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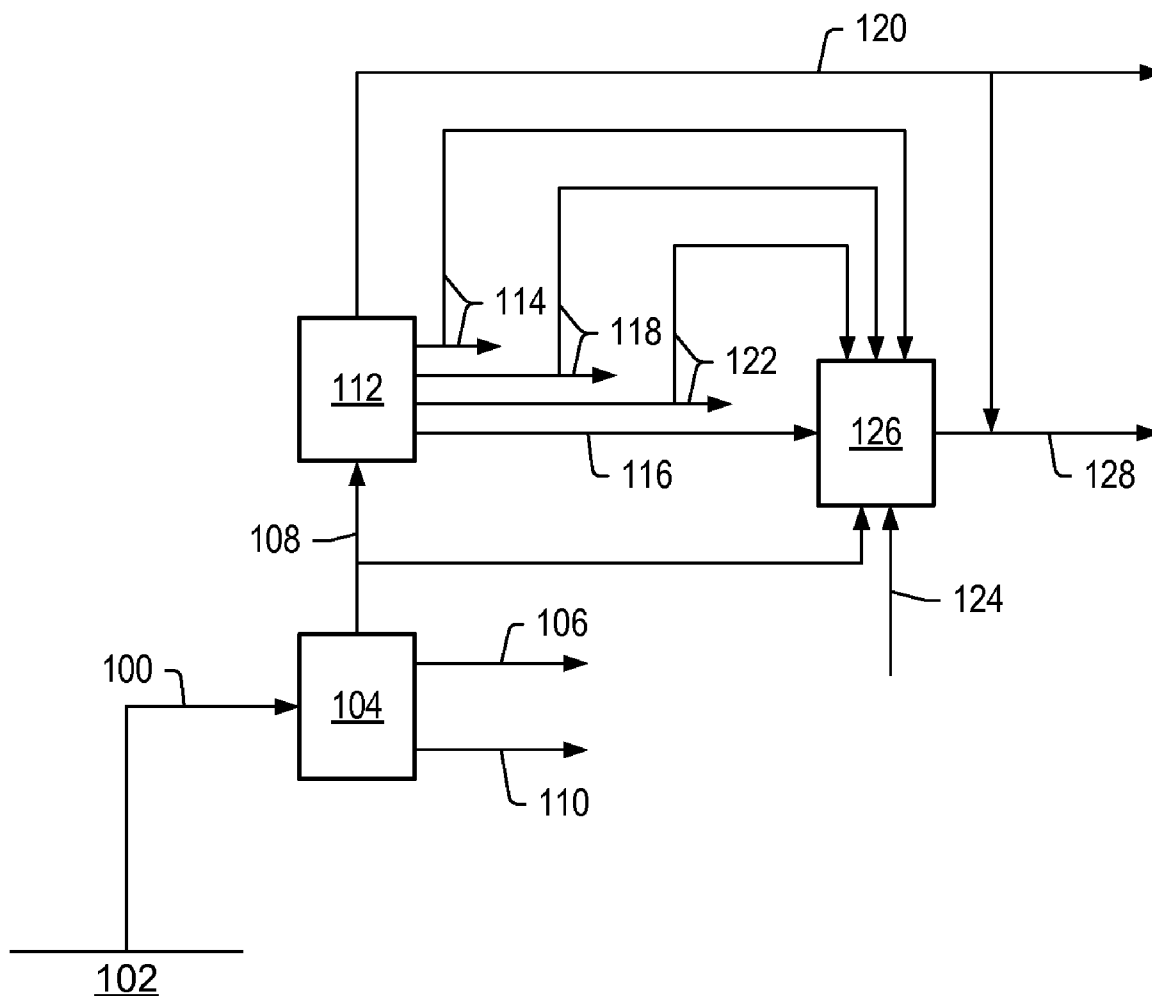
(19) **United States**(12) **Patent Application Publication**
MILAM et al.(10) **Pub. No.: US 2009/0260825 A1**(43) **Pub. Date: Oct. 22, 2009**(54) **METHOD FOR RECOVERY OF
HYDROCARBONS FROM A SUBSURFACE
HYDROCARBON CONTAINING FORMATION****Related U.S. Application Data**

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(76) Inventors: **Stanley Nemec MILAM**, Houston, TX (US); **Scott Lee WELLINGTON**, Bellaire, TX (US); **Mahendra Ladharam JOSHI**, Katy, TX (US); **Jingyu CUI**, Katy, TX (US); **Michael Anthony REYNOLDS**, Katy, TX (US)**Publication Classification**(51) **Int. Cl.**
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(57) **ABSTRACT**

Methods for treating a hydrocarbon containing formation are described herein. A comprising hydrogen sulfide is combusted in one or more surface facilities exterior to the hydrocarbon containing formation to produce a sulfur oxides stream. At least a portion of the sulfur oxides stream is provided to a hydrocarbon containing formation. Steam may be provided to the hydrocarbon containing formation. Mixing of the steam and/or water in the formation with the sulfur oxides generates heat of solution in the hydrocarbon containing formation for mobilizing formation fluids.

Correspondence Address:
SHELL OIL COMPANY
P O BOX 2463
HOUSTON, TX 772522463

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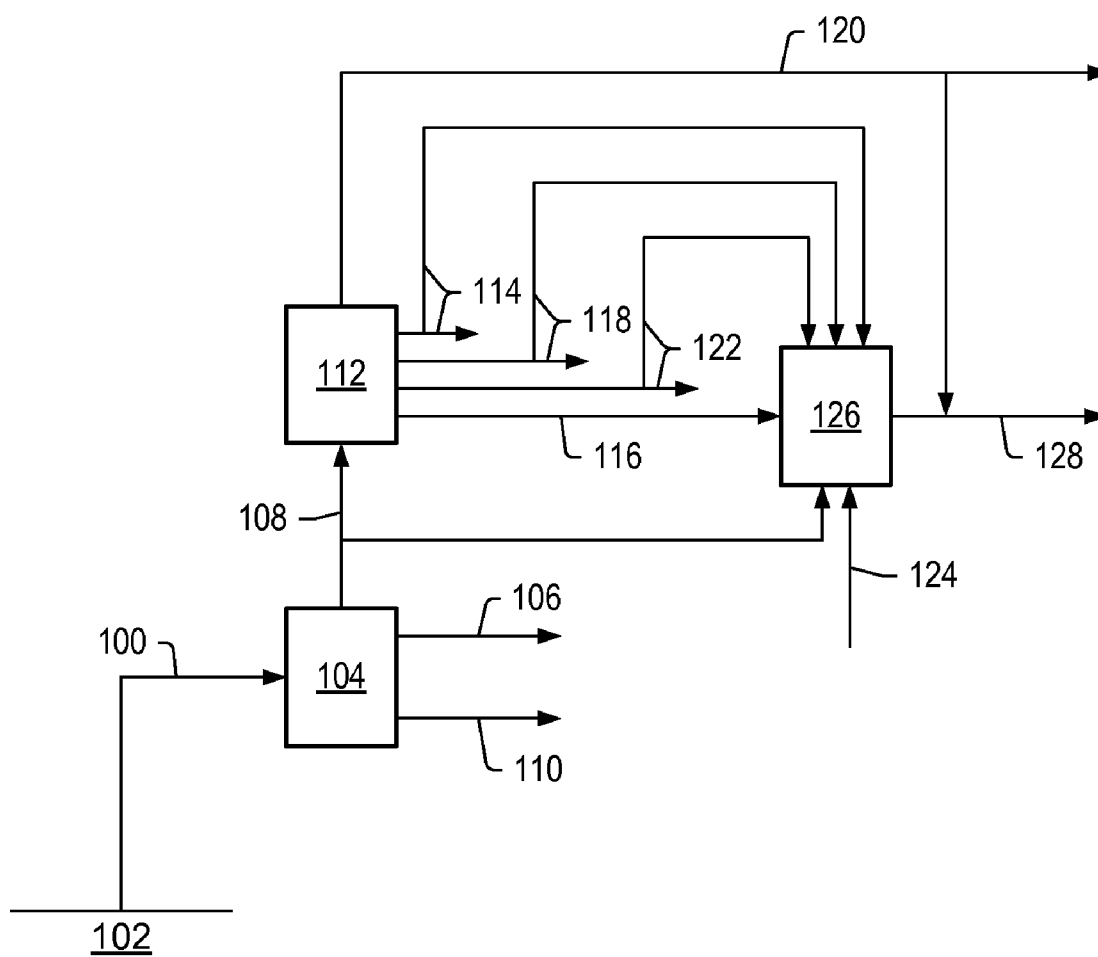


