-760, 510-650 or 510-570. The operating pressure (bars) can be in the range of about 1-20, 1-10 or 1-3, and in certain embodiments is mildly super-atmospheric. In certain embodiments of the process, steam is introduced or injected with the heated residue into the coking furnace, for instance in an amount of about 0.1-3, 0.5-3 or 1-3 wt%.

[106] In certain embodiments, a coking and separation zone is provided with units similar to those shown in FIGs. 4 or 5, with an additional material to enhance removal of HPNA and/or HPNA precursor compounds. Referring to FIG. 6, a coking and separation zone **620** is shown operating as a fluid coker integrated with a hydrocracking system **600**, which can be any suitable hydrocracking unit, for instance similar to any of the systems **100**, **200** or **300** described herein, and that generally produces a hydrocracked bottoms fraction **616** and a distillate fraction **614**. The coking and separation zone **620** generally includes a coking drum or vessel **650** that discharges a coker liquid and gas stream **656**; a coking fractionator **660** that discharges a thermally cracked hydrocarbon products stream **622**, or a first thermally cracked hydrocarbon products stream **652** and a second thermally cracked hydrocarbon products stream **622**, and a bottoms stream **646**; and a coking furnace **654** that receives a coker furnace feed **680**. The coker furnace feed **680** include one or more of a hydrocracker bottoms fraction **616** (corresponding to streams **116**, **216**, **316**), an additional feedstock **648** (corresponding to streams **148**, **248**, **348**), and/or the bottoms stream **646** from the coking product fractionator **660**. A source of additional material **672** is provided in fluid or particulate communication with the coking drum **650** inlet, for instance, via the initial feedstream. While schematically shown upstream of the coking furnace **654**, the additional material **672** can be added downstream of the coking furnace. In embodiments in which there is a coker recycle stream from the coking fractionator **660** to the coking drum or vessel **650**, the source of additional material can be integrated in the fractionator so that the coker recycle stream contains catalyst material. The additional material **672** can be added to the coker feed, or admixed with use

of a separate mixing zone, such as an in-line mixing apparatus or a separate mixing apparatus (not shown). In certain embodiments (not shown), additional material **672** can be metered or otherwise charged directly to the coking drum or vessel **650**.

[107] In embodiments in which additional material is catalyst material, suitable catalysts include those having functionality to stabilize the free radicals formed by the thermal cracking and to thereby enhance the thermal cracking reactions. The catalyst material can be in homogeneous oil-soluble form, heterogeneous supported catalysts, or a combination thereof.

[108] In certain embodiments, the additional material **672** is a heterogeneous catalyst material that can be added to the fractionator bottoms prior coking. Suitable heterogeneous catalyst materials include active metals deposited or otherwise incorporated on a support material. The heterogeneous catalyst materials used in embodiments herein are generally granular in nature, and the support material can be selected from the group consisting of silica, alumina, silica-alumina, titania-silica, molecular sieves, silica gel, activated carbon, activated alumina, silica-alumina gel, zinc oxide, clays (for instance, attapulgus clay), fresh catalyst materials (including zeolitic catalytic materials), used catalyst materials (including zeolitic catalytic materials), regenerated catalyst materials (including zeolitic catalytic materials) and combinations thereof. The active metals of the heterogeneous catalyst material include one or more active metal components of metals or metal compounds (oxides or sulfides) selected from the Periodic Table of the Elements IUPAC Groups 4, 5, 6, 7, 8, 9 and 10. In certain embodiments, the active metal component can be one or more metals or metal compounds (oxides or sulfides) including Mo, V, W, Cr or Fe. In certain embodiments the active metal component can be selected from the group consisting of vanadium pentoxide, molybdenum alicyclic and aliphatic carboxylic acids, molybdenum naphthenate, nickel 2-ethylhexanoate, iron pentacarbonyl, molybdenum 2-ethyl hexanoate, molybdenum di-thiocarboxylate, nickel naphthenate and iron naphthenate. In certain embodiments, Mo and Mo compounds are used as the active metal component of a heterogeneous catalyst material. The heterogeneous catalyst material is provided in particulate form of suitable dimension, such as granules, extrudates, tablets, or pellets, may be formed into various shapes such as spheres, cylinders, trilobes, quadrilobes or natural shapes, possess average particle diameters (mm) of about 0.01-4.0, 0.1-4.0, or 0.2-4.0, pore sizes (nm) of about 1-5,000 or 5-5,000, possess pore volumes (cc/g) of about 0.08 - 1.2, 0.3 - 1.2 or 0.5 - 1.2, in certain embodiments at least 1.0, and possess a surface area of at least about 100 m²/g.

[109] In embodiments in which additional material **672** is heterogeneous catalyst material, it can be added upstream of the coking furnace, or in an optional embodiment, downstream of the furnace. A mixing zone can be used to mix the catalyst and coker feed. In addition, as catalyst material can be metered or otherwise charged directly to the coking drum or vessel **650**, or metered or otherwise charged directly to the fractionating zone **660**, as noted herein. In embodiments in which heterogeneous catalyst is used, the amount (ppmw) can be about 1 - 20,000, 10 - 20,000, 100 - 20,000, 1 - 10,000, 10 - 10,000, 100 - 10,000, 1 - 5,000, 10 - 5,000, 100 - 5,000, 1 - 1,000, 10 - 1,000 or 100 - 1,000 relative to the weight of the total coker feedstream (stream **616** and in certain embodiments also stream **648**), and can be determined as is known in the art, for instance based upon factors including the characteristics of the crude oil and its residue, the type of catalyst used and the coking unit operating conditions.

[110] In certain embodiments, a homogenous catalyst is used. For instance, effective homogeneous catalysts include those that are oil-soluble and contain one or more active metal components of metals or metal compounds (oxides, sulfides, or salts of organo-metal complexes) selected from the Periodic Table of the Elements IUPAC Groups 4, 5, 6, 7, 8, 9 and 10. In certain embodiments, homogeneous catalysts are or contain as an active metal component a transition metal-based compound derived from an organic acid salt or an organo-metal compound containing Mo, V, W, Cr or Fe. In certain embodiments homogeneous catalysts can be, or contain an active metal compound, that is selected from the group consisting of vanadium pentoxide, molybdenum alicyclic and aliphatic carboxylic acids, molybdenum naphthenate, nickel 2-ethylhexanoate, iron pentacarbonyl, molybdenum 2-ethyl hexanoate, molybdenum di-thiocarboxylate, nickel naphthenate and iron naphthenate. In certain embodiments, Mo and Mo compounds are used as homogeneous catalyst material. The total concentration (ppmw, based on the total feedstock weight) of the catalyst material can be in the range of 100 - 20,000, 300 - 20,000, 500 - 20,000, 1,000 - 20,000, 100 - 5,000, 300 - 5,000, 500 - 5,000, 1,000 - 5,000, 100 - 1,500, 300 - 1,500, 500 - 1,500, 1,000 - 1,500, 100 - 1,200, 300 - 1,200 or 500 - 1,200.

[111] The homogeneous catalyst can be added upstream of the coking furnace, or in an optional embodiment, downstream of the furnace. Since the catalyst is homogeneous and oil-soluble, it can be added directly to the coking zone or in certain embodiments to the fractionator. If the homogeneous catalyst is prepared from metal oxides or conditioned before use, a separate step is carried for catalyst preparation as is known in the art. The amount of catalyst material (ppmw)

can range from 1-10,000, 10-10,000, 100-10,000, 1-5,000, 10-5,000, 100-5,000, 1-1,000, 10-1,000, 100-1,000, 1-100 or 10-100 relative to the weight of the total coker feedstream (stream **616** and in certain embodiments also stream **648**) can be determined as is known in the art, for instance based upon factors including the characteristics of the crude oil and its residue, the type of catalyst used and the coking unit operating conditions.

[112] In certain embodiments, the additional material used, alone or in combination with one or more types of catalyst materials, comprise adsorbent material. In this regard, the disclosure of commonly owned US Patents 9,023,192 and 9,234,146 are relevant and are incorporated by reference herein in their entireties. For example, adsorbent material is admixed with the coker feedstream(s) in a mixing zone, such as an in-line mixing apparatus or a mixer, to form a slurry of the coker feedstream(s) and adsorbent material. In certain optional embodiments, a source of catalyst material is provided along with the adsorbent material in fluid or solid communication with the coking drum or vessel **650** inlet. The optional catalyst material can be admixed in the same manner as the adsorbent material, or in a different manner. In embodiments in which optional catalyst material is used, the types and quantities of catalyst described herein for use in coking operations are applicable.

[113] The adsorbent material and/or heterogeneous catalyst material can be admixed with the coker feedstream(s) with or without a dedicated mixing zone. Other embodiments that are not shown are also possible. The adsorbent material and/or heterogeneous catalyst material can be metered or otherwise charged separately to the coking drum or vessel **650** whereby a source of material is provided in particulate communication or fluid communication (in which the material is formed in a slurry) with the coking drum or vessel **650** inlet. In further embodiments, the fractionating zone is configured for handling of adsorbent material and/or heterogeneous catalyst material, whereby a source of material is provided in particulate communication or fluid communication (in which the adsorbent material is formed in a slurry) with the fractionating zone **660**. The adsorbent material and/or heterogeneous catalyst material is metered or otherwise charged directly to the fractionating zone **660** so that a coker recycle, bottoms stream **646**, contains the adsorbent material and/or heterogeneous catalyst material, for instance similar to the process that is disclosed in commonly owned US Patent 9,023,192, which is incorporated by reference herein in its entirety. Coke **624**, which contains adsorbent material that has adsorbed undesirable

contaminants and/or heterogeneous catalyst material, is recovered from the coking drum or vessel **650**.

[114] The use of adsorbent material increases the quality of the thermally cracked distillates by removing some of the undesirable contaminants, for instance by selectively adsorbing sulfur- and/or nitrogen-containing compounds. Handling of adsorbent material that has adsorbed undesirable contaminants, and/or heterogeneous catalyst material, largely depends on the type of coker unit deployed. For instance, in delayed coker units, the adsorbent material and/or heterogeneous catalyst material is deposited with the coke on the inside surface of the coking drum(s). In a fluid coking process, the adsorbent material and/or heterogeneous catalyst material can pass with the coke particles that are discharged.

[115] Effective adsorbent materials are selected from the group consisting of silica, alumina, silica-alumina, titania-silica, molecular sieves, silica gel, activated carbon, activated alumina, silica-alumina gel, zinc oxide, clays (for instance, attapulgus clay), fresh catalyst materials (including zeolitic catalytic materials), spent catalyst materials (including zeolitic catalytic materials), regenerated catalyst materials (including zeolitic catalytic materials), and combinations thereof. In certain embodiments adsorbent material comprises activated carbon, clays, or mixtures thereof. The material is provided in particulate form of suitable dimension, such as granules, extrudates, tablets, or pellets, may be formed into various shapes such as spheres, cylinders, trilobes, quadrilobes or natural shapes, possess average particle diameters (mm) of about 0.01-4.0, 0.1-4.0, or 0.2-4.0, pore sizes (nm) of about 1-5,000 or 5-5,000, possess pore volumes (cc/g) of about 0.08 - 1.2, 0.3 - 1.2 or 0.5 - 1.2, in certain embodiments at least 1.0, and possess a surface area of at least about 100 m²/g. The quantity (weight basis, hydrocarbon to adsorbent) of the solid adsorbent material used in the embodiments herein is about 1000:1-3:1, 200:1-3:1, 100:1-3:1, 50:1-3:1, 20:1-3:1, 1000:1-3:1, 200:1-8:1, 100:1-8:1, 50:1-8:1, 20:1-8:1, 1000:1-3:1, 200:1-10:1, 100:1-10:1, 50:1-10:1 or 20:1-10:1.

[116] The fractionating zone, such as **460**, **560** or **660** described herein, includes design features to enable separation of cracker products from the coking drums/vessels, including a coker distillate stream that is recovered and the coker gas oil stream, and in certain embodiments a coker recycle stream. Components of the fractionating zone that are not shown but which are well-known can include feed/product and pump-around heat exchangers, charge heater(s), product strippers, cooling systems, hot and cold overhead drum systems including re-contactors and off-gas

compressors, and units for water washing of overhead condensing systems. Steam is typically injected to prevent cracking of heated feed. In certain embodiments, one or more flash vessels can be used as the fractionating zone. For instance, a first flash vessel can separate gases, and in certain embodiments all or a portion of a coker distillate stream, and a second flash vessel to separate a coker gas oil stream and the hydroprocessing feed and the coker recycle stream. In certain embodiments, in which a source of additional material is used and is integrated in the fractionator so that the coker recycle stream contains the additional material, the fractionator includes appropriate design features.

[117] The feeds to the fractionating zone, the coker liquid and gas stream **456**, **556** or **656**, can be introduced at different locations in the columns as is known. The effluents shown in the figures include the thermally cracked product streams **422**, **522** or **622**, or a first coker thermally cracked distillate stream **452**, **552** or **652** and a second thermally cracked product streams **422**, **522** or **622**. Other streams not shown can include light products and coker recycle. The light product stream typically includes gases H₂, H₂S, NH₃ and C₁-C₄ hydrocarbons. In certain embodiments the light product stream also includes hydrocarbons at or below the naphtha or light naphtha range, for instance, discharged as overhead gases and condensed in a separate vessel. A bottoms stream can be used as a coker recycle stream, and can correspond to that of a conventional vacuum residue (for instance, having an initial boiling point in the range of about 510-565°C). In certain embodiments the coker recycle stream can include lower boiling hydrocarbons, such as those in the heavy coker gas oil range or above, in certain embodiments having an initial boiling point in the range of about 450-510, 470-510 or 482-510°C.

