



(51) International Patent Classification:

C10G 45/46 (2006.01) *C10G 45/00* (2006.01)
B01J 29/06 (2006.01) *B01J 29/00* (2006.01)

(21) International Application Number:

PCT/US2012/022918

(22) International Filing Date:

27 January 2012 (27.01.2012)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

61/446,750 25 February 2011 (25.02.2011) US
11170738.6 21 June 2011 (21.06.2011) EP

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU,

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(54) Title: KEROGENE RECOVERY AND IN SITU OR EX SITU CRACKING PROCESS

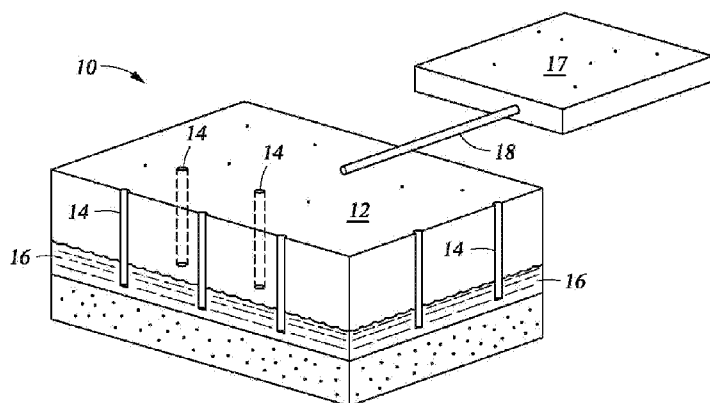


Fig. 1

(57) Abstract: A method of obtaining a thermal cracking feedstock for the production of olefins from an in-situ extracted oil-shale formation. The method comprises the steps of obtaining compositional analyses data for a set of in-situ extracted shale oils, the set of in-situ extracted shale oils produced at varied production temperatures and/or levels of lithostatic stress; determining from the compositional analyses data a value of a production temperature or a lithostatic stress that when achieved produces an in-situ extracted shale oil having a concentration of aromatics at or below a target level, the target level suitable for the production of olefins by thermal cracking; adjusting oil-shale formation extraction conditions to achieve the values for production temperature and/or lithostatic stress; and producing an in-situ extracted shale oil suitable for use as a thermal cracking feedstock for the production of olefins. A method for processing a hydrocarbon produced from a feed oil-shale formation to produce olefins is also provided.



TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

Published:

— *with international search report (Art. 21(3))*

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

CROSS-REFERENCE RELATED APPLICATIONS

[0001] This application claims priority from US Serial No. 61/446750, filed February 25, 2011, and EP 11170738.6, filed June 21, 2011, the disclosures of which are incorporated by reference in their entireties.

FIELD

[0002] This disclosure relates generally to integrated methods for chemicals manufacture from shale oil resources.

BACKGROUND

[0003] In the manufacture of chemicals, a variety of thermal, catalytic and separation-based technologies are employed, each frequently having their own feedstock requirements. For example, cracking, which is one pyrolysis process, is used to crack various hydrocarbon feedstocks into olefins, preferably light olefins, such as ethylene, propylene, and butenes. Conventional cracking processes may involve thermal cracking, partial oxidation or steam cracking systems. In particular, steam cracking systems are known to be effective for cracking high-quality feedstock, which contain a large fraction of volatile hydrocarbons, such as gas oil and naphtha.

[0004] Conventional thermal cracking utilizes a pyrolysis furnace which has two main sections: a convection section and a radiant section. The hydrocarbon feedstock typically enters the convection section of the furnace as a liquid (except for light low molecular weight feedstocks which enter as a vapor), wherein it is typically heated and vaporized by indirect contact with hot flue gas from the radiant section and, to a lesser extent, by direct contact with steam. The vaporized feedstock and steam mixture is then introduced into the radiant section where cracking takes place. Pyrolysis involves heating the feedstock sufficiently to cause thermal decomposition of the larger molecules. The resulting products, including olefins, leave the pyrolysis furnace for further downstream processing, including quenching.

[0005] The cracking economics sometimes favor cracking lower cost heavy feedstocks, such as crude oil, atmospheric residue and other feedstocks. These feedstocks often contain high molecular weight, non-volatile components with boiling points in excess of 590°C, otherwise known as asphaltenes, bitumen, or resid. The non-volatile components of these feedstocks have the tendency to lay down as coke in the convection section of conventional pyrolysis furnaces. Only very low levels of non-volatile components can be tolerated in the convection section downstream of the dry point where the lighter components have fully vaporized.

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[0006] Chemical manufacturing economics may favor additional feedstocks in the future. One potential feedstock is a kerogen-derived feedstock. Kerogen is a solid, carbonaceous material, which can become imbedded in rock formations. The kerogen-imbedded rock is referred to as oil-shale. Oil-shale is a vast fossil energy resource that has potential to yield liquids that may be used as a chemical feedstock.

[0007] Kerogens may decompose based upon exposure to heat over a period of time. Upon heating, kerogen molecularly decomposes to produce oil, gas, and carbonaceous coke. Small amounts of water may also be generated. The oil, gas, and water fluids are mobile within the rock matrix, while the carbonaceous coke remains essentially immobile.

[0008] Oil-shale formations are found in various areas world-wide. Oil-shale formations tend to reside at relatively shallow depths. These formations are often characterized by limited permeability. The decomposition rate of kerogen to produce mobile hydrocarbons is time and temperature dependent. Temperatures generally in excess of 270°C over the course of many months may be required for substantial conversion. At higher temperatures substantial conversion may occur within shorter times. When kerogen is heated, chemical reactions break the larger molecules forming the solid kerogen into smaller molecules of oil and gas (together with water and coke as byproducts). The thermal conversion process is referred to as retorting.

[0009] Attempts have been made for many years to extract oil from oil-shale formations. Commercial oil-shale retorting through surface mining has been conducted in the United States as well as Australia, Brazil, China, Estonia, France, Russia, South Africa, Spain, Scotland, and Sweden. However, the practice has been mostly discontinued in recent years because it proved to be uneconomical or because of environmental constraints. Further, surface retorting typically involves mining of the oil-shale, which limits application to very shallow formations.

[0010] Various documents describe the process of applying heat to the oil-shale formation in-situ to distill and produce hydrocarbons, such as in U.S. Patent Nos. 2,634,961; 2,732,195; 2,780,450; 2,789,805; 2,923,535; 4,886,118; and 6,688,387. Specifically, U.S. Patent No. 2,732,195 describes the introduction of heat supply channels through bore holes drilled into the formation. The bore holes received an electrical heat conductor which transferred heat to the surrounding oil-shale. Thus, the heat supply channels served as heat injection wells. The electrical heating elements in the heat injection wells were placed within sand, cement, or other heat-conductive material to permit the heat injection well to transmit heat into the surrounding oil-shale, while preventing the inflow of fluid. U.S. Patent No.

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2,732,195 describes heating the heater and heating material to between 500°C and 1000°C in some applications. Along with the heat injection wells, fluid producing wells were also completed in near proximity to the heat injection wells. As kerogen was retorted upon heat conduction into the rock matrix, the resulting oil and gas is recovered through the adjacent
5 production wells.

[0011] Further, other approaches may utilize different techniques to produce the hydrocarbons. For instance, U.S. Patent No. 4,458,757 describes a process for converting organic material of oil-shale into predominantly liquids, by heating the formation to temperatures from about 360°C to 475°C in an anionic atmosphere and collecting the
10 resulting liquids and gases via a microemulsion capable of extracting organic material from the heat treated oil-shale. Also, U.S. Patent No. 7,575,052 describes an in-situ heat treatment process that utilizes a circulation system to heat one or more treatment areas. U.S. Patent Application Publication No. 2010/0126727 describes an in-situ process for heating a formation with heaters to retort at least some hydrocarbons, which are then produced from
15 the formation.

[0012] As another example, U.S. Patent Application Publication No. 2008/0207970 describes a method of producing hydrocarbon fluids with improved hydrocarbon compound properties from a subsurface organic-rich rock formation, such as an oil-shale formation. The method includes the step of heating the organic-rich rock formation in-situ. In accordance
20 with the method, the heating of the organic-rich rock formation may retort at least a portion of the formation hydrocarbons, for example kerogen, to create hydrocarbon fluids. Thereafter, the hydrocarbon fluids may be produced from the formation. Hydrocarbon fluids with improved hydrocarbon compound properties are also proposed.

[0013] Despite these advances in the art of producing hydrocarbon fluids from kerogen, a
25 need exists for tailoring these fluids to the manufacture of chemicals and, in particular, to the production of advantaged feedstocks for the manufacture of chemicals.

SUMMARY

[0014] In one aspect, a method is provided of obtaining a thermal cracking feedstock for the production of olefins from an in-situ extracted oil-shale formation. The method
30 comprises the steps of obtaining compositional analyses data for a set of in-situ extracted shale oils, the set of in-situ extracted shale oils produced at varied production temperatures and/or levels of lithostatic stress; determining from the compositional analyses data a value of production temperature or lithostatic stress that when achieved produces an in-situ extracted shale oil having a concentration of aromatics at or below a target level, the target level

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suitable for the production of olefins by thermal cracking; adjusting oil-shale formation extraction conditions to achieve the values for production temperature and/or lithostatic stress; and producing an in-situ extracted shale oil suitable for use as a thermal cracking feedstock for the production of olefins.

5 **[0015]** In one or more embodiments, various features may be further clarified. For instance, the in-situ extracted shale oil may have a hydrogen content of at least about 12.0 weight percent (wt%). Further, the value for production temperature may be less than or equal to about 475°C, within the range of about 350°C to about 450°C, within the range of about 325°C to about 450°C, within the range of about 375°C to about 425°C, or less than or
10 equal to about 350°C. Also, the value for lithostatic stress may be between about 0 and about 17237 kiloPascals (kPa) gauge. Further, the compositional analysis includes gas and liquid chromatography and/or mass spectrometry.

[0016] Further, in one or more embodiments, a method is described for obtaining and processing hydrocarbons to produce olefins. The method comprises the steps of obtaining
15 hydrocarbons from a oil-shale formation, the hydrocarbons having a hydrogen content of at least about 12 wt%; introducing the hydrocarbons to a cracking reactor without prior hydrotreating; producing effluent from the hydrocarbons in the cracking reactor; and processing the effluent to produce olefins.

[0017] In yet another embodiment, a method for obtaining and processing hydrocarbons
20 is provided. The method comprises the steps of heating a portion of an oil-shale formation to a production temperature of less than or equal to about 475°C, to cause the separation of a kerogen-derived oil from the rock in the oil-shale formation; recovering the kerogen-derived oil from the oil-shale formation; passing at least a portion of the kerogen-derived oil to a cracking reactor; producing effluent from the at least the portion of the kerogen-derived oil in
25 the cracking reactor; and processing the effluent to produce olefins.

[0018] Further still, in yet another embodiment, a method for processing a hydrocarbon produced from an oil-shale formation to produce olefins is provided. The method comprises the steps of obtaining operational data about production of a hydrocarbon feed; determining whether the operational data indicates that the hydrocarbon feed was produced via an in-situ
30 method or an ex-situ method; and (i) if the operational data indicates that the hydrocarbon feed was produced via an in-situ method, processing the hydrocarbon feed without hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in a conversion process, such as a thermal cracking furnace; or (ii) if the operational data indicates that the

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hydrocarbon feed was produced via an ex-situ method, hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in the furnace.

[0019] These and other advantages, features and attributes of the disclosed methods and systems and their advantageous applications and/or uses will be apparent from the detailed description that follows, particularly when read in conjunction with the figures appended hereto.

BRIEF DESCRIPTION OF THE DRAWINGS

[0020] The disclosure is further explained in the description that follows with reference to the drawings illustrating, by way of non-limiting examples, various embodiments wherein:

10 [0021] FIG. 1 is a cross-sectional view of an exemplary subsurface area that includes an organic-rich rock matrix that defines the subsurface formation.

[0022] FIG. 2 is a flow chart of an exemplary oil and gas in-situ thermal recovery process from an organic-rich rock formation in accordance with the present techniques.

15 [0023] FIG. 3 is a cross-sectional view of an exemplary oil-shale formation that is within or connected to groundwater aquifers and a formation leaching operation in accordance with the present techniques.

[0024] FIG. 4 is a schematic flow diagram of an apparatus employed with a pyrolysis furnace for the manufacture of chemicals, in accordance with an exemplary embodiment.

DETAILED DESCRIPTION

20 [0025] Various aspects will now be described with reference to specific embodiments selected for purposes of illustration. It will be appreciated that the spirit and scope of the processes disclosed herein are not limited to the selected embodiments. Moreover, it is to be noted that the figures provided herein are not drawn to any particular proportion or scale, and that many variations can be made to the illustrated embodiments.

25 [0026] In one aspect, disclosed herein are methods for the manufacture of chemicals that integrate oil-shale resources, upstream production, and downstream manufacturing resources to provide enhanced efficiency and selectivity. The methods involve production of shale oils from oil-shale deposits using in-situ production methods combined with downstream processing to produce basic chemicals, such as olefins and aromatics that can be further
30 processed to produce a wide variety of finished derivative products, such as polyolefins and polyesters. Beneficially, certain hydrocarbons, such as shale oils, produced using in-situ methods have enhanced compositional characteristics for producing chemicals as compared to hydrocarbons, such as synthetic oils, produced using more conventional mining and ex-situ

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oil-shale retorting methods. Accordingly, the process includes a method of monitoring and adjusting formation extraction conditions for a formation, which enhances olefin recovery.

[0027] One embodiment disclosed herein includes an in-situ method of producing hydrocarbon fluids with enhanced properties from an organic-rich rock formation. The enhanced properties are associated with the extraction conditions from the formation. That is, the quality of the hydrocarbon fluids produced from in-situ heating and retorting of an organic-rich rock formation may be enhanced by selecting sections of the organic-rich rock formation with a certain lithostatic stress for in-situ heating and retorting. Further, it has been discovered that the temperature at which the in-situ retorting is accomplished has an effect on the composition of the produced fluid, that the effect of increasing temperature generally affects the composition of the produced fluid in the same direction as increasing lithostatic stress, and that the effect of decreasing temperature generally affects the composition of the produced fluid in the same direction as decreasing lithostatic stress. Moreover, it has been discovered that the pore pressure at which the in-situ retorting is conducted affects the composition of the produced fluid that the compositional effect of increasing pressure is generally in a direction opposite to the effects of increasing lithostatic stress and temperature. However, it is believed that the compositional effect of pressure is generally of a much lower magnitude than the effects of temperature and lithostatic stress.

[0028] The method may include creating the hydrocarbon fluid by retorting of a solid hydrocarbon and/or a heavy hydrocarbon present in the organic-rich rock formation. Certain embodiments may include the hydrocarbon fluid being partially, predominantly, substantially or completely created by retorting of the solid hydrocarbon and/or heavy hydrocarbon present in the organic-rich rock formation.

[0029] Further still, the method may include controlling the temperature or range of temperatures in the section of the organic-rich rock formation to effect the composition of the produced hydrocarbon fluids. For example, the heating rate of sources of in-situ heat may be set or adjusted to affect the temperature profile of the section of the organic-rich rock formation. The density or configuration of the sources of in-situ heat may be implemented or adjusted to effect the composition of the produced hydrocarbon fluid. Higher temperatures favor the production of aromatics and cyclic hydrocarbon compounds, while lower temperatures favor the production of normal and isoprenoid (or branched) hydrocarbon compounds. Alternatively, lower temperatures tend to decrease aromatic and cyclic hydrocarbon compound production while higher temperatures tend to decrease concentration of normal and isoprenoid (or branched) hydrocarbon compounds. Thus, the method may

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include exposing a section of the organic-rich rock formation to a maximum temperature above 270°C, e.g., a maximum temperature $\leq 750^\circ\text{C}$. Alternatively, the method may include heating the section of the organic-rich rock formation to a maximum temperature between 270°C and 600°C, between 270°C to 550°C, between 270°C to 500°C, between 270°C to 450°C, between 270°C to 400°C, or between 270°C to 350°C depending on the composition desired. Also, the method may include heating the section of the organic-rich rock formation to a maximum temperature between 350°C and 500°C, between 350°C to 550°C, between 350°C to 600°C, between 350°C to 650°C, between 350°C to 700°C, or between 350°C to 750°C depending on the composition desired. The method may include heating the section of the organic-rich rock formation by any method, including any of the methods described herein. For example, the method may include heating the section of the organic-rich rock formation by electrical resistance heating. Further, the method may include heating the section of the organic-rich rock formation through use of a heated heat transfer fluid.

