Office de la Propriété Intellectuelle du Canada

Un organisme d'Industrie Canada Canadian Intellectual Property Office

An agency of Industry Canada

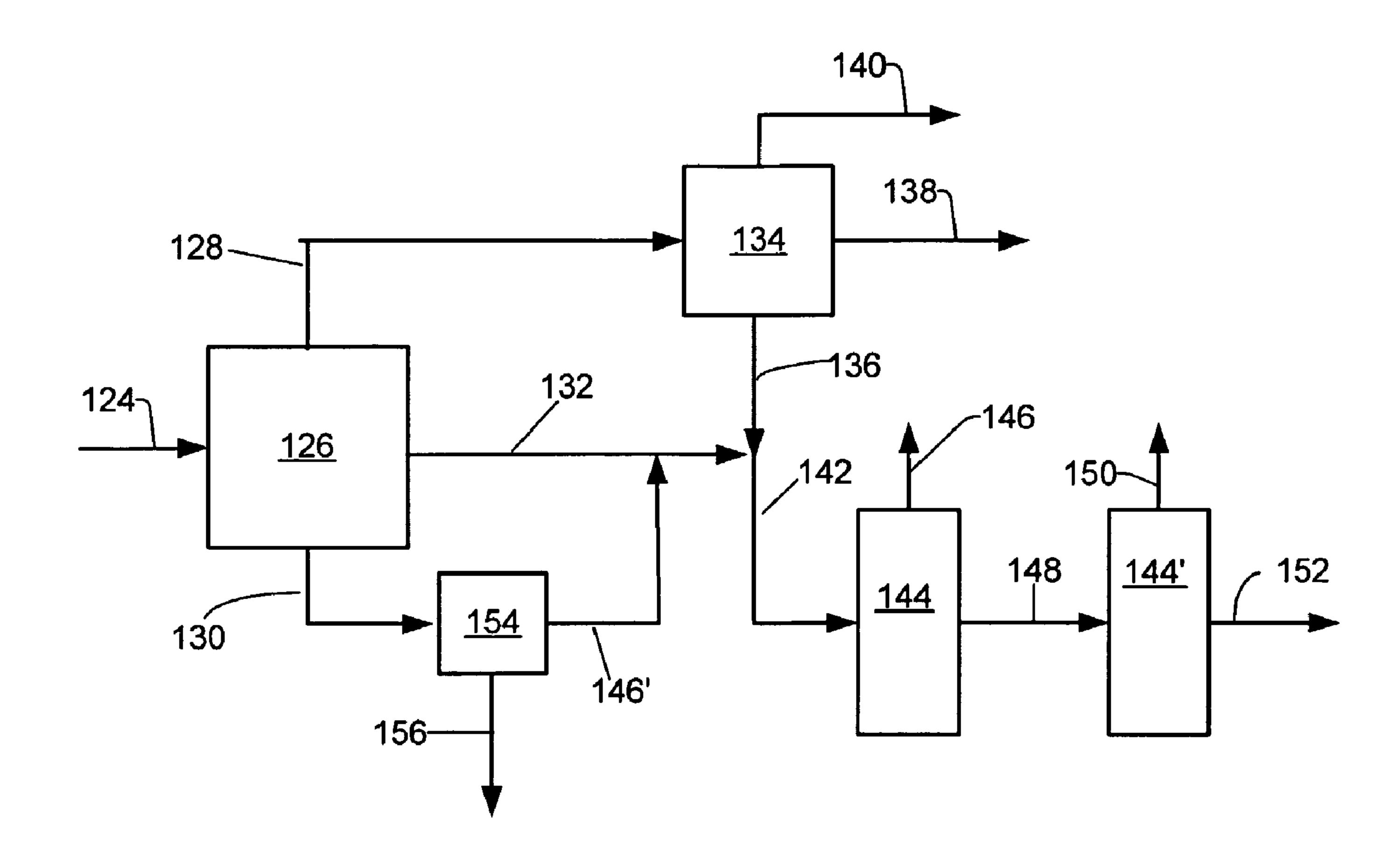
CA 2462957 C 2011/03/01

(11)(21) 2 462 957

(12) BREVET CANADIEN CANADIAN PATENT

(13) **C**

- (86) Date de dépôt PCT/PCT Filing Date: 2002/10/24
- (87) Date publication PCT/PCT Publication Date: 2003/05/01
- (45) Date de délivrance/Issue Date: 2011/03/01
- (85) Entrée phase nationale/National Entry: 2004/04/06
- (86) N° demande PCT/PCT Application No.: US 2002/034198
- (87) N° publication PCT/PCT Publication No.: 2003/036030
- (30) Priorités/Priorities: 2001/10/24 (US60/334,568); 2001/10/24 (US60/337,136); 2002/04/24 (US60/374,970); 2002/04/24 (US60/374,995)
- (51) Cl.Int./Int.Cl. *E21B 43/24* (2006.01), *B09C 1/02* (2006.01), *B09C 1/06* (2006.01), *C10G 45/00* (2006.01), *E21B 17/02* (2006.01), *E21B 43/16* (2006.01), *E21B 43/243* (2006.01), *E21B 47/022* (2006.01), *G01V 3/26* (2006.01)
- (72) Inventeurs/Inventors:
 WELLINGTON, SCOTT LEE, US;
 MADGAVKAR, AJAY MADHAV, US;
 RYAN, ROBERT CHARLES, US
- (73) Propriétaire/Owner: SHELL CANADA LIMITED, CA
- (74) Agent: SMART & BIGGAR
- (54) Titre: PROCEDE THERMIQUE IN SITU D'UNE FORMATION CONTENANT UN HYDROCARBURE ET BONIFICATION DES FLUIDES PRODUITS AVANT LA MISE EN OEUVRE D'UN AUTRE TRAITEMENT
- (54) Title: IN SITU THERMAL PROCESSING OF A HYDROCARBON CONTAINING FORMATION AND UPGRADING OF PRODUCED FLUIDS PRIOR TO FURTHER TREATMENT



(57) Abrégé/Abstract:

A method for hydrotreating a fluid in a heated formation in situ is described. The in situ treatment process may include providing heat from one or more heaters to at least a portion of the formation. The heat may be allowed to transfer from the one or more





CA 2462957 C 2011/03/01

(11)(21) 2 462 957

(13) **C**

(57) Abrégé(suite)/Abstract(continued):

heaters to a part of the formation. A fluid may be provided to the part of the formation. The temperature of the part of the formation and the hydrogen pressure may be controlled in the formation such that the fluid is hydrotreated. The resulting hydrotreated fluid may be produced form the formation. Separation of the produced hydrotreated fluid may be performed. The resulting products such as ammonia may be converted to other products.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau





(43) International Publication Date 1 May 2003 (01.05.2003)

PCT

(10) International Publication Number WO 03/036030 A3

(51) International Patent Classification⁷: E21B 43/24, C10G 45/00, E21B 43/16, 43/243

(21) International Application Number: PCT/US02/34198

(22) International Filing Date: 24 October 2002 (24.10.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/337,136	24 October 2001 (24.10.2001)	US
60/334,568	24 October 2001 (24.10.2001)	US
60/374,995	24 April 2002 (24.04.2002)	US
60/374,970	24 April 2002 (24.04.2002)	US

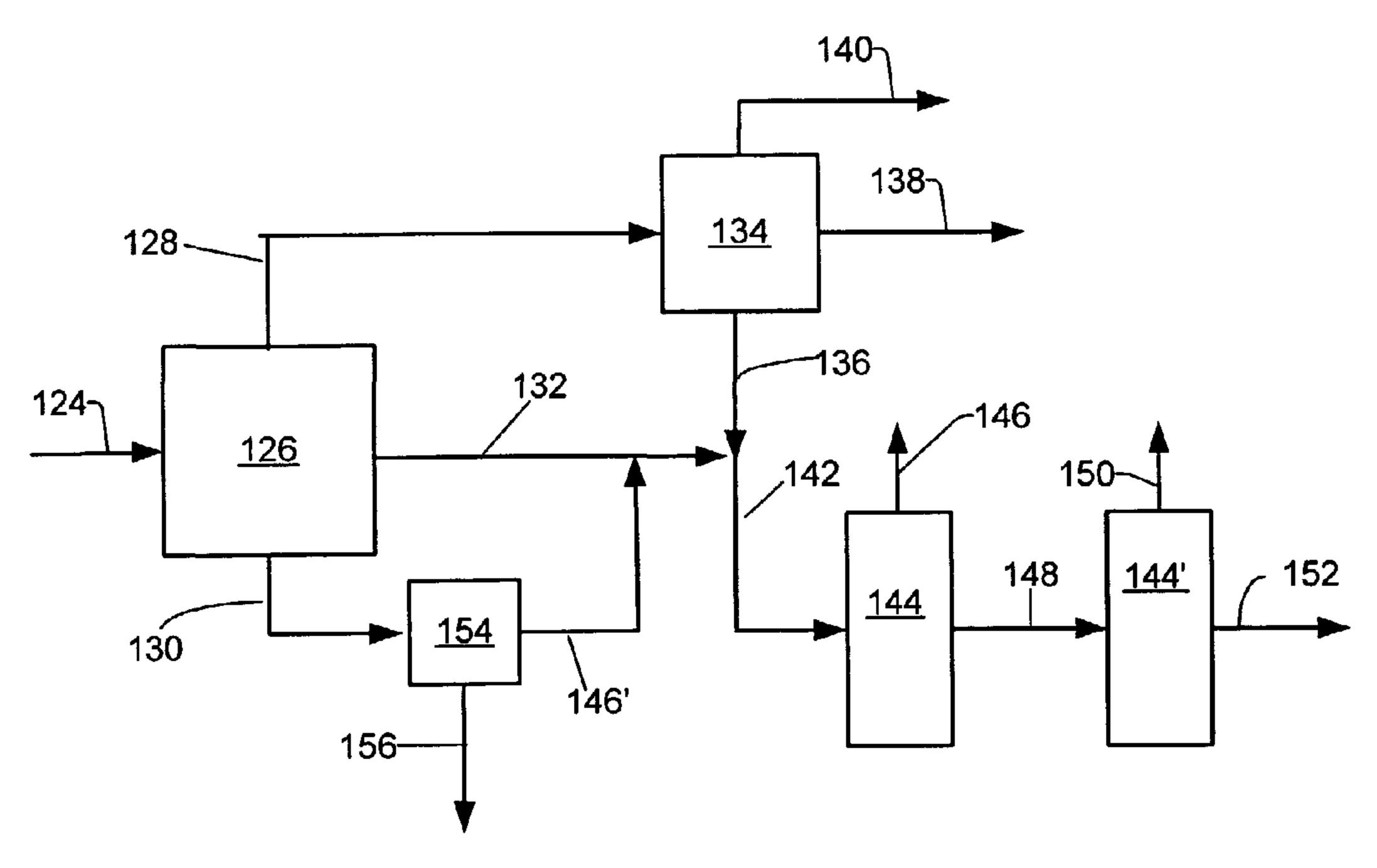
(71) Applicant (for AE, AG, AL, AM, AT, AU, AZ, BA, BB, BE, BG, BR, BY, BZ, CH, CN, CO, CR, CU, CY, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, FR, GB, GD, GE, GH, GM, GR, HR, HU, ID, IE, IL, IN, IS, IT, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MC, MD, MG, MK, MN, MW, MX, MZ, NL, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, SZ, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW only): SHELL OIL COMPANY

[US/US]; Department of Intellectual Property, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

- (71) Applicant (for CA only): SHELL CANADA LIMITED [CA/CA]; 400-4th Avenue, S.W., Calgary, Alberta T2P 2H5 (CA).
- (72) Inventors: WELLINGTON, Scott, Lee; 5109 Aspen Street, Bellaire, TX 77252-2463 (US). MADGAVKAR, Ajay, Madhav; 3102 Bentgrass Drive, Katy, TX 77450 (US). RYAN, Robert, Charles; 214 Cove Creek, Houston, TX 77042 (US).
- (74) Agent: CHRISTENSEN, Del, S.; SHELL OIL COM-PANY, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.