FIG. 1

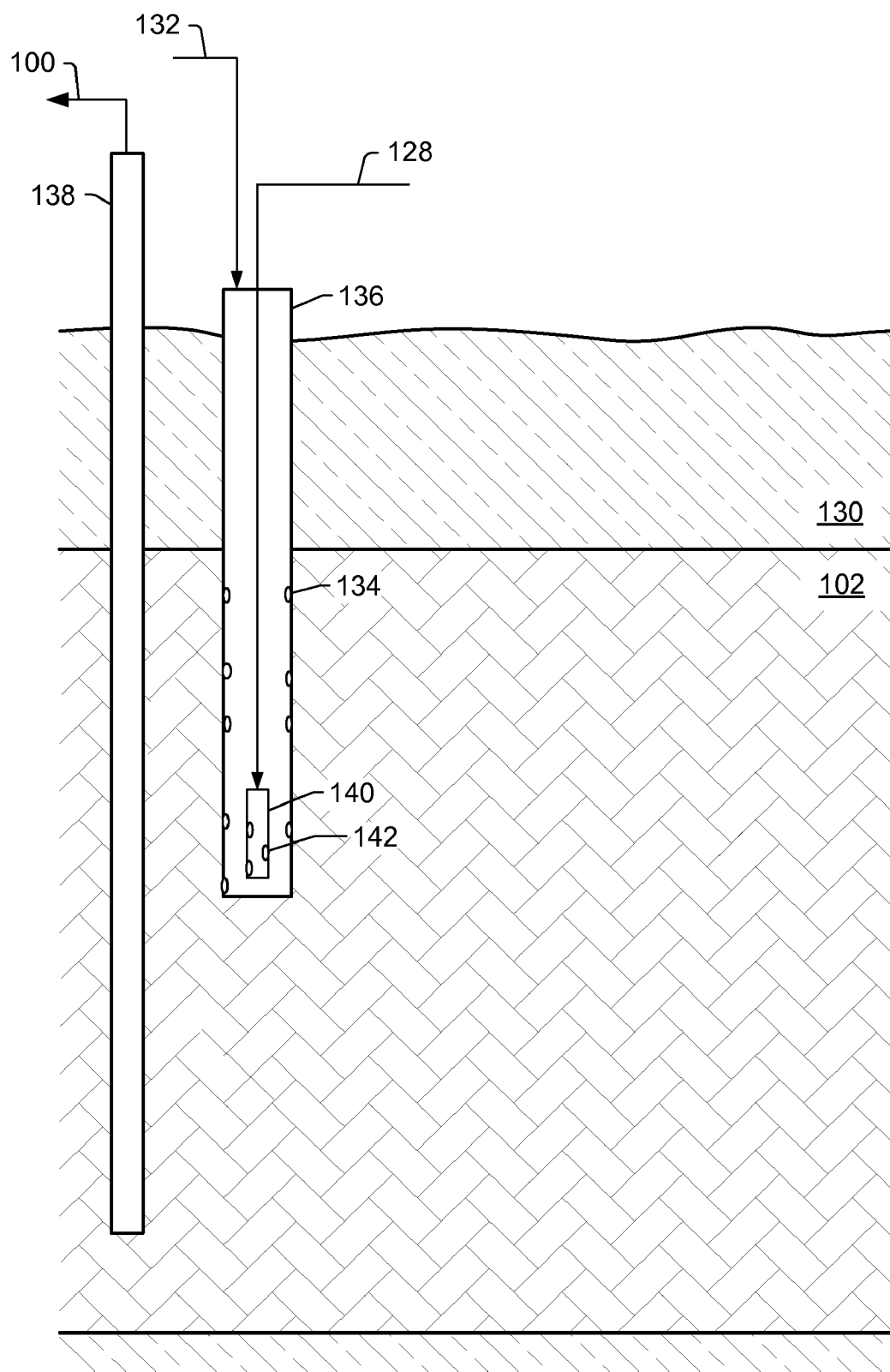


FIG. 2

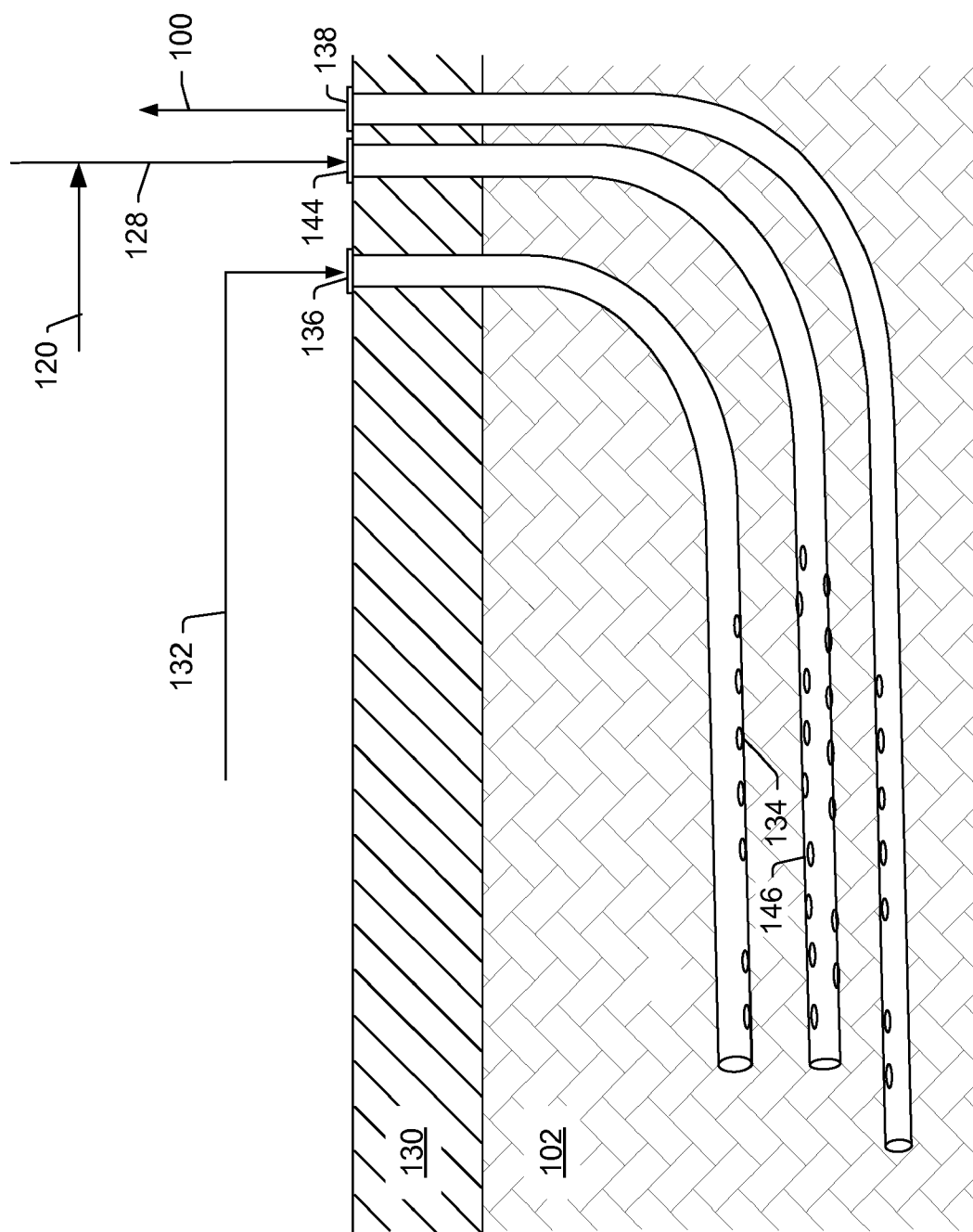


FIG. 3

METHOD FOR RECOVERY OF HYDROCARBONS FROM A SUBSURFACE HYDROCARBON CONTAINING FORMATION

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. Provisional Application Ser. No. 61/046,136 filed Apr. 18, 2008, which is hereby incorporated by reference in its entirety.