[0030] Further, the method may include maintaining a range of pressures in the section of the organic-rich rock formation to effect the composition of the produced hydrocarbon fluid. One method of maintaining a range of pressures in the section of the organic-rich rock formation includes selecting the section by estimating the section's lithostatic stress to limit the maximum pressure that such a section is predicted to experience by relying on the creation of fractures to relieve the pressure force due to in-situ heating. The effect of pressure when combined with lithostatic stress tends to alter the effect of lithostatic stress on the composition of the produced fluid. Lower pore pressures when combined with higher lithostatic stress tend to enhance production of aromatic and cyclic hydrocarbon compounds and decrease production of normal and isoprenoid (or branched) hydrocarbon compounds. Alternatively, higher pore pressures when combined with lower lithostatic stress tend to incrementally reduce production of aromatic and cyclic hydrocarbon compounds and increase production of normal and isoprenoid (or branched) hydrocarbon compounds. Thus, the method may include maintaining the pressure of a heated section of an organic-rich rock formation above 1379 kPa and producing a hydrocarbon fluid from the heated section of the organic-rich rock formation. In alternative embodiments, the method may include maintaining the pressure of a heated section of the organic-rich rock formation below 20684 kPa. In alternative embodiments, the method may include maintaining the pressure of a heated section of the organic-rich rock formation below 17237 kPa, below 13790 kPa, or below 10342 kPa depending on the composition desired. In alternative embodiments, the method may include allowing the pressure of a heated section of the organic-rich rock

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formation to reach a maximum pressure above 2758 kPa, above 3447 kPa, above 5516 kPa, above 6895 kPa, above 10342 kPa, or above 13790 kPa depending on the composition desired. In alternative embodiments, the method may include allowing the pressure of a heated section of the organic-rich rock formation to reach a maximum pressure between 1379 kPa and 6895 kPa, between 1379 kPa and 6205 kPa, between 1379 kPa and 5516 kPa, between 1379 kPa and 4826 kPa, or between 1379 kPa and 4137 kPa depending on the composition desired. In alternative embodiments, the method may include allowing the pressure of a heated section of the organic-rich rock formation to reach a maximum pressure between 5516 kPa and 20684 kPa, between 6205 kPa and 20684 kPa, between 6895 kPa and 20684 kPa, between 8273 kPa and 20684 kPa, or between 10342 kPa and 20684 kPa depending on the composition desired.

[0031] The impact of controlling production operations (e.g., extraction conditions, such as formation stress, temperature of the in-situ heating and retorting of organic-rich rock formations) on the ability to produce hydrocarbon fluids with certain desired properties is demonstrated in U.S. Patent Application Publication No. 2008/0207970, which is hereby incorporated by reference in its entirety for all that it discloses. From the production operational data in this reference, the temperature, pressure and lithostatic stress may affect the composition of fluids produced via in-situ heating and retorting.

[0032] Accordingly, the composition of the hydrocarbon fluids produced from in-situ heating and retorting may also be adjusted by selecting, maintaining and/or in some situations controlling one or more of the following: in-situ temperature, in-situ pressure, and/or in-situ lithostatic stress conditions of the organic-rich rock formation being heated in the in-situ process (e.g., the formation extraction conditions). By selecting, maintaining, and/or in some cases controlling the heating and retorting conditions of oil-shale, a condensable hydrocarbon fluid product that has desired compositional properties may be obtained. Such a product may be suitable for refining into gasoline and distillate products. Further, such a product, either before or after further fractionation, may have utility as a hydrocarbon feed for certain chemical processes.

[0033] Moreover, the composition of the produced shale oil can be beneficially tailored by using different operating conditions for in-situ heating. In particular, oils which are produced by gradually heating at lower temperatures and under conditions that limit lithostatic stress are preferred for producing ethylene and propylene by steam cracking or related chemical production conversion technologies, such as pyrolysis processes. Oils, which are produced by in-situ heating at higher temperatures and under conditions of higher

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lithostatic stress, contain higher concentrations of single ring aromatics that are preferred feedstocks for producing aromatic building blocks, such as benzene and paraxylene. Shale oils produced by in-situ heating contain lower concentrations of condensed ring aromatic structures, such as naphthalenes, phenanthrenes, and higher analogs which are undesirable in chemical processes.

5 **[0034]** Further, to produce advantaged feedstocks for use in the manufacture of chemicals, it is contemplated that advanced characterization methods be used to analyze the produced oils and optimize the severity of the production methods to produce oils that are better suited for manufacturing chemicals. As may be appreciated, in-situ retorting provides this capability, because in ex-situ retorting, the mined oil-shale is exposed to high temperatures above 475°C during the retorting process. Characterization methods suitable for this purpose include liquid and liquid-liquid chromatography and high resolution mass spectrometry, among others. In general, it is desirable to maintain effective production temperatures below about 400°C to produce oils with lower concentrations of naphthalenes and higher condensed ring aromatics. Of course, as noted herein, the effective temperature is somewhat subjective because the production temperatures varies in both time and space, but on average, the in-situ methods allow the oil to be produced at lower temperature, as compared to ex-situ methods, which are normally operated at temperatures above 475°C or even above 500°C.

20 **[0035]** In accordance with this aspect of tailoring produced shale oils for use in chemical manufacturing, provided is a method of obtaining a thermal cracking feedstock (e.g., hydrocarbon feed) for the production of olefins from an in-situ extracted oil-shale formation. The method comprises the steps of performing compositional analyses on a set of in-situ extracted shale oils, the set of in-situ extracted shale oils produced at varied production temperatures and/or levels of lithostatic stress; determining from the compositional analyses values for production temperature and/or lithostatic stress that when achieved produce an in-situ extracted shale oil having a concentration of aromatics at or below a target level, the target level suitable for the production of olefins by thermal cracking; adjusting oil-shale formation extraction conditions to achieve the values for production temperature and/or lithostatic stress; and producing an in-situ extracted shale oil suitable for use as a thermal cracking feedstock for the production of olefins. The concentration of aromatics may be less than 50 wt% aromatics in the in-situ extracted shale oil, or may be less than 62 wt% aromatics in the in-situ extracted shale oil.

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[0036] In one embodiment, compositional analysis data obtained for a plurality of in-situ extracted shale oil samples produced at varied production operation temperatures and/or levels of lithostatic stress can be stored in a computer database. The primary methods used for compositional analysis may include gas and liquid chromatography and mass spectrometry.

[0037] Mathematical solution techniques, such as multivariable linear regression (MVLR) or other known techniques may be employed to identify production conditions (e.g., extraction conditions) required to produce a target level for one or more compositional properties, such as the concentration of aromatics, hydrogen content, or the like, which when achieved, yields a feedstock suitable for a particular chemical process, such as the production of olefins by thermal cracking.

[0038] In one embodiment, the compositional analysis data are stored in a computer and analyzed using commercially available tools, such as MatLab[®], available from MathWorks of Natick, Massachusetts, to determine the relevant target level or levels of compositional properties required to yield a feedstock for producing chemicals, such as by cracking or other processes.

[0039] A wide variety of chemical processes can benefit from the feedstocks produced in accordance herewith. These include cracking processes, such as thermal or steam cracking and a wide variety of catalytic processes. In one embodiment, feedstocks are produced for use in thermal or steam cracking.

[0040] As may be appreciated from the above, knowledge of formation production operating conditions, whether by an in-situ or ex-situ process, and the compositional characteristics that correlate thereto, can serve to predict the concentration of aromatics, hydrogen content, or the like of the produced hydrocarbons. This information may be used in processing the hydrocarbons in a chemical refinery. In accordance herewith, in one embodiment, a method for processing a hydrocarbon feed produced from an oil-shale formation to produce olefins is provided. The method includes obtaining operational data about production of a hydrocarbon feed; and if the operational data indicates that the hydrocarbon feed was produced via an in-situ method, processing the hydrocarbon feed without hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in a conversion reactor, such as a pyrolysis furnace; or if the operational data indicates that the hydrocarbon feed was produced via an ex-situ method, hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in the conversion reactor (e.g., pyrolysis furnace).

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Reference is now made to FIGs. 1-4, wherein like numerals are used to designate like elements throughout.

Definitions

[0041] As used herein, the term "hydrocarbons" refers to organic material with molecular
5 structures containing carbon bonded to hydrogen. Hydrocarbons may also include other elements, such as, but not limited to, halogens, metallic elements, nitrogen, oxygen, and/or sulfur.

[0042] As used herein, the term "hydrocarbon fluids" refers to a hydrocarbon or mixtures of hydrocarbons that are gases or liquids. For example, hydrocarbon fluids may include a
10 hydrocarbon or mixtures of hydrocarbons that are gases and/or liquids at formation conditions, at processing conditions or at ambient conditions (15°C and 101 kilo Pascals (kPa)). Hydrocarbon fluids may include, for example, oil (e.g., a hydrocarbon fluid containing a mixture of condensable hydrocarbons), natural gas, coal bed methane, shale oil, pyrolysis oil, pyrolysis gas, a pyrolysis product of coal, and other hydrocarbons that are in a
15 gaseous or liquid state.

[0043] As used herein, the terms "produced fluids" and "production fluids" refer to liquids and/or gases removed from a subsurface formation. Produced fluids may include both hydrocarbon fluids and non-hydrocarbon fluids. Production fluids may include, but are not limited to, retorted shale oil, synthesis gas, a pyrolysis product of coal, carbon dioxide,
20 hydrogen sulfide, and water (including steam). Produced fluids may include both hydrocarbon fluids and non-hydrocarbon fluids.

[0044] As used herein, the term "condensable hydrocarbons" means those hydrocarbons that condense at 25°C and 101 kPa. Condensable hydrocarbons may include a mixture of hydrocarbons having carbon numbers greater than 4.

25 [0045] As used herein, the term "non-condensable hydrocarbons" means those hydrocarbons that do not condense at 25°C and 101 kPa. Non-condensable hydrocarbons may include hydrocarbons having carbon numbers less than 5.

[0046] As used herein, the term "heavy hydrocarbons" refers to hydrocarbon fluids that are highly viscous at ambient conditions (15°C and 101 kPa). Heavy hydrocarbons may
30 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 sulfur, oxygen and nitrogen. Additional elements may also be present in heavy hydrocarbons in trace amounts. Heavy hydrocarbons may be classified by American Petroleum Institute (API) gravity. Heavy hydrocarbons generally have an API gravity below about 20 degrees.

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Heavy oil, for example, generally has an API gravity of about 10-20 degrees, whereas tar generally has an API gravity below about 10 degrees. The viscosity of heavy hydrocarbons is generally greater than about 100 centipoise at 15°C.

[0047] As used herein, the term "solid hydrocarbons" refers to any hydrocarbon material that is found naturally in substantially solid form at formation conditions. Non-limiting examples include kerogen, coal, shungites, asphaltites, and natural mineral waxes.

[0048] As used herein, the term "formation hydrocarbons" refers to both heavy hydrocarbons and solid hydrocarbons that are contained in a subsurface formation. Formation hydrocarbons may be, but are not limited to, kerogen, oil-shale, coal, bitumen, tar, natural mineral waxes, and asphaltites.

[0049] As used herein, the term "tar" refers to 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 degrees.

[0050] As used herein, the term "kerogen" refers to a solid, insoluble hydrocarbon that principally contains carbon, hydrogen, nitrogen, oxygen, and sulfur. Oil-shale contains kerogen.

[0051] As used herein, the term "bitumen" refers to a non-crystalline solid or viscous hydrocarbon material that is substantially soluble in carbon disulfide.

[0052] As used herein, the term "organic-rich rock" refers to any rock matrix holding solid hydrocarbons and/or heavy hydrocarbons. Rock matrices may include, but are not limited to, sedimentary rocks, such as shales, siltstones, sands, silicilytes, carbonates, and diatomites, which may include oil-shale, kerogen, coal, and/or bitumen.

[0053] As used herein, the term "formation" refers to any finite subsurface region (e.g., geologic strata occurring below the earth's surface). The formation may contain one or more hydrocarbon-containing layers, one or more non-hydrocarbon containing layers, an overburden, and/or an underburden of any subsurface geologic formation.

[0054] As used herein, the term "organic-rich rock formation" refers to any formation containing organic-rich rock. Organic-rich rock formations include, for example, oil-shale formations, coal formations, and tar sands formations.

[0055] As used herein, the term "pyrolysis" refers to the breaking of chemical bonds through the application of heat. For example, pyrolysis may include transforming a compound into one or more other substances by heat alone. Pyrolysis may include modifying the nature of the compound by addition of hydrogen atoms which may be obtained from

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molecular hydrogen, water, carbon dioxide, or carbon monoxide. Heat may be transferred to a section of the formation to cause pyrolysis.

[0056] As used herein, the term "water-soluble minerals" refers to minerals that are soluble in water. Water-soluble minerals include, for example, nahcolite (sodium bicarbonate), soda ash (sodium carbonate), dawsonite ($\text{NaAl}(\text{CO}_3)(\text{OH})_2$), or combinations thereof. Substantial solubility may require heated water and/or a non-neutral pH solution.

[0057] As used herein, the term "migratory contaminant species" refers to species that are both soluble and moveable in water or an aqueous fluid, and are considered to be potentially harmful or of concern to human health or the environment. Migratory contaminant species may include inorganic and organic contaminants. Organic contaminants may include saturated hydrocarbons, aromatic hydrocarbons, and oxygenated hydrocarbons. Inorganic contaminants may include metal contaminants, and ionic contaminants of various types that may significantly alter pH or the formation fluid chemistry. Aromatic hydrocarbons may include, for example, benzene, toluene, xylene, ethylbenzene, and tri-methylbenzene, and various types of polyaromatic hydrocarbons such as anthracenes, naphthalenes, chrysenes and pyrenes. Oxygenated hydrocarbons may include, for example, alcohols, ketones, phenols, and organic acids such as carboxylic acid. Metal contaminants may include, for example, arsenic, boron, chromium, cobalt, molybdenum, mercury, selenium, lead, vanadium, nickel, or zinc. Ionic contaminants include, for example, sulfides, sulfates, chlorides, fluorides, ammonia, nitrates, calcium, iron, magnesium, potassium, lithium, boron, and strontium.

[0058] As used herein, the term "cracking" refers to a process involving decomposition and molecular rearrangements or recombination of organic compounds to produce a greater number of molecules than were initially present. In cracking, a series of reactions take place accompanied by a transfer of hydrogen atoms between molecules. For example, naphtha may undergo a thermal cracking reaction to produce ethylene and H_2 among other molecules.

[0059] As used herein, the term "thickness" of a layer refers to the distance between the upper and lower boundaries of a cross section of a layer, wherein the distance is measured normal to the average tilt of the cross section.

[0060] As used herein, the term "thermal fracture" refers to fractures created in a formation caused directly or indirectly by expansion or contraction of a portion of the formation and/or fluids within the formation, which is caused by increasing/decreasing the temperature of the formation and/or fluids within the formation, and/or by increasing/decreasing a pressure of fluids within the formation due to heating. Thermal

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fractures may propagate into or form in neighboring regions significantly cooler than the heated zone.

[0061] As used herein, the term "hydraulic fracture" refers to a fracture at least partially propagated into a formation, wherein the fracture is created through injection of pressurized fluids into the formation. The fracture may be artificially held open by injection of a proppant material. Hydraulic fractures may be substantially horizontal in orientation, substantially vertical in orientation, or oriented along any other plane.