[Continued on next page]

(54) Title: IN SITU THERMAL PROCESSING AND UPGRADING OF PRODUCED HYDROCARBONS



(57) Abstract: A method for hydrotreating a fluid in a heated formation in situ is described. The in situ treatment process may include providing heat from one or more heaters to at least a portion of the formation. The heat may be allowed to transfer from the one or more heaters to a part of the formation. A fluid may be provided to the part of the formation. The temperature of the part of the formation and the hydrogen pressure may be controlled in the formation such that the fluid is hydrotreated. The resulting hydrotreated fluid may be produced form the formation. Separation of the produced hydrotreated fluid may be performed. The resulting products such as ammonia may be converted to other products.

7.036020

3

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(88) Date of publication of the international search report: 13 November 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

— with international search report

IN SITU THERMAL PROCESSING OF A HYDROCARBON CONTAINING FORMATION AND UPGRADING OF PRODUCED FLUIDS PRIOR TO FURTHER TREATMENT

5

10

15

20

2.5

30

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates generally to methods and systems for production of hydrocarbons, hydrogen, and/or other products from various hydrocarbon containing formations. The present invention generally relates to separating out particular products from fluids produced from a hydrocarbon containing formation before further treating the produced fluids.

2. <u>Description of Related Art</u>

Hydrocarbons obtained from subterranean (e.g., sedimentary) formations are often used as energy resources, as feedstocks, and as consumer products. Concerns over depletion of available hydrocarbon resources and declining overall quality of produced hydrocarbons have led to development of processes for more efficient recovery, processing and/or use of available hydrocarbon resources. In situ processes may be used to remove hydrocarbon materials from subterranean formations. Chemical and/or physical properties of hydrocarbon material within a subterranean formation may need to be changed to allow hydrocarbon material to be more easily removed from the subterranean formation. The chemical and physical changes may include in situ reactions that produce removable fluids, composition changes, solubility changes, density changes, phase changes, and/or viscosity changes of the hydrocarbon material within the formation. A fluid may be, but is not limited to, a gas, a liquid, an emulsion, a slurry, and/or a stream of solid particles that has flow characteristics similar to liquid flow.

Hydrocarbons obtained from subterranean (e.g., sedimentary) formations are often used as energy resources, as feedstocks, and as consumer products. Concerns over depletion of available hydrocarbon resources and over declining overall quality of produced hydrocarbons have led to development of processes for more efficient recovery, processing and/or use of available hydrocarbon resources. In situ processes may be used to remove hydrocarbon materials from subterranean formations. Chemical and/or physical properties of hydrocarbon material within a subterranean formation may need to be changed to allow hydrocarbon material to be more easily removed from the subterranean formation. The chemical and physical changes may include in situ reactions that produce removable fluids, composition changes, solubility changes, density changes, phase changes, and/or viscosity changes of the hydrocarbon material within the formation. A fluid may be, but is not limited to, a gas, a liquid, an emulsion, a slurry, and/or a stream of solid particles that has flow characteristics similar to liquid flow.

There has been a significant amount of effort to develop methods and systems to economically produce hydrocarbons, hydrogen, and/or other products from hydrocarbon containing formations. At present, however, there are still many hydrocarbon containing formations that contain hydrocarbons and/or other products that may have low economic value. Thus, there may be a need for methods to upgrade hydrocarbons and/or other products to fluids of higher economic value.

40

35

SUMMARY OF THE INVENTION

In an embodiment, hydrocarbons within a hydrocarbon containing formation (e.g., a formation containing coal, oil shale, heavy hydrocarbons, or a combination thereof) may be converted in situ within the formation to

5

10

15

20

25 ·

yield a mixture of relatively high quality hydrocarbon products, hydrogen, and/or other products. One or more heaters may be used to heat a portion of the hydrocarbon containing formation to temperatures that allow pyrolysis of the hydrocarbons. Hydrocarbons, hydrogen, and other formation fluids may be removed from the formation through one or more production wells. In some embodiments, formation fluids may be removed in a vapor phase. In other embodiments, formation fluids may be removed in liquid and vapor phases or in a liquid phase. Temperature and pressure in at least a portion of the formation may be controlled during pyrolysis to yield improved products from the formation.

In certain embodiments, the fluids may be hydrotreated in situ in a heated formation. In situ treatment may include providing a fluid to a selected section of a formation. The in situ process may include controlling a H₂ partial pressure in the selected section of the formation. The H₂ partial pressure may be controlled by providing hydrogen to the part of the formation. The temperature within the part of the formation may be controlled such that the temperature remains within a range from about 200 °C to about 450 °C. At least some of the fluid may be hydrotreated within the part of the formation. A mixture including hydrotreated fluids may be produced from the formation. The produced mixture may include less than about 1% by weight ammonia. The produced mixture may include less than about 1% by weight hydrogen sulfide. The produced mixture may include less than about 1% oxygenated compounds. The heating may be controlled such that the mixture may be produced as a vapor.

In an embodiment, a method for hydrotreating a compound in a heated formation in situ may include controlling the H₂ partial pressure in a selected section of the formation, such that sufficient H₂ may be present in the selected section of the formation for hydrotreating. The method may further include providing a compound for hydrotreating to at least the selected section of the formation and producing a mixture from the formation that includes at least some of the hydrotreated compound.

In one embodiment, a method of separating ammonia from fluids produced from an in situ hydrocarbon containing formation may include separating at least a portion of the ammonia from the produced fluid. Fluids produced from a formation may, in some embodiments, may be hydrotreated to generate ammonia. In certain embodiments, ammonia may be converted to other products.

63293-3986

5

10

15

In another embodiment, there is provided a method for hydrotreating a fluid in a heated hydrocarbon containing formation in situ, comprising: providing heat from one or more heat sources to a portion of the hydrocarbon containing formation, wherein at least one of the heat sources is in at least one wellbore in the formation; allowing the heat to transfer from the one or more heat sources to a part of the formation wherein the heat provided from at least one of the one or more heat sources is transferred to at least a portion of the formation substantially by conduction; providing a fluid to the part of the formation; controlling a H₂ partial pressure in the part of the formation; hydrotreating at least some of the fluid in the part of the formation; and producing a mixture comprising hydrotreated fluids from the formation.

BRIEF DESCRIPTION OF THE DRAWINGS

Advantages of the present invention may become apparent to those skilled in the art with the benefit of the following detailed description of the preferred embodiments and upon reference to the accompanying drawings in which:

- FIG. 1 depicts an illustration of stages of heating a hydrocarbon containing formation.
- FIG. 2 depicts schematic view of an embodiment of a portion of an in situ conversion system for treating a hydrocarbon containing formation.
 - FIG. 3 depicts an embodiment of heater wells located in a hydrocarbon containing formation.
 - FIG. 4 depicts a schematic of an embodiment of a surface treatment configuration used to produce and separate ammonia.
- FIG. 5 depicts a schematic of an embodiment of a surface treatment configuration that produces ammonia on site.
 - FIG. 6 depicts a schematic of an embodiment of a surface treatment configuration used for the synthesis of urea.

FIG. 7 depicts a schematic of an embodiment of a surface treatment configuration that synthesizes ammonium sulfate.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings and may herein be described in detail. The drawings may not be to scale. It should be understood, however, that the drawings and detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the present invention as defined by the appended claims.

DETAILED DESCRIPTION OF THE INVENTION

10

15

20

25

30

35

40

The following description generally relates to systems and methods for treating a hydrocarbon containing formation (e.g., a formation containing coal (including lignite, sapropelic coal, etc.), oil shale, carbonaceous shale, shungites, kerogen, bitumen, oil, kerogen and oil in a low permeability matrix, heavy hydrocarbons, asphaltites, natural mineral waxes, formations wherein kerogen is blocking production of other hydrocarbons, etc.). Such formations may be treated to yield relatively high quality hydrocarbon products, hydrogen, and other products.

"Hydrocarbons" are generally defined as molecules formed primarily by carbon and hydrogen atoms.

Hydrocarbons may also include other elements, such as, but not limited to, halogens, metallic elements, nitrogen, oxygen, and/or sulfur.

A "formation" includes one or more hydrocarbon containing layers, one or more non-hydrocarbon layers, an overburden, and/or an underburden. An "overburden" and/or an "underburden" includes one or more different types of impermeable materials. For example, overburden and/or underburden may include rock, shale, mudstone, or wet/tight carbonate (i.e., an impermeable carbonate without hydrocarbons). In some embodiments of in situ conversion processes, an overburden and/or an underburden may include a hydrocarbon containing layer or hydrocarbon containing layers that are relatively impermeable and are not subjected to temperatures during in situ conversion processing that results in significant characteristic changes of the hydrocarbon containing layers of the overburden and/or underburden. For example, an underburden may contain shale or mudstone. In some cases, the overburden and/or underburden may be somewhat permeable.

A "heat source" is any system for providing heat to at least a portion of a formation substantially by conductive and/or radiative heat transfer. For example, a heat source may include electric heaters such as an insulated conductor, an elongated member, and/or a conductor disposed within a conduit. A heat source may also include heat sources that generate heat by burning a fuel external to or within a formation, such as surface burners, downhole gas burners, flameless distributed combustors, and natural distributed combustors. In addition, it is envisioned that in some embodiments heat provided to or generated in one or more heat sources may be supplied by other sources of energy. The other sources of energy may directly heat a formation, or the energy may be applied to a transfer media that directly or indirectly heats the formation. It is to be understood that one or more heat sources that are applying heat to a formation may use different sources of energy. For example, for a given formation some heat sources may supply heat from electric resistance heaters, some heat sources may provide heat from combustion, and some heat sources may provide heat from one or more other energy sources (e.g., chemical reactions, solar energy, wind energy, biomass, or other sources of renewable energy). A chemical reaction may include an exothermic reaction (e.g., an oxidation reaction). A heat source may include a heater that provides heat to a zone proximate and/or surrounding a heating location such as a heater well.