FIELD OF THE INVENTION

[0002] The present invention relates to methods for recovery of hydrocarbons from a subsurface hydrocarbon formation.

DESCRIPTION OF RELATED ART

[0003] Hydrocarbons obtained from subterranean formations are often used as energy resources, as feedstocks, and as consumer products. Concerns over depletion of available hydrocarbon resources have led to development of processes for more efficient recovery, processing, and/or use of available hydrocarbon resources.

[0004] Hydrocarbon formations may be treated in various ways to produce formation fluids. For example, application of heat, gases, and/or liquids to hydrocarbon formations to mobilize and/or produce formation fluids has been used to more efficiently recover hydrocarbons from hydrocarbon formations.

[0005] Combustion of fossil fuel and the resulting combustion by-products may be used to heat a formation. The combustion may take place in the formation, in a well, and/or near the surface. Combustion of fossil fuel generates carbon dioxide as a combustion by-product. Carbon dioxide is considered to have low economic value and is considered a contributor to the "greenhouse effect". Emissions such as carbon dioxide from fossil fuel combustion may be treated and/or sequestered in a formation. For example, flue gas from the combustion of fossil fuels has been used to displace heavy oil and bitumen in a subterranean formation to enhance recovery of the heavy oil and bitumen.

[0006] Combustion of sulfur compounds has also been used to heat a hydrocarbon formation, where the sulfur containing combustion products may act as a drive fluid for the more efficient production of hydrocarbons from the hydrocarbon formation. U.S. Pat. No. 4,379,489 to Rollmann describes a method for recovery of heavy oil from a subterranean reservoir that includes burning liquid sulfur in an oxygen-containing gas underground to form sulfur dioxide. The sulfur dioxide may act as a drive fluid for the recovery of oil or it may react with limestone in the formation to form carbon dioxide, an alternate drive fluid. The pressure of the oxygen-containing gas is maintained at a pressure sufficient to keep the sulfur dioxide in the liquid state.

[0007] An efficient, cost effective method for treating a hydrocarbon formation to more efficiently recover hydrocarbons from the hydrocarbon formation without the production of large quantities of carbon dioxide is desirable.

SUMMARY OF THE INVENTION

[0008] The present invention is directed to a method of treating a hydrocarbon containing formation comprising: providing a fuel comprising hydrogen sulfide to one or more surface facilities exterior to a hydrocarbon containing forma-

tion; combusting at least a portion of the fuel comprising hydrogen sulfide in the presence of an oxidant in at least one of the surface facilities to produce at least one combustion by-products stream comprising one or more sulfur oxides; contacting at least a portion of the combustion by-products stream comprising one or more sulfur oxides with water to generate heat; and transferring the heat generated by contacting the combustion by-products stream with water to the hydrocarbon containing formation.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Further 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:

[0010] FIG. 1 depicts a schematic of an embodiment of treating formation fluids produced from a hydrocarbon formation.

[0011] FIG. 2 depicts a representation of an embodiment of heating a portion of a hydrocarbon layer using a stream containing sulfur oxides in combination with a steam injection well.

[0012] FIG. 3 depicts a representation of an embodiment for heating a portion of a hydrocarbon layer using a well for introducing a stream containing sulfur oxides in combination with a steam injection well.

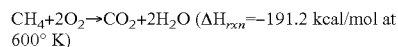
[0013] While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings and may herein be described in detail. The drawings may not be to scale. It should be understood, however, that the drawings and detailed 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 PRESENT INVENTION

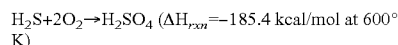
[0014] The present invention is directed to providing subsurface heat to a hydrocarbon formation where the heat is generated by combusting a fuel stream comprising hydrogen sulfide and transferring at least a portion of the heat of combustion to the hydrocarbon formation. Since the fuel stream is sulfur based, production of carbon dioxide is avoided upon combustion of the sulfur containing components of the fuel stream, reducing the overall production of carbon dioxide of the heating process relative to processes that utilize a fuel stream comprised mostly of hydrocarbons. Additional heat is provided to the hydrocarbon formation by injecting the combustion by-product stream, which includes sulfur oxides, into the hydrocarbon formation, where a heat of solution is generated by mixing of the sulfur oxides in the combustion by-product stream with water. The water that is mixed with the combustion by-product stream may be provided along with the combustion by-product stream to the hydrocarbon formation or may be present in the hydrocarbon formation.

[0015] The process of oxidizing hydrogen sulfide through a combustion process to produce sulfuric acid may have a heat value similar to methane combustion. For example, using data from "The Chemical Thermodynamics of Organic Compounds" by Stull et al.; Kreiger Publishing Company, Mala-

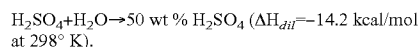
bar Fla., 1987, pp. 220, 229, 230, 233 and 234, the enthalpies of reaction for the combustion of methane and hydrogen sulfide can be calculated. Combustion of methane produces carbon dioxide as a by-product, as shown by the following reaction:



In contrast, oxidation (combustion) of hydrogen sulfide to form sulfuric acid has a calculated reaction enthalpy as shown in the following reaction:



More heat may be generated upon mixing the sulfuric acid in water by the heat of solution of sulfuric acid in water as shown below:



[0016] The total amount of heat content produced from the combustion of hydrogen sulfide and the dissolution of the sulfuric acid may range from -185 kcal/mol to -206 kcal/mol depending on the amount of water used to produce the sulfuric acid. Combustion of hydrogen sulfide as a fuel instead of methane in accordance with the process of the present invention, therefore, may be used to provide heat to a hydrocarbon formation in an amount comparable to the combustion of methane while producing no carbon dioxide. Furthermore, the use of fuels containing hydrogen sulfide in the process of the present invention provides a method to dispose of waste hydrogen sulfide from other processes (for example, sour gas and/or hydrotreating effluent streams) without creating elemental sulfur.

[0017] Terms used herein are as defined as follows.

[0018] "API gravity" refers to API gravity at 15.5° C. (60° F.). API gravity is as determined by ASTM Method D6822 or ASTM Method D1298.

[0019] "ASTM" refers to American Standard Testing and Materials.

[0020] A "formation" includes one or more hydrocarbon containing layers, one or more non-hydrocarbon layers, an overburden, and/or an underburden. "Hydrocarbon layers" refer to layers in the formation that contain hydrocarbons. The hydrocarbon layers may contain non-hydrocarbon material and hydrocarbon material. The "overburden" and/or the "underburden" include one or more different types of impermeable materials. In some cases, the overburden and/or the underburden may be somewhat permeable.

[0021] "Formation fluids" refer to fluids present in a formation and may include pyrolysis fluid, synthesis gas, mobilized hydrocarbons, and water (steam). Formation fluids may include hydrocarbon fluids as well as non-hydrocarbon fluids. The term "mobilized fluid" refers to fluids in a hydrocarbon containing formation that are able to flow as a result of treatment of the formation. "Produced fluids" refer to fluids removed from the formation.

[0022] A "heater" is any system or heat source 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, and/or combinations thereof.

[0023] "Heavy hydrocarbons" are viscous hydrocarbon fluids. Heavy hydrocarbons may include highly viscous hydrocarbon fluids such as heavy oil, tar, and/or asphalt.

Heavy hydrocarbons may include carbon and hydrogen, as well as smaller concentrations of compounds containing sulfur, oxygen, and nitrogen. Additional elements (for example, nickel, iron, vanadium, or mixtures thereof) may also be present in heavy hydrocarbons. Heavy hydrocarbons may be classified by API gravity. Heavy hydrocarbons generally have an API gravity below about 20. Heavy oil, for example, generally has an API gravity of about 10-20, whereas tar generally has an API gravity below about 10. The viscosity of heavy hydrocarbons is generally at least 100 centipoise at 15° C. Heavy hydrocarbons may include aromatics or other complex ring hydrocarbons.