[118] In certain embodiments, the feedstock to the delayed coker is mixed with hydrogen in a mixing zone, in certain embodiments an excess of hydrogen gas. A portion of the hydrogen gas is mixed with the feedstock to produce a hydrogen-enriched liquid hydrocarbon feedstock. This hydrogen-enriched liquid hydrocarbon feedstock and undissolved hydrogen can be supplied to a flashing zone in which at least a portion of undissolved hydrogen is flashed, and the hydrogen is recovered and recycled. The hydrogen-enriched liquid hydrocarbon feedstock from the flashing zone is supplied as a feed stream to the delayed coker reaction zone, for instance coker drums. The liquid product stream that is recovered from the reactor is further processed and/or recovered as provided here.

[119] The feed to the delayed coker are shown and described as the hydrocracker bottoms fraction (streams **116**, **216**, **316**, **416**, **516** and/or **616** above), alone or in combination with one or more additional feedstocks (streams **148**, **248**, **348**, **448**, **548** and/or **648** above). The additional feedstock can be co-processed along with the hydrocracking unit bottoms in the coking zone without treatment; alternatively, the additional feedstock can be subjected to a suitable pretreatment in a residue treatment zone. The quantity of additional feedstock can be such that 0-99, 10-99, 25-99, 50-99, 0-90, 10-90, 25-90, 50-90, 0-75, 10-75, 25-75 or 50-75 wt% of the total feed to the coking zone is obtained from the additional feedstock. The additional feedstock can be selected from the group consisting of atmospheric residue, vacuum residue, deasphalted oil, demetallized oil, other heavy oil fractions, and combinations thereof, and can be derived from crude oil, bitumens, oil sand, shale oil, coal oils or biomass oils. In certain embodiments an additional feedstock can have an initial boiling point corresponding to that of VGO described herein, an end point based on the characteristics of the heavy oil fraction. In further embodiments an additional feedstock can have an initial boiling point of about 425-565, 450-565, 425-540, 450-540, 425-530, 450-530, 425-510 or 450-510°C, in certain embodiments about 425, 450 or 475°C, and an end point based on the characteristics of the heavy oil fraction.

[120] In certain embodiments, all or a portion of the additional feedstock can be processed in a residue treatment zone. Treatment of the additional feedstock can be to any degree, depending on various factors including the desired coker liquid and gas product quantity/quality, the desired coke quantity/quality, the type and capacity of the coker unit and the operating conditions.

[121] In certain embodiments, the residue treatment zone produces a treated additional feedstock that, when combined with the hydrocracker bottoms fraction, produces a coker feedstock characterized by a S content of generally less than about 7.5, 3.5, 1.0 or 0.5 wt%, in certain embodiments 0.2-7.5, 0.2-3.5, 0.2-0.5, 1.0-7.5, 1.0-3.5 or 3.5-7.5 wt %, ; and a metals content of less than about 700, 400 or 100 ppmw, Such levels enable recovery of high quality petroleum green coke when the hydrocracker bottoms fraction and the suitably treated additional feedstock is thermally cracked. The recovered high quality petroleum green coke can be used as low S and metal content fuel grade coke, and/or as a raw material for production of low S and metal content marketable grades of coke including anode grade coke (sponge) and/or electrode grade coke (needle). Table 2 shows the properties of these types of coke. In accordance with certain embodiments of the process herein, calcination of the petroleum green coke recovered from the

coking drums produces sponge and/or needle grade coke, for instance, suitable for use in the aluminum and steel industries. Calcination is commonly known and occurs by thermal treatment to remove moisture and reduce the volatile combustible matter.

[122] The levels of the S and metals in the total feed to the coking zone is to be considered when determining whether such high quality petroleum coke product can be obtained. The hydrocracker bottoms fraction from the integrated hydrocracking operation generally has sufficiently low S and metals content. Therefore, additional feedstocks that would otherwise be unsuitable alone for production of high quality petroleum coke product, even after some degree of treatment, can be used in combination with the hydrocracker bottoms fraction to provide a total coker feed that possesses metals and S content compatible with the desired coke quality, such as the types of coke having properties set forth in Table 2.

Table 2

Property	Units	Fuel Coke	Calcined Sponge Coke	Calcined Needle Coke
Bulk Density	Kg/m ³	880	720-800	670-720
S	W% (max)	3.5-7.5	1.0-3.5	0.2-0.5
N	ppmw (max)	6,000	-	50
Ni	ppmw (max)	500	200	7
V	ppmw	150	350	-
Volatile Combustible Material	W% (max)	12	0.5	0.5
Ash Content	W% (max)	0.35	0.40	0.1
Moisture Content	W% (max)	8-12	0.3	0.1
Hardgrove Grindability Index (HGI)	W%	35-70	60-100	-
Coefficient of thermal expansion, E+7	°C	-	-	1-5

[123] As used herein, “high quality petroleum green coke” refers to petroleum green coke recovered from a coker unit that when calcined, possesses the properties as in Table 2, in certain embodiments possessing the properties in Table 2 concerning calcined sponge coke or calcined needle coke.

[124] In certain embodiments a residue treatment zone for treatment of the additional feedstock comprises residue hydrocracking, in which the additional feedstock is treated in the presence of

effective hydrotreating catalyst and an effective amount of hydrogen obtained from recycle within the residue hydroprocessing zone and from make-up hydrogen. A residue hydrotreating zone generally includes one or more inlets in fluid communication with a source of the additional feedstock and a source of hydrogen gas (including recycle and make-up hydrogen). One or more outlets of the residue hydrotreating reaction zone that discharge a hydrotreated residue is in fluid communication with one or more inlets of the coking zone, for instance via the coking furnace, directly to the coking drum or vessel if the temperature is sufficient, or the coking fractionator. In certain embodiments, one or more high pressure and low pressure separation stages are provided between the residue hydrotreating zone and the coking zone. In certain embodiments the residue hydrocracker a conversion of up to about 50 wt%. In addition to or alternatively, a stripper and/or a fractionator can be used between the residue hydrotreater and the coking zone.

[125] The additional feedstock stream and a hydrogen stream are charged to the hydrotreating reaction zone. The hydrogen stream contains an effective quantity of hydrogen to support the requisite degree of hydrotreating, feed type, and other factors, include recycle hydrogen from optional gas separation subsystems associated with the residue hydrotreating reaction zone and make-up hydrogen. In certain embodiments, a reaction zone can contain multiple catalyst beds and can receive one or more quench hydrogen streams between the beds.

[126] The residue hydrotreating reaction zone for treatment of the additional feedstock, prior to coking, can contain one or more fixed-bed, ebullated-bed, slurry-bed, moving bed, continuous stirred tank (CSTR) or tubular reactors, in series and/or parallel arrangement, and is operated under conditions typically effective for atmospheric or vacuum residue hydrotreating, the particular type of reactor, the feed characteristics, the desired product slate and the catalyst selection. For instance, these conditions can include a reaction temperature (°C) in the range of from about 330-520, 330-475, 330-450, 380-520, 380-475 or 380-450; a reaction pressure (bars) in the range of from about 90-300, 90-250, 90-200, 125-300, 125-250, 125-200, 140-300, 140-250 or 140-200; a hydrogen feed rate (SL/L) of up to about 670, 625, 610, 525 or 510, in certain embodiments from about 445-475, 445-510, 445-625, 500- 525, 510-550, 500-610, 500-665 or 500-545; and a feed rate liquid hourly space velocity (h^{-1}) in the range of from about 0.1-4, 0.3-1.5, 0.3-2.5, 1-3 or 1-4.

[127] An effective quantity of catalyst is provided for hydrotreatment of the additional feedstock, including those possessing hydrotreating functionality, for hydrodemetallization,

hydrodesulfurization and hydrodenitrification. Such catalysts generally contain one or more active metal component of metals or metal compounds (oxides or sulfides) selected from the Periodic Table of the Elements IUPAC Groups 6, 7, 8, 9 and 10. In certain embodiments, the active metal component is one or more of Co, Ni, W and Mo. The active metal component is typically deposited or otherwise incorporated on a support, such as amorphous alumina, amorphous silica alumina, zeolites, or combinations thereof. In certain embodiments, the catalyst used for hydrotreatment of the additional feedstock includes one or more beds selected from Co/Mo, Ni/Mo, Ni/W, and Co/Ni/Mo. Combinations of one or more beds of Co/Mo, Ni/Mo, Ni/W and Co/Ni/Mo, can also be used. The combinations can be composed of different particles containing a single active metal species, or particles containing multiple active species. In certain embodiments, a combination of Co/Mo catalyst and Ni/Mo catalyst are effective for hydrodemetallization, hydrodesulfurization and hydrodenitrification. One or more series of reactors can be provided, with different catalysts in the different reactors of each series. The residue hydrotreating catalyst material is provided in particulate form of suitable dimension, such as granules, extrudates, tablets, or pellets, may be formed into various shapes such as spheres, cylinders, trilobes, quadrilobes or natural shapes, possess average particle diameters (mm) of about 0.01-4.0, 0.1-4.0, or 0.2-4.0, pore sizes (nm) of about 1-5,000 or 5-5,000, possess pore volumes (cc/g) of about 0.08 - 1.2, 0.3 - 1.2 or 0.5 - 1.2, in certain embodiments at least 1.0, and possess a surface area of at least about 100 m²/g.

[128] In certain embodiments a residue treatment zone for treatment of the additional feedstock comprises solvent deasphalting. Solvent deasphalting operations are well-known processes in which suitable solvent is used to precipitate asphaltenes from the feed. The solvent deasphalting process produces a low contaminant and reduced asphaltenes product, known conventionally as deasphalted oil (DAO). The solvent deasphalting process is usually carried out with paraffinic C₃-C₇ solvents and occurs at or below the critical temperature of the solvent. In general, in a solvent deasphalting zone, a feed is mixed with solvent so that the DAO is solubilized in the solvent. The insoluble pitch precipitates out of the mixed solution. Separation of the DAO phase (solvent-DAO mixture) and the asphalt/pitch phase typically occurs in one or more vessels or extractors designed to efficiently separate the two phases and minimize contaminant entrainment in the DAO phase. The DAO phase is then heated to conditions at which the solvent becomes supercritical. In typical solvent deasphalting processed, separation of the solvent and DAO is facilitated in a DAO separator. Any entrained solvent in the DAO phase and the pitch phase is stripped out, typically

with a low pressure steam stripping apparatus. Recovered solvent is condensed and combined with solvent recovered under high pressure from the DAO separator. The solvent is then recycled back to be mixed with the feed.

[129] The asphalt phase contains a majority of the process reject materials from the charge, i.e., metals, asphaltenes, Conradson carbon, and is also rich in aromatic compounds and asphaltenes. In addition to the solvent deasphalting operations described herein, other solvent deasphalting operations, although less common, are suitable. For instance, a three-product unit, in which resin, DAO and pitch can be recovered, can be used, where a range of bitumens can be manufactured from various resin/pitch blends. Furthermore, although two extraction stages are described below, a single extraction stage can be effective to treat the additional feedstock, depending on the necessary degree of treatment.

[130] Solvent deasphalting is typically carried-out in liquid phase thus the temperature and pressure are set accordingly. There are commonly two stages for phase separation in solvent deasphalting. In a first separation stage, the temperature is maintained at a lower level than the temperature in the second stage to separate the bulk of the asphaltenes. The second stage temperature is selected to control the final DAO quality and quantity. Excessive temperature levels will result in a decrease in DAO yield, but the DAO will be lighter, less viscous, and contain less metals, asphaltenes, S, and N. Insufficient temperature levels have the opposite effect such that the DAO yield increases but the product quality is reduced. Operating conditions for solvent deasphalting units are generally based on a specific solvent and charge stock to produce a DAO of a specified yield and quality. Extraction temperature is generally fixed for a given solvent, with small adjustments to maintain the DAO quality. The composition of the solvent is also an important process variable. The solubility of the solvent increases with increasing critical temperature, such that $C_3 < iC_4 < nC_4 < iC_5$, i.e., the solubility of iC_5 is greater than that of nC_4 , the solubility of nC_4 is greater than that of iC_4 , the solubility of iC_4 is greater than that of C_3 . An increase in critical temperature of the solvent increases the DAO yield. However, solvents having higher critical temperatures afford less selectivity resulting in lower DAO quality. Solvent deasphalting units are operated at pressures that are high enough to maintain the solvent in the liquid phase, and depend on the deasphalting solvent composition. The volumetric ratio of the solvent to the solvent deasphalting unit charge is also a factor in selectivity, and to a lesser degree, on the DAO yield. A higher ratio results in a higher quality of the DAO for a fixed deasphalted

yield. Selection of the solvent is also considered in establishing operational solvent-to-oil ratios; generally the solvent-to-oil ratio decreases as the critical solvent temperature increases.

[131] In one embodiment, a solvent deasphalting zone generally includes a first phase separation zone and a second phase separation zone. The first phase separation zone includes one or more inlets in fluid communication with a source of the additional feedstock, and in fluid communication with a source of paraffinic hydrocarbon as deasphalting solvent, and includes, for example, one or more primary settler vessels suitable to accommodate the mixture of the additional feedstock and solvent. The first phase separation zone generally includes necessary components to operate at suitable temperature and pressure conditions, such as below the critical temperature and pressure of the solvent. The first phase separation zone also includes one or more outlets for discharging an asphalt phase, and one or more outlets for discharging a reduced asphalt content phase, which is the primary DAO phase. The outlet(s) discharging the asphalt phase are typically in fluid communication with a solvent-asphalt separation zone for recovery of solvent contained in the asphalt phase from the first phase separation zone.