A "heater" is any system for generating heat in a well or a near wellbore region. Heaters may be, but are not limited to, electric heaters, burners, combustors that react with material in or produced from a formation (e.g., natural distributed combustors), and/or combinations thereof. A "unit of heat sources" refers to a number of heat sources that form a template that is repeated to create a pattern of heat sources within a formation.

"Condensable hydrocarbons" are hydrocarbons that condense at 25 °C at one atmosphere absolute pressure. Condensable hydrocarbons may include a mixture of hydrocarbons having carbon numbers greater than 4. "Non-condensable hydrocarbons" are hydrocarbons that do not condense at 25 °C and one atmosphere absolute pressure. Non-condensable hydrocarbons may include hydrocarbons having carbon numbers less than 5.

"Upgrade" refers to increasing the quality of hydrocarbons. For example, upgrading heavy hydrocarbons may result in an increase in the API gravity of the heavy hydrocarbons.

10

15

20

25

30

35

40

Hydrocarbons in formations may be treated in various ways to produce many different products. In certain embodiments, such formations may be treated in stages. FIG. 1 illustrates several stages of heating a hydrocarbon containing formation. FIG. 1 also depicts an example of yield (barrels of oil equivalent per ton) (y axis) of formation fluids from a hydrocarbon containing formation versus temperature (°C) (x axis) of the formation.

Desorption of methane and vaporization of water occurs during stage 1 heating. Heating of the formation through stage 1 may be performed as quickly as possible. For example, when a hydrocarbon containing formation is initially heated, hydrocarbons in the formation may desorb adsorbed methane. The desorbed methane may be produced from the formation. If the hydrocarbon containing formation is heated further, water within the hydrocarbon containing formation may be vaporized. Water may occupy, in some hydrocarbon containing formations, between about 10 % to about 50 % of the pore volume in the formation. In other formations, water may occupy larger or smaller portions of the pore volume. Water typically is vaporized in a formation between about 160 °C and about 285 °C for pressures of about 6 bars absolute to 70 bars absolute. In some embodiments, the pressure in a formation may be maintained during an in situ conversion process between about 2 bars absolute and about 70 bars absolute. In some embodiments, the vaporized water may produce wettability changes in the formation and/or increase formation pressure. The wettability changes and/or increased pressure may affect pyrolysis reactions or other reactions in the formation. In certain embodiments, the vaporized water may be produced from the formation. In other embodiments, the vaporized water may be used for steam extraction and/or distillation in the formation or outside the formation. Removing the water from and increasing the pore volume in the formation may increase the storage space for hydrocarbons within the pore volume.

After stage 1 heating, the formation may be heated further, such that a temperature within the formation reaches (at least) an initial pyrolyzation temperature (e.g., a temperature at the lower end of the temperature range shown as stage 2). Hydrocarbons within the formation may be pyrolyzed throughout stage 2. A pyrolysis temperature range may vary depending on types of hydrocarbons within the formation. A pyrolysis temperature range may include temperatures between about 250 °C and about 900 °C. A pyrolysis temperature range for producing desired products may extend through only a portion of the total pyrolysis temperature range. In some embodiments, a pyrolysis temperature range for producing desired products may include temperatures between about 250 °C to about 400 °C. If a temperature of hydrocarbons in a formation is slowly raised through a temperature range from about 250 °C to about 400 °C, production of pyrolysis products may be substantially complete when the temperature approaches 400 °C. Heating the hydrocarbon containing formation with a plurality of heat sources may establish thermal gradients around the heat sources that slowly raise the temperature of hydrocarbons in the formation through a pyrolysis temperature range.

In some in situ conversion embodiments, a temperature of the hydrocarbons to be subjected to pyrolysis may not be slowly increased throughout a temperature range from about 250 °C to about 400 °C. The hydrocarbons in the formation may be heated to a desired temperature (e.g., about 325 °C). Other temperatures may be selected as the desired temperature. Heat from heat sources may allow the desired temperature to be relatively quickly and efficiently established in the formation. Energy input into the formation from the heat sources may be adjusted to maintain the temperature in the formation substantially at the desired temperature. The hydrocarbons may be maintained substantially at the desired temperature until pyrolysis declines such that production of desired formation fluids from the formation becomes uneconomical.

A pattern of heat sources may include many units of heat sources. There may be many heated portions, as well as many selected sections within the pattern of heat sources. In some embodiments, a large spacing may provide for a relatively slow heating rate of hydrocarbon material. The slow heating rate may allow for pyrolysis of hydrocarbon material with minimal coking or no coking within the formation away from areas in the vicinity of the heat sources. Heating from heat sources allows the selected section to reach pyrolysis temperatures so that all hydrocarbons within the selected section may be subject to pyrolysis reactions. In some in situ conversion embodiments, a majority of pyrolysis fluids are produced when the selected section is within a range from about 0 m to about 25 m from a heat source.

10

15

20

25

30

35

40

The spacing between heat sources may vary depending on a number of factors. The factors may include, but are not limited to, the type of a hydrocarbon containing formation, the selected heating rate, and/or the selected average temperature to be obtained within the heated portion. In some well pattern embodiments, the spacing between heat sources may be within a range of about 5 m to about 25 m. In some well pattern embodiments, spacing between heat sources may be within a range of about 8 m to about 15 m.

Heat may be generated by a heater positioned in an open wellbore. Generated heat may radiatively heat a portion of a hydrocarbon containing formation adjacent to the heater. Using an open wellbore completion may reduce casing and packing costs associated with filling the opening with a material to provide conductive heat transfer between the insulated conductor and the formation. In addition, heat transfer by radiation may be more efficient than heat transfer by conduction in a formation, so the heaters may be operated at lower temperatures using radiative heat transfer. Operating at a lower temperature may extend the life of the heat source and/or reduce the cost of material needed to form the heat source.

As shown in FIG. 2 in addition to heat sources 100, one or more production wells 102 will typically be placed within the portion of the hydrocarbon containing formation. Formation fluids may be produced through production wells 102. In some embodiments, production wells 102 may include a heat source. The heat source may heat the portions of the formation at or near the production well and allow for vapor phase removal of formation fluids. The need for high temperature pumping of liquids from the production well may be reduced or eliminated. Avoiding or limiting high temperature pumping of liquids may significantly decrease production costs. Providing heating at or through the production well may: (1) inhibit condensation and/or refluxing of production fluid when such production fluid is moving in the production well proximate the overburden, (2) increase heat input into the formation, and/or (3) increase formation permeability at or proximate the production well. In some in situ conversion process embodiments, an amount of heat supplied to production wells is significantly less than an amount of heat applied to heat sources that heat the formation.

Because permeability and/or porosity increases in the heated formation, produced vapors may flow considerable distances through the formation with relatively little pressure differential. Increases in permeability

may result from a reduction of mass of the heated portion due to vaporization of water, removal of hydrocarbons, and/or creation of fractures. Fluids may flow more easily through the heated portion. In some embodiments, production wells may be provided in upper portions of hydrocarbon layers.

FIG. 3 illustrates an embodiment of hydrocarbon containing layer 104 that may be at a near-horizontal angle with respect to an upper surface of ground 106. An angle of hydrocarbon containing layer 104, however, may vary. For example, hydrocarbon containing layer 104 may dip or be steeply dipping. As shown in FIG. 3, production wells 102 may extend into a hydrocarbon containing formation near the top of heated portion 108 heated by heater well 110. Extending production wells significantly into the depth of the heated hydrocarbon layer may be unnecessary.

Fluid generated within a hydrocarbon containing formation may move a considerable distance through the hydrocarbon containing formation as a vapor. The considerable distance may be over 1000 m depending on various factors (e.g., permeability of the formation, properties of the fluid, temperature of the formation, and pressure gradient allowing movement of the fluid). Due to increased permeability in formations subjected to in situ conversion and formation fluid removal, production wells may only need to be provided in every other unit of heat sources or every third, fourth, fifth, or sixth units of heat sources.

10

15

20

25

30

35

40

During an in situ process, production wells may be operated such that the production wells are at a lower pressure than other portions of the formation. In some embodiments, a vacuum may be drawn at the production wells. Maintaining the production wells at lower pressures may inhibit fluids in the formation from migrating outside of the in situ treatment area.

Certain embodiments may include controlling the heat provided to at least a portion of the formation such that production of less desirable products in the portion may be substantially inhibited. Controlling the heat provided to at least a portion of the formation may also increase the uniformity of permeability within the formation. For example, controlling the heating of the formation to inhibit production of less desirable products may, in some embodiments, include controlling the heating rate to less than a selected amount (e.g., 10 °C, 5 °C, 3 °C, 1 °C, 0.5 °C, or 0.1 °C) per day.

Substantially uniform heating of the hydrocarbon containing formation may result in a substantially uniform increase in permeability. For example, uniformly heating may generate a series of substantially uniform fractures within the heated portion due to thermal stresses generated in the formation. Heating substantially uniformly may generate pyrolysis fluids from the portion in a substantially homogeneous manner. Water removed due to vaporization and production may result in increased permeability of the heated portion. In addition to creating fractures due to thermal stresses, fractures may also be generated due to fluid pressure increase. As fluids are generated within the heated portion a fluid pressure within the heated portion may also increase. As the fluid pressure approaches a lithostatic pressure of the heated portion, fractures may be generated. Substantially uniform heating and homogeneous generation of fluids may generate substantially uniform fractures within the heated portion. In some embodiments, a permeability of a heated section of a hydrocarbon containing formation may not vary by more than a factor of about 10.

Certain embodiments for treating heavy hydrocarbons in a relatively low permeability formation may include providing heat from one or more heat sources to pyrolyze some of the heavy hydrocarbons and then to vaporize a portion of the heavy hydrocarbons. The heat sources may pyrolyze at least some heavy hydrocarbons in a selected section of the formation and may pressurize at least a portion of the selected section. During the heating, the pressure within the formation may increase substantially. The pressure in the formation may be controlled such

that the pressure in the formation may be maintained to produce a fluid of a desired composition. Pyrolyzation fluid may be removed from the formation as vapor from one or more heater wells by using the back pressure created by heating the formation.

After pyrolysis of hydrocarbons, a large amount of carbon and some hydrogen may still be present in the formation. A significant portion of remaining carbon in the formation can be produced from the formation in the form of synthesis gas. Synthesis gas generation may take place during stage 3 heating depicted in FIG. 1. Stage 3 may include heating a hydrocarbon containing formation to a temperature sufficient to allow synthesis gas generation. For example, synthesis gas may be produced within a temperature range from about 400 °C to about 1200 °C.