[0062] As used herein, the term "wellbore" refers to a hole in the subsurface made by drilling or insertion of a conduit into the subsurface. A wellbore may have a substantially circular cross section, or other cross-sectional shapes (e.g., circles, ovals, squares, rectangles, triangles, slits, or other regular or irregular shapes). As used herein, the term "well", when referring to an opening in the formation, may be used interchangeably with the term "wellbore."

[0063] As used herein, "non-volatile components" are the fraction of a hydrocarbon stream with a nominal boiling point above 590°C as measured by ASTM D-6352-98 or D-2887. The boiling point distribution of the hydrocarbon stream is measured by Gas Chromatograph Distillation (GCD) according to the methods described in ASTM D-6352-98 or D-2887, extended by extrapolation for materials boiling above 700°C. Non-volatile components can include coke precursors, which are moderately heavy and/or reactive molecules, such as multi-ring aromatic compounds, which can condense from the vapor phase and then form coke under the operating conditions encountered in the thermal cracking of a hydrocarbon feedstock used in the manufacture of chemicals. T_{50} as used herein shall mean the temperature, determined according to the boiling point distribution described above, at which 50 weight percent (wt%) of a particular hydrocarbon sample has reached its boiling point. Likewise T_{95} or T_{98} mean the temperature at which 95 wt% or 98 wt% of a particular sample has reached its boiling point. Nominal final boiling point shall mean the temperature at which 99.5 wt% of a particular sample has reached its boiling point.

[0064] Unless otherwise stated, all percentages, parts, ratios, etc., are by weight. Unless otherwise stated, a reference to a compound or component includes the compound or component by itself, as well as in combination with other compounds or components, such as mixtures of compounds.

[0065] Further, when an amount, concentration, or other value or parameter is given as a list of upper preferable values and lower preferable values, this is to be understood as

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specifically disclosing all ranges formed from any pair of an upper preferred value and a lower preferred value, regardless of whether ranges are separately disclosed.

In-situ oil-shale production and processing

[0066] FIG. 1 is a cross-sectional view of an exemplary oil-shale development area 10, which includes an organic-rich rock matrix that defines a subsurface formation 16 and a fluid processing facility 17, which includes a hydrocarbon processing system, such as the hydrocarbon processing system 200 of FIG. 4 discussed further below. Below the surface 12, a subsurface formation 16 contains formation hydrocarbons (e.g., kerogen) and possibly valuable water-soluble minerals (e.g., nahcolite). The subsurface formation 16 may be any formation, including a rock matrix containing coal or tar sands, for example, which may include regions that are permeable, semi-permeable or non-permeable.

[0067] To access a subsurface formation 16, a plurality of wellbores 14 may be formed. While the wellbores 14 may be substantially vertical in orientation relative to the surface 12, as shown, it is understood that some or all of the wellbores 14 may deviate into an obtuse or even horizontal orientation depending upon the specific configuration or layout of the wellbores 14. In the arrangement of FIG. 1, each of the wellbores 14 penetrate through the surface 12 and into the subsurface formation 16. The completions may be either open or cased hole, which may also include hydraulic fractures that are propped or unpropped.

[0068] In the view of FIG. 1, the wellbores 14 are shown, which may be utilized for different functions, such as heating, producing, injecting and monitoring. It may be desirable to arrange the various wellbores in a pre-planned pattern. For instance, heater wells may be arranged in a variety of patterns including, but not limited to triangles, squares, hexagons, and other polygons. The pattern may include a regular polygon to promote uniform heating through at least the portion of the formation in which the heater wells are placed. This configuration may include one production well surrounded by heater wells in a configuration, such as 5-spot, 7-spot, or 9-spot arrays, with alternating rows of production and heater wells. Also, a ratio of heater wells to production wells disposed within a organic-rich rock formation may be greater than about 5, 8, 10, 20, or more. Further, the well spacing may be located in relatively close proximity, being from 3.05 meters (m) to up to 91 m in separation, from 9.1 m to 61 m, from 15.2 m to 30.5 m, or from 4.6 m to 7.6 m. Typically, the wellbores 14 extend through shallow depths, having a total depth from 61 m to 1524 m, but may alternatively be between 305 m and 1219 m, 366 m and 1128 m, or 457 m and 1067 m below the surface. In some configurations the subsurface formation being accessed for in-situ retorting is at a depth greater than 61 m, greater than 152 m, greater than 305 m, or greater

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than 457 m below the surface. Alternatively, conversion and production occur at depths between 152 m and 762 m.

[0069] As may be appreciated, the wellbores 14 are selected for certain functions and may be designated as heat injection wells, water injection wells, oil production wells and/or water-soluble mineral solution production wells. In one aspect, the wellbores 14 are dimensioned to serve two, three, or all four of these functions. Suitable tools and equipment may be sequentially run into and removed from the wellbores 14 to serve the various functions.

[0070] A fluid processing facility 17 is also shown in fluid communication with the wellbores 14. That is the fluid processing facility 17 is equipped to receive produced fluids from the subsurface formation 16 through one or more pipelines or flow lines 18. The fluid processing facility 17 may include equipment suitable for receiving and separating oil, gas, and water produced from the heated formation along with equipment for processing the hydrocarbons into other products, such as olefins and polyolefins. The fluid processing facility 17 may further include equipment for separating out dissolved water-soluble minerals and/or migratory contaminant species, including, for example, dissolved organic contaminants, metal contaminants, or ionic contaminants in the produced water recovered from the subsurface formation 16. The contaminants may include, for example, aromatic hydrocarbons such as benzene, toluene, xylene, and tri-methylbenzene. The contaminants may also include polyaromatic hydrocarbons such as anthracene, naphthalene, chrysene and pyrene. Metal contaminants may include species containing arsenic, boron, chromium, mercury, selenium, lead, vanadium, nickel, cobalt, molybdenum, or zinc. Ionic contaminant species may include, for example, sulfates, chlorides, fluorides, lithium, potassium, aluminum, ammonia, and nitrates. As an example, the processing facility may include a non-hydrocarbon separating unit configured to separate one or more dissolved water-soluble minerals and/or migratory contaminant species product (e.g., water, nahcolite or other sodium minerals) from the produced fluids. This may be in fluid communication with a furnace that may be configured to crack a portion of the remaining produced fluids into a effluent that may be further processed to olefins for other processes.

[0071] To operate, each of the wellbores 14 may be designated as heater wells that are arranged around a production well (e.g., as one or more different layers that surround the production well, such as a 5-spot pattern). The heater wells heat the formation to breakdown the kerogen so that the hydrocarbons may migrate to the production well. This arrangement of heater wells may be configured to avoid passing the hydrocarbons through a zone of

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substantially increasing formation temperature, and may be configured to optimize the thermal conductivity of the formation (e.g., via use of an elongation in a particular direction, such as the direction of most efficient thermal conductivity). Once the formation hydrocarbons are migrated to the production well, these produced fluids may be provided to the fluid processing facility 17 for further processing. This may involve separating non-hydrocarbon products and cracking the hydrocarbons to produce an olefin product. Accordingly, to recover and process oil, gas, and sodium (or other) water-soluble minerals, a series of steps may be undertaken, as shown in FIG. 2.

[0072] FIG. 2 is a flow chart 100 of an oil and gas in-situ thermal recovery process from an organic-rich rock formation in accordance with an exemplary embodiment. It should be understood that the order of the steps from FIG. 2 may be changed for some of the steps, and that the sequence of steps is merely for illustration.

[0073] First, formation hydrocarbons, such as oil-shale, may be present in one or more subsurface formations. Also, the organic-rich rock formations may be separated by rock layers that are hydrocarbon-free or that otherwise have little or no commercial value. Therefore, it may be desirable for the operator of a field under hydrocarbon development to undertake an analysis as to which of the subsurface, organic-rich rock formations to target or the order that different formations should be developed. As shown in block 110, the subsurface formation (e.g., an organic-rich rock or oil-shale formation, such as subsurface formation 16 of FIG. 1) is identified within the development area, such as development area 10 of FIG. 1.

[0074] The organic-rich rock formation may be selected for development based on various factors. That is, the targeted development area within the subsurface formation may be identified by measuring or modeling various factors, such as the depth, thickness and organic richness of the oil-shale as well as evaluating the position of the organic-rich rock formation relative to other rock types, structural features (e.g., faults, anticlines or synclines), or hydrogeological units (e.g., aquifers). This is accomplished by creating and interpreting maps and/or models of depth, thickness, organic richness and other data from available tests and sources. These models and maps may be used to perform flow and reservoir simulations to assess the pathways and temperature history of hydrocarbon fluids generated in-situ as they migrate from their points of origin to production wells. This may involve performing geological surface surveys, studying outcrops, performing seismic surveys, and/or obtaining core samples from the subsurface formation. The samples may be analyzed to assess kerogen

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content and hydrocarbon fluid generating capability of the material within the subsurface formation and regions outside the subsurface formation.

[0075] One of the factors that may be considered is the thickness of the hydrocarbon containing layer within the formation. Greater pay zone thickness may indicate a greater potential volumetric production of hydrocarbon fluids. Each of the hydrocarbon containing layers may have a thickness that varies depending on, for example, conditions under which the formation hydrocarbon containing layer was formed. Therefore, an organic-rich rock formation typically is selected for treatment if that formation includes at least one formation hydrocarbon-containing layer having a thickness sufficient for economical production of produced fluids.

[0076] The organic-rich rock formation may also be chosen if the thickness of several layers that are closely spaced together is sufficient for economical production of produced fluids. For example, an in-situ conversion process for formation hydrocarbons may include selecting and treating a layer within an organic-rich rock formation having a thickness of greater than about 5 meters (m), 10 m, 50 m, or even 100 m. In this manner, heat loss (as a fraction of total injected heat) to layers formed above and below an organic-rich rock formation may be less than the heat loss from a thin layer of formation hydrocarbons. A process as described herein, however, may also include selecting and treating layers that may include layers substantially free of formation hydrocarbons or thin layers of formation hydrocarbons.

[0077] Subsurface formation permeability may also be assessed via rock samples, outcrops, or studies of ground water flow. Furthermore, the connectivity of the development area to ground water sources may be assessed. Thus, an organic-rich rock formation may be chosen for development based on the permeability or porosity of the formation matrix even if the thickness of the formation is relatively thin.

[0078] The richness of one or more organic-rich rock formations may also be considered. Richness may depend on many factors including the conditions under which the formation hydrocarbon containing layer was formed, an amount of formation hydrocarbons in the layer, and/or a composition of formation hydrocarbons in the layer. A thin and rich formation hydrocarbon layer may be able to produce significantly more valuable hydrocarbons than a much thicker, less rich formation hydrocarbon layer. Of course, producing hydrocarbons from a formation that is both thick and rich is desirable.

[0079] The kerogen content of the subsurface formation may be ascertained from data based upon analysis of outcrop or core samples using a variety of analysis techniques. Such

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data may include organic carbon content, hydrogen index, and modified Fischer assay analyses, for example. Subsurface permeability may also be assessed via rock samples, outcrop samples, and/or studies of ground water flow. Furthermore, the connectivity of the development area to ground water sources may be assessed.

5 **[0080]** Other factors may be taken into consideration when selecting a formation for development. Such factors include depth of the perceived pay zone, stratigraphic proximity of fresh ground water to kerogen-containing zones, continuity of thickness, and other factors. For instance, the assessed fluid production content within a formation also effects eventual volumetric production. Further, amount of nahcolite or other sodium minerals contained in
10 the formation may also be considered. Moreover, the selection of a formation for development may include obtaining compositional analysis data for in-situ extracted shale oil and determining from the compositional analysis data a value of oil-shale formation extraction conditions that include a production temperature or a lithostatic stress that when achieved produces an in-situ extracted shale oil having a concentration of aromatics at or
15 below a target level. The compositional analysis data may include in-situ extracted shale oils produced at varied production temperatures and/or levels of lithostatic stress.

[0081] Next, a plurality of wellbores (e.g., wellbores 14 of FIG. 1) may be formed across the development area, as shown in block 115. The wellbores may be used for one or more of the functions, as described above. However, it is noted that for purposes of the wellbore
20 formation step of block 115, only a portion of the wells may be completed initially. For instance, at the beginning of the project, heat injection wells may be utilized, while a majority of the hydrocarbon production wells may not be utilized until a later stage. Production wells may be brought in once conversion begins, such as after four to twelve months of heating.

[0082] It is understood different strategies for the arrangement and depth of the wellbores
25 may be developed and may vary based upon anticipated reservoir characteristics, economic constraints, and work scheduling constraints. In addition, the specific configuration and use of the wellbores, such as for heating, may be determined based on these different constraints. This selection step is represented by block 120. Of course, this designation may be done initially, and as may be appreciated, the operation of the wellbores may change over time.

30 **[0083]** Various methods for applying heat to the subsurface formation may be utilized. The present methods are not limited to the heating technique employed in the heat injection wells or heater wells. The heating step is represented generally by block 130. Preferably, for in-situ processes, the heating of a production zone takes place over a period of months, or even four or more years. The step involves heating the subsurface formation to a temperature

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sufficient to pyrolyze (e.g., retort) at least a portion of the oil-shale to convert the kerogen to hydrocarbon fluids. The bulk of the area near the wellbore (e.g., the target zone of the formation) may be heated to between 270°C to 800°C. Alternatively, the targeted volume of the subsurface formation is heated to at least 350°C to create production fluids. This conversion is represented in block 135. The resulting liquids and hydrocarbon gases may be refined into products which resemble common commercial petroleum products or used in the manufacture of chemicals, which are described in detail below. Generated gases include light alkanes, light alkenes, H₂, CO₂, CO, and NH₃. The heater wells may include, for example, electrical resistance heating element.

[0084] Conversion of the oil-shale creates permeability in the oil-shale section of rocks that were originally impermeable. Preferably, the heating and conversion processes of blocks 130 and 135, occur over a period of time, such as a heating period from three months to four or more years. Also, as an optional part of block 135, the formation may be heated to a temperature sufficient to convert at least a portion of nahcolite, if present, to soda ash. Heat applied to mature the oil-shale and recover oil and gas also converts nahcolite to sodium carbonate (soda ash), a related sodium mineral. The process of converting nahcolite (sodium bicarbonate) to soda ash (sodium carbonate) is described herein.

[0085] The purpose for heating the organic-rich rock formation is to pyrolyze at least a portion of the solid formation hydrocarbons to create hydrocarbon fluids. The solid formation hydrocarbons may be retorted in-situ by raising the organic-rich rock formation, (or zones within the formation), to a production temperature. In certain embodiments, the temperature of the formation may be slowly raised through the production temperature range. For example, an in-situ conversion process may include heating at least a portion of the organic-rich rock formation to raise the average temperature of the zone above 270°C at a rate less than a selected amount (e.g., about 10°C, 5°C, 3°C, 1°C, 0.5°C, or 0.1°C) per day. The formation may be heated such that a temperature within the formation reaches (at least) an initial production temperature (e.g., a temperature at the lower end of the temperature range where pyrolyzation begins to occur).

[0086] The production temperature range may vary depending on the types of hydrocarbons within the formation, the heating methodology, and the distribution of heating sources. The bulk of the target zone of the formation may be heated to within the production temperature range. For example, a production temperature range may include production temperatures (e.g., values) between 270°C and 900°C, between 270°C to 800°C, between 300°C to 600°C, between 270°C to 500°C, between 350°C and 450°C, between 325°C and

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450°C, or between 375°C and 425°C. This can be achieved, e.g., by exposing the formation to a temperature $\leq 900^\circ\text{C}$. In certain embodiments, the heated zone may have an average temperature that is less than 375°C, less than 400°C, or less than 475°C. Specifically, the formation may be heated to production temperatures less than or equal to 350°C and the aromatics content is less than 50 wt%. Preferably, for in-situ processes the heating of a production zone takes place over a period of months, or even four or more years. Alternatively, the formation may be heated for one to fifteen years, alternatively, three to ten years, one and a half to seven years, or two to five years.