[132] The second phase separation zone includes one or more inlets in fluid communication with the reduced asphalt content phase outlet from the first phase separation zone, and includes, for example, one or more secondary settler vessels suitable to accommodate the feed. The second phase separation zone generally includes necessary components to operate at temperature and pressure conditions below critical properties of the solvent. The second phase separation zone includes one or more outlets for discharging an asphalt phase. In certain embodiments the outlet for discharging the asphalt phase is in fluid communication with the solvent-asphalt separation zone for recovery of solvent. In further embodiments the outlet discharging the asphalt phase is in fluid communication with an inlet of first phase separation zone via a recycle stream.

[133] The second phase separation zone also includes one or more outlets for discharging a reduced asphalt content phase stream, which is the secondary DAO phase. The secondary DAO phase is typically in fluid communication one or more inlets of a solvent-DAO separation zone. The solvent-DAO separation zone contains one or more flash vessels or fractionation units operable to separate solvent and DAO. The separation zone includes one or more outlets for discharging a solvent stream, which is in fluid communication with one or more inlets of the first phase separation zone, and one or more outlets for discharging DAO. The outlet discharging DAO

is in fluid communication with the coking zone as described herein, as the additional feedstock that has been subjected to pretreatment.

[134] The solvent-asphalt separation zone is used and includes one or more inlets in fluid communication with the outlet(s) discharging asphalt streams. The separation zone contains one or more flash vessels or fractionation units operable to separate solvent and asphaltic materials, and can include, for instance, necessary heat exchangers to increase the temperature before a separation vessel. The solvent-asphalt separation zone also includes one or more outlets for discharging a recycle solvent stream, which is in fluid communication with the first phase separation zone, and an outlet for discharging an asphalt stream. In certain embodiments, the outlet discharging the asphalt stream is in fluid communication with a gasification zone or an asphalt pool.

[135] The solvent stream is derived from one or more solvent sources comprising an integrated process solvent stream such as light naphtha from the hydrocracker products or the coker light products, recycle solvent stream from the solvent-DAO separation zone and/or the solvent-asphalt separation zone, and/or make-up solvent which can be those used in typical solvent deasphalting processes such as C₃-C₇ paraffinic hydrocarbons. The following Table 3 provides critical temperature and pressure data for C₃-C₇ paraffinic solvents.

Table 3

Carbon Number	Temperature, ° C	Pressure, bar
C ₃	97	42.5
C ₄	152	38.0
C ₅	197	34.0
C ₆	235	30.0
C ₇	267	27.5

[136] In operation of a deasphalting process herein, the mixture of the additional feedstock and solvent is passed to first phase separation zone in which phase separation occurs. The additional feedstock and solvent are mixed, for example using an in-line mixer or a separate mixing vessel. Mixing can occur as part of the first phase separation zone or prior to entering the first phase separation zone. The first phase separation zone serves as the first stage for the extraction of DAO from the feedstock. The two phases formed in the first phase separation zone are an asphalt phase

and a primary DAO phase. The temperature at which the contents of the first phase separation zone are maintained is sufficiently low to maximize recovery of the DAO from the feedstock. In certain embodiments conditions in the first phase separation zone are maintained below the critical temperature and pressure of the solvent. In general, components with a higher degree of solubility in the solvent will pass with the primary DAO phase. The primary DAO phase includes a major portion of the solvent, a minor portion of the asphalt content of the feedstock and a major portion of the DAO content of the feedstock. The asphalt phase generally contains a minor portion of the solvent and is discharged, typically from the bottom of the vessel. In the second phase separation zone, the DAO phase from the first phase separation zone, which contains some asphalt, enters a separation vessel, for example, a secondary settler. An asphalt phase separates and forms at the bottom of the secondary settler that, due to increased temperature, is approaching the critical temperature of the solvent. The rejected asphalt from the secondary settler contains a relatively small amount of solvent and DAO. In certain embodiments all or any portion of the asphalt phase is recycled back to first phase separation zone for the recovery of remaining DAO. In other embodiments all or any portion of the asphalt phase from the secondary settler is mixed with the asphalt stream from the primary settler. All or any portion of the asphalt stream from first phase separation zone, and/or the asphalt stream from second phase separation zone can be charged to a solvent-asphalt separation zone. The asphalt can optionally be heated in heater before being passed to the inlet of the solvent-asphalt separation zone. Additional solvent is flashed from the solvent-asphalt separation zone and recycled to the first phase separation zone. A bottoms asphalt stream from the solvent-asphalt separation zone can optionally be passed to a steam stripper for steam stripping of the asphalt as conventionally known to recover a steam stripped asphalt phase, and a steam/solvent mixture for solvent recovery and recycle. The asphalt stream, containing precipitated asphaltenes, is removed from the solvent deasphalting unit on regular basis to facilitate the deasphalting process.

[137] The secondary DAO phase is passed to the solvent-DAO separation zone to recover solvent for recycle. Solvent is flashed and discharged for recycle to the first phase separation zone in certain embodiments in a continuous operation. A DAO stream from the separation zone can be passed to the coking zone as the treated additional feedstock, or can optionally be subjected to steam stripping as is conventionally known to recover a steam stripped DAO as the as the treated additional feedstock, and a steam/solvent mixture for solvent recovery and recycle.

[138] In certain embodiments an enhanced solvent deasphalting process can be used, as described herein and in US Patents 7,566,394, 7,799,211 / 8,986,622, or 7,763,163 / 7,867,381, which are commonly owned and incorporated by reference herein in their entireties.

[139] In certain embodiments a residue treatment zone for treatment of the additional feedstock comprises an enhanced solvent deasphalting zone, in which adsorbent material is included in the first phase separation zone. The enhanced solvent deasphalting zone generally includes a mixing zone, a first phase separation zone, an adsorbent stripping zone, a solvent-asphalt separation zone, and a second phase separation zone. For instance, a similar enhanced solvent deasphalting process is described in commonly owned US Patent Number 7,566,394, which is incorporated by reference herein in its entirety.

[140] The mixing zone includes one or more inlets in fluid communication with a source of the additional feedstock, a source of solid adsorbent material, and a source of deasphalting solvent. In certain embodiments the mixing zone is equipped with suitable mixing apparatus such as rotary stirring blades or paddles, which provide a gentle, but thorough mixing of the contents. The mixing zone can be operated as an ebullated bed, fixed-bed, tubular or continuous stirred-tank reactor. The mixing zone includes one or more outlets for discharging a slurry containing the mixture of the feed, deasphalting solvent and adsorbent material. In certain embodiments mixing can occur in one or more in-line apparatus so that the slurry is formed and send to the first phase separation zone.

[141] The slurry outlet is in fluid communication with one or more inlets of the first phase separation zone. The first phase separation zone includes, for example, one or more primary settler vessels suitable to accommodate the mixture of the additional feedstock, deasphalting solvent and adsorbent material. The first phase separation zone can be similar to that used in typical solvent deasphalting described above and generally includes necessary components to operate at temperature and pressure conditions below the critical temperature and pressure of the deasphalting solvent. The first phase separation zone also includes one or more outlets for discharging a light phase stream, and one or more outlets for discharging a bottoms phase stream.

[142] A second phase separation zone includes one or more inlets in fluid communication with the light phase stream outlet for separation of deasphalting solvent from DAO. The second phase separation zone includes, for example, one or more settler vessels suitable to accommodate the mixture of DAO and deasphalting solvent. The second phase separation zone can be similar to

that used in typical solvent deasphalting and generally includes necessary components to operate at suitable temperature and pressure conditions, such as below the critical properties of the deasphalting solvent. The second phase separation zone includes one or more outlets for discharging a recycle deasphalting solvent stream, and one or more outlets for discharging a DAO stream. The recycle deasphalting solvent stream outlet is in fluid communication with inlet(s) to the mixing zone.

[143] The bottoms phase stream outlet, and a source of stripping solvent, are in fluid communication with one or more inlets of the adsorbent stripping zone to separate and clean the adsorbent material. The adsorbent stripping zone can include one or more filtration vessels, and includes one or more outlets for discharging stripped adsorbent material and one or more outlets for discharging an asphalt stream. The adsorbent material outlet is in fluid communication with an inlet of the mixing zone to recycle adsorbent material. A portion of the adsorbent material can also be discharged in a continuous, periodic or as-needed manner, for instance, as spent adsorbent material. The adsorbent stripping zone also includes one or more outlets for discharging a stripping solvent-asphalt mixture that is in fluid communication with an inlet of the solvent-asphalt separation zone, such as a flash vessel or fractionator, to separate stripping solvent. The solvent-asphalt separation zone further includes outlets for discharging an asphalt stream and a recycle stripping solvent stream. The recycle stripping solvent stream outlet is in fluid communication with inlet(s) of the adsorbent stripping zone. In certain embodiments, the asphalt stream outlets and/or the adsorbent material outlet (via the spent adsorbent) are in fluid communication with a gasification zone or an asphalt pool.

[144] The deasphalting solvent stream is derived from one or more solvent sources comprising an integrated process solvent stream such as light naphtha from the hydrocracker products or the coker light products, a recycle deasphalting solvent stream from the second phase separation zone, and in certain embodiments make-up deasphalting solvent. Make-up deasphalting solvent can be a solvent from another source that is used in typical solvent deasphalting processes as described herein. The stripping solvent stream is derived from one or more solvent sources comprising an integrated process solvent stream such as light naphtha from the hydrocracker products or the coker light products, a recycle stripping solvent stream from the solvent-asphalt separation zone, and in certain embodiments make-up stripping solvent.

[145] In operation of the enhanced solvent deasphalting zone in which adsorbent material is included in the first phase separation zone, the additional feedstock, adsorbent material, and the deasphalting solvent stream are charged to the mixing zone and mixed to provide the slurry. The rate of agitation for a given vessel and mixture of adsorbent, solvent and feedstock is selected so that there is minimal, if any, attrition of the adsorbent granules or particles. For example, mixing can be carried out for 30 to 150 minutes. In addition, the additional feedstock, adsorbent material, and the deasphalting solvent stream can be mixed in an in-line mixer to produce the slurry. The slurry is passed to the first phase separation zone, which operates under temperature and pressure conditions effective to facilitate separation of the feed mixture into an upper layer comprising light and less polar fractions that are removed as the light phase stream, and the bottoms phase stream comprising asphaltenes and the solid adsorbent. In certain embodiments, vertical flash drum can be utilized for this separation step. Conditions in the mixing vessel and first phase separation zone are generally maintained below the critical temperature and pressure of the deasphalting solvent as described above in the embodiments using conventional solvent deasphalting. The light phase stream is passed to the second separation vessel which is maintained at an effective temperature and pressure to separate deasphalting solvent from the DAO, such as between the boiling and critical temperature of the solvent, and under a pressure of for instance between about 1-3 bars. The deasphalting solvent stream is recovered and recycled to the mixing zone, in certain embodiments in a continuous operation. The DAO stream from the second separation zone can be passed to the coking zone as the treated additional feedstock, or can optionally be subjected to steam stripping as is conventionally known to recover a steam stripped DAO as the as the treated additional feedstock, and a steam/solvent mixture for solvent recovery and recycle.

[146] The asphalt and adsorbent slurry are mixed with a stripping solvent stream in an adsorbent stripping zone to separate and clean the adsorbent material by desorption. In certain embodiments, the adsorbent slurry and asphalt mixture is washed with two or more aliquots of the stripping solvent in the adsorbent stripping zone in order to dissolve and remove the adsorbed process reject materials. The clean solid adsorbent stream is recovered, and all or a portion is recycled to the mixing zone. A portion of the adsorbent material can also be discharged in a continuous, periodic or as-needed manner, for instance, as spent adsorbent material. An asphalt stream is recovered, and contains asphaltenes and process reject materials that were desorbed from the adsorbent. A solvent-asphalt mixture is withdrawn from the adsorbent stripping zone and is it is sent to a

separation zone to discharge an asphalt stream and a clean stripping solvent stream which can be recycled to the adsorbent stripping zone, in certain embodiments in a continuous operation.

[147] In certain embodiments a residue treatment zone for treatment of the additional feedstock comprises an enhanced solvent deasphalting zone, in which adsorbent material is included in the second phase separation zone. The enhanced solvent deasphalting zone generally includes a first phase separation zone, a second phase separation zone, an adsorbent stripping zone and a solvent-DAO separation zone. For instance, a similar enhanced solvent deasphalting process is described in commonly owned US Patent Number 7,566,394, which is incorporated by reference herein in its entirety.

[148] The first phase separation zone includes one or more inlets in fluid communication with a source of the additional feedstock, and a source of deasphalting solvent. The first phase separation zone includes, for example, one or more primary settler vessels suitable to accommodate the mixture of the additional feedstock and deasphalting solvent. The first phase separation zone can be similar to that used in typical solvent deasphalting described above and generally includes necessary components to operate at temperature and pressure conditions below the critical temperature and pressure of the deasphalting solvent. The first phase separation zone also includes one or more outlets for discharging a light phase stream and one or more outlets for discharging a bottoms phase stream.