10

15

20

25

30

35

40

FIG. 2 shows a schematic view of an embodiment of a portion of an in situ conversion system for treating a hydrocarbon containing formation. Heat sources 100 may be placed within at least a portion of the hydrocarbon containing formation. Heat sources 100 may include, for example, electric heaters such as insulated conductors, conductor-in-conduit heaters, surface burners, flameless distributed combustors, and/or natural distributed combustors. Heat sources 100 may also include other types of heaters. Heat sources 100 may provide heat to at least a portion of a hydrocarbon containing formation. Energy may be supplied to the heat sources 100 through supply lines 112. The supply lines may be structurally different depending on the type of heat source or heat sources being used to heat the formation. Supply lines for heat sources may transmit electricity for electric heaters, may transport fuel for combustors, or may transport heat exchange fluid that is circulated within the formation.

Production wells 102 may be used to remove formation fluid from the formation. Formation fluid produced from production wells 102 may be transported through collection piping 114 to treatment facilities 116. Formation fluids may also be produced from heat sources 100. For example, fluid may be produced from heat sources 100 to control pressure within the formation adjacent to the heat sources. Fluid produced from heat sources 100 may be transported through tubing or piping to collection piping 114 or the produced fluid may be transported through tubing or piping directly to treatment facilities 116. Treatment facilities 116 may include separation units, reaction units, upgrading units, fuel cells, turbines, storage vessels, and other systems and units for processing produced formation fluids.

An in situ conversion system for treating hydrocarbons may include barrier wells 118. In some embodiments, barriers may be used to inhibit migration of fluids (e.g., generated fluids and/or groundwater) into and/or out of a portion of a formation undergoing an in situ conversion process. Barriers may include, but are not limited to naturally occurring portions (e.g., overburden and/or underburden), freeze wells, frozen barrier zones, low temperature barrier zones, grout walls, sulfur wells, dewatering wells, injection wells, a barrier formed by a gel produced in the formation, a barrier formed by precipitation of salts in the formation, a barrier formed by a polymerization reaction in the formation, sheets driven into the formation, or combinations thereof.

An in situ conversion process for hydrocarbons may include providing heat to a portion of a hydrocarbon containing formation and controlling a temperature, rate of temperature increase, and/or pressure within the heated portion. A temperature and/or a rate of temperature increase of the heated portion may be controlled by altering the energy supplied to heat sources in the formation.

In certain embodiments, one or more conduits may be provided to supply additional components (e.g., nitrogen, carbon dioxide, reducing agents such as gas containing hydrogen, etc.) to formation openings, to bleed off fluids, and/or to control pressure. Formation pressures tend to be highest near heating sources. Providing pressure control equipment in heat sources may be beneficial. In some embodiments, adding a reducing agent proximate the

heating source assists in providing a more favorable pyrolysis environment (e.g., a higher hydrogen partial pressure). Since permeability and porosity tend to increase more quickly proximate the heating source, it is often optimal to add a reducing agent proximate the heating source so that the reducing agent can more easily move into the formation.

Formation fluids including pyrolyzation fluids may be produced from the formation. The pyrolyzation fluids may include, but are not limited to, hydrocarbons, hydrogen, carbon dioxide, carbon monoxide, hydrogen sulfide, ammonia, nitrogen, water, and mixtures thereof. As the temperature of the formation increases, the amount of condensable hydrocarbons in the produced formation fluid tends to decrease. At high temperatures, the formation may produce mostly methane and/or hydrogen. If a hydrocarbon containing formation is heated throughout an entire pyrolysis range, the formation may produce only small amounts of hydrogen towards an upper limit of the pyrolysis range. After all of the available hydrogen is depleted, a minimal amount of fluid production from the formation will typically occur.

10

15

20

25

30

40

In an in situ conversion process embodiment, a heated formation may be used to upgrade materials.

Materials to be upgraded may be produced from the same portion of the formation and recycled, produced from other formations, or produced from other portions of the same formation.

Upgrading may include, but is not limited to, changing a product composition, a boiling point, or a freezing point. Examples of materials that may be upgraded include, but are not limited to, heavy hydrocarbons, tar, emulsions (e.g., emulsions from surface separation of tar from sand), naphtha, asphaltenes, and/or crude oil. In certain embodiments, surface mined tar may be injected into a formation for upgrading. Such surface mined tar may be partially treated, heated, or emulsified before being provided to a formation for upgrading. The material to be upgraded may be provided to the heated portion of the formation. The material may be upgraded in the formation. For example, upgrading may include providing heavy hydrocarbons having an API gravity of less than about 20°, 15°, 10°, or 5° into a heated portion of the formation. The heavy hydrocarbons may be cracked or distilled in the heated portion. The upgraded heavy hydrocarbons may have an API gravity of greater than about 20° (or above about 25° or above 30°). The upgraded heavy hydrocarbons may also have a reduced amount of sulfur and/or nitrogen. A property of the upgraded hydrocarbons (e.g., API gravity or sulfur content) may be measured to determine the relative upgrading of the hydrocarbons.

In an in situ conversion process embodiment, heavy hydrocarbons may be produced from a heated formation. The heavy hydrocarbons may be recycled back into the same formation to be upgraded. The upgraded products may be produced from the formation. In another embodiment, the heavy hydrocarbon may be produced from one formation and upgraded in another formation at a different temperature. The residence time and temperature of the formation may be controlled to produce a desirable product. For example, a portion of fluid initially produced from a tar sands formation undergoing an in situ conversion process may be heavy hydrocarbons, especially if the hydrocarbons are produced from a relatively deep depth within a hydrocarbon containing layer of the tar sands formation. The produced heavy hydrocarbons may be reintroduced into the formation through or adjacent to a heat source to facilitate upgrading of the heavy hydrocarbons.

In an in situ conversion process embodiment, crude oil produced from a formation by conventional methods may be upgraded in a heated formation of the in situ conversion process system. The crude oil may be provided to a heated portion of the formation to upgrade the oil. In some embodiments, only a heavy fraction of the crude oil may be introduced into the heated formation. The heated portion of the formation may upgrade the quality

of the introduced portion of the oil and/or remove some of the undesired components within the introduced portion of the crude oil (e.g., sulfur and/or nitrogen).

In some embodiments, hydrogen or any other hydrogen donor fluid may be added to heavy hydrocarbons injected into a heated formation. The hydrogen or hydrogen donor may increase cracking and upgrading of the heavy hydrocarbons in the heated formation. In certain embodiments, heavy hydrocarbons may be injected with a gas (e.g., hydrogen or carbon dioxide) to increase and/or control the pressure within the heated formation.

Hydrogen content of a hydrocarbon containing formation may significantly influence a composition of hydrocarbon fluids producible from the formation. Pyrolysis of hydrocarbons within heated portions of the formation may generate hydrocarbon fluids that include a double bond or a radical. Hydrogen within the formation may reduce the double bond to a single bond. Reaction of generated hydrocarbon fluids with each other and/or with additional components in the formation may be inhibited. For example, reduction of a double bond of the generated hydrocarbon fluids to a single bond may reduce polymerization of the generated hydrocarbons. Such polymerization may reduce the amount of fluids produced and may reduce the quality of fluid produced from the formation.

10

15

20

25

30

35

40

Hydrogen within the formation may neutralize radicals in the generated hydrocarbon fluids. Hydrogen present in the formation may inhibit reaction of hydrocarbon fragments by transforming the hydrocarbon fragments into relatively short chain hydrocarbon fluids. The hydrocarbon fluids may enter a vapor phase. Vapor phase hydrocarbons may move relatively easily through the formation to production wells. Increase in the hydrocarbon fluids in the vapor phase may significantly reduce a potential for producing less desirable products within the selected part of the formation.

A lack of bound and free hydrogen in the formation may negatively affect the amount and quality of fluids that can be produced from the formation. If too little hydrogen is naturally present, then hydrogen or other reducing fluids may be added to the formation.

In an in situ conversion process embodiment, a heated portion of a formation may be used as a hydrotreating zone. A temperature and pressure of a portion of the formation may be controlled so that molecular hydrogen is present in the hydrotreating zone. For example, a heat source or selected heat sources may be operated at high temperatures to produce hydrogen and coke. The hydrogen produced by the heat source or selected heat sources may diffuse or be drawn by a pressure gradient created by production wells towards the hydrotreating zone. The amount of molecular hydrogen may be controlled by controlling the temperature of the heat source or selected heat sources. In some embodiments, hydrogen or hydrogen generating fluid (e.g., hydrocarbons introduced through or adjacent to a hot zone) may be introduced into the formation to provide hydrogen for the hydrotreating zone.

In an in situ conversion process embodiment, a compound or compounds may be provided to a hydrotreating zone to hydrotreat the compound or compounds. In some embodiments, the compound or compounds may be generated in the formation by pyrolysis reactions of native hydrocarbons. In other embodiments, the compound or compounds may be introduced into the hydrotreating zone. Examples of compounds that may be hydrotreated include, but are not limited to, oxygenates, olefins, nitrogen containing carbon compounds, sulfur containing carbon compounds, crude oil, synthetic crude oil, pitch, hydrocarbon mixtures, and/or combinations thereof.

Hydrotreating in a heated formation may provide advantages over conventional hydrotreating. The heated reservoir may function as a large hydrotreating unit, thereby providing a large reactor volume in which to hydrotreat materials. The hydrotreating conditions may allow the reaction to be run at low hydrogen partial pressures and/or at

low temperatures (e.g., less than about 0.007 to about 1.4 bars or about 0.14 to about 0.7 bars partial pressure hydrogen and/or about 200 °C to about 450 °C or about 200 °C to about 250 °C). Coking within the formation generates hydrogen, which may be used for hydrotreating. Even though coke may be produced, coking may not cause a decrease in the throughput of the formation because of the large pore volume of the reservoir.

The heated formation may have lower catalytic activity for hydrotreating compared to commercially available hydrotreating catalysts. The formation provides a long residence time, large volume, and large surface area, such that the process may be economical even with lower catalytic activity. In some formations, metals may be present. These naturally present metals may be incorporated into the coke and provide some catalytic activity during hydrotreating. Advantageously, a stream generated or introduced into a hydrotreating zone does not need to be monitored for the presence of catalyst deactivators or destroyers.

10

15

20

25

30

35

40

In an embodiment, the hydrotreated products produced from an in situ hydrotreating zone may include a hydrocarbon mixture and an inorganic mixture. The produced products may vary depending upon, for example, the compound provided. Examples of products that may be produced from an in situ hydrotreating process include, but are not limited to, hydrocarbons, ammonia, hydrogen sulfide, water, or mixtures thereof. In some embodiments, ammonia, hydrogen sulfide, and/or oxygenated compounds may be less than about 40 weight % of the produced products.