[0087] In connection with the heating step of block 130, the subsurface formation may optionally be fractured to aid heat transfer or later hydrocarbon fluid production. The optional fracturing step is shown in block 125. Fracturing may be accomplished by creating thermal fractures within the formation through application of heat. By heating the organic-rich rock and transforming the kerogen to oil and gas, the permeability of portions of the formation are increased via thermal fracture formation and subsequent production of a portion of the hydrocarbon fluids generated from the kerogen. Alternatively, a process known as hydraulic fracturing may be used. Hydraulic fracturing is a process known in the art of oil and gas recovery where a fracture fluid is pressurized within the wellbore above the fracture pressure of the formation, thus developing fracture planes within the formation to relieve the pressure generated within the wellbore. Hydraulic fractures may be used to create additional permeability in portions of the formation and/or be used to provide a planar source for heating.

[0088] Further, it may be desirable that the progression of heat through the subsurface in accordance with blocks 130 and 135 to be uniform. However, for various reasons the heating and maturation of formation hydrocarbons in the formation may not proceed uniformly despite a regular arrangement of heater and production wells, which may be because of heterogeneities in the oil-shale properties and formation structure, uneven distribution of preferred pathways relating from fractures, and/or uneven fluid maturation. To detect these conditions (e.g., uneven flow conditions), monitor wells, which may be part of the production and heater wells, may be instrumented with sensors. Sensors may include equipment to measure temperature, pressure, flow rates, and/or compositional information. Data from these sensors can be processed via simple rules or input to detailed simulations to reach decisions on how to adjust heater and production wells to improve subsurface performance. Production well performance may be adjusted by controlling backpressure or throttling on the well. Heater well performance may also be adjusted by controlling energy input. Sensor

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readings may also sometimes imply mechanical problems with a well or downhole equipment which requires repair, replacement, or abandonment.

[0089] In one embodiment, flow rate, compositional, temperature and/or pressure data are utilized from two or more wells as inputs to a computer algorithm to control heating rate and/or production rates. Unmeasured conditions at or in the neighborhood of the well are then estimated and used to control the well. For example, in-situ fracturing behavior and kerogen maturation are estimated based on thermal, flow, and compositional data from a set of wells. In another example, well integrity is evaluated based on pressure data, well temperature data, and estimated in-situ stresses. In a related embodiment the number of sensors is reduced by equipping only a subset of the wells with instruments, and using the results to interpolate, calculate, or estimate conditions at un-instrumented wells. Certain wells may have only a limited set of sensors (e.g., wellhead temperature and pressure only) where others have a much larger set of sensors (e.g., wellhead temperature and pressure, bottomhole temperature and pressure, production composition, flow rate, electrical signature, casing strain, etc.). In this manner, the in-situ operations may control the heating of the produced fluid, which may be based on or optimized for the subsequent cracking processes in the fluid processing facility.

[0090] Further, there are various methods for applying heat to a subsurface formation. Heating methods include using electrical resistance heaters disposed in a wellbore or outside of a wellbore, using electrical resistive heating elements in a cased or uncased wellbore (e.g., directly passing electricity through a conductive material such that resistive losses cause it to heat the conductive material), burning a fuel external to or within the subsurface formation, using downhole combustors, in-situ combustion, radio-frequency (RF) electrical energy, microwave energy, or injecting a hot fluid into the oil-shale formation to directly heat it and circulating the fluid (or it may not be circulated).

[0091] Examples of these methods include, for example, Intl. Patent Publication No. 2005/010320 that describes the use of electrically conductive fractures to heat the oil-shale. In this process, thermal conduction heats the oil-shale to conversion temperatures in excess of 300°C causing artificial maturation. Further, Intl. Patent Publication No. 2005/045192 describes an alternative heating means that employs the circulation of a heated fluid within an oil-shale formation. In this process, fracture temperatures of 320°C to 400°C are maintained for up to five to ten years prior to the fluid pressure increase driving the generated oil to the heated fractures.

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[0092] Other examples may include downhole steam generation. In downhole steam generation, a combustor in the well is used to boil water placed in the wellbore for injection into the formation. Applications of the downhole heat technology have been described in F. M. Smith, "A Down-hole burner--Versatile tool for well heating," 25th Technical Conference on Petroleum Production, Pennsylvania State University, pp 275-285 (October 19-21, 1966);
5 H. Brandt, W. G. Poynter, and J. D. Hummell, "Stimulating Heavy Oil Reservoirs with Downhole Air-Gas Burners," World Oil, pp. 91-95 (September 1965); and C. I. DePriester and A. J. Pantaleo, "Well Stimulation by Downhole Gas-Air Burner," Journal of Petroleum Technology, pp. 1297-1302 (December 1963).

10 [0093] As a further alternative, certain embodiments of the methods disclosed herein may utilize downhole burners to heat a targeted oil-shale zone, which may include conduction, convection, and radiative methods for heat transfer. Downhole burners of various designs have been discussed in the patent literature for use in oil-shale and other largely solid hydrocarbon deposits. Examples include U.S. Patent Nos. 2,887,160; 2,847,071; 2,895,555;
15 3,109,482; 3,225,829; 3,241,615; 3,254,721; 3,127,936; 3,095,031; 5,255,742; and 5,899,269. Downhole burners operate through the transport of a combustible fuel (typically natural gas) and an oxidizer (typically air) to a subsurface position in a wellbore. The fuel and oxidizer react downhole to generate heat. The combustion gases are removed (typically by transport to the surface, but possibly via injection into the formation). Often times,
20 downhole burners utilize pipe-in-pipe arrangements to transport fuel and oxidizer downhole, and then to remove the flue gas back up to the surface. The downhole burners may or may not generate a flame.

[0094] Certain wellbores may be designated as oil and gas production wells, as noted in block 140. Oil and gas production may not be initiated until it is determined that the kerogen
25 has been sufficiently retorted to allow maximum recovery of fluids (e.g., oil and gas) from the subsurface formation. In some instances, dedicated production wells may not be drilled until after heat injection wells of block 130 have been in operation for a period of several weeks or months. Thus, block 140 may include the formation of additional wellbores after initial heating operations have begun. In other instances, selected heater wells may be
30 converted to production wells.

[0095] After certain wellbores have been designated as oil and gas production wells, oil and/or gas is produced from the wellbores 14. The oil and/or gas production process is shown at block 145. In this block 145, any water-soluble minerals, such as nahcolite and converted soda ash, may remain substantially trapped in the subsurface formation as finely

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disseminated crystals or nodules within the oil-shale beds, and may not be produced. However, some nahcolite and/or soda ash may be dissolved in the water created during heat conversion in block 135 within the formation.

[0096] In block 150, the process 100 may optionally designate certain wellbores as water or aqueous fluid injection wells. Aqueous fluids are solutions of water with other species. The water may constitute "brine," and may include dissolved inorganic salts of chloride, sulfates and carbonates of Group I and II elements of The Periodic Table of Elements. The "Periodic Table of the Elements" means the Periodic Chart of the Elements as tabulated on the inside cover of The Merck Index, 12th Edition, Merck & Co., Inc., 1996. Organic salts can also be present in the aqueous fluid. The water may alternatively be fresh water containing other species. The other species may be present to alter the pH of the water. Alternatively, the other species may reflect the availability of brackish water not saturated in the species to be leached from the subsurface formation. Preferably, the water injection wells are selected from some or all of the wellbores used for heat injection or for oil and/or gas production. However, block 150 may include the drilling of yet additional wellbores for use as dedicated water injection wells in some instances. In this respect, it may be desirable to complete water injection wells along a periphery of the development area to create a boundary of high pressure.

[0097] Next, optionally water or an aqueous fluid is injected through the water injection wells and into the subsurface formation, which is shown at block 155. The water may be in the embodiment of steam or pressurized hot water. Alternatively, the injected water may be injected at a lower temperature and becomes heated as it contacts the previously heated formation. The injection process may further induce fracturing, such as fingered caverns and brecciated zones in the nahcolite-bearing intervals some distance, for example up to 200 ft out, from the water injection wellbores. In one aspect, a gas cap, such as nitrogen, may be maintained at the top of each "cavern" to prevent or minimize vertical growth.

[0098] In addition, certain wellbores may be designated as water or water-soluble mineral solution production wells, as shown in block 160. These wells may be the same as wells used to previously produce hydrocarbons or inject heat. These recovery wells may be used to produce an aqueous solution of dissolved water-soluble minerals and other species, including, for example, migratory contaminant species. For example, the solution may be one primarily of dissolved soda ash, is shown in block 165. Alternatively, single wellbores may be used to both inject water and then to recover a sodium mineral solution. Thus, block 165 includes the

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option of using the same wellbores for both water injection and solution production in block 165.

[0099] Temporary control of the migration of the migratory contaminant species, especially during the retorting process, can be obtained via placement of the injection and production wells such that fluid flow out of the heated zone is minimized. Typically, this involves placing injection wells at the periphery of the heated zone so as to cause pressure gradients which prevent flow inside the heated zone from leaving the zone.

[00100] After the recovery, a produced fluid may be subjected to various processing steps to convert the produced fluid into various products, as shown in blocks 170 to 180. At block 170, the produced fluid may be subjected to one or more non-hydrocarbon separating processes. These separation processes may separate from the produced fluid one or more dissolved water-soluble mineral products, one or more migratory contaminant species products, one or more water products. Then, at least a portion of the remaining produced fluid may be cracked in a conversion reactor, such as a steam cracking furnace or other suitable pyrolysis reactor, as shown in block 175. This cracking process may involve temperatures between about 550°C and 1000°C depending on the specific design of the conversion process. Catalytic conversion processes typically operate at the lower temperature range, which is from 550°C to 750°C. In particular, thermal cracking, such as steam cracking, are typically practiced at higher temperatures from 700°C to 1000°C, or between 800°C and 950°C. Further, because the remaining produced fluid (e.g., the hydrocarbon feed) is from an in-situ recovery method, the process does not have to utilize a hydrotreater or hydrogen diluent for the cracking process. Once cracked, the effluent from the cracking process may be further processed or converted into other petrochemical products, such as polyolefins. These processes may include any of a variety of catalytic or non-catalytic chemical manufacturing processes depending on the desired product to be produced.

[00101] Beneficially, it has been discovered that shale oils produced using certain in-situ methods have enhanced compositional characteristics for producing chemicals as compared to shale oils produced using more conventional mining and surface retort methods. These characteristics include increased hydrogen content and reduced concentrations of sulfur, oxygen, and/or nitrogen. Accordingly, the proposed process utilizes this information (e.g., certain oil-shale formation extraction conditions) to enhance the processing of hydrocarbons into olefins. That is, the process may utilize and adjust extraction conditions to enhance chemical recovery.

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[00102] Further, in one or more embodiments, it may be desirable to control the migration of produced or generated fluids. In some instances, this includes the use of injection wells, particularly around the periphery of the field. Such wells may inject water, steam, CO₂, heated methane, or other fluids to drive generated fluids inwardly towards production wells.

5 In some embodiments, physical barriers may be placed around the area of the organic-rich rock formation under development. One example of a physical barrier may include the creation of freeze walls. Freeze walls are formed by circulating refrigerant through peripheral wells to substantially reduce the temperature of the formation. This, in turn, prevents or limits the retorting of kerogen present at the periphery of the field and the
10 outward migration of oil and gas. Freeze walls also cause native water in the formation along the periphery to freeze.

[00103] In addition, as noted above, several different types of wells may be used in the development of an organic-rich rock formation, including, for example, an oil-shale field. For example, the process may utilize heater wells, production wells, injection wells, and
15 monitoring well (e.g., wells may be configured with one or more devices that measure a temperature, a pressure, and/or a property of a fluid in the wellbore). Each of the different wells in a development area may be used for more than one purpose. That is, wells initially completed for one purpose may later be used for another purpose, thereby lowering project costs and/or decreasing the time required to perform certain tasks. As an example, one or
20 more of the production wells may also be used as injection wells for later injecting water into the organic-rich rock formation. Alternatively, one or more of the production wells may also be used as solution production wells for later producing an aqueous solution from the organic-rich rock formation. Also, each well may also be configured to provide two or more functions for one or more subsurface zones, such as heating, producing, injecting, and
25 monitoring.

[00104] FIG. 3 is a cross-sectional view of an exemplary subsurface formation that is within or connected to ground water aquifers and a formation leaching operation in accordance with the present techniques. Four separate zones 23, 24, 25, and 26 are within the subsurface formation. The water aquifers are below the ground surface 27, and are
30 categorized as an upper aquifer 20 and a lower aquifer 22. Intermediate to the aquifers 20 and 22 is an aquitard 21, which is zone or bed of low permeability adjacent to an aquifer. It can be seen that certain zones of the formation are both aquifers or aquitards and oil-shale zones. A plurality of wells 28, 29, 30, and 31 is shown traversing vertically downward through the formation and each performs a specific function. One of the wells (e.g., water

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injection well 31) is operated to inject water into the formation, while another well (e.g., water production well 30) is operated to produce fluids from the formation. In this manner, water is circulated along a flow path 32 through at least the lower aquifer 22.

[00105] In this configuration, the water is circulated through an oil-shale volume 33 that was heated to recover hydrocarbon fluids and that resides within or is connected to an aquifer 22. In particular, as indicated by the arrows, water is introduced via the water injection well 31. This circulation forces water into the previously heated oil-shale volume 33 and water-soluble minerals and migratory contaminants species are swept to the water production well 30. The water, water-soluble minerals, and migratory contaminant species may then be processed in a facility 34 (e.g., a fluid processing facility 17 of FIG. 1), wherein the water-soluble minerals (e.g., nahcolite or soda ash) and the migratory contaminants may be substantially removed from the circulation. Further, hydrocarbon feedstocks are also separated from the circulation to be processed into olefins. Then, the water is re-injected into the oil-shale volume 33 via water injection well 31 and the formation leaching process is repeated. This leaching process continues until levels of migratory contaminant species are at environmentally acceptable levels within the previously heated oil-shale volume 33. This may involve one cycle, two cycles, five cycles, or ten or more cycles of the formation leaching process, where a single cycle indicates injection and production of approximately one pore volume of water. It is understood that there may be numerous water injection and water production wells in other oil-shale developments. Moreover, the system may include monitoring wells 28 and 29, which can be utilized during the oil-shale heating phase, the shale oil production phase, the leaching phase, or during any combination of these phases to monitor for migratory contaminant species and/or water-soluble minerals.

[00106] In one or more embodiments, shale oils produced by in-situ heating methods can be advantageously processed in a hydrocarbon processing system, which includes a thermal cracker reactor. In one embodiment, a method is provided for obtaining and processing hydrocarbons to produce olefins. The method comprises the steps of obtaining hydrocarbons from a oil-shale formation, the hydrocarbons having a hydrogen content of at least about 12 wt%; introducing the hydrocarbons to a cracking reactor without prior hydrotreating; producing effluent from the hydrocarbons in the cracking reactor; and processing the effluent to produce olefins.

[00107] In another embodiment, a method for obtaining and processing hydrocarbons is provided. The method comprises the steps of heating a portion of an oil-shale formation to a production temperature of less than or equal to about 475°C to cause the separation of a

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kerogen-derived oil from the rock in the oil-shale formation; recovering the kerogen-derived oil from the oil-shale formation; passing at least a portion of the kerogen-derived oil to a cracking reactor; producing effluent from the at least the portion of the kerogen-derived oil in the cracking reactor; and processing the effluent to produce olefins.