[149] A second phase separation zone includes one or more inlets in fluid communication with the light phase stream outlet and a source of solid adsorbent material. The second phase separation zone provides contact and residence time with the adsorbent material, and facilitates separation of deasphalting solvent from DAO. The second phase separation zone includes, for example, one or more settler vessels suitable to accommodate the mixture of DAO, deasphalting solvent and adsorbent material. The second phase separation zone can be similar to that used in typical solvent deasphalting described above and generally includes necessary components to operate at suitable temperature and pressure conditions, such as below the critical properties of the deasphalting solvent. The second phase separation zone includes one or more outlets for discharging a recycle deasphalting solvent stream, and one or more outlets for discharging a slurry of DAO and adsorbent material. The recycle deasphalting solvent stream outlet is in fluid communication with inlet(s) to the first phase separation zone.

[150] The slurry outlet, and a source of stripping solvent, are in fluid communication with one or more inlets of the adsorbent stripping zone to separate and clean the adsorbent material. The adsorbent stripping zone can include one or more filtration vessels and includes one or more outlets for discharging stripped adsorbent material and one or more outlets for discharging an asphalt stream. The adsorbent material outlet is in fluid communication with an inlet of the second phase separation zone or associated mixing zone to recycle adsorbent material. A portion of the adsorbent material can also be discharged in a continuous, periodic or as-needed manner, for instance, as spent adsorbent material. The adsorbent stripping zone also includes one or more outlets for discharging a solvent-DAO stream that is in fluid communication with an inlet of a solvent-DAO separation zone, such as a flash vessel or fractionator, to separate stripping solvent. The solvent-DAO separation zone includes one or more outlets for discharging a recycle stripping solvent stream, one or more outlets for discharging a DAO stream, and one or more outlets for discharging an asphalt stream. The recycle stripping solvent stream outlet is in fluid communication with inlet(s) of the adsorbent stripping zone. In certain embodiments, the asphalt outlets and/or the adsorbent material outlet (via the spent adsorbent) are in fluid communication with a gasification zone or an asphalt pool.

[151] The deasphalting solvent stream is derived from one or more solvent sources comprising an integrated process solvent stream such as light naphtha from the hydrocracker products or the coker light products, a recycle deasphalting solvent stream from the second phase separation zone, and in certain embodiments make-up deasphalting solvent. Make-up deasphalting solvent can be a solvent from another source that is used in typical solvent deasphalting processes as described herein. The stripping solvent stream is derived from one or more solvent sources comprising an integrated process solvent stream such as light naphtha from the hydrocracker products or the coker light products, a recycle stripping solvent stream from the solvent-asphalt separation zone, and in certain embodiments make-up stripping solvent.

[152] In operation of the enhanced solvent deasphalting zone in which adsorbent material is included in the second phase separation zone, the additional feedstock and the deasphalting solvent stream are charged to first phase separation zone. The first phase separation zone operates under temperature and pressure conditions effective to facilitate separation of the feed mixture into an upper layer comprising light and less polar fractions that are removed as the light phase stream, and the bottoms phase stream containing asphaltenes. Conditions in the first separation vessel are

maintained below the critical temperature and pressure of the deasphalting solvent, as described above in the embodiment using conventional solvent deasphalting. The light phase stream is mixed with an effective quantity of solid adsorbent material, including fresh and recycled adsorbent material, for instance using an in-line mixing apparatus and/or a separate mixing zone, to produce a slurry of DAO, deasphalting solvent, and solid adsorbent material. The slurry is passed to the second phase separation zone and is maintained at an effective temperature and pressure to separate solvent from the DAO, such as between the boiling and critical temperature of the deasphalting solvent, and under a pressure of between 1-3 bars. In addition, the mixture is maintained in the second phase separation zone for a time sufficient to adsorb on the adsorbent material any remaining asphaltenes. The deasphalting solvent is separated from the DAO and adsorbent material, and the deasphalting solvent is recovered and recycled to the first phase separation zone. The slurry of DAO and adsorbent from the second phase separation zone is mixed with the stripping solvent stream in the adsorbent stripping zone to separate and clean the adsorbent material. In certain embodiments, the adsorbent slurry and DAO is washed with two or more aliquots of the stripping solvent in the adsorbent stripping zone in order to dissolve and remove the adsorbed compounds. The clean solid adsorbent is recovered, and all or a portion is recycled to the second phase separation zone. A portion of the adsorbent material can also be discharged in a continuous, periodic or as-needed manner, for instance, as spent adsorbent material. A stripping solvent-DAO mixture is withdrawn from the adsorbent stripping zone, and an asphalt stream is also discharged, which contains asphaltenes and process reject materials that were desorbed from the adsorbent. The stripping solvent-DAO mixture is sent to solvent-DAO separation zone, including an inlet for receiving the stripping solvent-DAO mixture, and outlets for discharging an asphalt stream, a clean solvent stream which is recycled to adsorbent stripping zone, and a DAO stream.

[153] In certain embodiments a residue treatment zone for treatment of the additional feedstock includes an oxidation treatment step. The additional feedstock is contacted with an oxidant to produce an intermediate charge containing oxidized organosulfur compounds, and passing that intermediate charge to any of the herein described deasphalting or enhanced processes. In this manner, the oxidized portion of the additional feedstock has a polarity that results in shifting to the asphalt phase due to its insoluble nature in the deasphalting solvent. An example of a process and system that can be integrated in this manner is disclosed in commonly owned US Patent

Number 10,125,319, which is incorporated by reference herein in its entirety. Furthermore, integration with a coking unit to enable production of higher grades of coke is disclosed in commonly owned US Patent Number 9,896,629, which is incorporated by reference herein in its entirety. For example, an additional feedstock is introduced an oxidizer column vessel, typically after passage through one or more heat exchangers, and optionally in the presence of a homogeneous catalyst. Gaseous oxidant is typically compressed and routed to distributors in the oxidizer column. The oxidized additional feedstock is passed to any of the herein described deasphalting processes including with or without adsorbent material. The gaseous oxidant can be air, oxygen, nitrous oxide or ozone. The oxygen to oil ratio is in the range of about 1-50, 1-20, 3-50 or 30:20 V: V %, or equivalent ratio for other gaseous oxidants. The oxidizing unit operates at a temperature range of about 100-300, 150-300, 100-200 or 150-200°C at the inlet, and about 250-300°C in the oxidation zone, and at a pressure level ranging from about ambient to 60 bars, or ambient to 30 bars. Catalyst that optionally can be added to the oxidation step can be, for example homogeneous transition metal catalysts, active metal components of which are Mo(VI), W(VI), V(V), Ti(IV), possessing high Lewis acidity with weak oxidation potential.

[154] In certain embodiments a residue treatment zone for treatment of the additional feedstock comprises comprise adsorptive treatment. The additional feedstock is treated by contacting with an effective type(s) and quantity of adsorbent material, and under effective conditions, to remove asphaltenes and other contaminants, accompanied by atmospheric and vacuum separation. The resulting mixture is then subjected to atmospheric separation to recover an atmospheric light fraction and an atmospheric heavy fraction, with the adsorbent material passing with the heavy fraction. At this stage, asphaltenes from the feed are adsorbed on and/or within the pores of the adsorbent material. The atmospheric heavy fraction is further separated in a vacuum separation zone to recover vacuum light fraction and a vacuum heavy fraction, with the adsorbent material passing with the heavy fraction. The adsorbent material is regenerated using one or more internal solvent sources as described herein, and recycled for contacting with the feed. An example of a process and system that can be integrated in this manner is disclosed in commonly owned US Patent Numbers 7,799,211 and 8,986,622, which are incorporated by reference herein in their entireties.

[155] For example, an adsorptive treatment and separation zone includes a mixing zone, an atmospheric separation zone, a vacuum separation zone, a filtration/regeneration zone, and a

stripping solvent separation zone. The mixing zone includes one or more inlets in fluid communication with the additional feedstock, and a source of solid adsorbent material. The mixing zone can be operated as an ebullated bed, fixed-bed, tubular or continuous stirred-tank reactor. In certain embodiments, the mixing zone operates as a mixing vessel, equipped with suitable mixing apparatus such as rotary stirring blades or paddles, which provide a gentle, but thorough mixing of the contents. The mixing zone includes one or more outlets for discharging a mixture of the additional feedstock and adsorbent material. In certain embodiments, not shown, mixing can occur in one or more in-line apparatus so that the slurry is formed and send to the atmospheric flash separation zone. The atmospheric separation zone includes one or more inlets in fluid communication with the outlet discharging the mixture/slurry of the feed and adsorbent material. The atmospheric separation zone includes suitable flash or fractionation vessels operating generally at atmospheric conditions with one or more outlets for discharging an atmospheric light fraction, and one or more outlets for discharging an atmospheric heavy fraction which contains the adsorbent material. The vacuum separation zone includes one or more inlets in fluid communication with the outlet discharging the atmospheric heavy fraction containing the adsorbent material. The vacuum separation zone includes suitable flash or fractionation vessels operating generally at vacuum conditions with one or more outlets for discharging a vacuum light fraction, and one or more outlets for discharging a vacuum heavy fraction which contains the adsorbent material. The outlets discharging the atmospheric light fraction and the vacuum light fraction are in fluid communication with the coking zone described herein as the treated additional feedstock.

[156] The filtration/regeneration zone includes one or more inlets in fluid communication with the outlet discharging the vacuum heavy fraction, and one or more inlets in fluid communication with a source of stripping solvent. The filtration/regeneration zone can include one or more filtration vessels for discharging regenerated adsorbent material that is in fluid communication with the mixing zone. A portion of the adsorbent material can also be discharged in a continuous, periodic or as-needed manner, for instance, as spent adsorbent material. In certain embodiments, the spent adsorbent material outlet is in fluid communication with a gasification zone or an asphalt pool. In certain embodiments, parallel vessels are used so that the system is operated in swing mode. The filtration/regeneration zone also includes one or more outlets outlet for discharging a stream containing vacuum residue, and one or more outlets for discharging a stream containing a

mixture of asphaltenes and other process reject materials from the adsorbent material. In certain embodiments the outlet discharging vacuum residue is in fluid communication with the coking zone described herein as part of the additional feedstock, or a separate unit such as a gasification zone.

[157] A stripping solvent separation zone includes one or more inlets in fluid communication with the outlet discharging a stream containing a mixture of stripping solvent, asphaltenes and other process reject materials. The stripping solvent separation zone contains one or more flash vessels or fractionation units operable to separate stripping solvent from the mixture, and includes one or more outlets for discharging a stripping solvent stream, which is in fluid communication with one or more inlets of the filtration/regeneration zone, and one or more outlets for discharging asphaltenes and other process reject materials. In certain embodiments the outlet discharging asphaltenes and other process reject materials is in fluid communication with a gasification zone, or an asphalt pool. In general, the stripping solvent stream is derived from one or more solvent sources comprising an integrated process solvent stream such as light naphtha from the hydrocracker products or the coker light products, a recycle stripping solvent stream, and in certain embodiments a make-up stripping solvent stream.

[158] In operation of the adsorptive treatment and separation zone, the additional feedstock and solid adsorbent material are fed to the mixing zone and mixed to form a slurry. The rate of agitation for a given vessel and mixture of adsorbent, solvent and feedstock is selected so that there is minimal, if any, attrition of the adsorbent granules or particles. The solid adsorbent/crude oil slurry mixture is transferred to the atmospheric separator to separate and recover the atmospheric light fraction. The atmospheric heavy fraction from the atmospheric separator is sent to the vacuum separator. The vacuum light fraction stream is withdrawn from the vacuum separator and the bottoms stream containing vacuum flash residue and solid adsorbent are sent to the adsorbent regeneration zone. The atmospheric light fraction and the vacuum light fraction stream are passed to the coking zone as treated additional feedstock. Vacuum residue is withdrawn from the adsorbent regeneration zone and the bottoms are removed and separated so that the reusable regenerated adsorbents are recycled back and introduced with fresh adsorbent material and the feedstock into mixing zone. A spent portion of the adsorbent material is discharged in a continuous, periodic or as-needed manner. In certain embodiments, the adsorbent regeneration zone is operated in swing mode so that production of the regenerated absorbent is continuous;

when adsorbent material one regeneration column is spent and no longer effective for adsorption, the flow is directed to the other column. The adsorbed compounds are desorbed in the process herein using solvent treatment, for instance, at a pressure in the range of about 1-30 bars temperature range of from about 20-250°C or 20-205°C. The adsorbed compounds are desorbed with a stripping solvent to remove at least some of the process reject materials so that at least a portion of the adsorbent material can be recycled. The stream containing stripping solvent and rejected components from the regeneration unit is sent to a separation zone, recovered stripping solvent is recycled back to the adsorbent regeneration zone, and rejected components are discharged.

[159] In certain embodiments a residue treatment zone for treatment of the additional feedstock comprises comprise adsorptive treatment. The additional feedstock is treated by contacting with an effective type(s) and quantity of adsorbent material, and under effective conditions, to remove asphaltenes and other contaminants, with a packed bed or slurry column. The additional feedstock is passed through at least one packed bed column containing adsorbent material, or is mixed with adsorbent material and passed through a slurry column. Asphaltene and other contaminants are adsorbed. The adsorbent material is regenerated with stripping solvent and recycled for contacting with the additional feedstock. An example of a process and system that can be integrated in this manner is disclosed in commonly owned US Patent Numbers 7,763,163 and 7,867,381, which are incorporated by reference herein in their entireties.