Formation fluid produced from a hydrocarbon containing formation during treatment may include a mixture of different components. To increase the economic value of products generated from the formation, formation fluid may be treated using a variety of treatment processes. Processes utilized to treat formation fluid may include distillation (e.g., atmospheric distillation, fractional distillation, and/or vacuum distillation), condensation (e.g., fractional), cracking (e.g., thermal cracking, catalytic cracking, fluid catalytic cracking, hydrocracking, residual hydrocracking, and/or steam cracking), reforming (e.g., thermal reforming, catalytic reforming, and/or hydrogen steam reforming), hydrogenation, coking, solvent extraction, solvent dewaxing, polymerization (e.g., catalytic polymerization and/or catalytic isomerization), visbreaking, alkylation, isomerization, deasphalting, hydrodesulfurization, catalytic dewaxing, desalting, extraction (e.g., of phenols, other aromatic compounds, etc.), and/or stripping.

Formation fluids may undergo treatment processes in a first in situ treatment area as the formation fluid is generated and produced, in a second in situ treatment area where a specific treatment process occurs, and/or in surface treatment units. A "surface treatment unit" is a unit used to treat at least a portion of formation fluid at the surface. Surface treatment units may include, but are not limited to, reactors (e.g., hydrotreating units, cracking units, ammonia generating units, fertilizer generating units, and/or oxidizing units), separating units (e.g., air separating units, liquid-liquid extraction units, adsorption units, absorbers, ammonia recovery and/or generating units, vapor/liquid separating units, distillation columns, reactive distillation columns, and/or condensing units), reboiling units, heat exchangers, pumps, pipes, storage units, and/or energy producing units (e.g., fuel cells and/or gas turbines). Multiple surface treatment units used in series, in parallel, and/or in a combination of series and parallel are referred to as a surface facility configuration. Surface facility configurations may vary dramatically due to a composition of formation fluid as well as the products being generated.

Surface treatment configurations may be combined with treatment processes in various surface treatment systems to generate a multitude of products. Products generated at a site may vary with local and/or global market conditions, formation characteristics, proximity of formation to a purchaser, and/or available feedstocks. Generated products may be utilized on site, transferred to another site for use, and/or sold to a purchaser.

Feedstocks for surface treatment units may be generated in treatment areas and/or surface treatment units. A "feedstock" is a stream containing at least one component required for a treatment process. Feedstocks may include, but are not limited to, formation fluid, synthetic condensate, a gas stream, a water stream, a gas fraction, a light fraction, a middle fraction, a heavy fraction, bottoms, a naphtha fraction, a jet fuel fraction, a diesel fraction, and/or a fraction containing a specific component (e.g., heart fraction, phenols containing fraction, etc.). In some embodiments, feedstocks are hydrotreated prior to entering a surface treatment unit. For example, a hydrotreating unit used to hydrotreat a synthetic condensate may generate hydrogen sulfide to be utilized in the synthesis of a fertilizer such as ammonium sulfate. Alternatively, one or more components (e.g., heavy metals) may have been removed from formation fluids prior to entering the surface treatment unit.

In alternate embodiments, feedstocks for in situ treatment processes may be generated at the surface in surface treatment units. For example, a hydrogen stream may be separated from formation fluid in a surface treatment unit and then provided to an in situ treatment area to enhance generation of upgraded products. In addition, a feedstock may be injected into a treatment area to be stored for later use. Alternatively, storage of a feedstock may occur in storage units on the surface.

10

15

20

25

30

40

The composition of products generated may be altered by controlling conditions within a treatment area and/or within one or more surface treatment units. Conditions within the treatment area and/or one or more surface treatment units which affect product composition include, but are not limited to, average temperature, fluid pressure, partial pressure of H₂, temperature gradients, composition of formation material, heating rates, and composition of fluids entering the treatment area and/or the surface treatment unit. Many different surface facility configurations exist for the synthesis and/or separation of specific components from formation fluid.

Controlling formation conditions to control the pressure of hydrogen in the produced fluid may result in improved qualities of the produced fluids. In some embodiments, it may be desirable to control formation conditions so that the partial pressure of hydrogen in a produced fluid is greater than about 0.5 bars absolute, as measured at a production well.

In an embodiment, a portion of a hydrocarbon containing formation may be heated to increase a partial pressure of H₂. In some embodiments, an increased H₂ partial pressure may include H₂ partial pressures in a range from about 0.5 bars to about 7 bars. Alternatively, an increased H₂ partial pressure range may include H₂ partial pressures in a range from about 5 bars to about 7 bars. For example, a majority of hydrocarbon fluids may be produced wherein a H₂ partial pressure is within a range of about 5 bars to about 7 bars. A range of H₂ partial pressures within the pyrolysis H₂ partial pressure range may vary depending on, for example, temperature and pressure of the heated portion of the formation.

Maintaining a H₂ partial pressure within the formation of greater than atmospheric pressure may increase an API value of produced condensable hydrocarbon fluids. Maintaining an increased H₂ partial pressure may increase an API value of produced condensable hydrocarbon fluids to greater than about 25° or, in some instances, greater than about 30°. Maintaining an increased H₂ partial pressure within a heated portion of a hydrocarbon containing formation may increase a concentration of H₂ within the heated portion. The H₂ may be available to react with pyrolyzed components of the hydrocarbons. Reaction of H₂ with the pyrolyzed components of hydrocarbons may reduce polymerization of olefins into tars and other cross-linked, difficult to upgrade, products. Therefore, production of hydrocarbon fluids having low API gravity values may be inhibited.

An in situ conversion process may generate significant amounts of H₂ and hydrocarbon fluids within the formation. Generation of hydrogen within the formation, and pressure within the formation sufficient to force

hydrogen into a liquid phase within the formation, may produce a reducing environment within the formation without the need to introduce a reducing fluid (e.g., H₂ and/or non-condensable saturated hydrocarbons) into the formation. A hydrogen component of formation fluid produced from the formation may be separated and used for desired purposes. The desired purposes may include, but are not limited to, fuel for fuel cells, fuel for combustors, and/or a feed stream for surface hydrogenation units.

In an embodiment, a method for treating a hydrocarbon containing formation in situ may include adding hydrogen to a selected section of the formation when the selected section is at or undergoing certain conditions. For example, the hydrogen may be added through a heater well or production well located in or proximate the selected section. Since hydrogen is sometimes in relatively short supply (or relatively expensive to make or procure), hydrogen may be added when conditions in the formation optimize the use of the added hydrogen. For example, hydrogen produced in a section of a formation undergoing synthesis gas generation may be added to a section of the formation undergoing pyrolysis. The added hydrogen in the pyrolysis section of the formation may promote formation of aliphatic compounds and inhibit formation of olefinic compounds that reduce the quality of hydrocarbon fluids produced from formation.

10

15

20

25

30

35

40

In some embodiments, hydrogen may be added to the selected section after an average temperature of the formation is at a pyrolysis temperature (e.g., when the selected section is at least about 270 °C). In some embodiments, hydrogen may be added to the selected section after the average temperature is at least about 290 °C, 320 °C, 375 °C, or 400 °C. Hydrogen may be added to the selected section before an average temperature of the formation is about 400 °C. In some embodiments, hydrogen may be added to the selected section before the average temperature is about 300 °C or about 325 °C.

The average temperature of the formation may be controlled by selectively adding hydrogen to the selected section of the formation. Hydrogen added to the formation may react in exothermic reactions. The exothermic reactions may heat the formation and reduce the amount of energy that needs to be supplied from heat sources to the formation. In some embodiments, an amount of hydrogen may be added to the selected section of the formation such that an average temperature of the formation does not exceed about 400 °C.

A valve may maintain, alter, and/or control a pressure within a heated portion of a hydrocarbon containing formation. For example, a heat source disposed within a hydrocarbon containing formation may be coupled to a valve. The valve may release fluid from the formation through the heat source. In addition, a pressure valve may be coupled to a production well within the hydrocarbon containing formation. In some embodiments, fluids released by the valves may be collected and transported to a surface unit for further processing and/or treatment.

In conventional treatment processes, hydrocarbon fluids produced from a formation may be separated into at least two streams, including a gas stream and a synthetic condensate stream. The gas stream may contain one or more components and may be further separated into component streams using one or more surface treatment units.

Formation fluid may be hydrotreated prior to separation into a gas stream and a liquid hydrocarbon condensate stream. Alternatively, the gas stream and/or the liquid hydrocarbon condensate stream may be hydrotreated in separate hydrotreating units prior to further separation into component streams. "Synthetic condensate" is the liquid component of formation fluid that condenses.

Hydrotreating a fluid may alter many properties of the fluid. Hydrotreating may increase the hydrogen content of the hydrocarbons within the fluid and/or the volume of fluid. In addition, hydrotreating may reduce a content of heteroatoms such as oxygen, nitrogen, or sulfur in the fluid. For example, nitrogen removed from the fluid during hydrotreating may be converted into ammonia. Removed sulfur may be converted into hydrogen

sulfide. Feedstocks for hydrotreating units may include, but are not limited to, formation fluid and/or any fluid generated or separated in a surface treatment unit (e.g., synthetic condensate, light fraction, middle fraction, heavy fraction, bottoms, heart cut, pyrolysis gasoline, and/or molecular hydrogen generated at an olefin generating plant).

Ammonia may be generated during an in situ conversion process. In situ ammonia may be generated during a pyrolysis stage from some of the nitrogen present in hydrocarbon material. Hydrogen sulfide may also be produced within the formation from some of the sulfur present in the hydrocarbon containing material. The ammonia and hydrogen sulfide generated in situ may be dissolved in water condensed from the formation fluids.

10

15

20

25

30

35

40

In some embodiments, ammonia may be formed from nitrogen present in hydrocarbons when fluids are being hydrotreated. FIG. 4 depicts a configuration of surface treatment units that may separate ammonia and other gases from water produced in the formation. Formation fluid 124 may be separated at wellhead 126 into gas stream 128, synthetic condensate 130, and water stream 132. Gas treating unit 134 may separate gas stream 128 into gas mixture 136, light hydrocarbon mixture 138, and/or hydrogen fraction 140. Gas mixture 136 may include, but is not limited to, hydrogen sulfide, carbon dioxide, and/or ammonia. Gas mixture 136 may be blended with water stream 132 to form aqueous mixture 142. Aqueous mixture 142 may flow to stripping unit 144, where aqueous mixture 142 is separated into ammonia stream 146 and aqueous mixture 148. Aqueous mixture 148 may flow to stripping unit 144' to be separated into gas stream 150 and water stream 152. Ammonia stream 146 may be stored as an aqueous solution or in anhydrous form. Alternately, ammonia stream 146 may be provided to surface treatment units requiring ammonia, such as a urea synthesis unit or an ammonium sulfate synthesis unit. Synthetic condensate 130 may flow to hydrotreating unit 154 to form ammonia containing stream 146' and hydrotreated synthetic condensate 156. Ammonia containing stream 146' may be blended with water stream 132 prior to entering stripping unit 144.