[0024] "Hydrocarbons" are generally defined as molecules formed primarily by carbon and hydrogen atoms. Hydrocarbons as used herein may also include metallic elements and/or other compounds that contain, but are not limited to, halogens, nitrogen, oxygen, and/or sulfur. Hydrocarbon compounds that contain sulfur are referred to as "organosulfur compounds." Hydrocarbons may be, but are not limited to, kerogen, bitumen, pyrobitumen, oils, natural mineral waxes, and asphaltites. Hydrocarbons may be located in or adjacent to mineral matrices in the earth. Matrices may include, but are not limited to, sedimentary rock, sands, silicities, carbonates, diatomites, and other porous media. "Hydrocarbon fluids" are fluids that include hydrocarbons. Hydrocarbon fluids may include, entrain, or be entrained in non-hydrocarbon fluids such as hydrogen, nitrogen, carbon monoxide, sulfur oxides, carbonyl sulfide, carbon dioxide, hydrogen sulfide, water, ammonia, or mixtures thereof.

[0025] As used herein, when two or more elements are described as "operatively connected" the elements are defined to be directly or indirectly connected to allow direct or indirect fluid flow between the elements. The term "fluid flow" as used in the definition of operatively connected refers to the flow of a gas or a fluid. As used in the definition of "operatively connected" the term "indirect fluid flow" means that the flow of a fluid or a gas between two defined elements may be directed through one or more additional elements to change one or more aspects of the fluid or gas as the fluid or gas flows between the two defined elements. Aspects of a fluid or a gas that may be changed in indirect fluid flow include physical characteristics, such as the temperature or the pressure of a gas or a fluid, and/or the composition of the gas or fluid, e.g. by separating a component of the gas or fluid, for example, by condensing water from a gas stream containing steam.

[0026] "Oxidant" refers to compounds suitable to support combustion. Examples of oxidants include air, oxygen, and/or enriched air. "Enriched air" refers to air having a larger mole fraction of oxygen than air in the atmosphere. Air is typically enriched to increase combustion-supporting ability of the air.

[0027] "Tar" is a viscous hydrocarbon that generally has a viscosity greater than about 10,000 centipoise at 15° C. The specific gravity of tar generally is greater than 1.000. Tar may have an API gravity less than 10.

[0028] "Tar sands formation" refers to a formation in which hydrocarbons are predominantly present in the form of heavy hydrocarbons and/or tar entrained in a mineral grain framework or other host lithology (for example, sand or carbonate). Examples of tar sands formations include formations such as the Athabasca formation, the Grosmont formation, and the Peace River formation, all three in Alberta, Canada; and the Faja formation in the Orinoco belt in Venezuela.

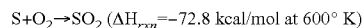
[0029] “Water” refers to the liquid and vapor phases of water. For example, water, steam and super-heated steam.

[0030] In the process of the present invention, heat is provided to a hydrocarbon containing formation. A fuel comprising hydrogen sulfide is provided to one or more surface facilities exterior to the hydrocarbon producing formation, and is combusted in the one or more surface facilities in the presence of an oxidant to produce a combustion by-products stream comprising one or more sulfur oxides. At least a portion of the combustion by-products stream is contacted with water to generate a heat of solution, and the generated heat is transferred to the hydrocarbon formation. Heat from the combustion of the fuel comprising hydrogen sulfide may also be transferred to the hydrocarbon formation by contacting the hot combustion by-products stream with the hydrocarbon formation or by transferring heat from the hot combustion by-products stream to water and then contacting the heated water with the hydrocarbon formation. The heat provided to the hydrocarbon formation may be utilized to mobilize formation fluids so that the formation fluids may be collected and produced from the hydrocarbon formation.

[0031] A drive process may be used in conjunction with the process of the present invention to treat hydrocarbon formations and to mobilize and drive formation fluids to production wells so that the formation fluids may be recovered from the hydrocarbon formation. The drive process may include, but is not limited to, a steam injection process such as cyclic steam injection, a steam assisted gravity drainage process, a solvent injection process, or a vapor solvent and steam assisted gravity drainage process; or a carbon dioxide injection process.

[0032] The fuel comprising hydrogen sulfide utilized in the process of the present invention may include from 1% to 100%, or from 3% to 90%, or from 10% to 80%, or from 20% to 50% of hydrogen sulfide by volume; or at least 1%, or at least 5% or at least 10%, or at least 20%, or at least 25%, or at least 30% of hydrogen sulfide by volume. Hydrogen sulfide content in a stream may be measured using ASTM Method D2420. The fuel stream containing hydrogen sulfide may contain hydrocarbons (for example, methane and ethane) and/or hydrogen. The fuel stream comprising hydrogen sulfide may include other sulfur containing compounds, for example sulfur oxides and organosulfur compounds including methyl thiol, thiophene, thiophene compounds, carbon disulfide, and carbonyl sulfide. The fuel stream comprising hydrogen sulfide may have at least 0.1 grams, or at least 0.3 grams, or at least 0.5 grams, or at least 0.7 grams, or at least 0.9 grams of atomic sulfur per gram of fuel as determined by ASTM Method D4294.

[0033] The fuel stream comprising hydrogen sulfide may be mixed with elemental sulfur for combustion in the presence of an oxidant. Mixing of the fuel stream comprising hydrogen sulfide and elemental sulfur for combustion provides additional sulfur for the formation of sulfur oxides to be combined with water to provide a heat of solution to the hydrocarbon formation as well as additional heat of combustion as shown in the following formula:



Additionally, combustion of elemental sulfur in combination with the fuel stream comprising hydrogen sulfide in the process of the present invention provides a method for disposing of elemental sulfur, where such elemental sulfur may have accumulated from processing of sulfur-contaminated hydrocarbons.

[0034] The fuel stream comprising hydrogen sulfide may also be mixed with a hydrocarbon fuel stream for combustion in the presence of an oxidant. The hydrocarbon fuel stream may comprise gaseous hydrocarbons, and may include methane, ethane, propane, and butane.

[0035] In the process of the present invention, the oxidant with which the fuel stream comprising hydrogen sulfide is combusted is an oxygen-containing gas or liquid. The oxidant is preferably selected from compressed air, oxygen-enriched air, or oxygen gas. Compressed air may be provided as the oxidant in the process of the invention by compressing air by conventional air compressing processes, for example, air may be compressed by passing the air through a turbine compressor. Oxygen-enriched air, which may contain from 0.5 vol. % to 15 vol. % more oxygen than air, may be produced by compressing air and passing the compressed air through a membrane that increases the amount of oxygen in the air. Oxygen gas may be provided as the oxidant by conventional air separation technology.

[0036] The surface facilities in which the fuel stream comprising hydrogen sulfide is combusted in the presence of the oxidant may be any conventional facility for effecting combustion of a fuel stream comprising hydrocarbons that is equipped to handle combustion of hydrogen sulfide. The surface facilities may include one or more conventional combustor reactors in which the fuel stream comprising hydrogen sulfide and the oxidant may be mixed, and the temperature in the combustor reactor may be raised to a temperature above the autoignition temperature of the mixture to initiate combustion of the mixture.

[0037] The surface facilities are located exterior to the hydrocarbon formation operatively connected to the hydrocarbon formation in gaseous or liquid communication with the hydrocarbon formation so that combustion by-products may be delivered from the surface facilities to the hydrocarbon formation. The surface facilities may also be in thermal communication with the hydrocarbon formation so that heat from the combustion of the fuel stream comprising hydrogen sulfide and the oxidant may be provided to the hydrocarbon formation. In an embodiment, one or more combustor reactors in one or more surface facilities are operatively connected in gaseous or liquid communication with the hydrocarbon formation through a wellbore that extends into the hydrocarbon formation and is operatively connected in gaseous or liquid communication with the hydrocarbon formation.