[160] For example, an adsorptive treatment zone includes an adsorbent contacting zone and a solvent-asphalt separation zone. The adsorbent contacting zone contains one or more vessels which contain an effective of adsorbent material, and can be for example one or more packed bed columns. The adsorbent contacting zone generally includes one or more inlets in fluid communication with a source of the additional feedstock, and one or more outlets for discharging an adsorbent treated stream, during an adsorption mode of operation. In addition, the adsorbent contacting zone comprises one or more inlets in fluid communication with a source of a stripping solvent and one or more outlets for discharging a stream of stripping solvent and rejected components during a desorption mode of operation. The outlet discharging the adsorbent treated stream is in fluid communication with the coking zone described herein as the treated additional feedstock. The solvent-asphalt separation zone includes one or more inlets in fluid communication with the stream of stripping solvent and rejected components, and contains one or more flash

vessels or fractionation units operable to separate solvent and asphaltic materials, and can include, for instance, necessary heat exchangers to increase the temperature before a separation vessel. The solvent-asphalt separation zone also includes one or more outlets for discharging a bottoms stream containing rejected materials, and one or more outlets for discharging a recycle stripping solvent stream that is in fluid communication with the adsorbent contacting zone during desorbing operations. In certain embodiments, the bottoms stream outlet is in fluid communication with a gasification zone or an asphalt pool. In general, the stripping solvent stream is derived from one or more solvent sources comprising an integrated process solvent stream such as light naphtha from the hydrocracker products or the coker light products, a recycle stripping solvent stream, and in certain embodiments a make-up stripping solvent stream.

[161] The contacting zone operates in an adsorption mode and a desorption mode. In the adsorption mode, the additional feedstock is passed to the contacting zone and flows under the effect of gravity or by pressure over the adsorbent material to absorb asphaltenes and other contaminants, and under effective conditions to adsorb at least a portion of asphaltenes and other contaminants in the feed. For instance, effective adsorption conditions include a pressure in the range of about 1-30 bars and a temperature in the range of about 20-250°C or 20-205°C. The cleaned feedstock is removed from the contacting zone and passed as treated additional feedstock to the coking zone described herein. In a desorption mode, adsorbed asphaltenes and other contaminants are eluted with stripping solvent under effective conditions to remove at least a portion thereof. For instance, effective desorption conditions include a pressure in the range of about 1-30 bars and a temperature in the range of about 20-250°C or 20-205°C. The stream of stripping solvent and rejected materials is passed to the solvent-asphalt separation zone, and the mixture is separated, for instance by flash separation or fractionation, into the relatively light recycle stripping solvent stream and the relatively heavy bottoms stream which contains the asphaltenes and other contaminants that were stripped from the adsorbent material. In certain embodiments, parallel vessels are used in the adsorbent contacting zone and the system is operated in swing mode so that production of the cleaned feedstock can be continuous. When the adsorbent material in a first vessel becomes spent and no longer effective for adsorption, the flow of the feedstream is directed to another column containing fresh or regenerated adsorbent material. The feedstream enters the top of one of the columns and flows under the effect of gravity or by pressure over the adsorbent material to absorb asphaltenes and other contaminants. The cleaned feedstock

is removed from the bottom of that column. Concurrently, stripping solvent is fed to the other column to carry out desorption operations as described above.

[162] In another embodiment, adsorptive treatment zone includes an adsorbent slurry contacting zone, a filtration/regeneration zone, and a solvent-asphalt separation zone. The adsorbent slurry contacting zone includes one or more inlets in fluid communication with a source of the additional feedstock, and a source of adsorbent material. The adsorbent slurry contacting zone can be operated as an ebullated bed, fixed-bed, tubular or continuous stirred-tank reactor. In certain embodiments, the adsorbent slurry contacting zone operates as a mixing vessel, equipped with suitable mixing apparatus such as rotary stirring blades or paddles, which provide a gentle, but thorough mixing of the contents. The adsorbent slurry contacting zone includes one or more outlets for discharging a mixture of the additional feedstock and adsorbent material. In certain embodiments mixing can occur in one or more in-line apparatus so that the slurry is formed and sent to the filtration/regeneration zone. The filtration/regeneration zone includes one or more inlets in fluid communication with the outlet discharging the mixture of the additional feedstock and adsorbent material, and one or more inlets in fluid communication with a source of stripping solvent. The filtration/regeneration zone includes one or more filtration vessels and includes one or more outlets for discharging a regenerated adsorbent material that is in fluid communication with the adsorbent slurry contacting zone. A portion of the adsorbent material can also be discharged in a continuous, periodic or as-needed manner, for instance, as spent adsorbent material. In certain embodiments, the spent adsorbent material outlet is in fluid communication with a gasification zone or an asphalt pool. The filtration/regeneration zone also includes one or more outlets for discharging a stream containing adsorbent treated additional feedstock, and one or more outlets for discharging a stream containing a mixture of solvent, asphaltenes and other process reject materials from the adsorbent material. The outlet discharging the adsorbent treated additional feedstock is in fluid communication with the coking zone described herein as the treated additional feedstock. The solvent-asphalt separation zone includes one or more inlets in fluid communication with the stream of stripping solvent and rejected components, and contains one or more flash vessels or fractionation units operable to separate solvent and asphaltic materials, and can include, for instance, necessary heat exchangers to increase the temperature before a separation vessel. The solvent-asphalt separation zone also includes one or more outlets for discharging a bottoms stream containing rejected materials, and one or more outlets for discharging a recycle

stripping solvent stream that is in fluid communication with the adsorbent contacting zone during desorbing operations. In certain embodiments, the bottoms stream outlet is in fluid communication with a gasification zone or an asphalt pool. In general, the stripping solvent stream is derived from one or more solvent sources comprising an integrated process solvent stream such as light naphtha from the hydrocracker products or the coker light products, a recycle stripping solvent stream, and in certain embodiments a make-up stripping solvent stream.

[163] In operation of the adsorptive treatment zone including an adsorbent slurry contacting zone, the additional feedstock and adsorbent material are charged to the adsorbent slurry contacting zone under conditions effective for adsorption of asphaltenes and other contaminants, and to provide a slurry. The rate of agitation for a given vessel and mixture of adsorbent and feedstock is selected so that there is minimal, if any, attrition of the adsorbent granules or particles. For example, mixing can be carried out for 30 to 150 minutes, at a pressure in the range of about 1-30 bars and a temperature in the range of about 20-250°C or 20-205°C. In addition, the additional feedstock and adsorbent material can be mixed in an in-line mixer to produce the slurry. The slurry is passed to the filtration/regeneration zone for contact with stripping solvent under effective conditions to strip at least a portion of the adsorbed asphaltenes and other contaminants. The treated feedstock is removed from the contacting zone and passed as treated additional feedstock to the coking zone described herein. The stream containing the mixture of solvent, asphaltenes and other process reject materials is passed to the solvent-asphalt separation zone for recovery of solvent. The mixture is separated, for instance by flash separation or fractionation, into the relatively light recycle solvent stream and the relatively heavy bottoms stream which contains the asphaltenes and other contaminants that were stripped from the adsorbent material. Regenerated adsorbent material is discharged and at least a portion is typically recycled to the adsorbent slurry contacting zone, and spent adsorbent can be removed.

[164] Solid adsorbent materials or mixture of solid adsorbent materials for use in the embodiments herein that are effective to capture asphaltenes and other contaminants include in the additional feedstock are those that are characterized by high surface area, large pore volumes, and a wide pore diameter distribution. Types of adsorbent materials that are effective include molecular sieves, silica gel, activated carbon, activated alumina, silica-alumina gel, zinc oxide, clays such as attapulgus clay, fresh zeolitic catalyst materials, used zeolitic catalyst materials, spent catalysts from other refining operations, and mixtures of two or more of these materials. Effective

adsorbent materials are provided in particulate form of suitable dimension, such as granules, extrudates, tablets, or pellets, and may be formed into various shapes such as spheres, cylinders, trilobes, quadrilobes or natural shapes. In certain embodiments, having average particle diameters (mm) in the range of from about 0.01-4.0, 0.1-4.0, or 0.2-4.0, average pore diameters (nm) in the range of from 1-5,000 or 5-5,000, pore volumes (cc/g) in the range of from about 0.08 - 1.2, 0.3 - 1.2, 0.5 - 1.2, 0.08 - 0.5, 0.1 - 0.5, or 0.3 - 0.5, and a surface area of at least about 100 m²/g. The quantity (weight basis, feed:adsorbent) of the solid adsorbent material used in the embodiments herein is about 0.1:1 - 20:1, 0.1:1 - 10:1, 1:1 - 20:1, or 1:1 - 10:1. In certain embodiment, solid adsorbent material is attapulgus clay and has an average pore size in the range of from 10 angstroms to 750 angstroms. In a further embodiment, solid adsorbent material is activated carbon and has an average pore size in the range of from 5 angstroms to 400 angstroms.

[165] Spent solid adsorbent material can include adsorbed heavy polynuclear aromatic molecules, compounds containing S, compounds containing N, and/or compounds containing metals and/or metals. In certain embodiments, solid adsorbent material is “spent” when more than 50% of its original pore volume has been blocked by deposited carbonaceous material and other contaminants. In further embodiments, solid adsorbent material is considered “spent” when less than 50% of its original pore volume has been blocked by deposited carbonaceous material and other contaminants, for example, 25-49, 25-45, or 25-40%, particularly where the partially spent material is intermingled in an asphalt pool.

[166] Suitable stripping solvents include benzene, toluene, xylenes, tetrahydrofuran, methylene chloride. Solvents can be selected based on their Hildebrand solubility factors or on the basis of two-dimensional solubility factors. The overall Hildebrand solubility parameter is a well-known measure of polarity and has been tabulated for numerous compounds. (See, for example, *Journal of Paint Technology*, Vol. 39, No. 505, February 1967). The solvents can also be described by two-dimensional solubility parameters, that is, the complexing solubility parameter and the field force solubility parameter. (See, for example, I. A. Wiehe, *Ind. & Eng. Res.*, 34(1995), 661). The complexing solubility parameter component which describes the hydrogen bonding and electron donor-acceptor interactions measures the interaction energy that requires a specific orientation between an atom of one molecule and a second atom of a different molecule. The field force solubility parameter which describes van der Waal's and dipole interactions measures the interaction energy of the liquid that is not impacted by changes in the orientation of the molecules.

[167] In certain embodiments the stripping solvent is a non-polar solvent or combination of solvents have an overall Hildebrand solubility parameter of less than about 8.0 or a complexing solubility parameter of less than 0.5 and a field force parameter of less than 7.5. Suitable non-polar solvents include, for example, saturated aliphatic hydrocarbons such as pentanes, hexanes, heptanes, paraffinic naphthas, C5-C11, kerosene C12-C15, diesel C16-C20, normal and branched paraffins, mixtures of any of these solvents. In certain embodiments the solvents are C5-C7 paraffins and C5-C11 paraffinic naphthas.

[168] In certain embodiments the stripping solvent is a polar solvent or combination of solvents having an overall solubility parameter greater than about 8.5 or a complexing solubility parameter of greater than one and a field force parameter value greater than 8. Examples of polar solvents meeting the desired solubility parameter are toluene (8.91), benzene (9.15), xylene (8.85), and tetrahydrofuran (9.52). Suitable polar solvents include toluene and tetrahydrofuran.

Examples

[169] Example 1 – A sample of 100 grams of vacuum residue derived from Arab Heavy crude oil is delayed coked at 499°C to produce coke, light gases, (C₁-C₄) and distillates. The properties of feed streams are summarized in Table 4 and the yields are summarized in Table 5.

[170] Example 2 – A sample of 10 grams of hydrocracker bottoms was mixed with 90 grams of vacuum residue derived from Arab Heavy crude oil. The mixture is delayed coked at 499°C to produce coke, light gases, (C₁-C₄) and distillates. The properties of feed streams are summarized in Table 4 and the yields are summarized in Tables 5 and 6. Table 5 summarizes the results obtained from calculated MCR content of the samples. Table 6 summarizes the results obtained from actual MCR measurement. The reproducibility of MCR analysis is 0.26 W%. It is apparent that the hydrocracking recycle oil impacts the MCR measurement, which is an indicator for coke formation.

[171] Example 3 – A sample of 25 grams of hydrocracker bottoms was mixed with 75 grams of vacuum residue derived from Arab Heavy crude oil. The mixture is delayed coked at 499°C to produce coke, light gases, (C₁-C₄) and distillates. The properties of feed streams are summarized in Table 4 and the yields are summarized in Tables 5 and 6. Table 5 summarizes the results obtained from calculated MCR content of the samples. Table 6 summarizes the results obtained from actual MCR measurement. The reproducibility of MCR analysis is 0.26 W%. It is apparent

that the hydrocracking recycle oil impacts the MCR measurement, which is an indicator for coke formation.

[172] Example 4 – 50 grams of hydrocracker bottoms was mixed with 50 grams of vacuum residue derived from Arab Heavy crude oil. The mixture is delayed coked at 499°C to produce coke, light gases, (C₁-C₄) and distillates. The properties of feed streams are summarized in Table 4 and the yields are summarized in Tables 5 and 6. Table 5 summarizes the results obtained from calculated MCR content of the samples. Table 6 summarizes the results obtained from actual MCR measurement. The reproducibility of MCR analysis is 0.26 W%. It is apparent that the hydrocracking recycle oil impacts the MCR measurement, which is an indicator for coke formation.

[173] Example 5 – 75 grams of hydrocracker bottoms was mixed with 25 grams of vacuum residue derived from Arab Heavy crude oil. The mixture is delayed coked at 499°C to produce coke, light gases, (C₁-C₄) and distillates. The properties of feed streams are summarized in Table 4 and the yields are summarized in Tables 5 and 6. Table 5 summarizes the results obtained from calculated MCR content of the samples. Table 6 summarizes the results obtained from actual MCR measurement. The reproducibility of MCR analysis is 0.26 W%. It is apparent that the hydrocracking recycle oil impacts the MCR measurement, which is an indicator for coke formation.