In some embodiments, ammonia may be generated on site in surface treatment units using an ammonia synthesis process as shown in FIG. 5. Air stream 160 may flow to air separating unit 162 to separate nitrogen stream 164 and stream 166 from air stream 160. Nitrogen stream 164 may be heated with heat exchanger 168 to form heated nitrogen feedstock 140' prior to flowing into ammonia generating unit 172. Hydrogen fraction 140' may flow to ammonia generating unit 172 to react with nitrogen stream 164 to form ammonia stream 174. Ammonia generated during in situ or surface treatment processes may be stored in an aqueous solution or as anhydrous ammonia. In some instances, ammonia in either form may be sold commercially. Alternatively, ammonia may be used on site to generate a number of different products that have commercial value (e.g., fertilizers such as ammonium sulfate and/or urea). Production of fertilizer may increase the economic viability of a treatment system used to treat a formation. Precursors for fertilizer production may be produced in situ or while treating formation fluid at surface facilities.

Ammonia and carbon dioxide generated during treatment either in situ or at a surface treating unit may be used to generate urea for use as a fertilizer, as illustrated in FIG. 6. Ammonia stream 174 and carbon dioxide stream 176 may react in urea generating unit 178 to form urea stream 180.

As illustrated in FIG. 7 ammonium sulfate may be generated by treating formation fluid in a surface treatment unit. Wellhead 126 may separate formation fluid 124 into a mixture of non-condensable hydrocarbon fluids 182 and synthetic condensate 130. Separation unit 184 may be used to separate non-condensable hydrocarbon fluids 182 into hydrogen stream 140', hydrogen sulfide stream 186, methane stream 188, carbon dioxide stream 176', and non-condensable hydrocarbon fluids 182'.

Hydrogen sulfide stream 186 may flow to oxidation unit 190 to be converted to sulfuric acid stream 192. Additional hydrogen sulfide may, in certain embodiments, be provided to oxidation unit 190 from hydrogen sulfide stream 186'. In some embodiments, hydrogen sulfide stream 186' may be provided from a hydrotreating unit. The hydrotreating unit may be a surface facility in a different section of a treatment system or part of a different configuration of a treatment system. Ammonia stream 174 and sulfuric acid stream 192 may flow into fertilizer synthesis unit 194 to produce ammonium sulfate stream 196. Alternatively, a portion of sulfuric acid produced in an oxidation unit may be sold commercially.

5

10

15

20

25

In some embodiments, ammonia produced during treatment of a formation may be used to generate ammonium carbonate, ammonium bicarbonate, ammonium carbamate, and/or urea. Separated ammonia may be provided to a stream containing carbon dioxide (e.g., synthesis gas and/or carbon dioxide separated from formation fluid) such that the separated ammonia reacts with carbon dioxide in the stream to generate ammonium carbonate, ammonium bicarbonate, ammonium carbamate, and/or urea. Utilization of separated ammonia in this manner may reduce carbon dioxide emissions from a treatment process. Ammonium carbonate, ammonium bicarbonate, ammonium carbamate, and/or urea may be commercially marketed to a local market for use (e.g., as a fertilizer or a material to make fertilizer). Ammonium carbonate, ammonium bicarbonate, ammonium carbamate, and/or urea may capture or sequester carbon dioxide in geologic formations.

Further modifications and alternative embodiments of various aspects of the invention may be apparent to those skilled in the art in view of this description. Accordingly, this description is to be construed as illustrative only and is for the purpose of teaching those skilled in the art the general manner of carrying out the invention. It is to be understood that the forms of the invention shown and described herein are to be taken as the presently preferred embodiments. Elements and materials may be substituted for those illustrated and described herein, parts and processes may be reversed, and certain features of the invention may be utilized independently, all as would be apparent to one skilled in the art after having the benefit of this description of the invention. Changes may be made in the elements described herein without departing from the spirit and scope of the invention as described in the following claims. In addition, it is to be understood that features described herein independently may, in certain embodiments, be combined.

63293-3986

<u>CLAIMS:</u>

10

1. A method for hydrotreating a fluid in a heated hydrocarbon containing formation in situ, comprising:

providing heat from one or more heat sources to a portion of the

hydrocarbon containing formation, wherein at least one of the heat sources is in at least one wellbore in the formation;

allowing the heat to transfer from the one or more heat sources to a part of the formation wherein the heat provided from at least one of the one or more heat sources is transferred to at least a portion of the formation substantially by conduction;

providing a fluid to the part of the formation;

controlling a H₂ partial pressure in the part of the formation;

hydrotreating at least some of the fluid in the part of the formation; and

- 15 producing a mixture comprising hydrotreated fluids from the formation.
 - 2. The method of claim 1, wherein the mixture is produced from the formation when a partial pressure of hydrogen in the part of the formation is at least about 0.5 bars absolute.
- The method of claim 1 or 2, wherein the one or more heat sources are arranged in wellbores that traverse the hydrocarbon containing formation in a well pattern such that the spacing between adjacent heat sources is between 5 and 25 meters.
- 4. The method of any one of claims 1 to 3, wherein the fluid provided to 25 the formation comprises hydrogen.

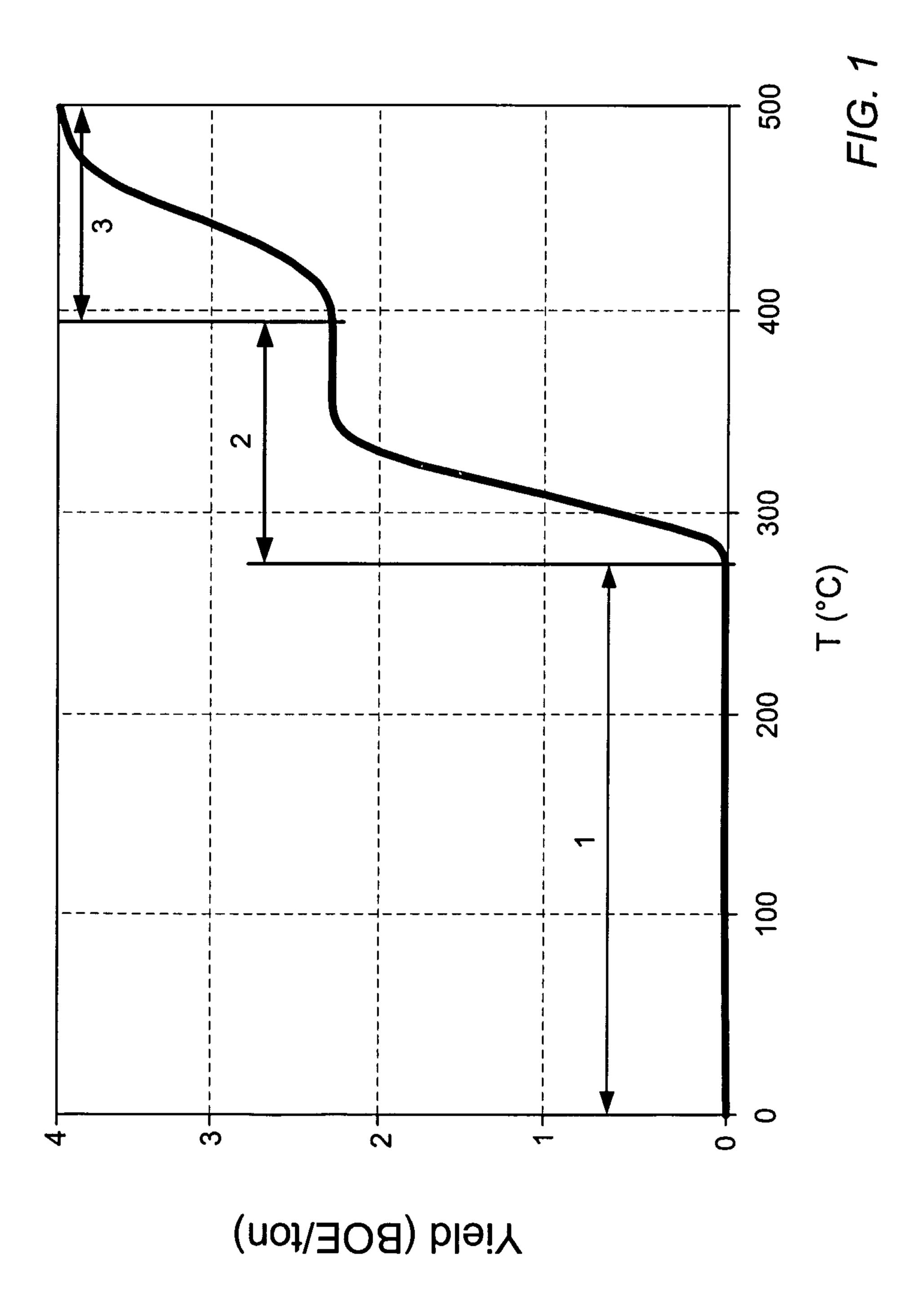
- 5. The method of any one of claims 1 to 4, further comprising controlling the heat such that a temperature within the part of the formation is in a range from about 200°C to about 450°C.
- 6. The method of any one of claims 1 to 4, further comprising providing hydrogen to the part of the formation after a temperature of the part of the formation is between greater than about 270°C and less than about 400°C.
 - 7. The method of any one of claims 1 to 6, further comprising controlling a temperature of a majority of the part of the formation by selectively adding hydrogen to the formation.
- 10 8. The method of claim 7, further comprising controlling the temperature such that the temperature is less than about 400°C.
 - 9. The method of claim 7, further comprising controlling the temperature such that the temperature is less than about 375°C.
- 10. The method of any one of claims 1 to 9, further comprising controlling a heating rate such that the temperature is less than about 400°C.
 - 11. The method of any one of claims 1 to 10, wherein the provided fluid comprises an olefin, pitch, an oxygenated compound, a sulfur containing compound, a nitrogen containing compound, and/or crude oil.
- 12. The method of any one of claims 1 to 11, wherein the produced mixture comprises a hydrocarbon mixture, less than about 1% by weight ammonia, less than about 1% by weight hydrogen sulfide, and/or less than about 1% oxygenated compounds.
- 13. The method of any one of claims 1 to 12, further comprising producing the mixture from the formation through a production well, wherein the heating is controlled such that the mixture can be produced from the formation as a vapor.