[0038] In the process of the present invention, combustion of the fuel stream comprising hydrogen sulfide in the presence of an oxidant produces a combustion by-products stream comprising sulfur oxides. In some embodiments, the combustion by-products stream includes from 1% to 100%, or from 3% to 90%, or from 10% to 80%, or from 20% to 50% of sulfur oxides by volume, or at least 1%, or at least 5%, or at least 10%, or at least 20%, or at least 25%, or at least 30% of sulfur oxides by volume. The combustion by-products stream may include, but is not limited to, hydrogen sulfide, sulfur dioxide, sulfur trioxide, nitrogen, nitrogen oxide, carbon dioxide, carbonyl sulfide, organosulfur compounds, water and/or oxygen.

[0039] The ratio of total sulfur to oxidant may be controlled during the combustion process. By selecting the amount of total sulfur (from the fuel comprising hydrogen sulfide and, optionally, from elemental sulfur) relative to the amount of oxidant present on the basis of atomic sulfur to atomic oxygen ratio or on a stoichiometric basis—and adjusting the

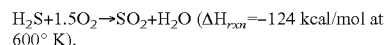
amount of total sulfur to the selected amount, the composition of the combustion by-products produced (for example, hydrogen sulfide, sulfur dioxide and/or sulfur trioxide) may be controlled. The amount of the fuel stream comprising hydrogen sulfide may be controlled, the amount of elemental sulfur may be controlled, and/or the amount the oxidant stream may be controlled to produce a selected ratio of total sulfur to oxidant for combustion such that a preferred combustion by-product stream composition is produced.

[0040] The amounts of the fuel stream comprising hydrogen sulfide, elemental sulfur, and the oxidant stream provided for combustion in the process of the present invention may be controlled in a manner such that combustion generates substantially sulfur trioxide in the combustion by-product stream. To produce a sulfur trioxide-rich combustion by-product stream, the ratio of total sulfur to oxidant may be controlled so that excess oxidant is combusted relative to the amount of total sulfur in the fuel stream comprising hydrogen sulfide and the elemental sulfur. Combusting a total sulfur-lean mixture produces more sulfur trioxide than sulfur dioxide as a combustion by-product. The sulfur trioxide may react with water in the hydrocarbon formation to form sulfuric acid. Sulfur trioxide is readily converted to sulfuric acid, thus heat of solution may be produced and delivered to the hydrocarbon formation more rapidly than when the total sulfur amount combusted is a stoichiometric amount or deficient amount relative to the amount of oxidant.

[0041] Alternatively, the amounts total sulfur and the oxidant provided for combustion in the process of the present invention may be controlled in a manner such that combustion generates substantially sulfur dioxide in the combustion by-product stream. To produce a sulfur dioxide-rich combustion by-product stream, the ratio of hydrogen sulfide and elemental sulfur to oxidant may be controlled so that a deficient amount of oxidant is combusted relative to the total amount of sulfur. Using an excess of total sulfur relative to oxidant produces a combustion by-products stream rich in sulfur dioxide that also contains hydrogen sulfide, and allows hydrogen sulfide and/or sulfur dioxide to be introduced into a layer of the hydrocarbon containing formation. A portion of the hydrogen sulfide and/or sulfur dioxide may contact at least a portion of the formation fluids and solvate and/or dissolve a portion of the heavy hydrocarbons in the formation fluids. Solvation and/or dissolution of at least a portion of the heavy hydrocarbons may facilitate movement of the heavy hydrocarbons towards the production well. Furthermore, introduction of at least a portion of the combustion by-product stream comprising sulfur dioxide into the formation fluids may increase a shear rate applied to hydrocarbon fluids in the formation and decrease the viscosity of non-Newtonian hydrocarbon fluids within the formation. The sulfur dioxide may also drive formation fluids towards production wells. The introduction of the sulfur dioxide rich combustion by-products stream into the formation may thereby increase a portion of the formation available for production, and may increase a ratio of energy output of the formation (energy content of products produced from the formation) to energy input into the formation (energy costs for treating the formation).

[0042] In a further alternative, the amounts of the total sulfur and the oxidant provided for combustion in the process of the present invention may be controlled to provide stoichiometrically equivalent amounts of total sulfur and the oxygen. Combustion of a stoichiometric amount of hydrogen sulfide

with oxygen may generate predominately sulfur dioxide and water as the combustion by-products as shown in the following reaction:



In addition to the heat value that is obtained from combustion of hydrogen sulfide, the introduction of heated sulfur dioxide/water combustion by-product stream into the hydrocarbon formation may facilitate recovery of hydrocarbons from the formation. The heat from the sulfur dioxide may transfer heat to fluids in the formation and the heated fluids may flow towards production wells. Furthermore, as discussed above, the sulfur dioxide in the combustion by-product stream may reduce the viscosity of hydrocarbon formation fluids in the hydrocarbon formation and thereby increase the amount of hydrocarbons available to be recovered from the formation. The heat of solution of sulfur dioxide, although less than the heat of solution of sulfuric acid, may also be transferred to the formation fluids of the hydrocarbon formation thereby mobilizing the formation fluids.

[0043] The combustion by-products stream is contacted with water to generate heat, and the heat is transferred to the hydrocarbon formation. A heat of solution is generated upon contact of the combustion by-products stream with water. Combustion by-products sulfur dioxide, sulfur trioxide, and sulfuric acid, formed by contact of sulfur trioxide with water, generate a heat of solution upon being mixed with water. In addition, heat from the combustion of the fuel stream comprising hydrogen sulfide and the oxidant may be transferred to the water by contacting hot combustion by-products stream with the water to form steam or superheated steam which then may be contacted with the hydrocarbon formation to provide heat to the hydrocarbon formation. If desired, hot combustion by-products from other combustion processes, e.g. combustion of a fuel comprising hydrocarbons, may be combined with the combustion by-products stream from combustion of the fuel comprising hydrogen sulfide to provide additional heat to the hydrocarbon formation.

[0044] The water with which the combustion by-products stream is contacted to generate heat may be water present in the hydrocarbon formation or may be water that is provided to the hydrocarbon formation in conjunction with the combustion by-products stream. In a preferred embodiment, the water is steam provided to the hydrocarbon formation by a steam injection process, where the steam and the combustion by-products stream are injected into a portion of the hydrocarbon layer through a wellbore.

[0045] The combustion by-products stream, in conjunction with water or alone, may be injected into a portion of the hydrocarbon containing formation under pressure. The combustion by-products stream may have a pressure, or may be pressurized to a pressure, of at least 6 MPa, at least 10 MPa, or at least 12 MPa, or equal to the formation pressure, and be injected into the hydrocarbon formation at that pressure through a well or a steam injection well. The combustion by-products stream may be introduced into one or more wells located at depths below the hydrocarbon formation surface of about 100, 200, 500, 1000, 1500, 2500, 5000, or 10000 meters. Heating the hydrocarbon containing formation at shallow depths may allow recovery of hydrocarbons that are not readily accessible through conventional hydrocarbon recovery methods.

[0046] In an embodiment of the process of the present invention, the combustion by-products stream is injected into

a portion of a hydrocarbon formation in combination with a steam injection process. The steam injection process may include steam drive, cyclic steam injection, SAGD, or other processes of steam injection into a hydrocarbon formation. The combustion by-products stream may be injected into a portion of the hydrocarbon formation together with the water/steam through one or more wells and/or the combustion by-products stream and water/steam may be injected into a portion of the hydrocarbon formation in separate wells so that the combustion by-products mix with the injected water in the hydrocarbon formation.

[0047] In an embodiment of the process of the present invention, the combustion by-product stream comprising sulfur oxides and, optionally, water/steam may be combined with carbon dioxide and introduced into the hydrocarbon formation. Introduction of the combustion by-product stream comprising sulfur oxides in combination with steam and/or carbon dioxide may provide heat and/or sufficient drive to mobilize heavy hydrocarbons in the hydrocarbon layer.

[0048] Heat may be transferred to formation fluids (including water), to fluids introduced into the formation, and/or to a portion of the hydrocarbon containing formation through heat of reaction, heat of solvation, conductive heat, or convective heat. Fluids introduced into the formation and/or the combustion by-products stream may transfer heat to at least a portion of the hydrocarbon containing formation and/or formation fluids.