[174] Referring to FIG. 7, the recycle content is plotted against the coke yield for examples 1-5. As is apparent hydrocracking recycle oil stream minimizes the coke yield. In the presence of hydrocracking recycle oil the coke yield drops down. This is due to the hydrogen donor effect of the recycle oil stream. The hydrocracking recycle oil is rich in hydrogen, 14 W%, and donates hydrogen to stabilize the free radicals formed during the coking process, thereby minimizing the coke formation.

[175] While not shown, the skilled artisan will understand that additional equipment, including exchangers, furnaces, pumps, columns, and compressors to feed the reactors, maintain proper operating conditions, and to separate reaction products, are all part of the systems described.

[176] The method and system of the present invention have been described above and in the attached drawings; however, modifications will be apparent to those of ordinary skill in the art and the scope of protection for the invention is to be defined by the claims that follow.

Table 4

Example	1		2	3	4	5
Feedstock	Vacuum Residue	Recycle Oil	Blend	Blend	Blend	Blend
VR Content, W%	100	0	90	75	50	25
API Gravity, °	4.0	32.1	6.4	10.1	16.7	24.0
SG	1.0440	0.8651	1.0261	0.9993	0.9546	0.9098
Carbon Content, W%	83.61	86.00	83.85	84.21	84.81	85.40
Hydrogen, W%	10.15	14.00	10.54	11.11	12.08	13.04
S, W%	5.34	0.01	4.81	4.01	2.67	1.34
N, W%	0.48	1.00	0.54	0.61	0.74	0.87
Oxygen, W%	0.00		0.00	0.00	0.00	0.00
CCR (calc), W%	23.05	0.08	20.75	17.31	11.57	5.82
CCR (measured), W%	23.05	0.08	16.96	15.96	10.19	5.54
C5-Asphaltenes, W%	0.05	0.00	0.05	0.04	0.03	0.01
Ni, ppmw	59	0	53	44	29	15
V, ppmw	176	0	158	132	88	44

Table 5

Example	1	2	3	4	5
Recycle Oil	0	10	25	50	75
Vacuum Residue	100	90	75	50	25
Coke	36.9	33.2	27.7	18.5	9.3
Gas	11.1	10.8	10.3	9.5	8.6
Naphtha	19.2	18.4	17.2	15.3	13.3
Gas Oil	19.2	22.5	27.3	33.9	37.5
VGO	13.6	15.1	17.5	22.9	31.3
Total	100.0	100.0	100.0	100.0	100.0

Table 6

Example	1	2	3	4	5
Recycle Oil	0	10	25	50	75
Vacuum Residue	100	90	75	50	25
Coke	36.9	27.1	25.5	16.3	8.9
Gas	11.1	10.2	10.1	9.3	8.6
Naphtha	19.2	17.1	16.8	14.8	13.2
Gas Oil	19.2	27.8	29.0	35.1	37.6
VGO	13.6	17.7	18.6	24.6	31.8
Total	100.0	100.0	100.0	100.0	100.0

Claims

1. A process for separation of heavy poly nuclear aromatic (HPNA) compounds and/or HPNA precursor compounds from a hydrocracker bottoms fraction prior to recycling within a hydrocracking operation, the process comprising:

subjecting the hydrocracker bottoms fraction to thermal cracking in a coking zone to produce thermally cracked hydrocarbon products and coke, wherein the coke contains HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms fraction; and

recycling all or a portion of the thermally cracked hydrocarbon products within the hydrocracking operation.

2. A hydrocracking process comprising:

subjecting a hydrocarbon stream to one or more hydrocracking stages to produce a hydrocracked effluent;

fractionating the hydrocracked effluent to recover one or more hydrocracked product fractions and a hydrocracker bottoms fraction containing heavy poly-nuclear aromatic (HPNA) compounds and/or HPNA precursor compounds;

subjecting the hydrocracker bottoms fraction to thermal cracking in a coking zone to produce thermally cracked hydrocarbon products and coke, wherein the coke contains HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms fraction; and

recycling all or a portion of the thermally cracked hydrocarbon products to at least one of the one or more hydrocracking stages.

3. A two stage hydrocracking process comprising:
 - subjecting the hydrocarbon stream to a first hydrocracking stage to produce a first hydrocracked effluent;
 - fractionating the first hydrocracked effluent to recover one or more hydrocracked product fractions and a hydrocracker bottoms fraction containing heavy poly-nuclear aromatic (HPNA) compounds and/or HPNA precursor compounds;
 - subjecting the hydrocracker bottoms fraction to thermal cracking in a coking zone to produce thermally cracked hydrocarbon products and coke, wherein the coke contains HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms fraction; and
 - passing all or a portion of the thermally cracked hydrocarbon products to at least one of the one or more hydrocracking stages.
4. The process as in claim 3, wherein the second hydrocracked effluent is fractionated with the first hydrocracked effluent.
5. The process as in any of claims 1-4, wherein the coking zone produces a coker liquid and gas stream that is fractioned into one or more streams forming recycled thermally cracked hydrocarbon products.
6. The process as in claim 5, wherein the recycled thermally cracked hydrocarbon products comprise coker gas oil.
7. The process as in claim 5, wherein the recycled thermally cracked hydrocarbon products comprise coker gas oil and coker middle distillates.
8. The process as in claim 5, wherein the recycled thermally cracked hydrocarbon products comprise coker gas oil, coker middle distillates and coker naphtha.
9. The process as in any of claims 1-8, wherein the coking zone is a delayed coker.
10. The process as in claim 9, wherein the delayed coker operating conditions include a temperature (°C) in a coking drums of the delayed coker of about 425-650, 425-510, 425-505, 425-500, 450-650, 450-510, 450-505, 450-500, 485-650, 485-510, 485-505, 485-500, 470-650, 470-510, 470-505 or 470-500; a pressure (bars) in the coking drum of about 1-20, 1-10 or 1-3, and a steam introduction rate of about 0.1-3, 0.5-3 or 1-3 wt% relative to the heated residue.
11. The process as in any of claims 1-8, wherein the coking zone is a fluid coker.
12. The process as in claim 11, wherein the fluid coker operating conditions include a temperature (°C) in a coking drums of the delayed coker of about 450-760, 450-650, 450-570, 470-

760, 470-650, 470-570, 510-760, 510-650 or 510-570; a pressure (bars) in the coking drum of about 1-20, 1-10 or 1-3; and a steam introduction rate of about 0.1-3, 0.5-3 or 1-3 wt% relative to the heated residue.

13. The process as in any of claims 1-12, wherein adsorbent material or catalytic material is added to the coking zone.

14. The process as in claim 13, wherein catalytic material is added, and wherein catalytic material is a heterogeneous catalyst selected from the group consisting of silica, alumina, silica-alumina, titania-silica, molecular sieves, silica gel, activated carbon, activated alumina, silica-alumina gel, zinc oxide, clays, fresh catalyst materials, used catalyst materials, regenerated catalyst materials and combinations thereof.

15. The process as in claim 14, wherein the heterogeneous catalyst includes one or more active metal components of metals or metal compounds selected from the Periodic Table of the Elements IUPAC Groups 4, 5, 6, 7, 8, 9 and 10.

16. The process as in claim 15, wherein the active metal component is a metal or metal compound selected from the group consisting of Mo, V, W, Cr, Fe and combinations thereof.

17. The process as in claim 16 wherein the active metal component is a metal or metal compound selected from the group consisting of vanadium pentoxide, molybdenum alicyclic and aliphatic carboxylic acids, molybdenum naphthenate, nickel 2-ethylhexanoate, iron pentacarbonyl, molybdenum 2-ethyl hexanoate, molybdenum di-thiocarboxylate, nickel naphthenate, iron naphthenate and combinations thereof.

18. The process as in claim 13, wherein catalytic material is added, and wherein catalytic material is a homogeneous catalyst that is oil-soluble and contains one or more active metal components of metals or metal compounds selected from the Periodic Table of the Elements IUPAC Groups 4, 5, 6, 7, 8, 9 and 10.

19. The process as in 18 wherein the homogeneous catalyst is, or contains as an active metal component, a transition metal-based compound derived from an organic acid salt or an organo-metal compound containing Mo, V, W, Cr, Fe and combinations thereof.

20. The process as in 18 wherein the homogeneous catalyst is, or contains as an active metal compound, a compounds selected from the group consisting of vanadium pentoxide, molybdenum alicyclic and aliphatic carboxylic acids, molybdenum naphthenate, nickel 2-ethylhexanoate, iron

pentacarbonyl, molybdenum 2-ethyl hexanoate, molybdenum di-thiocarboxylate, nickel naphthenate, iron naphthenate and combinations thereof.

21. The process as in claim 13, wherein adsorbent material is added, and wherein adsorbent material is selected from the group consisting of silica, alumina, silica-alumina, titania-silica, molecular sieves, silica gel, activated carbon, activated alumina, silica-alumina gel, zinc oxide, clays, fresh catalyst materials, spent catalyst materials, regenerated catalyst materials, and combinations thereof.

22. The process as in any of claims 1-21, further comprising introducing additional feed to the coking zone.

23. The process as in claim 22, wherein the additional feed is selected from the group consisting of atmospheric residue, vacuum residue, deasphalted oil and demetallized oil.

24. The process as in claim 22 or 23, wherein the additional feed comprises 0-99, 10-99, 25-99, 50-99, 0-90, 10-90, 25-90, 50-90, 0-75, 10-75, 25-75 or 50-75 wt% of total feed to the coking zone.

25. The process as in any of claims 22-24, further comprising subjecting the additional feedstock to treatment prior to introducing to the coking zone.

26. The process as in claim 25, wherein the treatment of the additional feedstock comprises residue hydrocracking.

26. The process as in claim 25, wherein the treatment of the additional feedstock comprises solvent deasphalting.

27. The process as in claim 26, wherein solvent deasphalting includes introducing adsorbent material to a vessel within solvent deasphalting.

28. The process as in claim 25, wherein the treatment of the additional feedstock comprises oxidation of the additional feedstock.

29. The process as in claim 25, wherein the treatment of the additional feedstock comprises contacting the additional feedstock with adsorbent material.

30. A system for removal of heavy poly nuclear aromatic (HPNA) compounds and/or HPNA precursor compounds from a hydrocracker bottoms fraction comprising:

a coking reaction and separation zone having one or more inlets in fluid communication with a hydrocracker bottoms outlet of a hydrocracking fractionating zone, and one or more outlets for discharging thermally cracked hydrocarbon products in fluid communication with a hydrocracking operation as a bottoms recycle stream, and one or more outlets for coke containing HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms fraction.

31. A hydrocracking system comprising:

a hydrocracking reaction zone having one or more inlets in fluid communication with a source of an initial feedstock and a recycle stream, and one or more outlets discharging an effluent stream;

a fractionating zone having one or more inlets in fluid communication with the outlet(s) for discharging the effluent stream, one or more outlets discharging a hydrocracked product fractions, and one or more outlets discharging a hydrocracker bottoms fraction containing heavy poly-nuclear aromatic (HPNA) compounds and/or HPNA precursor compounds; and

a coking reaction and separation zone having one or more inlets in fluid communication with a hydrocracker bottoms outlet of the hydrocracking fractionating zone, and one or more outlets for discharging thermally cracked hydrocarbon products in fluid communication with inlet(s) of the hydrocracking reaction zone as a bottoms recycle stream, and one or more outlets for coke containing HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms fraction.

32. A two stage hydrocracking system comprising:

a first hydrocracking reaction zone having one or more inlets in fluid communication with a source of an initial feedstock and a recycle stream, and one or more outlets for discharging a first hydrocracked effluent stream;

a fractionating zone having one or more inlets in fluid communication with the outlet(s) for discharging the first hydrocracked effluent stream, one or more outlets discharging a hydrocracked product fractions, and one or more outlets discharging a hydrocracker bottoms fraction containing heavy poly-nuclear aromatic (HPNA) compounds and/or HPNA precursor compounds;

a coking reaction and separation zone having one or more inlets in fluid communication with a hydrocracker bottoms outlet of the hydrocracking fractionating zone, and one or more outlets for discharging thermally cracked hydrocarbon products, and one or more outlets for coke containing HPNA compounds and/or HPNA precursor compounds from the hydrocracker bottoms fraction;

a second hydrocracking reaction zone having one or more inlets in fluid communication with the outlet(s) for discharging the thermally cracked hydrocarbon products, and one or more outlets discharging a second hydrocracked effluent stream.

33. The system as in claim 32, wherein the outlet(s) for discharging the second hydrocracked effluent is in fluid communication with the fractioning zone.