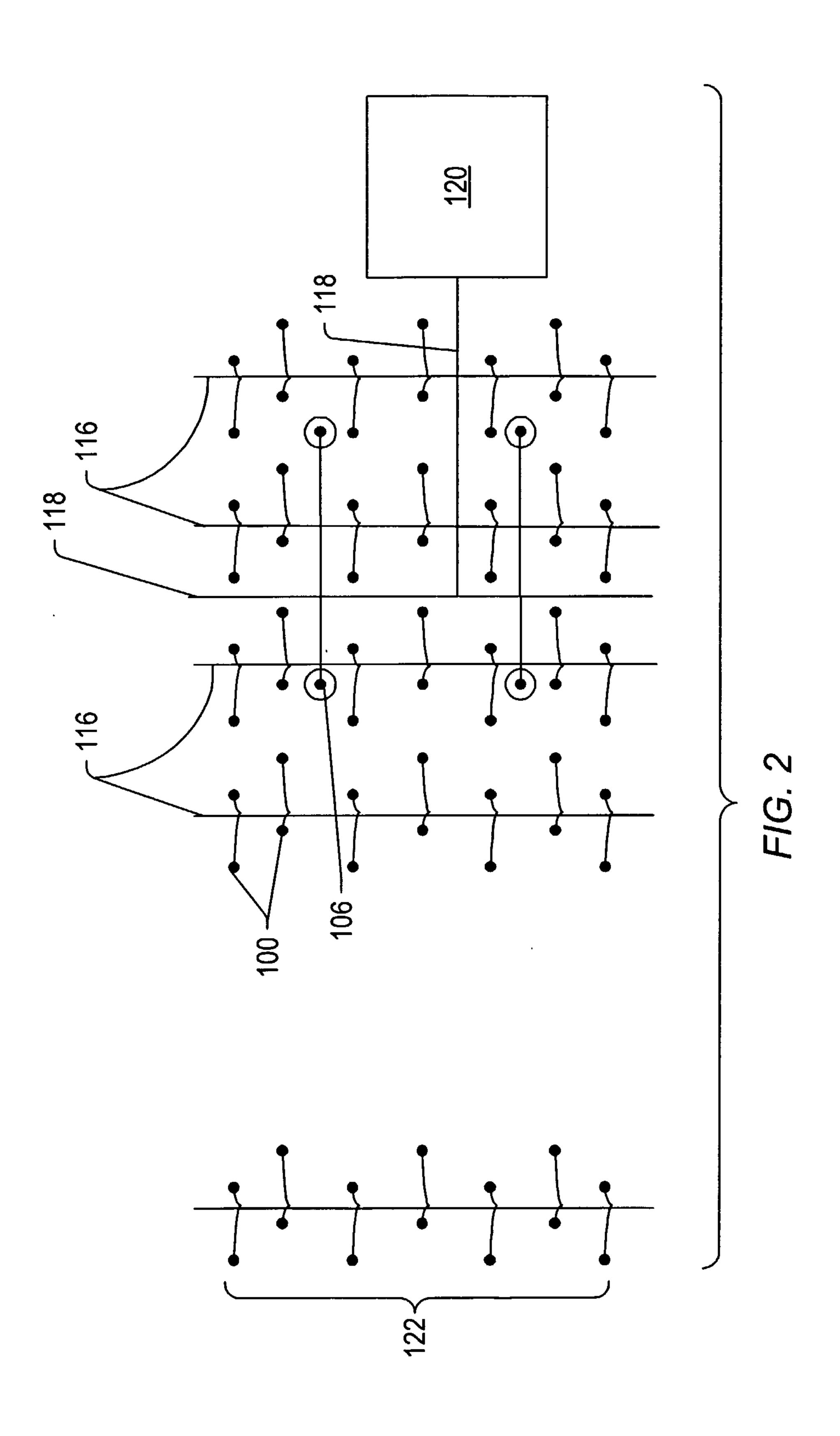
63293-3986

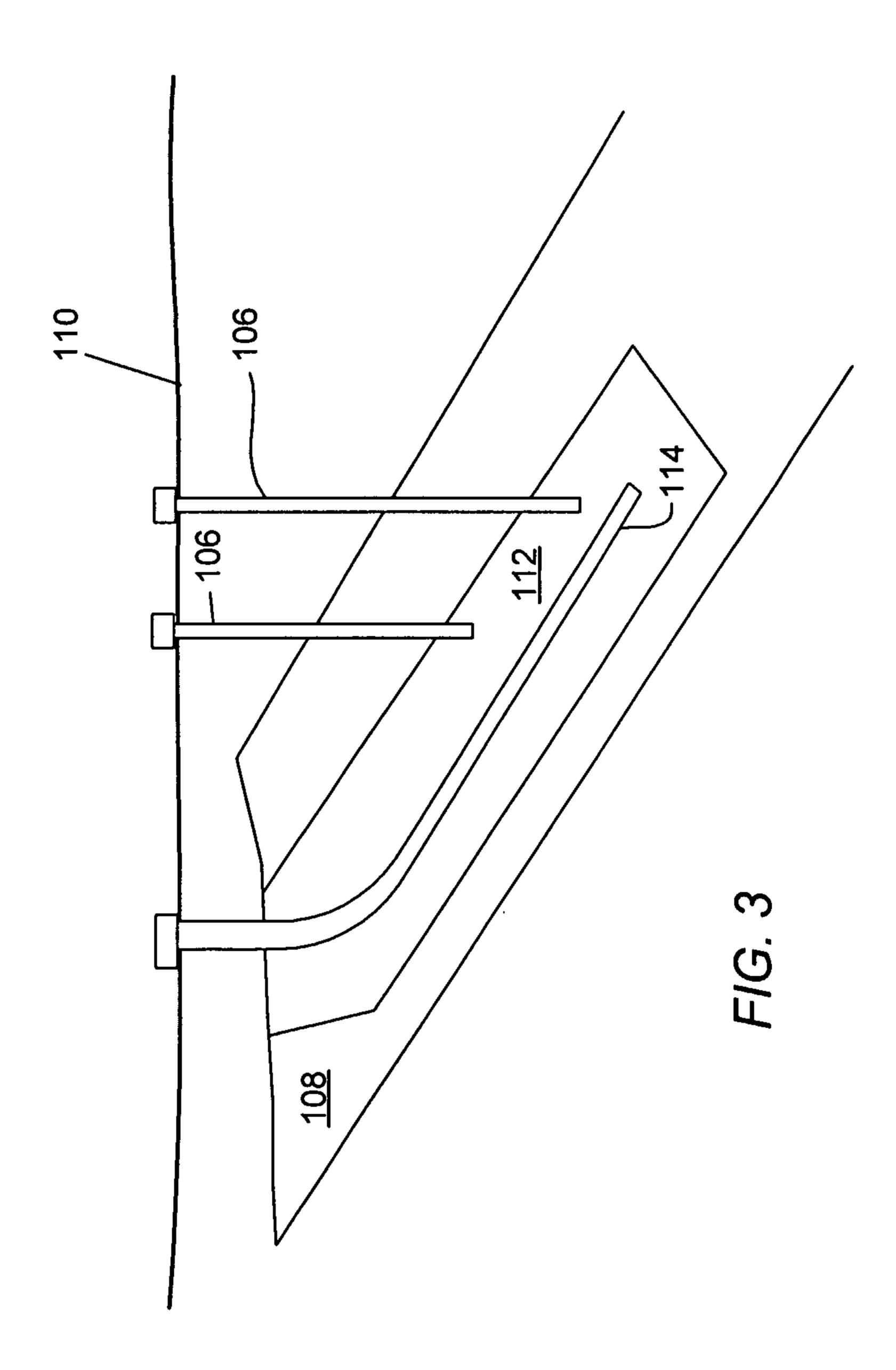
10

20

- 14. The method of any one of claims 1 to 13, wherein the produced mixture comprises ammonia and further comprising separating at least a portion of the ammonia from the hydrotreated fluids.
- 15. The method of claim 14, further comprising using at least a portion of the separated ammonia to generate ammonium sulfate.
 - 16. The method of claim 14, further comprising using at least a portion of the separated ammonia to generate urea.
 - 17. The method of claim 14, wherein the produced fluids further comprise carbon dioxide, and further comprising separating at least a portion of the carbon dioxide from the produced fluids, and reacting at least the portion of the carbon dioxide with at least a portion of ammonia to form urea.
 - 18. The method of claim 14, wherein the produced fluids further comprise hydrogen sulfide, and further comprising separating at least a portion of the hydrogen sulfide from the produced fluids, converting at least some hydrogen sulfide into sulfuric acid, and reacting at least some sulfuric acid with at least a portion of the ammonia to form ammonium sulfate.
 - 19. The method of claim 14, wherein the produced fluids further comprise hydrogen sulfide, and further comprising separating at least a portion of the hydrogen sulfide from the produced fluids, and converting at least some hydrogen sulfide into sulfuric acid.
 - The method of claim 14, further comprising generating ammonium bicarbonate using at least a portion of the ammonia.
 - The method of claim 14, further comprising providing at least a portion of the ammonia to a fluid comprising carbon dioxide to generate ammonium bicarbonate.
 - The method of claim 14, further comprising providing at least a portion of the ammonia to at least some synthesis gas to generate ammonium bicarbonate.