5 [00108] In yet another embodiment, provided is a process for cracking a shale-oil derived hydrocarbon feedstock. The process comprises heating the hydrocarbon feedstock; feeding the hydrocarbon feedstock to a flash/separation vessel; separating the hydrocarbon feedstock into a vapor phase and a liquid phase; removing the vapor phase from the flash/separation vessel; and cracking the vapor phase in a radiant section of a pyrolysis furnace to produce an
10 effluent comprising olefins, the pyrolysis furnace comprising a radiant section and a convection section. Steam, which may optionally comprise sour or treated process steam and may optionally be superheated, may be added at any step or steps in the process prior to cracking the vapor phase.

[00109] The flash/separation vessel can be used as a low cost separation device to keep
15 residual solids and heavy vacuum residual oils from entering the radiant section of the steam cracking furnace where they are prone to coking and fouling processes. The flash/separation vessel can be easily operated at different temperatures and or stripping rates in order to tune the operation to the feedstock properties. In another preferred embodiment, the shale oil may be mixed with conventional heavy petroleum feedstocks such as atmospheric resid before
20 processing into a steam cracker furnace with a flash/separation vessel. Because shale oils tend be lighter feedstocks, co-processing the shale oil with petroleum resids can facilitate management and separation of residual solids. An exemplary hydrocarbon processing system that includes a steam cracking unit along with other units is described further below in FIG. 4.

25 [00110] FIG. 4 is an exemplary hydrocarbon processing system 200, which is illustrated as one embodiment of a fluid processing facility, such as fluid processing facility 17 of FIG. 1. The hydrocarbon processing system 200 may include a non-hydrocarbon separation unit 250, furnace 201, flash/separator vessel 205, centrifugal separator 238, and an upgrading unit 260. This process may utilize these units to convert the produced fluid into olefins and other
30 products.

[00111] In this configuration, the produced fluid may be provided to the non-hydrocarbon separation unit 250 via line 252. The non-hydrocarbon separation unit 250 may include water scrubbing, oil scrubbing, cyclone separation, electrostatic separation, filtration, and/or moving bed adsorption. As may be appreciated, each of these systems may be combined

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together in one or more units to overcome certain limitations within the system. For instance, water scrubbing is effective to remove solids, but it limits the recovery of heat in the effluent. Oil scrubbing may be utilized for heat recovery, but it may present problems with fouling and emulsion formation. Cyclone separation may be limited to remove solids, but not other smaller or fine solids. Electrostatic separation may have problems with clogging and short-circuiting-due to carbon deposit buildup. Adsorption and filtration are limited to handling small amounts of solids and may be problematic for larger amounts of solids. As a result, one or more of these techniques may be coupled together in series to provide the separation. The solid-liquid phase of the produced fluid may be conducted away from the non-hydrocarbon separation unit 250 as a first or non-hydrocarbon product via line 254. The remaining portion of the produced fluid may be withdrawn from non-hydrocarbon separation unit 250 and passed to the furnace 201 via line 256.

[00112] The furnace 201 may be utilized to crack at least a portion of the remaining produced fluid. The furnace 201, which may be any of a variety of furnaces, includes a convection section 203 and a radiant section 240. Examples of such furnaces include U.S. Patent Nos. 7,097,758, 7,563,357, and 7,588,737. The convection section 203 includes various convection section tube banks (e.g., first tube bank 202, second tube bank 206, third tube bank (not shown) and fourth tube bank 223), which may use hot flue gases from the radiant section 240 of the furnace 201 to heat fluids within the respective tube banks.

[00113] Along the flow path through the furnace 201, other fluids may be added, such as steam and/or other hydrocarbons. For instance, the mixing can be accomplished using any mixing device known within the art, such as a first sparger 204 or second sparger 208 of a double sparger assembly 209. In particular, a fluid may pass through a fluid valve 214 and a primary dilution steam may be passed via primary dilution line 217 through a primary dilution steam valve 215 to be mixed with the heated hydrocarbon feed in the respective spargers 204 or 208 to form a mixture stream in line 211. Also, a secondary dilution steam stream 218 can be heated in the superheater section 216 of the convection section, may be combined with water via water line 226 through an intermediate desuperheater 225 (control valve and water atomizer nozzle), and mixed with the heated mixture steam. Optionally, the secondary dilution steam stream 218 may be further split into a flash steam stream in flash steam line 219, which is mixed with the heavy hydrocarbon mixture, and a bypass steam stream in bypass line 221, which is mixed with the vapor phase from the flash before the vapor phase is cracked in the radiant section 240. The flash steam stream may be combined with the mixture stream to form a flash stream in flash line 220.

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[00114] Along with the addition of certain fluids, certain portions of the hydrocarbon feed or mixtures may be removed from the process as well. For example, a flash/separator vessel 205 may be utilized to separate the flash stream 220 into two phases a vapor phase comprising predominantly volatile hydrocarbons and steam and a liquid phase comprising predominantly non-volatile hydrocarbons. The flash/separation vessel 205 may include any vessel or vessels used to separate the hydrocarbon feedstock into a vapor phase and at least one liquid phase, which is intended to include fractionation and any other method of separation, for example, but not limited to, drums, distillation towers, and centrifugal separators. The vapor phase is preferably removed from the flash/separator vessel 205 as an overhead vapor stream is further processed in a centrifugal separator 238, which removes trace amounts of entrained and/or condensed liquid, before being passed via overhead line 213, vapor phase control valve 236, and crossover pipe 224 to the radiant section 240 for cracking. The liquid phase of the flashed mixture stream is removed from a boot or cylinder 235 on the bottom of the flash/separator vessel 205 as a bottoms stream 227. This stream 227 may be further processed in a pump 237 and cooler 228 with the cooled stream 229 being split into a recycle stream 230 and export stream 222.

[00115] Once the mixture is exposed to heat in the radiant section 240, the reactor product or effluent may be further processed. For instance, the effluent may be passed to the upgrading unit 260. The upgrading unit 260 may purify or process the effluent in one or more units, such as include a demethanator tower (to remove H_2 , CH_4 , N_2 and CO) and a C_2 splitter to remove ethane and upgrade ethylene to polymer grade ethylene. The upgrading unit 260 may also include C_2 or C_3 refrigeration train, compression and additional distillation towers. This upgrading unit 260 may separate the effluent into one or more products, such as an ethylene product and an acetylene product. The one or more products, which are provided via line 262 may include different light gas products (e.g., hydrogen, carbon monoxide, nitrogen, methane, and the like), ethylene, acetylene and/or heavier products (e.g., ethane and C_3^+ products). Further, the upgrading unit 260 may include an ethylene polymerization unit. As an example, U.S. Patent Nos. 6,822,057; 7,045,583; 7,354,979; and 7,728,084 describe different ethylene polymerization processes that may be utilized.

[00116] To operate, various stages may heat the hydrocarbon feed to different temperatures. For instance, the hydrocarbon feed may be heated to temperatures between about $150^\circ C$ and $260^\circ C$ in the first tube bank 202, while the mixture stream may be heated in the second tube bank to temperatures between $315^\circ C$ and $540^\circ C$, which is also the temperature utilized in the flash/separator vessel 205. The vapor phase from the

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flash/separator vessel 205 is further heated in fourth or lower convection section tube bank 223 to temperatures between 425°C to 705°C, while the tubes of the radiant section 240 may further expose the vapor phase to temperatures between about 700°C and 1000°C. Further, the temperature of the recycled stream via line 230 may be at temperatures between 260°C to 315°C.

[00117] In addition, the process may be integrated to recover heat. For instance, the process may include optional cooling of the effluent from the cracking furnace 201 (not shown) in one or more transfer line heat exchangers, a primary fractionator, and a water quench tower or indirect condenser. As a specific example, the effluent may be passed to one or more transfer-line exchanger (not shown) to provide a cooled effluent for further processing. The one or more transfer-line exchanger may be coupled between the outlet from the furnace 201 (not shown) and upgrading unit 260, or may be coupled between the upgrading unit and other units. A utility fluid, such as boiler feed water or recovered fluid comprising water from the non-hydrocarbon separation unit 250, may also pass through the transfer-line exchanger to a steam drum to recover heat from the cracking process by generating high pressure steam. As a further enhancement, the steam drum may be coupled to the third tube bank in the convection section to generating high pressure steam. A steam control valve may be coupled between various lines to provide a water source that controls the temperature of the steam.

[00118] Regardless, the heated utility fluid may be utilized in the process to further enhance operations. For example, the heated utility fluid may be utilized to heat the produced fluids prior to the non-hydrocarbon separation unit 250 to further enhance the separation of the different products. Further, the heated utility fluid may be utilized to generate electricity (e.g., drive turbines to produce electricity) for pumps, compressors and other equipment utilized in the process for processing the produced fluids or in obtaining the produced fluids from the formation. Examples of other integrations with the furnace 201 and a transfer-line exchanger may be found in U.S. Patent No. 7,820,035, for example.

[00119] As may be appreciated, the flash/separation vessel 205 separates the heated hydrocarbon feedstock into two phases: a vapor phase comprising predominantly steam and volatile hydrocarbons from the hydrocarbon feedstock and a liquid phase comprising less-volatile hydrocarbons along with a significant fraction of the non-volatile components and/or coke precursors. It is understood that vapor-liquid equilibrium at the operating conditions described herein may result in very small quantities of non-volatile components and/or coke precursors present in the vapor phase. Additionally, and varying with the design of the

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flash/separation vessel, minute quantities of liquid containing non-volatile components could be entrained in the vapor phase. In the process disclosed herein, these quantities are sufficiently small to allow decoking downstream of the flash/separation vessel on the same schedule as for decoking in the radiant section of the furnace. The vapor phase can be considered to have substantially no non-volatile components or coke precursors when coke buildup in the convection section between the flash/separation vessel is at a sufficiently low rate that decoking is not required any more frequently than typical decoking required for the radiant section is required. Typically, at least about 2%, more preferably about 5%, of the total hydrocarbons are in the liquid phase after being flashed.

[00120] In addition to maintaining a constant temperature of the mixture stream 212 entering the flash/separation vessel 205, it is generally also desirable to maintain a constant hydrocarbon partial pressure of the flash stream 220 to maintain a constant ratio of vapor to liquid in the flash/separation vessel 205. By way of examples, the constant hydrocarbon partial pressure can be maintained by maintaining constant flash/separation vessel pressure through the use of control valves 236 on the vapor phase line 213, and by controlling the ratio of steam to hydrocarbon feedstock in stream 220.

[00121] Further, the hydrocarbon partial pressure of the flash stream is set and controlled at between about 25 kPa and about 175 kPa, such as between about 35 kPa and about 100 kPa, for example between about 40 kPa and about 75 kPa. As an example, the flash may be a one-stage process with or without reflux. In this configuration, the flash/separation vessel 205 is normally operated at about 275 kPa to about 1400 kPa pressure, and its temperature is usually the same or slightly lower than the temperature of the flash stream 220 before entering the flash/separation vessel 205. Typically, the pressure at which the flash/separation vessel 205 operates is about 275 to about 1400 kPa, for example about 600 to about 1100 kPa, as a further example about 700 to about 1000 kPa, and in yet another example, the pressure of the flash/separation vessel 205 can be about 700 to about 760 kPa. The temperature at which the flash/separation vessel 205 operates, or the temperature of the inlet stream to the flash/separation vessel, is about 315°C to about 560°C, such as about 370°C to about 490°C, for example about 400°C to about 480°C. Depending on the temperature of the mixture stream 212, generally about 50 wt% to about 99 wt% of the mixture stream being flashed is in the vapor phase, such as about 75 wt% to about 95 wt%.

Additional modifications to the in-situ oil-shale production and processing

[00122] In the production of oil and gas resources, it may be desirable to use the produced hydrocarbons as a source of power for ongoing operations. This may be applied to the

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development of oil and gas resources from oil-shale. As a specific example of energy efficiency, heat may be supplied by surface burners or downhole burners or by circulating hot fluids (such as methane gas or naphtha) into the formation through, for example, wellbores via, for example, natural or artificial fractures. Some burners may be configured to perform flameless combustion. Alternatively, some methods may include combusting fuel within the formation, such as via a natural distributed combustor, which generally refers to a heater that uses an oxidant to oxidize at least a portion of the carbon in the formation to generate heat, and wherein the oxidation takes place in the vicinity proximate to a wellbore. The present methods are not limited to the heating technique employed.

[00123] Further, the fuel for the burners or hot fluids may be provided from the fluid processing facility. Specifically, the fuel for the downhole burners may be supplied from a portion of the hydrocarbons separated from the produced fluid, while the hot fluids may be generated via heat integration with the furnace 201, heat exchanger and other suitable units.

[00124] As another embodiment, when electrically resistive heaters are used in connection with in-situ shale oil recovery, large amounts of power are required. Accordingly, a specific hydrogen content for low-BTU fuels may also be desirable to achieve appropriate burn properties. Accordingly, the H₂ content of the fuel gas may be adjusted via separation or addition in the surface equipment in the facilities to optimize turbine performance. Adjustment of H₂ content in non-shale oil surface facilities utilizing low BTU fuels has been discussed in the patent literature (e.g., U.S. Patent Nos. 6,684,644 and 6,858,049).

[00125] Further, in certain embodiments, as noted above, monitoring of the operations may be beneficial. That is, monitoring may be utilized to optimize the temperatures that the produced fluids are extracted from the formation, which may enhance olefin production. For instance, the process of heating formation hydrocarbons within an organic-rich rock formation, for example, by retorting, may generate fluids, such as water (which is vaporized within the formation) and other fluids, such as hydrocarbons, oxides of carbon, ammonia, molecular nitrogen, and molecular hydrogen. These produced fluids which tend to expand upon heating. Therefore, as temperatures within a heated portion of the formation increase, a pressure within the heated portion may also increase as a result of increased fluid generation, molecular expansion, and vaporization of water. The pressure within a heated portion of an organic-rich rock formation depends on other reservoir characteristics, which may include, for example, formation depth, distance from a heater well, a richness of the formation hydrocarbons within the organic-rich rock formation, the degree of heating, and/or a distance from a producer well. Thus, some correlation exists between subsurface pressure in an oil-

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shale formation and the fluid pressure generated during retorting. This, in turn, indicates that formation pressure may be monitored to detect the progress of a kerogen conversion process.

[00126] Accordingly, it may be desirable to monitor the formation pressure of an oil-shale field during development. Pressure within a formation may be determined at a number of different locations. Such locations may include, but may not be limited to, at a wellhead and at varying depths within a wellbore. In some embodiments, pressure may be measured at a producer well. In an alternate embodiment, pressure may be measured at a heater well. In still another embodiment, pressure may be measured downhole of a dedicated monitoring well.

[00127] Alternatively, pressure generated by expansion of pyrolysis fluids or other fluids generated in the formation may increase for certain configurations. This assumes that an open path to a production well or other pressure sink does not yet exist in the formation. In one aspect, a fluid pressure may be allowed to increase to or above a lithostatic stress. In this instance, fractures in the hydrocarbon containing formation may form when the fluid pressure equals or exceeds the lithostatic stress. For example, fractures may form from a heater well to a production well. The generation of fractures within the heated portion may reduce pressure within the portion due to the production of produced fluids through a production well. In certain embodiments, the lithostatic stress (e.g., value) is between 0 kPa and 6894 kPa, while the aromatics content is less than 62 wt%.

[00128] Once retorting has begun within a subsurface formation, fluid pressure may vary depending upon various factors. These include, for example, thermal expansion of hydrocarbons, generation of fluids, rate of conversion, and withdrawal of generated fluids from the formation. For example, as fluids are generated within the formation, fluid pressure within the pores may increase. Removal of generated fluids from the formation may then decrease the fluid pressure within the near wellbore region of the formation.

[00129] In certain embodiments, a mass of at least a portion of an organic-rich rock formation may be reduced due, for example, to retorting of formation hydrocarbons and the production of hydrocarbon fluids from the formation. As such, the permeability and porosity of at least a portion of the formation may increase. Any in-situ method that effectively produces oil and gas from oil-shale creates permeability in what was originally a very low permeability rock. The extent to which this occurs is illustrated by the large amount of expansion that accommodates fluids generated from kerogen that are unable to flow.