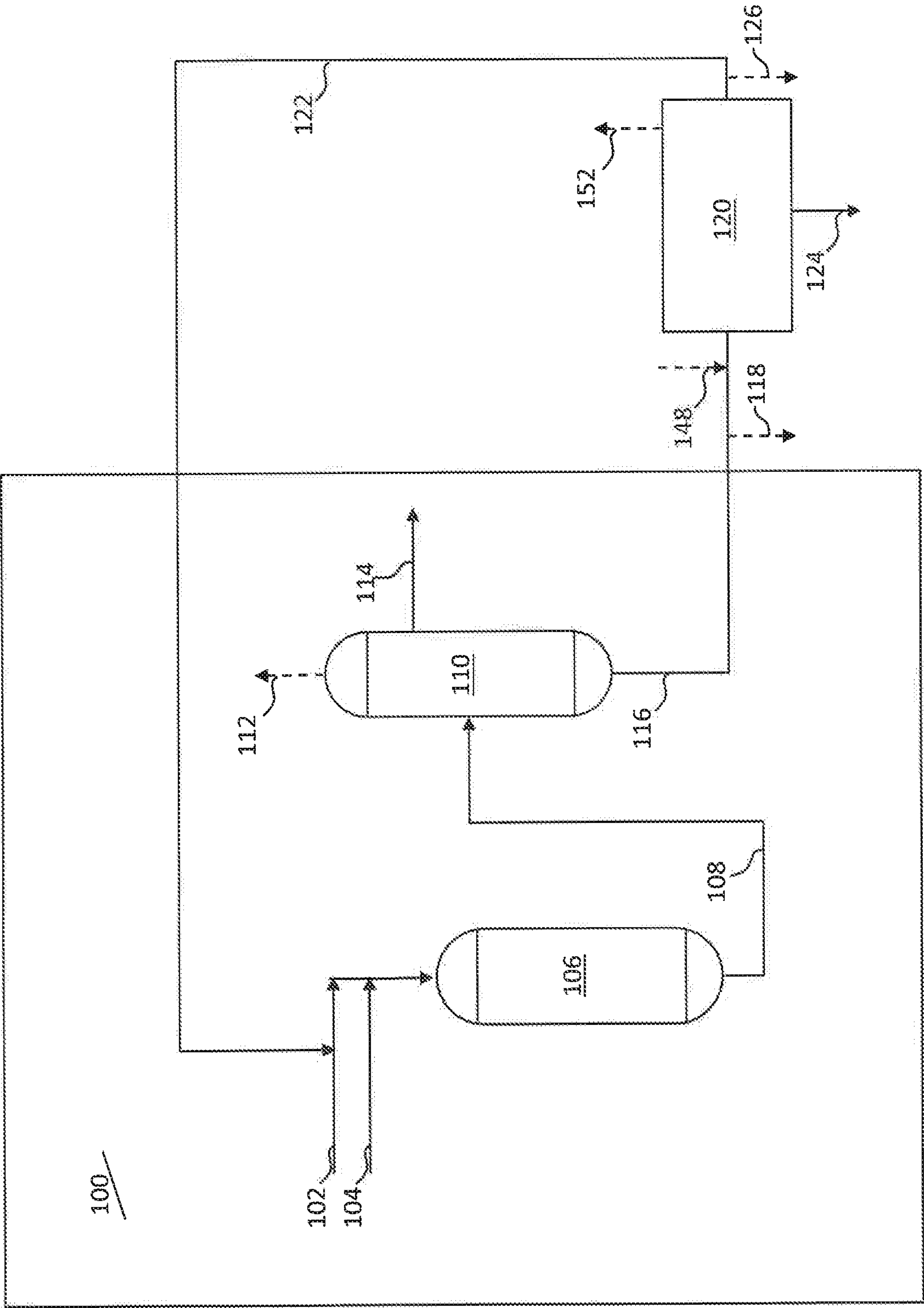


FIG. 1

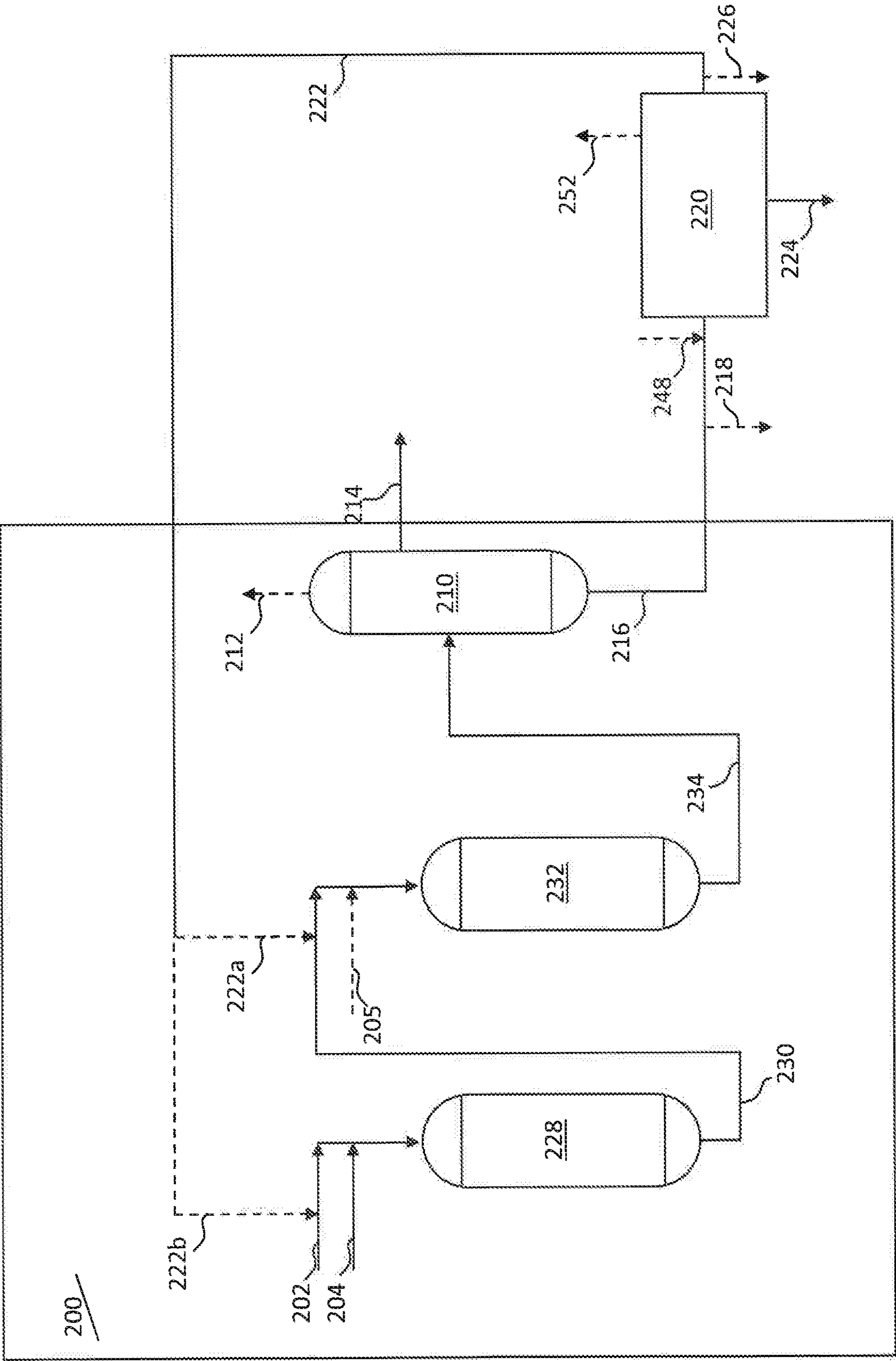
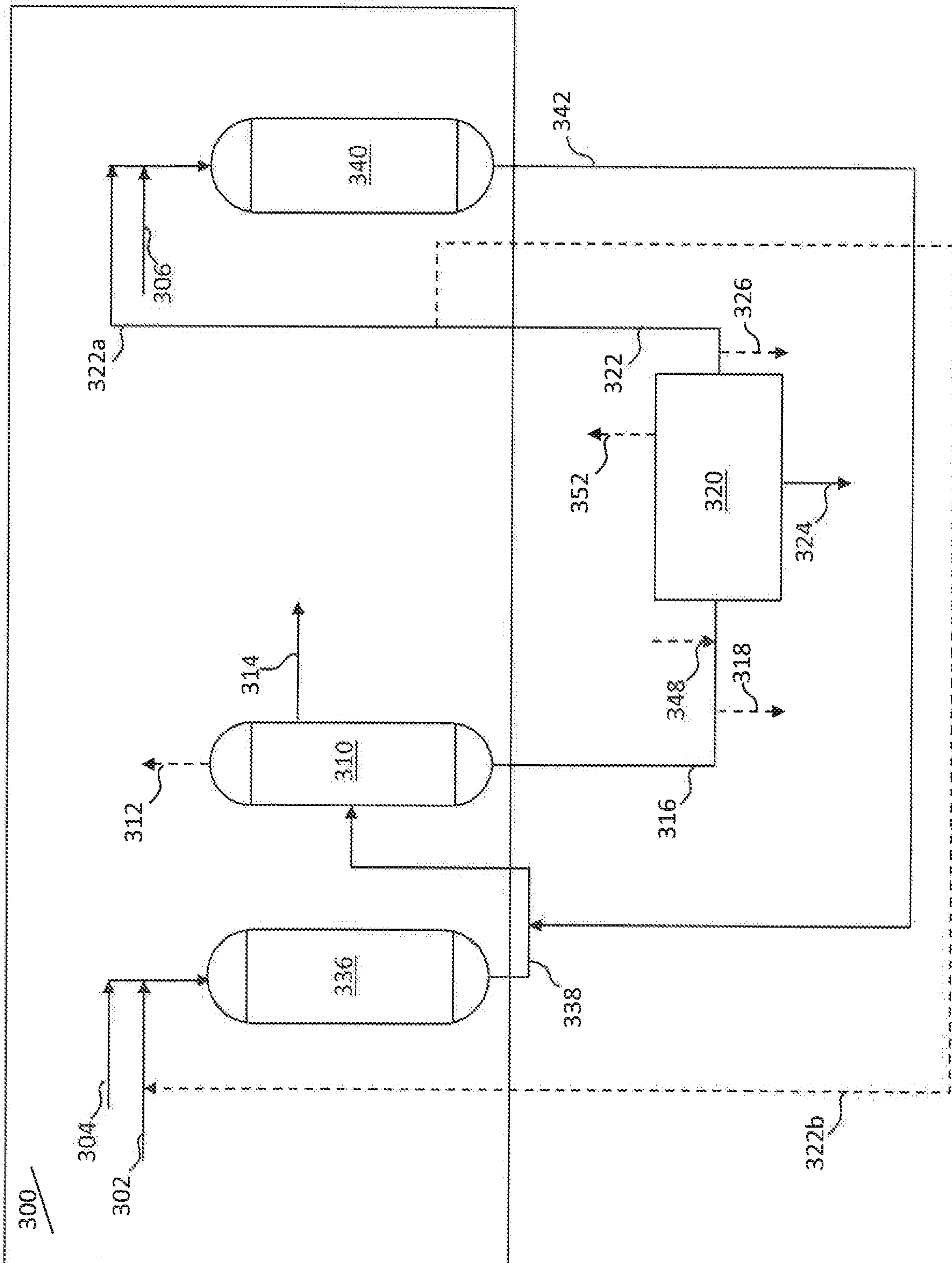


FIG. 2



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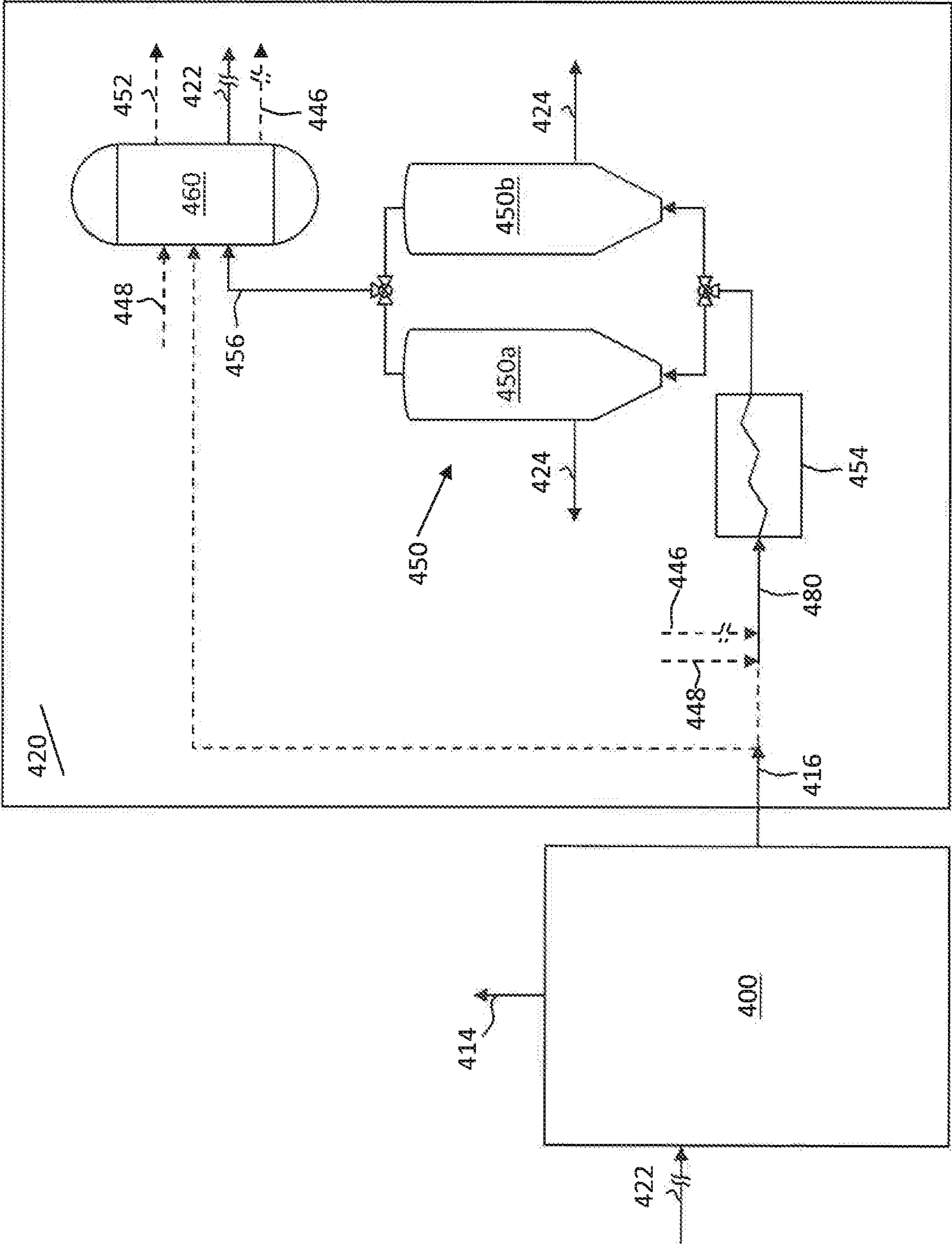