[0049] Convective heat transfer may occur when non-condensable non-miscible gases such as nitrogen contact the formation fluids and/or the hydrocarbon containing formation. When the oxidant stream is formed of compressed air or oxygen-enriched air, the combustion by-product stream may include nitrogen gas. Convective heat transfer may also occur when superheated miscible solvent vapors (for example, hydrogen sulfide, carbon dioxide, and/or sulfur dioxide vapors) contact the formation fluids and/or the hydrocarbon containing formation. Convective heat transfer may also occur when superheated non-miscible solvent vapors such as water contact the formation fluids and/or the hydrocarbon containing formation.

[0050] Conductive heat transfer may occur when hot liquid steam condensate contacts the formation fluids and/or the hydrocarbon containing formation. Conductive heat transfer may occur when hot liquid miscible solvent (for example, hydrogen sulfide, carbon dioxide, and/or sulfur dioxide) contacts the formation fluids and/or the hydrocarbon containing formation.

[0051] Heat of reaction heat transfer may occur when one compound reacts with another compound. For example, sulfur oxides form solutions with liquid water in the hydrocarbon containing formation and/or with water/steam in the well to generate a heat of reaction. Heat of reaction also occurs as oxygen reacts with hydrocarbons or sulfur compounds to form carbon oxides or sulfur oxides.

[0052] Heat of solution may occur when at least one component is dissolved in a solvent. For example, heat is generated when sulfuric acid is dissolved in water.

[0053] Heat that is transferred to the hydrocarbon formation may mobilize formation fluids. One or more production wells may be located in a position to collect the mobilized formation fluids so that the formation fluids may be recovered from the hydrocarbon formation.

[0054] In an embodiment of the process of the present invention, the fuel stream comprising hydrogen sulfide may

be produced from a hydrocarbon formation, preferably the hydrocarbon formation to be heated by combustion of the fuel stream comprising hydrogen sulfide. FIG. 1 depicts a schematic representation of treatment of formation fluids produced from a hydrocarbon formation. The fuel stream comprising hydrogen sulfide may be obtained by separating the hydrogen sulfide from formation fluid produced from hydrocarbon containing formations, gas reservoirs, surface facilities, or combinations thereof. Formation fluid **100** produced from hydrocarbon layer **102** enters fluid separation unit **104** and is separated into liquid stream **106**, gas stream **108** and aqueous stream **110**. Liquid stream **106** may be transported to other processing units and/or storage units. Gas stream **108** may include, but is not limited to, hydrocarbons, carbonyl sulfide, sulfur oxides, hydrogen sulfide, organosulfur compounds, hydrogen, carbon dioxide, or mixtures thereof. Gas stream **108** may enter gas separation unit **112** to separate gas hydrocarbon stream **114** from the gas stream. In gas separation unit **112**, treatment of gas stream **108** separates at least a portion of hydrogen sulfide stream **116**, at least a portion of carbon dioxide stream **118**, at least a portion of sulfur dioxide stream **120**, and/or at least a portion of hydrogen stream **122** from gas hydrocarbon stream **114**. The gas separation unit may treat gases from reservoirs, gas fields and/or waste streams from other surface facilities.

[0055] Gas separation unit **112** may include a physical treatment system and/or a chemical treatment system. The physical treatment system includes, but is not limited to, a membrane unit, a pressure swing adsorption unit, a liquid absorption unit, and/or a cryogenic unit. The chemical treatment system may include units that use amines (for example, diethanolamine or di-isopropanolamine), zinc oxide, sulfolane, water, or mixtures thereof in the treatment process. In some embodiments, gas separation unit **112** uses a Sulfinol gas treatment process for removal of sulfur compounds. Carbon dioxide may be removed using Catacarb® (Catacarb, Overland Park, Kans., U.S.A.) and/or Benfield (UOP, Des Plaines, Ill., U.S.A.) gas treatment processes. The gas separation unit may be a rectified adsorption and high pressure fractionation unit. Carbon dioxide stream **118** may be sequestered and/or used as a drive fluid. Gas hydrocarbon stream **114** and/or hydrogen stream **122** may be used as fuel. For example, gas hydrocarbon stream **114** and/or hydrogen stream **122** may be combusted to heat water or drive turbines to produce electricity. Gas hydrocarbon stream **114** may be used as a fuel in downhole heaters to heat steam and/or layers of a formation.

[0056] The gas separation unit **112** may use a regenerable process to remove sulfur oxides from the gas stream. In such a process, at least a portion of gas stream **108** contacts a material and/or compound that adsorbs at least a portion of the sulfur dioxide from the stream. The adsorbent may be treated to release the sulfur dioxide to form sulfur dioxide stream **120**. Sulfur dioxide stream **120** may include sulfur dioxide and some sulfur trioxide. In some embodiments, sulfur dioxide stream **120** is separated from gas stream **108** using a process as described in U.S. Pat. No. 5,480,619 to Johnson et al. and/or a Cansolv® SO₂ Scrubbing System (Cansolv Technologies, Montreal Canada). Sulfur dioxide stream **120** may contain at least 50% by volume, at least 80% by volume, or at least 99% by volume of sulfur dioxide. Sulfur dioxide content in a stream may be measured using ISO Method 7935.

Sulfur dioxide stream **120** may be stored and/or combined with one or more streams to form a concentrated sulfur dioxide stream.

[0057] Hydrogen sulfide stream **116** may be stored and/or combined with one or more streams to form a concentrated hydrogen sulfide stream. Hydrogen sulfide stream **116** may include from 1% to about 100%, from 3% to 90%, from 10% to 80%, or from 20% to 50% of hydrogen sulfide by volume. Hydrogen sulfide content in a stream may be measured using ASTM Method D2420. In some embodiments, hydrogen sulfide stream **116** includes hydrocarbons (for example, methane and/or ethane) and/or hydrogen. At least a portion of the hydrogen sulfide stream **116** may be used as fuel for down-hole heaters.

[0058] The hydrogen sulfide stream **116** may be dried to remove moisture. For example, hydrogen sulfide stream **116** may be dried by contacting the hydrogen sulfide stream with ethylene glycol to remove water.

[0059] At least a portion of hydrogen sulfide stream **116** enters combustor **126**. At least a portion of gas stream **108**, at least a portion of hydrocarbon stream **114** and/or at least a portion of carbon dioxide stream **118** may enter combustor **126**. In combustor **126**, hydrogen sulfide stream **116**, gas stream **108**, hydrocarbon stream **114**, or mixtures thereof may be reacted with oxidant stream **124** to generate heat and combustion by-products stream **128**. In some embodiments, gas stream **108**, hydrocarbon stream **114**, and/or carbon dioxide stream **118** are not used.

[0060] Combustion by-products stream **128** includes one or more sulfur oxides. The combustion by-products stream **128** may include sulfur dioxide, sulfur trioxide, hydrogen sulfide, oxygen, and/or nitrogen. In some embodiments, at least a portion of sulfur dioxide stream **120** may be combined with a portion of combustion by-products stream **128** to form a stream concentrated in sulfur dioxide.

[0061] Elemental sulfur may be combusted with the hydrogen sulfide stream **116**. Elemental sulfur may be provided to the combustor and/or may be combined with hydrogen sulfide stream **116** and may be burned in combustor **126** along with hydrogen sulfide stream **116** to form combustion by-product stream **128**. In some embodiments, the combined hydrogen sulfide stream and elemental sulfur combusted in combustor **126** have at least 0.1 grams, at least 0.3 grams, at least 0.5 grams, at least 0.7 grams, at least 0.9 grams or at least 0.99 grams of atomic sulfur per gram of combined hydrogen sulfide stream **116** and elemental sulfur as determined by ASTM Method D4294.

[0062] The heat generated from combustor **126** may be used to heat water for a stream that includes steam. The stream may be used for a drive process. Combusting the fuel that includes hydrogen sulfide may produce at least 25% of the heat required to heat the stream that includes steam. In some embodiments, at least 25%, at least 50%, at least 75%, at least 95% or all of the heat necessary to heat water for the drive process, other surface facility processes, other hydrocarbon recovery processes, or combinations thereof is generated through the combustion of the fuel comprising hydrogen sulfide stream **116** and, optionally, elemental sulfur.