[00130] As an example, a simulated in-situ retorting process has been performed for one ton of Green River oil-shale (e.g., material before conversion and material after conversion).

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The simulated process was carried out at 16547 kPa and 400°C on oil-shale having a total organic carbon content of 22 wt% and a Fisher assay of 42 gallons/ton. Before the conversion, a total of 437 liters of rock matrix existed. This matrix comprised 206 liters of mineral, i.e., dolomite, limestone, etc., and 231 liters of kerogen imbedded within the material. As a result of the conversion the material expanded to 746 liters. This represented 206 liters of mineral (the same number as before the conversion), 189 liters of hydrocarbon liquid, 268 liters of hydrocarbon vapor, and 57 liters of coke. It can be seen that substantial volume expansion occurred during the conversion process, which increases permeability of the rock structure.

[00131] In one embodiment, heating a portion of an organic-rich rock formation in-situ to a production temperature may increase permeability of the heated portion. For example, permeability may increase due to formation of thermal fractures within the heated portion caused by application of heat. As the temperature of the heated portion increases, water may be removed due to vaporization. The vaporized water may escape and/or be removed from the formation. In addition, permeability of the heated portion may also increase as a result of production of hydrocarbon fluids from pyrolysis of at least some of the formation hydrocarbons within the heated portion on a macroscopic scale.

[00132] Certain systems and methods described herein may be used to treat formation hydrocarbons in at least a portion of a relatively low permeability formation (e.g., in "tight" formations that contain formation hydrocarbons). Such formation hydrocarbons may be heated to pyrolyze at least some of the formation hydrocarbons in a selected zone of the formation. Heating may also increase the permeability of at least a portion of the selected zone. Hydrocarbon fluids generated from pyrolysis may be produced from the formation, thereby further increasing the formation permeability.

[00133] Permeability of a selected zone within the heated portion of the organic-rich rock formation may also rapidly increase while the selected zone is heated by conduction. For example, permeability of an impermeable organic-rich rock formation may be less than about 0.1 millidarcy before heating. In some embodiments, pyrolyzing at least a portion of organic-rich rock formation may increase permeability within a selected zone of the portion to greater than about 10 millidarcies, 100 millidarcies, 1 darcy, 10 darcies, 20 darcies, or 50 darcies. Therefore, a permeability of a selected zone of the portion may increase by a factor of more than about 10, 100, 1,000, 10,000, or 100,000. In one embodiment, the organic-rich rock formation has an initial total permeability less than 1 millidarcies, alternatively less than 0.1 or 0.01 millidarcies, before heating the organic-rich rock formation. In one embodiment, the

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organic-rich rock formation has a post heating total permeability of greater than 1 millidarcy, alternatively, greater than 10, 50, or 100 millidarcies, after heating the organic-rich rock formation.

[00134] Further, the organic-rich rock formation may optionally be fractured to aid heat transfer or hydrocarbon fluid production. The fracturing may be accomplished naturally by creating thermal fractures within the formation through application of heat. Thermal fracture formation is caused by thermal expansion of the rock and fluids and by chemical expansion of kerogen transforming into oil and gas. Thermal fracturing can occur both in the immediate region undergoing heating, and in cooler neighboring regions. The thermal fracturing in the neighboring regions is due to propagation of fractures and tension stresses developed due to the expansion in the hotter zones. Thus, by both heating the organic-rich rock and transforming the kerogen to oil and gas, the permeability is increased not only from fluid formation and vaporization, but also via thermal fracture formation. The increased permeability aids fluid flow within the formation and production of the hydrocarbon fluids generated from the kerogen.

[00135] In addition, a process known as hydraulic fracturing may be used. Hydraulic fracturing is a process known in the art of oil and gas recovery where a fracture fluid is pressurized within the wellbore above the fracture pressure of the formation, thus developing fracture planes within the formation to relieve the pressure generated within the wellbore. Hydraulic fractures may be used to create additional permeability and/or be used to provide an extended geometry for a heater well. As noted above in Intl. Patent Application Publication No. 2005/010320 one such method is described.

[00136] In connection with the production of hydrocarbons from a rock matrix, particularly those of shallow depth, a concern may exist with respect to subsidence. This is particularly true in the in-situ heating of organic-rich rock where a portion of the matrix itself is thermally converted and removed. That is initially, the formation may contain formation hydrocarbons in solid forms, such as, for example, kerogen, and water-soluble minerals. Initially, the formation may also be substantially impermeable to fluid flow.

[00137] The in-situ heating of the matrix convert at least a portion of the formation hydrocarbons to create hydrocarbon fluids. This creates permeability within a matured (pyrolyzed) organic-rich rock zone in the organic-rich rock formation. The combination of conversion and increased permeability assists in the movement of hydrocarbon fluids that are to be produced from the formation. At the same time, the loss of supporting matrix material also creates the potential for subsidence relative to the earth surface.

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[00138] In some embodiments, compositions and properties of the hydrocarbon fluids produced by an in-situ conversion process may vary depending on, for example, conditions within an organic-rich rock formation, as noted above. Controlling heat and/or heating rates of a selected section in an organic-rich rock formation may increase or decrease production of selected produced fluids.

[00139] In one or more embodiments, an operating system may be utilized to control the operating conditions of the formation and the associated processing of the hydrocarbons and other produced fluids. In particular, the operating system may include monitoring devices coupled to one or more computer systems, which are coupled to control devices that may adjust the operational settings of different units or components (e.g., adjust the operating conditions). The computer system and other devices may include, for example, one or more general purpose computer systems, microprocessors, digital signal processors, micro-controllers, and the like, programmed according to the teachings of the exemplary embodiments, as will be appreciated by those skilled in the computer and software arts. The devices and subsystems of the exemplary embodiments can communicate with each other using any suitable protocol and can be implemented using one or more programmed computer systems or devices. For instance, one or more interface components may include, for example, internet access, telecommunications in any suitable form (e.g., voice, modem, and the like), wireless communications media, and the like. For example, employed communications networks or links can include one or more wireless communications networks, cellular communications networks, G3 communications networks, Public Switched Telephone Network (PSTNs), Packet Data Networks (PDNs), the Internet, intranets, a combination thereof, and the like.

[00140] The computer system may include memory or computer readable medium for storing a set of instructions and measured data and a processor for executing the set of instructions. Accordingly, the computer systems and devices may store information relating to various processes described herein. This information can be stored in one or more memories, such as, for example, a floppy disk, a flexible disk, hard disk, magnetic tape, any other suitable magnetic medium, a CD-ROM, CDRW, DVD, any other suitable optical medium, punch cards, paper tape, optical mark sheets, any other suitable physical medium with patterns of holes or other optically recognizable indicia, a RAM, a PROM, an EPROM, a FLASH-EPROM, any other suitable memory chip or cartridge, a carrier wave or any other suitable medium from which a computer can read. The data may be organized using data

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structures (e.g., records, tables, arrays, fields, graphs, trees, lists, and the like) included in one or more memories or storage devices listed herein.

[00141] The set of instructions or computer readable instructions may be configured to facilitate operating the system in an enhanced manner. These instructions may be implemented as any specific combination of hardware circuitry and/or software. The computer readable instructions may be embedded on a tangible computer readable medium and configured to cause one or more computer processors to perform the steps of obtaining compositional analyses on a set of in-situ extracted shale oils, the set of in-situ extracted shale oils produced at varied production temperatures and/or levels of lithostatic stress; determining from the compositional analyses values for production temperature and/or lithostatic stress that when achieved produce an in-situ extracted shale oil having a concentration of aromatics at or below a target level, the target level suitable for the production of olefins by cracking; adjusting oil-shale formation extraction conditions to achieve the values for production temperature and/or lithostatic stress; and monitoring the production of an in-situ extracted shale oil, which may optionally be suitable for use as a cracking feedstock for the production of olefins. Further, the set of instructions may also be utilized to interact with a human user, and the like.

[00142] In one embodiment, operating conditions may be determined by measuring at least one property of the organic-rich rock formation. The measured properties may be input into a computer system. The measured data may include at least one property of the produced fluids that is to be produced from the formation. The set of instructions may be executed to determine a set of operating conditions for the extraction of the hydrocarbons from the formation, which may be based on the one or more measured properties (e.g., measured data) along with a model of the formation. The set of instructions may also be configured to monitor the operating conditions within the formation (via monitoring devices located in monitoring well) that may be communicated to the computer system. This measured data (e.g., pressure, temperature, and composition measurements) may be utilized by a set of instructions to calculate different operating conditions for the extraction operations. In this manner, the determined set of operating conditions may be configured to increase production of selected produced fluids from the formation.

[00143] Certain heater well embodiments may include an operating system that is coupled to any of the heater wells such as by insulated conductors or other types of wiring. The operating system may be configured to interface with the heater well. The operating system may receive a signal (e.g., an electromagnetic signal) from a heater that is representative of a

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temperature distribution of the heater well. Additionally, the operating system may be further configured to control the heater well, either locally or remotely. For example, the operating system may alter a temperature of the heater well by altering a parameter of equipment coupled to the heater well. Therefore, the operating system may monitor, alter, and/or control the heating of at least a portion of the formation. For example, the operating system may transmit a signal to the heater well control unit to turn down and/or off the downhole heater after an average temperature in a formation may have reached a selected temperature. Turning down and/or off the heater well may reduce input energy costs, substantially inhibit overheating of the formation, and allow heat to substantially transfer into colder regions of the formation. That is, the optimization of the heater system to avoid overheating the formation may be useful for producing shale oils with higher average hydrogen content that are preferred for producing olefins. Further, this mode of operation reduces olefin and aromatic generation by decreasing the average production temperature.

[00144] Temperature (and average temperatures) within a heated organic-rich rock formation may vary, depending on, for example, proximity to a heater well, thermal conductivity and thermal diffusivity of the formation, type of reaction occurring, type of formation hydrocarbon, and the presence of water within the organic-rich rock formation. At points in the field where monitoring wells are established, temperature measurements may be taken directly in the wellbore. Further, the temperature in the vicinity of heater wells (e.g., the immediately surrounding formation) may be measured or understood. However, it is desirable to interpolate temperatures to points in the formation intermediate temperature sensors and heater wells.

[00145] In accordance with one aspect of the production processes disclosed herein, a temperature distribution within the organic-rich rock formation may be computed using a numerical simulation model, which may be stored on a computer system. The numerical simulation model may calculate a subsurface temperature distribution through interpolation of known data points and assumptions of formation conductivity. In addition, the numerical simulation model may be used to determine other properties of the formation under the assessed temperature distribution. For example, the various properties of the formation may include, but are not limited to, permeability of the formation.

[00146] The numerical simulation model may also include assessing various properties of a fluid formed within an organic-rich rock formation under the assessed temperature distribution. For example, the various properties of a formed fluid may include, but are not limited to, a cumulative volume of a fluid formed in the formation, fluid viscosity, fluid

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density, and a composition of the fluid formed in the formation. Such a simulation may be used to assess the performance of a commercial-scale operation or small-scale field experiment. For example, a performance of a commercial-scale development may be assessed based on, but not limited to, a total volume of product that may be produced from a research-scale operation.

[00147] Some embodiments include producing at least a portion of the hydrocarbon fluids from the organic-rich rock formation. The produced fluid may contain hydrocarbon fluids along with aqueous fluids. The aqueous fluids may contain water-soluble minerals and/or migratory contaminant species. In such instance, the produced fluid may be separated into a hydrocarbon stream and an aqueous stream at a surface facility. Thereafter the water-soluble minerals and/or migratory contaminant species may be recovered from the aqueous stream and the hydrocarbon stream (e.g., hydrocarbon feed) may be further converted into olefins.

[00148] In view thereof, a method for processing a hydrocarbon produced from a oil-shale formation to produce olefins is provided. The method comprises the steps of obtaining production data about production of a hydrocarbon feed; and (i) if the operational data indicates that the hydrocarbon feed was produced via an in-situ method, processing the hydrocarbon feed without hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in a pyrolysis furnace; or (ii) if the operational data indicates that the hydrocarbon feed was produced via an ex-situ method, hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in the pyrolysis furnace.

[00149] It is to be understood that the exemplary embodiments are for exemplary purposes, as many variations of the specific hardware used to implement the exemplary embodiments are possible, as will be appreciated by those skilled in the relevant art(s). For example, the functionality of one or more of the devices and subsystems of the exemplary embodiments can be implemented via one or more programmed computer systems or devices.

[00150] To implement such variations as well as other variations, a single computer system can be programmed to perform the special purpose functions of one or more of the devices and subsystems of the exemplary embodiments. On the other hand, two or more programmed computer systems or devices can be substituted for any one of the devices and subsystems of the exemplary embodiments. Accordingly, principles and advantages of distributed processing, such as redundancy, replication, and the like, also can be implemented, as desired, to increase the robustness and performance of the devices and subsystems of the exemplary embodiments.

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[00151] The produced hydrocarbon fluids may include an oil component (or condensable component) and a gas component (or non-condensable component). Condensable hydrocarbons produced from the formations typically include paraffins, cycloalkanes, mono-aromatics, and di-aromatics as components. Such condensable hydrocarbons may also
5 include other components such as tri-aromatics and other hydrocarbon species.

[00152] In certain embodiments, a majority of the hydrocarbons in the produced fluid ($\geq$ 50.0 wt% based on the weight of the produced fluids) may have a carbon number of less than approximately 25. Alternatively, less than about 15 wt% of the hydrocarbons in the fluid may have a carbon number greater than approximately 25. The non-condensable
10 hydrocarbons may include, but are not limited to, hydrocarbons having carbon numbers less than 5. Further, in certain embodiments, the API gravity of the condensable hydrocarbons in the produced fluid may be approximately 20 or above (e.g., above 25, 30, 40, 50, etc.). In certain embodiments, the hydrogen to carbon atomic ratio in produced fluid may be at least approximately 1.7 (e.g., at least 1.8, 1.9, etc.).

[00153] One embodiment disclosed herein includes an in-situ method of producing hydrocarbon fluids with improved properties from an organic-rich rock formation. It has been surprisingly discovered that the quality of the hydrocarbon fluids produced from in-situ heating and retorting of an organic-rich rock formation may be improved by selecting
15 sections of the organic-rich rock formation with higher lithostatic stress for in-situ heating and retorting.

[00154] The method may include in-situ heating of a section of the organic-rich rock formation that has a high lithostatic stress to embodiment hydrocarbon fluids with enhanced properties. The method may include creating the hydrocarbon fluid by retorting of a solid hydrocarbon and/or a heavy hydrocarbon present in the organic-rich rock formation.
25 Embodiments may include the hydrocarbon fluid being partially, predominantly or substantially completely created by retorting of the solid hydrocarbon and/or heavy hydrocarbon present in the organic-rich rock formation. The method may include heating the section of the organic-rich rock formation by any method, including any of the methods described herein. For example, the method may include heating the section of the organic-
30 rich rock formation by electrical resistance heating. Further, the method may include heating the section of the organic-rich rock formation through use of a heated heat transfer fluid. The method may include heating the section of the organic-rich rock formation to above 270°C. Alternatively, the method may include heating the section of the organic-rich rock formation between 270°C and 500°C.

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[00155] The method may include heating in-situ a section of the organic-rich rock formation having a lithostatic stress greater than 1379 kPa and producing a hydrocarbon fluid from the heated section of the organic-rich rock formation. In alternative embodiments, the heated section of the organic-rich rock formation may have a lithostatic stress greater than 2758 kPa. In alternative embodiments, the heated section of the organic-rich rock formation may have a lithostatic stress greater than 800 psi, greater than 6895 kPa, greater than 8274 kPa, greater than 10342 kPa, or greater than 13790 kPa. It has been found that in-situ heating and retorting of organic-rich rock formations with increasing amounts of stress lead to the production of hydrocarbon fluids with improved properties.