FIG. 4

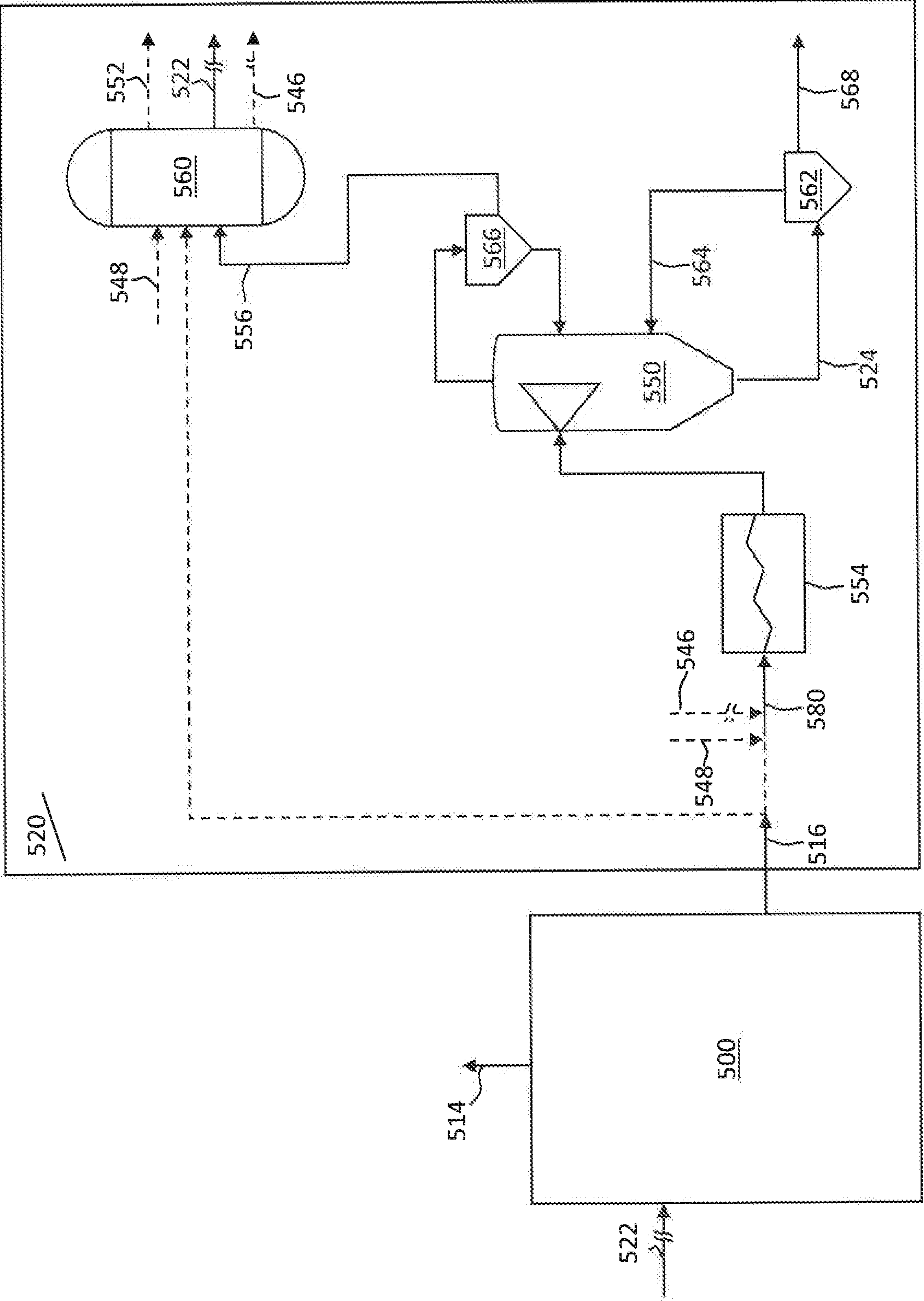


FIG. 5

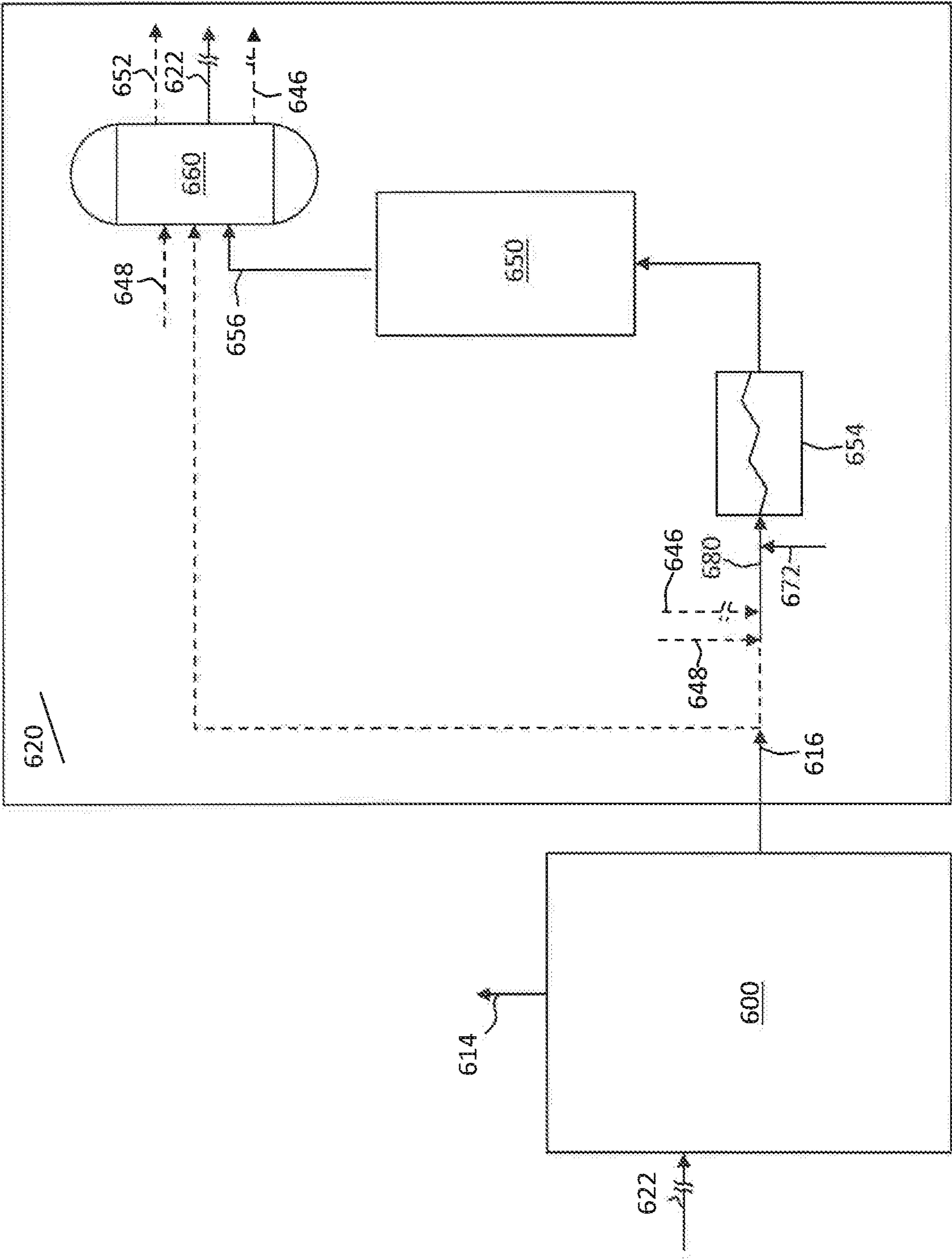
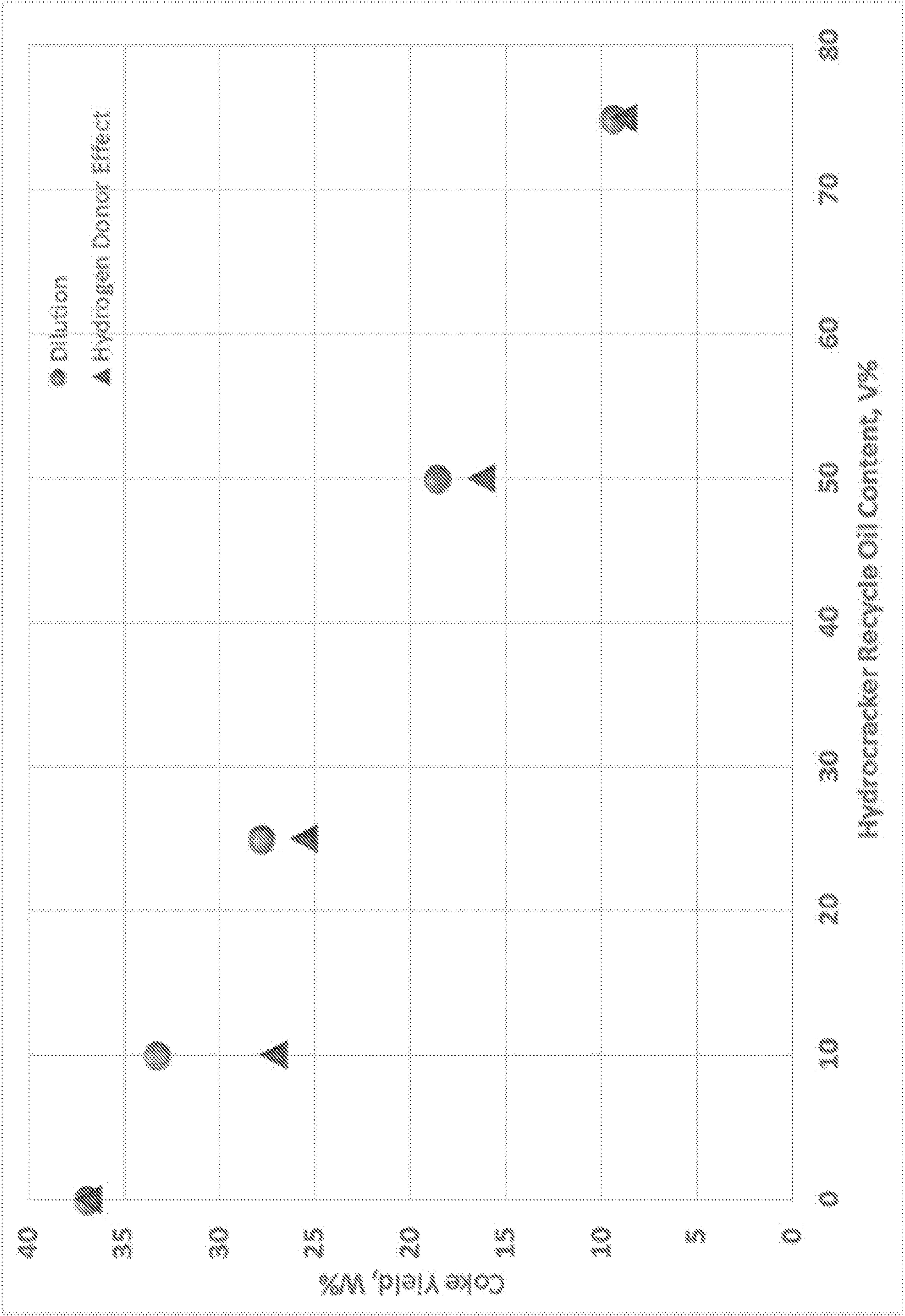


FIG. 6



INTERNATIONAL SEARCH REPORT

International application No

PCT/US2020/065881

A. CLASSIFICATION OF SUBJECT MATTER
 INV. C10G47/00 C10G9/00 C10G69/06 C10B55/00 C10G75/00
 ADD.

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 C10H C10B

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 792 390 A (STAGGS DARRELL W [US] ET AL) 20 December 1988 (1988-12-20) figure 1 column 4, line 50 - column 9, line 63 examples 1-2; tables 1-5 claims 1-27	1-33
A	----- US 2011/079541 A1 (KOSEOGLU OMER REFA [SA]) 7 April 2011 (2011-04-07) figure 2 paragraph [0040] - paragraph [0050] paragraph [0051] - paragraph [0055]; example 1; tables 1-2	1-33
A	----- US 2018/187100 A1 (KOSEOGLU OMER REFA [SA]) 5 July 2018 (2018-07-05) paragraph [0050] - paragraph [0103]; figures 1-6 examples 1-3; tables 1-4 -----	1-33



Further documents are listed in the continuation of Box C.



See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search

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Date of mailing of the international search report

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2020/065881

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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			US 2012189505 A1 26-07-2012
			WO 2011043904 A1 14-04-2011

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			EP 3565876 A1 13-11-2019
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			KR 20190104037 A 05-09-2019
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			WO 2018129022 A1 12-07-2018