[0063] In some embodiments, a method of treating a hydrocarbon containing formation includes combusting a fuel having a sulfur content of at least 0.1 grams of atomic sulfur per gram of fuel, in one or more surface facilities to produce at least one combustion by-products stream. The combustion by-products stream includes one or more sulfur oxides. At

least a portion of the sulfur oxides stream is provided to at least a portion of a hydrocarbon containing formation. A stream that includes steam is provided to a plurality of wellbores in the hydrocarbon containing formation. At least a portion of the sulfur oxides stream is contacted with at least a portion of the steam provided to the hydrocarbon formation and/or water in the formation to generate heat.

[0064] The composition of combustion by-products stream **128** to be injected may be controlled. In some embodiments, the composition of combustion by-products stream **128** to be injected may be controlled by mixing various streams of hydrogen sulfide combustion products. In some embodiments, the composition of combustion by-products stream **128** is adjusted by combining sulfur dioxide stream **120** with combustion by-products stream **128**. In some embodiments, combustion by-products stream **128** is heated and directly introduced into the formation and/or a wellbore. In some embodiments at least a portion of the fuel that includes hydrogen sulfide produces hot water and further comprising providing at least a portion of the hot water to the hydrocarbon containing formation.

[0065] FIGS. 2 and 3 depict representations of systems for producing hydrocarbons from a hydrocarbon containing formation (for example, a tar sands formation). Hydrocarbon layer **102** includes one or more portions with heavy hydrocarbons. Hydrocarbon layer **102** may be below overburden **130**. Hydrocarbons may be produced from hydrocarbon layer **102** using more than one process.

[0066] Hydrocarbons may be produced from a portion of hydrocarbon layer **102** using a steam injection process. In the steam injection process, a stream that includes steam **132** is introduced into hydrocarbon layer **102** through openings **134** in injection well **136**. As shown in FIG. 2, the steam injection process uses a substantially vertical well. It should be understood that any well configuration (for example, substantially horizontal or substantially diagonal) may be used. In some embodiments, the terminus of steam injection well **136** is at a depth of below 100, 200, 500, 1000, 1500, 2500, 5000, or 10000 meters.

[0067] In some embodiments, heated carbon dioxide alone or in combination with steam **132** is introduced into injection well **136**. Introduction of at least a portion of heated carbon dioxide may facilitate movement of formation fluids to production well **138** by heating, driving and/or reducing the viscosity of the formation fluids. The injection of at least portion of the carbon dioxide into the wellbore may be beneficial as an abatement of carbon dioxide emissions. In some embodiments, steam **132** includes carbon dioxide, nitrogen and/or sulfur dioxide. For example, steam **132** may be combined with at least a portion of sulfur dioxide stream **120** and/or at least a portion of combustion by-products stream **128**.

[0068] In some embodiments, a portion of hydrocarbon layer **102** is treated using heaters prior to the steam injection process. Heaters may be used to increase the temperature and/or permeability of a portion of the hydrocarbon layer **102**. Some hydrocarbons may be produced through production well **138** by heating the hydrocarbon layer. Formation fluids **100** removed through production well **138** may be sent to surface facilities (as shown in FIG. 1). In some embodiments, hydrocarbon layer **102** is not heated prior to steam injection. The pattern and number of injection wells, heater wells and

production wells may be any number or geometry sufficient to achieve production of formation fluids from a hydrocarbon containing formation.

[0069] In some embodiments, injection well 136 includes a heater or a series of heaters. In some embodiments, heaters are inserted in injection well 136 after some hydrocarbons have been produced from hydrocarbon layer 102. In some embodiments, heaters in injection well 136 may combust fuel to heat steam injected in the injection well.

[0070] In some embodiments, a portion of steam 132 is introduced into injection well 136 at temperatures of at least 200° C., at least 225° C., at least 250° C., or at least 260° C. and at pressures ranging from about 1 MPa to about 15 MPa. The steam injected into the formation may move and/or drive heavy hydrocarbon towards production well 138.

[0071] A portion of combustion by-products stream 128 may enter injection well 136 via conduit 140. In some embodiments, sulfur dioxide stream 120 is combined with combustion by-products stream 128. In some embodiments, at least a portion of the combustion by-products stream that includes one or more sulfur oxides is mixed with a stream that includes steam prior to providing the stream comprising steam to the hydrocarbon containing formation.

[0072] In some embodiments, conduit 140 may include openings 142 to allow combustion by-products stream 128 to mix with steam 132 and/or water present in the formation. Steam 132, the mixture of steam 132 and combustion by-products stream 128, and/or the mixture of combustion by-products stream and formation water may transfer heat to hydrocarbon layer 102. Steam 132, the mixture of steam 132 and combustion by-products stream 128, and/or the combustion by-products stream 128 itself enters into hydrocarbon layer 102 through openings 134 in injection well 136.

[0073] In some embodiments, combustion by-products stream 128 is injected directly into steam 132 in injection well 136 and/or mixed with steam 132 prior to injection into the injection well. Combustion by-product streams from other processes may also be combined with steam 132 prior to introduction of steam 132 into injection well 136. Combining at least a portion of combustion by-products stream 128 and, optionally, other combustion by-products stream(s) provides heat to at least a portion of steam 132.

[0074] At least a portion of sulfur dioxide stream 120 may be combined with a stream that includes steam 132 at the wellhead of injection well 136 as well. Combining at least a portion of the sulfur dioxide stream 120 with steam 132 may heat at least a portion of the steam and provides the stream with an additional formation fluid drive agent.

[0075] Openings 142 may be opened and/or closed to allow combustion by-products stream 128 to be introduced into specific portions of injection well 136 and/or hydrocarbon layer 102. The position of conduit 140 may be adjusted to allow the conduit to be positioned in various parts of the injection well 136. A portion of steam 132 may be introduced into the portion of injection well 136 between the outer wall of conduit 140 and the inner wall of injection well 136.

[0076] In some embodiments, the portion between outer wall of conduit 140 and inner wall of injection well 136 is a conduit that communicates with the injection well and the conduit. A portion of steam 132 and combustion by-products stream 128 may be introduced into conduit 140 and between the outer wall of conduit 140 and the inner wall of injection well 136.

[0077] As shown in FIG. 3, a portion of combustion by-products stream 128 may enter injection well 144 positioned between injection well 136 and production well 138 in hydrocarbon layer 102. Injection well 144 may include openings 146 to allow combustion by-products stream 128 to enter the formation and mix with formation water and/or with steam 132 as the steam flows into the formation through openings 134 into hydrocarbon layer 102. Mixing of steam, cooled steam, and/or formation water with the combustion by-products stream releases heat into the hydrocarbon formation.

[0078] Injection wells 136, 144 may be fabricated from materials known in the art to be resistant to sulfur oxides. For example, injection wells 136, 144 may be made from Hastelloy® C276, alloy 230, alloy 800H, alloy 370H, nickel/copper/iron alloys, or cobalt-chromium alloys.

[0079] Heat from steam 132 may form a first heated zone. Hydrocarbons in hydrocarbon layer 102 may be mobilized by the heat and produced from production well 138.

[0080] In some embodiments, sulfur oxides in combustion by-product stream 128 in water may generate additional convective and/or conductive heat in hydrocarbon layer 102 and form a second heated zone. Heat from the second heated zone may transfer to a portion of hydrocarbon layer 102 and mobilize formation fluids towards production well 138.

[0081] Contact of at least a portion of the combustion by-products stream 128 with water 132 may heat the water in injection well 136 and/or hydrocarbon layer 102 to form a second heated zone. The second heated zone may heat a portion of the hydrocarbon layer 102 proximate the end of injection well 136 and/or extend into hydrocarbon layer 102. Due to the heat from the combustion by-products stream, an increased amount of hydrocarbons may be produced per volume as compared to conventional drive fluid processes. The first and second heat zones may overlap.