10 [00156] The lithostatic stress of a section of an organic-rich formation can normally be estimated by recognizing that it generally is equal to the weight of the rocks overlying the formation. The density of the overlying rocks can be expressed in units of psi/ft (pressure per square inch). Generally, this value falls between 0.8 and 1.1 psi/ft and can often be approximated as 0.9 psi/ft. As a result, the lithostatic stress of a section of an organic-rich formation can be estimated by multiplying the depth of the organic-rich rock formation interval by 0.9 psi/ft. Thus the lithostatic stress of a section of an organic-rich formation occurring at about 1,000 ft can be estimated to be (0.9 psi/ft) multiplied by (1,000 ft) or 6205 kPa. If a more precise estimate of lithostatic stress is desired the density of overlying rocks can be measured using wireline logging techniques or by making laboratory measurements on samples recovered from coreholes.

20 [00157] It has been found that in-situ heating and retorting of organic-rich rock formations with differing amounts of stress lead to the production of hydrocarbon fluids with changed properties. The method may include in-situ heating of a section of the organic-rich rock formation that has a selected lithostatic stress to embodiment hydrocarbon fluids with desired properties. Selecting or maintaining a higher lithostatic stress increases the production of aromatic and cyclic hydrocarbon compounds, while decreasing the production of normal and isoprenoid (or branched) hydrocarbon compounds. Alternatively, maintaining a lower lithostatic stress decreases the production of aromatic and cyclic hydrocarbon compounds, while increasing the production of normal and isoprenoid (or branched) hydrocarbon compounds. The method may include heating in-situ a section of the organic-rich rock formation having a lithostatic stress greater than 1379 kPa and producing a hydrocarbon fluid from the heated section of the organic-rich rock formation. In alternative embodiments, the heated section of the organic-rich rock formation may have a lithostatic stress greater than 2758 kPa. In alternative embodiments, the heated section of the organic-rich rock formation

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may have a lithostatic stress greater than 5516 kPa, greater than 6895 kPa, greater than 8274 kPa, greater than 10342 kPa, or greater than 13790 kPa depending on the composition desired. In alternative embodiments, the heated section of the organic-rich rock formation may have a lithostatic stress less than 5516 kPa, less than 6895 kPa, less than 10342 kPa, less than 17237 kPa, or less than 20684 kPa depending on the composition desired. In alternative
5 embodiments, the heated section of the organic-rich rock formation may have a lithostatic stress between 1379 kPa and 6895 kPa, between 1379 kPa and 6205 kPa, between 1379 kPa and 5516 kPa, between 1379 kPa and 4826 kPa, or between 1379 kPa and 4137 kPa depending on the composition desired. In alternative embodiments, the heated section of the
10 organic-rich rock formation may have a lithostatic stress between 5516 kPa and 20684 kPa, between 6205 kPa and 20684 kPa, between 6895 kPa and 20684 kPa, between 8274 kPa and 20684 kPa, or between 10342 kPa and 20684 kPa depending on the composition desired.

[00158] The organic-rich rock formation may be, for example, a heavy hydrocarbon formation or a solid hydrocarbon formation. Particular examples of such formations may
15 include an oil-shale formation, a tar sands formation or a coal formation. Particular formation hydrocarbons present in such formations may include oil-shale, kerogen, coal, and/or bitumen.

[00159] The hydrocarbon fluid produced from the organic-rich rock formation may include both a condensable hydrocarbon portion (e.g., liquid) and a non-condensable
20 hydrocarbon portion (e.g., gas). The hydrocarbon fluid may additionally be produced together with non-hydrocarbon fluids. Exemplary non-hydrocarbon fluids include, for example, water, carbon dioxide, hydrogen sulfide, hydrogen, ammonia, and/or carbon monoxide.

[00160] The condensable hydrocarbon portion of the hydrocarbon fluid may be a fluid
25 present within different locations associated with an organic-rich rock development project. For example, the condensable hydrocarbon portion of the hydrocarbon fluid may be a fluid present within a production well that is in fluid communication with the organic-rich rock formation. The production well may serve as a device for withdrawing the produced hydrocarbon fluids from the organic-rich rock formation. Alternatively, the condensable
30 hydrocarbon portion may be a fluid present within processing equipment adapted to process hydrocarbon fluids produced from the organic-rich rock formation. Exemplary processing equipment is described herein. Alternatively, the condensable hydrocarbon portion may be a fluid present within a fluid storage vessel. Fluid storage vessels may include, for example, fluid storage tanks with fixed or floating roofs, knock-out vessels, and other intermediate,

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temporary or product storage vessels. Alternatively, the condensable hydrocarbon portion may be a fluid present within a fluid transportation pipeline. A fluid transportation pipeline may include, for example, piping from production wells to processing equipment or fluid storage vessels, piping from processing equipment to fluid storage vessels, or pipelines
5 associated with collection or transportation of fluids to or from intermediate or centralized storage locations.

Examples

[00161] Laboratory testing facilities were developed to simulate in-situ retorting at different conditions. The testing methods utilized a Parr bomb, model number 243HC5,
10 which is available from Parr Instrument Company, with a custom loadframe that allowed oil-shale samples to be heated at well defined temperatures with or without application of additional mechanical stress and or gas pressure. The tests were performed under a number of conditions and the oils produced were analyzed for detailed molecular composition using a variety of techniques. The primary methods used for detailed compositional analysis
15 included gas and liquid chromatography and mass spectrometry.

[00162] Table 1 compares the composition of oils produced from Green River Shale samples produced by simulated in-situ retorting at several conditions with that produced in earlier studies using ex-situ retorting methods at both long and short reaction times. The experiments illustrate the effect of several parameters on the composition of the shale oil
20 produced. Temperatures ranged from 350°C to 393°C, while run durations were varied between one and twenty-eight days. Hydrostatic pressure was applied using argon with initial pressures ranging from 345 kPa to 3447 kPa. Layer normal uniaxial stress was applied in some experiments at either 2758 kPa or 6895 kPa with the sample constrained laterally. All experiments were conducted as a closed system. In all cases liquids and gas were sampled
25 after cooling the experiment to room temperature (e.g., about 21°C).

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TABLE 1**Compositional Characteristics for Shale Oils Produced Under Different Conditions**

Experiment	1	2	3	4	5	6	6
Pyrolysis Type	Simulated <i>In-situ</i>	Simulated <i>In-situ</i>	Simulated <i>In-situ</i>	<i>Ex-situ</i>	<i>Ex-situ</i>	<i>Ex-situ</i>	<i>Ex-situ</i>
Temp (°C)	375	393	393	496	510	538	499
Rxn Time	24 hr	24 hr	24 hr	10 min	10 min	6 sec	17 min
Applied Stress (kPa)	None	None	6895	None	None	None	None
C5+ Oil Composition (wt%)							
Hydrogen	12.9	12.4	11.0	11.9	11.6	10.7	9.8
Oxygen	NM	NM	NM	1.2	1.6	3.0	1.0
Sulfur	0.4	0.4	0.6	0.8	0.8	0.7	1.0
Nitrogen	0.05	0.06	0.11	1.3	1.9	1.6	2.3
Aromatics	33.6	42.2	61.5	NM	NM	NM	NM
Alkanes	44.0	38.4	18.9	NM	NM	NM	NM
Alkenes	9.3	9.1	13.5	NM	NM	NM	NM
Cyclic Alkanes	13.2	10.2	6.2	NM	NM	NM	NM
Benzenes	14.8	17.7	28.2	NM	NM	NM	NM
Naphthalenes	8.5	12.5	17.0	NM	NM	NM	NM

NM=not measured

[00163] From the data presented in Table 1, various observations are noted. First, oil samples produced by simulated in-situ retorting at 371°C to 399°C had significantly higher overall hydrogen content when compared to shale oil produced at higher temperature using ex-situ methods. Second, oils produced at lower average temperature and low applied stress had the highest overall hydrogen content. These oils also had the lowest nitrogen and sulfur content. Third, oils produced at higher temperature and with applied mechanical stress or gas pressure tended to have lower hydrogen and higher aromatic content.

[00164] It is believed based on extensive steam cracking experience with yields for steam cracking gas oils and naphthas with different characteristics that shale oil fluids may produce higher yields of light olefins along with higher yields of steam cracked naphtha than many other conventional crudes, such as Zafiro crude. In particular, shale oil fluids produced by in situ retorting are expected to produce higher olefin yields as compared to oils produced using conventional ex-situ retort methods, based on at least the higher hydrogen content in the oil as noted in the table. The steam cracked naphtha may be useful as a gasoline blending component and as a source of feedstock for producing aromatics, such as benzene and paraxylene. Further, the shale oil is believed to produce lower yields of undesirable tar as

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compared to the other crudes. These results indicate that shale oils produced by in-situ retorting may be highly attractive steam cracking feeds in a steam cracking furnace unit equipped with an integrated knock out drum separation device for heavy hydrocarbons boiling above about 560°C.

5 [00165] While the focus of this disclosure has been the use of in-situ-derived shale oils, it is to be understood to not be so limited. In particular, various aspects disclosed herein may be employed with ex-situ-derived shale oils. However, it is to be recognized that ex-situ-derived shale oils may require hydrotreating prior to cracking such a feed in the pyrolysis furnace. Hydrotreating can be used to increase hydrogen content and to reduce sulfur,
10 oxygen, and nitrogen to low levels.

[00166] When numerical lower limits and numerical upper limits are listed herein, ranges from any lower limit to any upper limit are contemplated.

[00167] This application is a may include processes and equipment, as noted in U.S. Serial Nos. 11/973,898; 60/997,654; 60/997,650; 60/997,646; 60/997,645; 60/997,648; 60/997,653;
15 60/997,649; 60/851,432; 60/851,534; 60/851,535; 60/851,819; 60/851,786; and 60/851,820, which are hereby incorporated by reference in their entirety. All patents, test procedures, and other documents cited herein are fully incorporated by reference to the extent such disclosure is not inconsistent and for all jurisdictions in which such incorporation is permitted.

[00168] The embodiments of the present techniques may also comprise embodiments such
20 as in the following exemplary claims:

1. A method of producing and processing a hydrocarbon feed for the production of olefins from an in-situ extracted oil-shale formation, comprising:
 - obtaining compositional analysis data for in-situ extracted shale oils;
 - determining from the compositional analysis data a value of oil-shale formation
25 extraction conditions that include a production temperature or a lithostatic stress that when achieved produces an in-situ extracted shale oil having a concentration of aromatics at or below a target level, the target level suitable for the production of olefins by thermal cracking;
 - adjusting the oil-shale formation extraction conditions for an oil-shale formation to
30 achieve the in-situ extracted shale oil having a concentration of aromatics at or below the target level; and
 - producing an in-situ extracted shale oil, which may optionally be suitable for use as a thermal cracking feedstock for the production of olefins.

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2. The method of paragraph 1, comprising obtaining compositional analysis data for in-situ extracted shale oils that are produced at varied production temperatures.
3. The process of any one of paragraphs 1 and 2, wherein the compositional analysis data are for in-situ extracted shale oils produced at varied production temperatures and/or
5 levels of lithostatic stress.
4. The method of paragraph 1, wherein adjusting the oil-shale formation extraction conditions comprises adjusting the production temperature applied to the oil-shale formation to less than or equal to 475°C.
5. The method of paragraph 1, wherein adjusting the oil-shale formation extraction
10 conditions comprises adjusting the production temperature applied to the oil-shale formation to between 325°C and 450°C.
6. The method of paragraph 1, wherein the concentration of aromatics is less than 50 wt% aromatics in the in-situ extracted shale oil.
7. The method of paragraph 1, wherein the concentration of aromatics is less than 62
15 wt% aromatics in the in-situ extracted shale oil.
8. The method of paragraph 1, wherein the compositional analyses includes gas and liquid chromatography and/or mass spectrometry.
9. A method for producing olefins, the method comprising:
obtaining a hydrocarbon feed having a hydrogen content of at least 12 wt% and at
20 least a portion of the hydrocarbon feed is produced from an oil-shale formation, wherein the at least a portion of the hydrocarbon feed is greater than 30 wt% of the hydrocarbon feed;
cracking the hydrocarbon feed in a pyrolysis reactor without prior hydroprocessing, such as hydrotreating, to produce an effluent; and
processing the effluent to produce olefins.
- 25 10. The method of paragraph 9, wherein the at least a portion of the hydrocarbon feed was produced at a production temperature of less than or equal to 475°C.
11. The method of paragraph 10, wherein the at least a portion of the hydrocarbon feed was produced at the production temperature being between 325°C and 450°C.
12. The method of paragraph 11, wherein the at least a portion of the hydrocarbon feed
30 was produced at the production temperature being between 375°C and 425°C.
13. The method of paragraph 9, comprising separating the effluent into olefins and aromatic products.
14. The method of paragraph 9, comprising separating non-hydrocarbon products from the hydrocarbon feed prior to cracking the hydrocarbon feed in the pyrolysis reactor.

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15. The method of paragraph 9, comprising combining the hydrocarbons obtained from the oil-shale formation with a heavy petroleum feedstock prior to form the hydrocarbon feed.

16. The method of paragraph 15, wherein the heavy petroleum feedstock is selected from atmospheric resid and crude oil.

5 17. A method for obtaining and processing hydrocarbons comprising:

heating a portion of an oil-shale formation to a production temperature of less than or equal to 475°C to cause the separation of a kerogen-derived oil from the rock in the oil-shale formation;

10 recovering the kerogen-derived oil from the oil-shale formation as an in-situ extracted shale oil;

cracking at least a portion of the in-situ extracted shale oil in a cracking reactor to produce effluent; and

processing the effluent to produce olefins or aromatics.

15 18. The method of paragraph 17, wherein the kerogen-derived oil is produced at a temperature within the range of 325°C to 450°C.

19. The method of paragraph 17, wherein the kerogen-derived oil is produced at a temperature within the range of 375°C to 425°C.

20. The method of paragraph 17, comprising:

obtaining compositional analysis data for in-situ extracted shale oil;

20 determining from the compositional analysis data a value of a production temperature or a lithostatic stress that when achieved produces an in-situ extracted shale oil having a concentration of aromatics at or below a target level; and

adjusting oil-shale formation extraction conditions for the oil-shale formation to achieve the value for production temperature and/or lithostatic stress.

25 21. The method of paragraph 20, wherein the compositional analysis data are for in-situ extracted shale oils produced at varied production temperatures and/or levels of lithostatic stress.

22. The method of paragraph 17, wherein the kerogen-derived oil is produced at a temperature of less than or equal to about 350°C and the aromatics content is less than 50
30 wt%.

23. The method of paragraph 17, further comprising the step of separating in a separation vessel a cracked product and a byproduct stream.

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24. The method of paragraph 23, further comprising the step of combining the hydrocarbons obtained from the oil-shale formation with a heavy petroleum feedstock prior to said step of introducing the hydrocarbons to the cracking reactor.

25. The method of paragraph 24, wherein the heavy petroleum feedstock is selected from atmospheric resid and crude oil.

26. A method for processing a hydrocarbon feed produced from an oil-shale formation to produce olefins, comprising:

obtaining operational data about production of a hydrocarbon feed; and (i) if the operational data indicates that the hydrocarbon feed was produced via an in-situ method, processing the hydrocarbon feed without hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in a pyrolysis furnace; or (ii) if the operational data indicates that the hydrocarbon feed was produced via an ex-situ method, hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in the pyrolysis furnace.

27. A method for processing a hydrocarbon feed produced from an oil-shale formation to produce olefins, comprising:

obtaining operational data about production of a hydrocarbon feed;

determining whether the operational data indicates that the hydrocarbon feed was produced via an in-situ method or an ex-situ method; and

processing the hydrocarbon feed without hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in a pyrolysis furnace to produce olefins, if the hydrocarbon feed is determined to be produced via the in-situ method.

28. The method of any one of paragraphs 26 and 27, wherein the operational data indicates that the hydrocarbon feed was produced via an in-situ method and the production temperature is less than or equal to about 475°C.