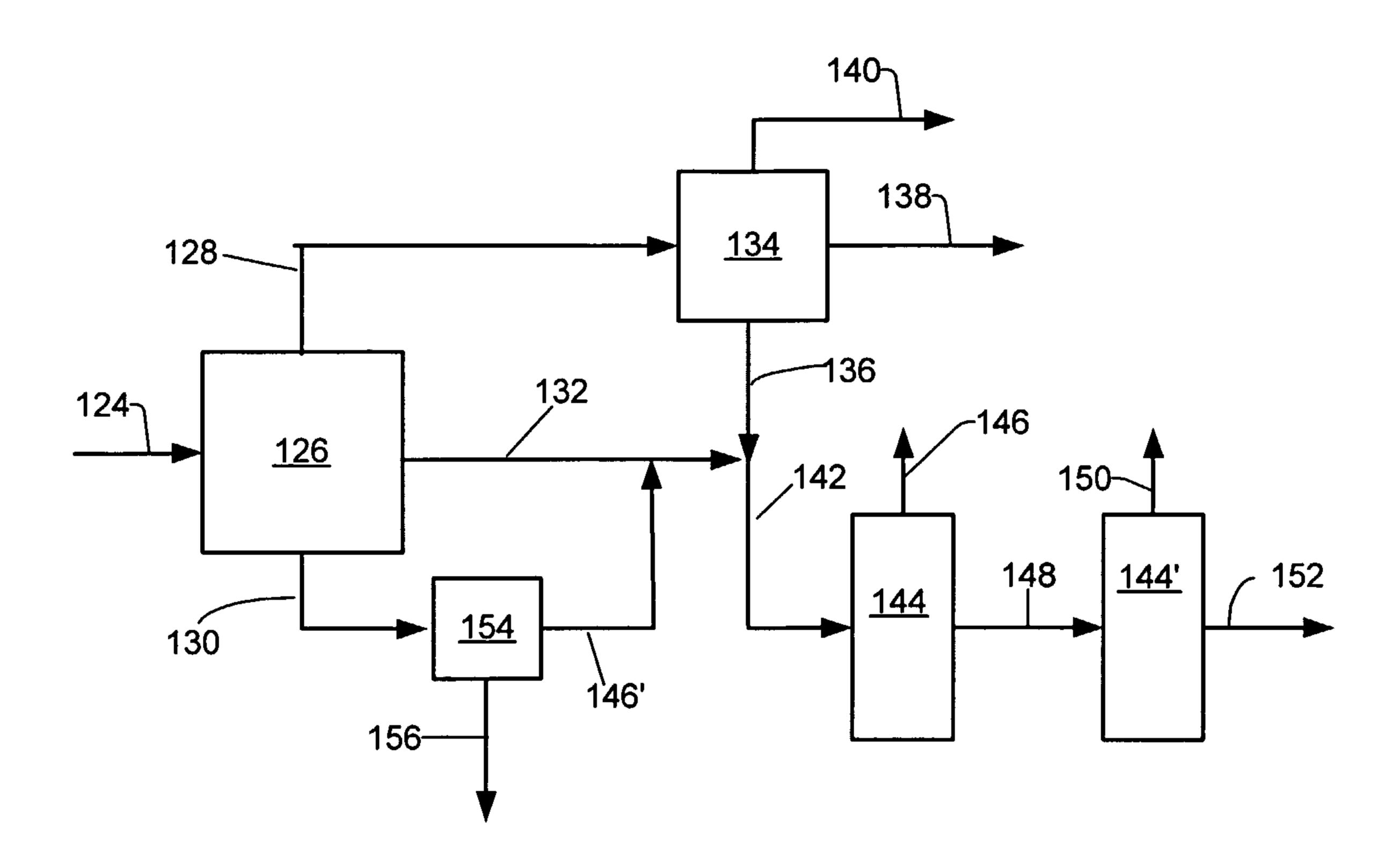


FIG. 4

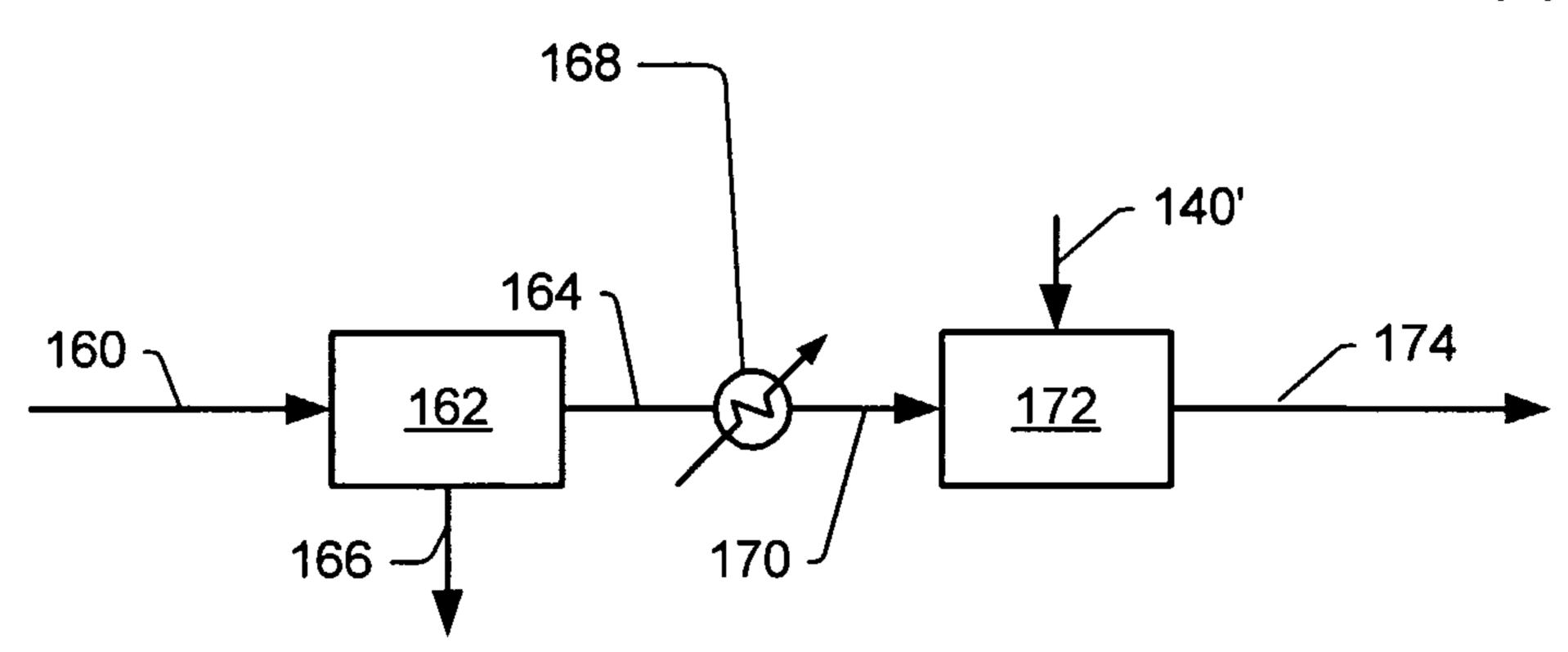


FIG. 5

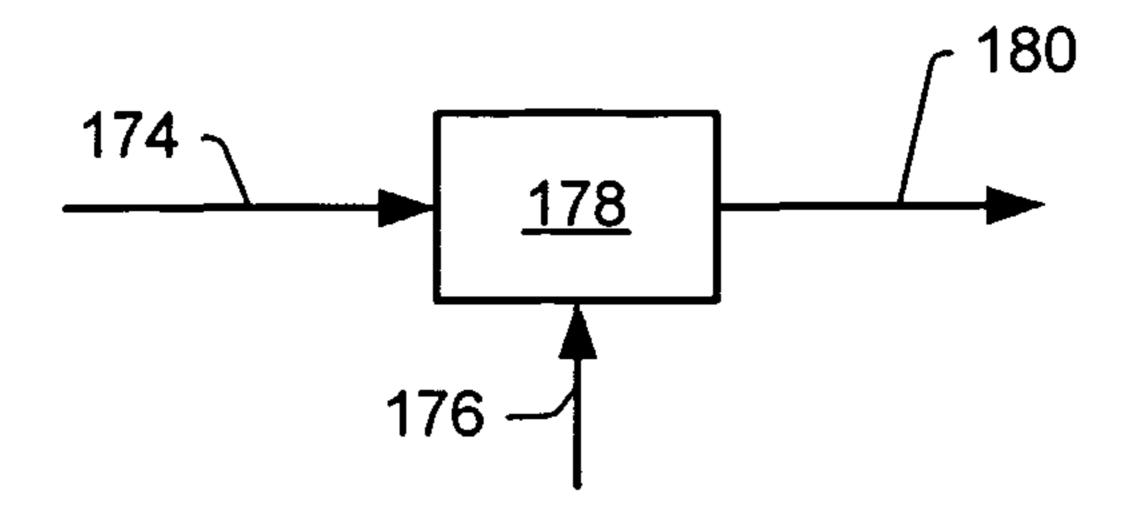


FIG. 6

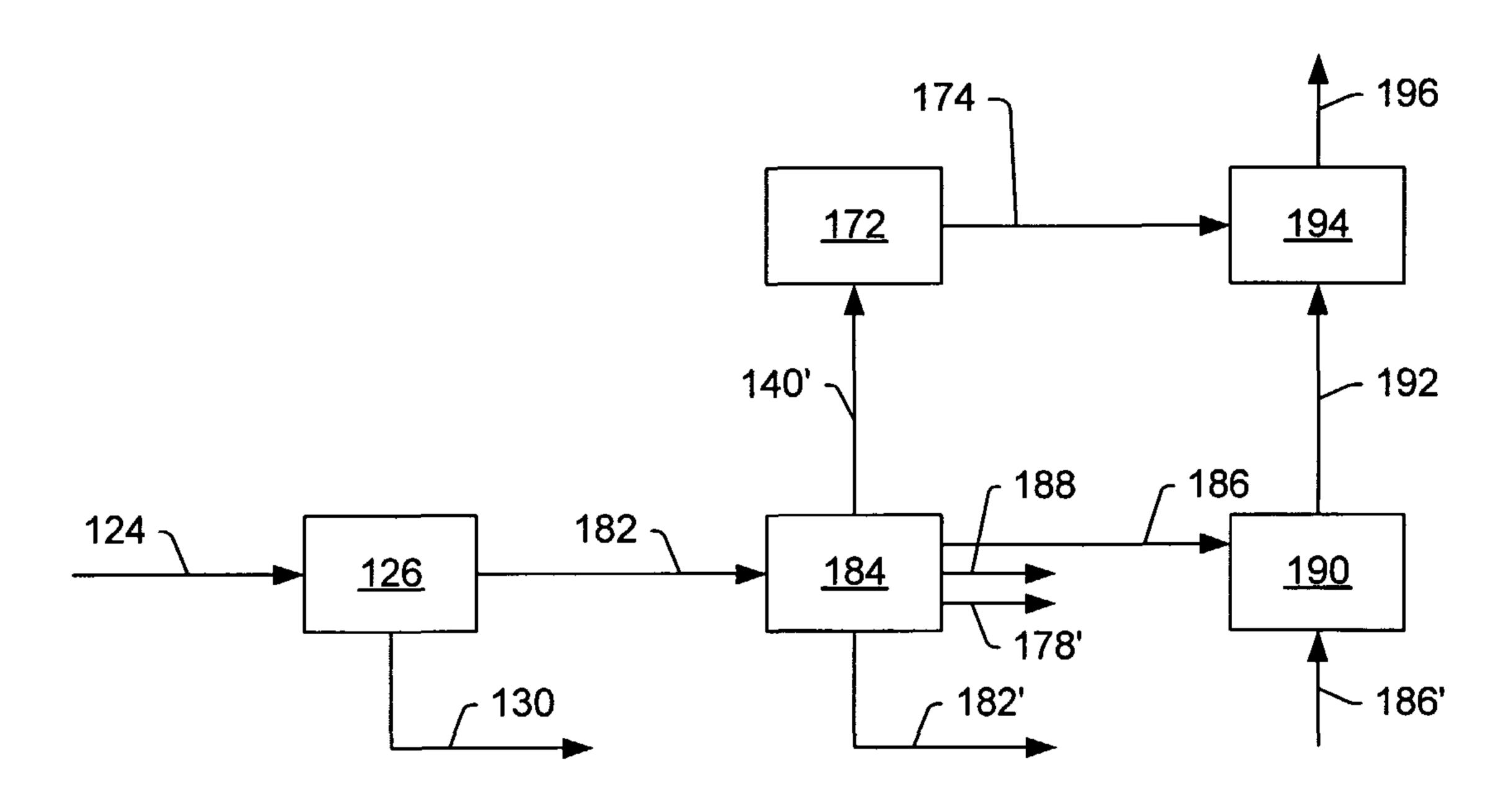


FIG. 7