[0082] In some embodiments, the second heated zone is a substantial distance from injection well 136. For example, the combustion by-products stream may drive the steam into the formation. As the steam condenses, the sulfur oxides in the combustion by-products stream may react with the condensed water and/or water in the formation to generate heat from the formation of sulfuric acid. The sulfuric acid may mix with water and release heat of solution. Released heat and/or generated heat from the combustion by-products stream may heat the formation sufficiently to mobilize hydrocarbons toward production well 138. The combination of steam heating in combination with latent heating (heating after the steam condenses) may facilitate recovery of hydrocarbons from the formation. The combination of sensible heat for all introduced components and latent heat may reduce energy and/or heating requirements for producing hydrocarbons from the formation as compared to the energy and/or heating requirements for conventional hydrocarbon recovery processes.

[0083] In some embodiments, a portion of combustion by-products stream 128 and/or sulfur dioxide stream 120 may be compressed to form a liquid stream. Liquid sulfur dioxide may enhance dissolution of organic compounds. In some embodiments, a portion of the sulfur dioxide stream and/or a portion of the combustion by-products stream may be compressed prior to injection into the hydrocarbon formation and/or a wellbore.

[0084] In some embodiments, the formation contains limestone. As the sulfur oxides contact the formation in the presence of water, the limestone reacts with the sulfur oxides and

produces carbon dioxide. The carbon dioxide may serve as an additional drive fluid to push the fluids towards production well **138**.

[0085] In some embodiments, as the combustion by-products stream and/or the sulfur dioxide stream is/are introduced into the formation, the stream(s) may increase a shear rate applied to hydrocarbon fluids in the formation and decrease the viscosity of non-Newtonian hydrocarbon fluids within the formation. The introduction of combustion by-products stream and/or the sulfur dioxide stream(s) into the formation may increase a portion of the formation available for production. Introduction of the combustion by-products stream and/or the sulfur dioxide stream(s) may increase a ratio of energy output of the formation (energy content of products produced from the formation) to energy input into the formation (energy costs for treating the formation).

[0086] In some embodiments, combustion of the fuel containing hydrogen sulfide and hydrocarbon gases in the presence of the oxidant produces a combustion by-products stream that includes sulfur oxides, and other non-hydrocarbon gases, for example, nitrogen, nitrogen oxide, organosulfur compounds, carbonyl sulfide, and carbon dioxide. The production of carbon dioxide, nitrogen and/or nitrogen oxide during combustion of hydrocarbons in the fuel stream may facilitate heating steam **132**, driving steam **132** into hydrocarbon layer **102** and/or move formation fluids towards production well **138**.

[0087] Formation fluids (for example, heavy hydrocarbons) produced from production well **138** may be treated in a surface facility (for example, in surface facilities described in FIG. 1) to form a gas stream and a liquid stream. The gas stream may include hydrogen sulfide, hydrocarbon gases, sulfur dioxide, nitrogen, nitrogen oxide, organosulfur compounds, carbonyl sulfide, and/or carbon dioxide. Some of the gas stream may enter a combustor (for example, see combustor **126** in FIG. 1). At least a portion of the sulfur dioxide in the gas stream produced from production well **138** may be oxidized in the presence of oxidant in the combustor **126** and form combustion by-products stream **128** enriched in sulfur trioxide. The enriched sulfur trioxide stream may be introduced into hydrocarbon layer **102**, mix with steam **132**, and release heat of solution. Recycling of sulfur dioxide in such a manner, provides a method to substantially abate all of the sulfur emissions produced by combustor **126**, thus reducing emissions as compared to gas emissions generated by combustion of hydrocarbons alone (for example, generation of carbon dioxide).

[0088] In some embodiments, the sulfur dioxide is separated from the produced gas stream in a surface facility (for example, in surface facilities described in FIG. 1) to produce sulfur dioxide stream **120** and combined with combustion by-products stream **128**. In some embodiments, the sulfur dioxide stream **120** is directly introduced into injection well **144** and/or hydrocarbon containing formation **102**.

[0089] Steam **132** may include one or more surfactants and/or one or more foaming agents. Surfactants include thermally stable surfactants (for example, sulfonates, alkyl benzene sulfonates, ethoxylated sulfates, and/or phosphates). The use of foaming agents and/or surfactants may change the surface tension between the hydrocarbons and the formation to facilitate mobilization of hydrocarbons towards production well **138**. A foaming agent may be used to inhibit foaming of the formations fluids when carbon dioxide and surfactants are present.

[0090] Steam **132** may include hydrogen sulfide and or hydrogen. The hydrogen sulfide and/or hydrogen may solvate, dilute, and/or hydrogenate a portion of the heavy hydrocarbons to form a mixture that may move toward production well **138**. Formation of the mixture may increase production of hydrocarbons in hydrocarbon layer **102**. Solubilization, dilution and/or hydrogenation of a portion of the heavy hydrocarbons may allow an increase in the amount of hydrocarbons produced from the hydrocarbon layer. The solvents and/or hydrogen sulfide may be separated from the mixture and injected with steam **132** or used as a fuel in other processes and/or for heaters. In some embodiments, heat from hydrogenation of hydrocarbons transfers to a portion of hydrocarbon layer **102**.

[0091] Further modifications and alternative embodiments of various aspects of the invention will 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 examples of 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.

What is claimed is:

1. A method of treating a hydrocarbon containing formation, comprising:
 - providing a fuel comprising hydrogen sulfide to one or more surface facilities exterior to a hydrocarbon containing formation;
 - combusting at least a portion of the fuel comprising hydrogen sulfide in the presence of an oxidant in at least one of the surface facilities to produce at least one combustion by-products stream comprising one or more sulfur oxides;
 - contacting at least a portion of the combustion by-products stream comprising one or more sulfur oxides with water to generate heat; and
 - transferring the heat generated by contacting the combustion by-products stream with water to the hydrocarbon containing formation.
2. The method of claim 1 further comprising the step of:
 - providing a stream comprising steam to a portion of the hydrocarbon containing formation, wherein at least a portion of the stream comprising steam comprises at least a portion of the water contacted with the combustion by-products stream to generate heat.
3. The method claim 2 further comprising the step of providing at least a portion of the combustion by-products stream comprising one or more sulfur oxides to at least a portion of a hydrocarbon containing formation; wherein at least a portion of the stream comprising steam is contacted with the combustion by-products stream in the hydrocarbon formation.
4. The method of claim 2, further comprising heating at least a portion of the stream comprising steam with at least a

portion of the combustion by-products stream prior to providing the stream comprising steam to the hydrocarbon containing formation.

5. The method of claim 2 wherein the at least a portion of the stream comprising steam is contacted with the combustion by-products stream in the wellbore adjacent the hydrocarbon formation.

6. The method of claim 2 wherein at least a portion of the water contacted with the combustion by-products stream is water present in the hydrocarbon formation.

7. The method of claim 1 wherein at least a portion of the water contacted with the combustion by-products stream is water present in the hydrocarbon formation.

8. The method of claim 1, wherein the fuel comprises at least 1% hydrogen sulfide by volume as determined by ASTM Method D2420.

9. The method of claim 1, wherein the fuel comprises elemental sulfur.

10. The method of claim 1, wherein providing the combustion by-products stream comprising one or more sulfur oxides comprises introducing the combustion by-products stream comprising one or more sulfur oxides into one or more wells

in the hydrocarbon containing formation positioned proximate a portion of hydrocarbon formation containing the steam.

11. The method of claim 1, wherein providing the combustion by-products stream comprising one or more sulfur oxides comprises introducing combustion by-products stream comprising one or more sulfur oxides into a downstream portion of a steam injection well.

12. The method of claim 1, wherein at least one of the sulfur oxides comprises sulfur dioxide and contacting comprises solvating at least a portion of the formation fluids with the sulfur dioxide.

13. The method of claim 1, further comprising the steps of mobilizing at least a portion of hydrocarbons in the hydrocarbon containing formation with the generated heat; and recovering at least a portion of the mobilized hydrocarbons.

14. The method of claim 1, wherein the hydrogen sulfide is obtained by separating the hydrogen sulfide from formation fluid produced from hydrocarbon containing formations, gas reservoirs, surface facilities, or combinations thereof.

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