29. The method of paragraph 28, wherein the production temperature is within the range of about 325°C to about 450°C.

30. The method of paragraph 29, wherein the production temperature is within the range of about 375°C to about 425°C.

31. The method of any one of paragraphs 26 and 27, wherein the operational data indicates that the hydrocarbon feed was produced via an in-situ method and the production temperature is less than or equal to about 350°C and the aromatics content is less than 50 wt%.

32. A computer program product for facilitating processing a hydrocarbon feed produced from an oil-shale formation to produce olefins, including one or more computer readable

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instructions embedded on a tangible computer readable medium and configured to cause one or more computer processors to perform the steps of:

- 5 (a) obtaining compositional analyses on a set of in-situ extracted shale oils, the set of in-situ extracted shale oils produced at varied production temperatures and/or levels of lithostatic stress;
- (b) determining from the compositional analyses values for production temperature and/or lithostatic stress that when achieved produce an in-situ extracted shale oil having a concentration of aromatics at or below a target level, the target level suitable for the production of olefins by cracking;
- 10 (c) adjusting oil-shale formation extraction conditions to achieve the values for production temperature and/or lithostatic stress; and
- (d) monitoring production of an in-situ extracted shale oil.

33. The method of paragraph 32, wherein the in-situ extracted shale oil has a hydrogen content of at least about 12.0 wt%.

15 34. The method of paragraph 32, wherein the value for production temperature is within the range of about 325°C to about 450°C.

35. The method of paragraph 32, wherein the value for lithostatic stress is between about 0 and about 6894 kPa and the aromatics content is less than 62 wt%.

20 36. The method of paragraph 32, wherein the compositional analyses includes gas and liquid chromatography and/or mass spectrometry.

[00169] While the illustrative embodiments disclosed herein have been described with particularity, it will be understood that various other modifications will be apparent to and can be readily made by those skilled in the art without departing from the spirit and scope of the disclosure. Accordingly, it is not intended that the scope of the claims appended hereto
25 be limited to the examples and descriptions set forth herein, but rather that the claims be construed as encompassing all the features of patentable novelty which reside herein, including all features which would be treated as equivalents thereof by those skilled in the art to which this disclosure pertains.

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CLAIMS

What is claimed is:

1. A method of processing a hydrocarbon feed for the production of olefins from an in-situ extracted oil-shale formation, comprising:
 - 5 obtaining compositional analysis data for in-situ extracted shale oils;
determining from the compositional analysis data a value of oil-shale formation extraction conditions that include a production temperature or a lithostatic stress that when achieved produces an in-situ extracted shale oil having a hydrogen content ≥ 12.0 wt% and an aromatics content ≤ 50.0 wt% based on the weight of the in-situ extracted shale oil;
 - 10 adjusting the oil-shale formation extraction conditions for an oil-shale formation to achieve the in-situ extracted shale oil having a concentration of aromatics at or below the target level, the extraction conditions including:
 - (a) exposing the formation to a temperature $\leq 900^{\circ}\text{C}$,
 - (b) exposing the in-situ extracted shale oil to a production temperature $\leq 475^{\circ}\text{C}$, and
 - 15 (c) a lithostatic stress ≤ 17237 kPa (gauge); and
producing an in-situ extracted shale oil having a hydrogen content ≥ 12.0 wt% and an aromatics content ≤ 62.0 wt% based on the weight of the in-situ extracted shale oil.
2. The method of claim 1, wherein the extraction conditions include exposing the formation to an average temperature $\leq 475^{\circ}\text{C}$ and exposing the in-situ extracted shale oil to a
20 temperature in the range of 350°C to 450°C .
3. The method of claims 1 or 2, wherein adjusting the oil-shale formation extraction conditions comprise exposing the formation to a temperature less than or equal to 475°C .
4. The method of any of claims 1 - 3, wherein adjusting the oil-shale formation extraction conditions comprise exposing the formation to a temperature in the range of 325°C
25 to 450°C .
5. The method of any of claims 1 - 4, wherein the lithostatic stress is ≤ 6894 kPa.
6. The method of any of claims 1 - 5, wherein the concentration of aromatics is less than 50.0 wt% aromatics in the in-situ extracted shale oil.
7. A method for producing olefins, the method comprising:
 - 30 obtaining a hydrocarbon feed having a hydrogen content of at least 12 wt% and at least 30.0 wt% of the hydrocarbon feed being produced from an oil-shale formation, based on the weight of the hydrocarbon feed;
cracking the hydrocarbon feed in a pyrolysis reactor without prior hydrotreating to produce an effluent; and

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processing the effluent to produce olefins.

8. The method of claim 7, wherein the portion of the hydrocarbon feed produced from the shale formation is produced at a production temperature of less than or equal to 475° C.

9. The method of claims 7 or 8, wherein the portion of the hydrocarbon feed produced
5 from the shale formation is produced at the production temperature being between 325°C and 450°C.

10. The method of any of claims 7 - 9, comprising separating the effluent into olefins and aromatic products.

11. The method of claim 7, comprising separating non-hydrocarbon products from the
10 hydrocarbon feed prior to cracking the hydrocarbon feed in the pyrolysis reactor.

12. The method of any of claims 7 - 9, comprising combining the hydrocarbons obtained from the oil-shale formation with a heavy petroleum feedstock prior to form the hydrocarbon feed.

13. The method of claim 12, wherein the heavy petroleum feedstock is selected from
15 atmospheric resid and crude oil.

14. A method for processing a hydrocarbon feed produced from an oil-shale formation to produce olefins, comprising:

obtaining operational data about production of a hydrocarbon feed;

determining whether the operational data indicates that the hydrocarbon feed was
20 produced via an in-situ method or an ex-situ method; and

processing the hydrocarbon feed without hydrotreating the hydrocarbon feed prior to cracking the hydrocarbon feed in a pyrolysis furnace to produce olefins is determined to be produced via the in-situ method.

15. The method of claim 14, wherein the operational data indicates that the hydrocarbon
25 feed was produced via an in-situ method and the production temperature is less than or equal to about 475°C.

16. The method of claims 14 or 15, wherein the production temperature is within the range of about 325°C to about 450°C.

17. The method of any of claims 14 - 16, wherein the operational data indicates that the
30 hydrocarbon feed was produced via an in-situ method and the production temperature is less than or equal to about 350°C and the aromatics content is less than 50 wt%.

18. A computer program product for facilitating processing a hydrocarbon feed produced from an oil-shale formation to produce olefins, including one or more computer readable

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instructions embedded on a tangible computer readable medium and configured to cause one or more computer processors to perform the steps of:

- 5 (a) obtaining compositional analyses on a set of in-situ extracted shale oils, the set of in-situ extracted shale oils produced at varied production temperatures and/or levels of lithostatic stress;
 - (b) determining from the compositional analyses values for production temperature and/or lithostatic stress that when achieved produce an in-situ extracted shale oil having a concentration of aromatics at or below a target level, the target level suitable for the production of olefins by cracking;
 - 10 (c) adjusting oil-shale formation extraction conditions to achieve the values for production temperature and/or lithostatic stress; and
 - (d) monitoring production of an in-situ extracted shale oil.
19. The method of claim 18, wherein the in-situ extracted shale oil has a hydrogen content of at least 12.0 wt%.
- 15 20. The method of claims 18 or 19, wherein the production temperature is in the range of 325°C to 450°C.
21. The method of any of claims 18 - 20, wherein the value for lithostatic stress is in the range of 0 to 6894 kPa and the aromatics content is less than 62 wt% based on the weight of the in-situ extracted shale oils.
- 20 22. The method of any of claims 18 - 21, wherein the compositional analyses include gas and liquid chromatography and/or mass spectrometry.

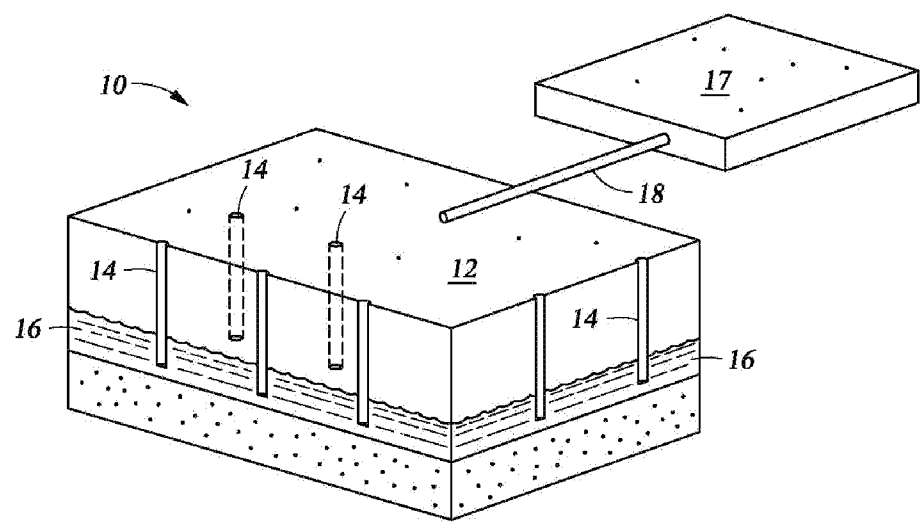
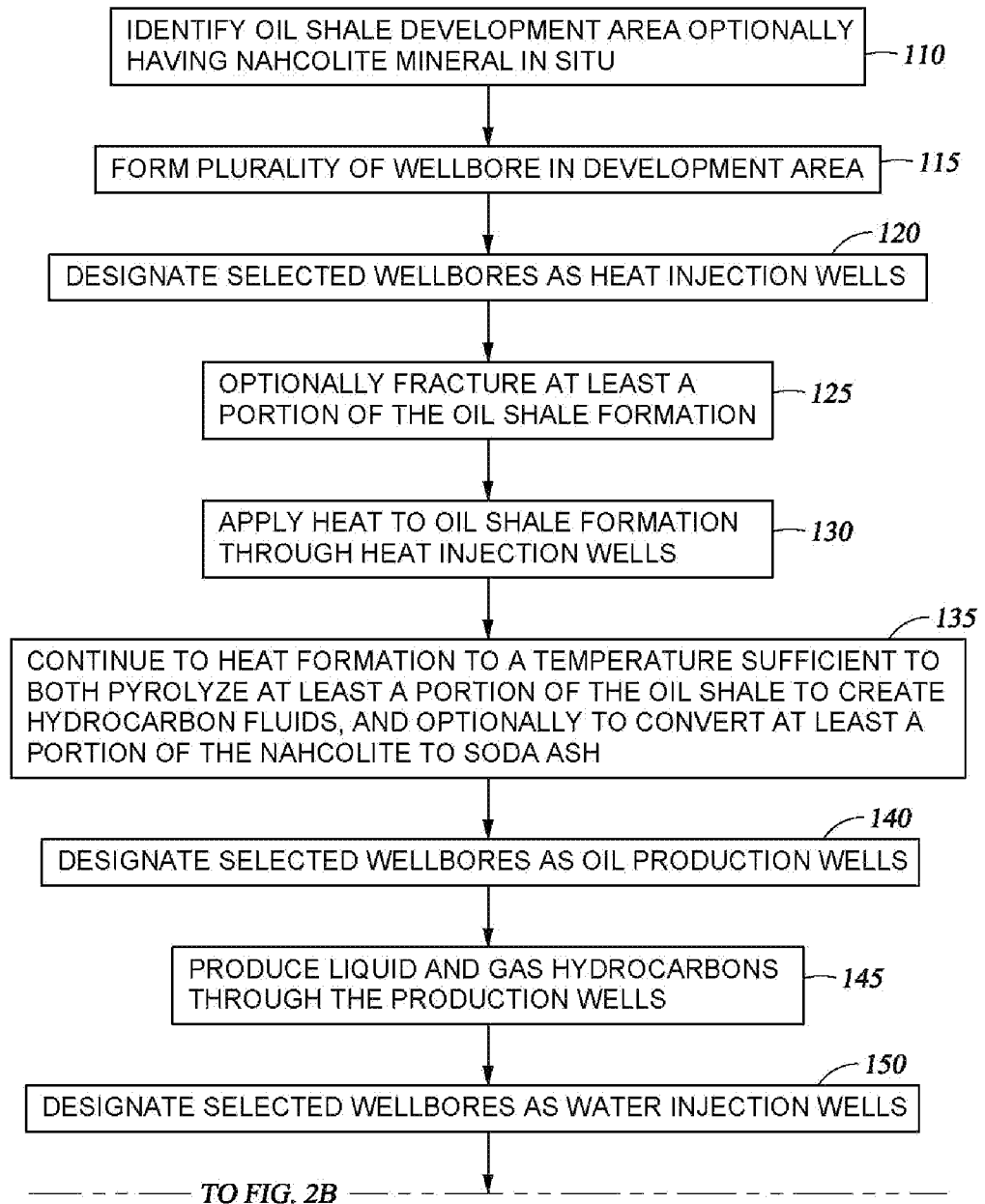
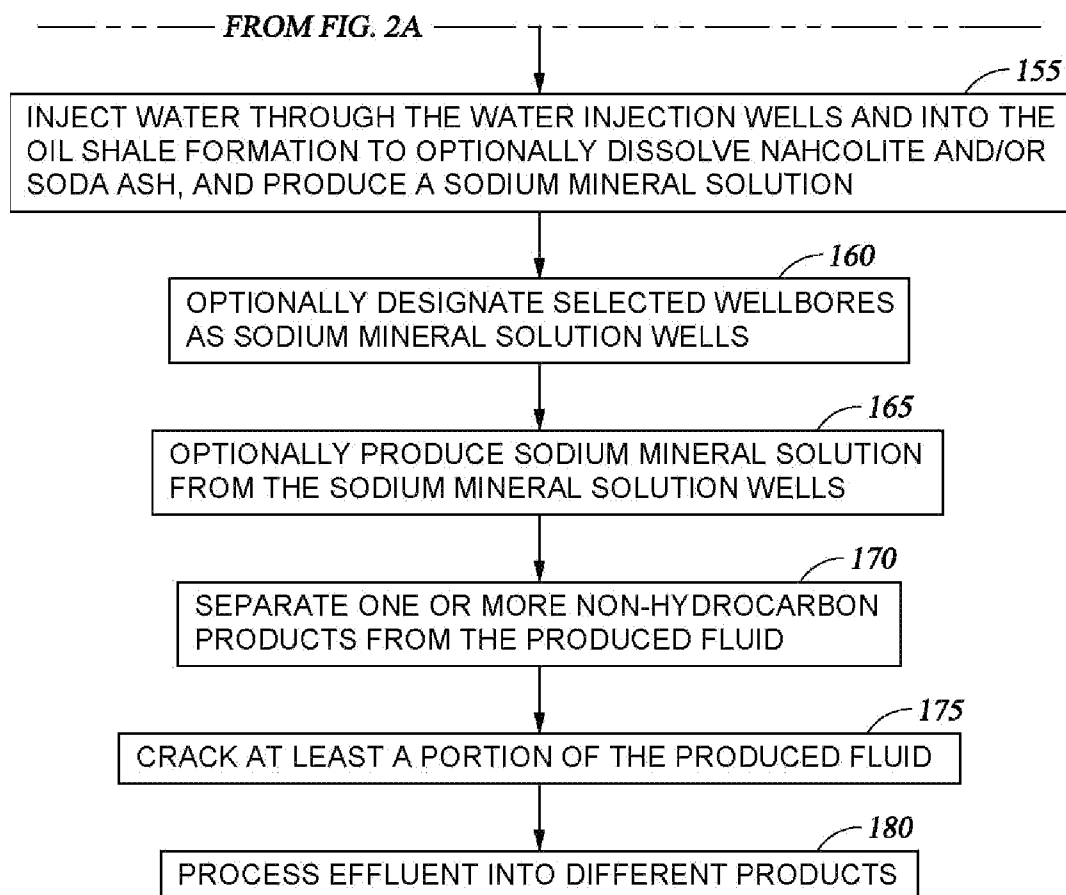


Fig. 1

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Fig. 2A

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*Fig. 2B*

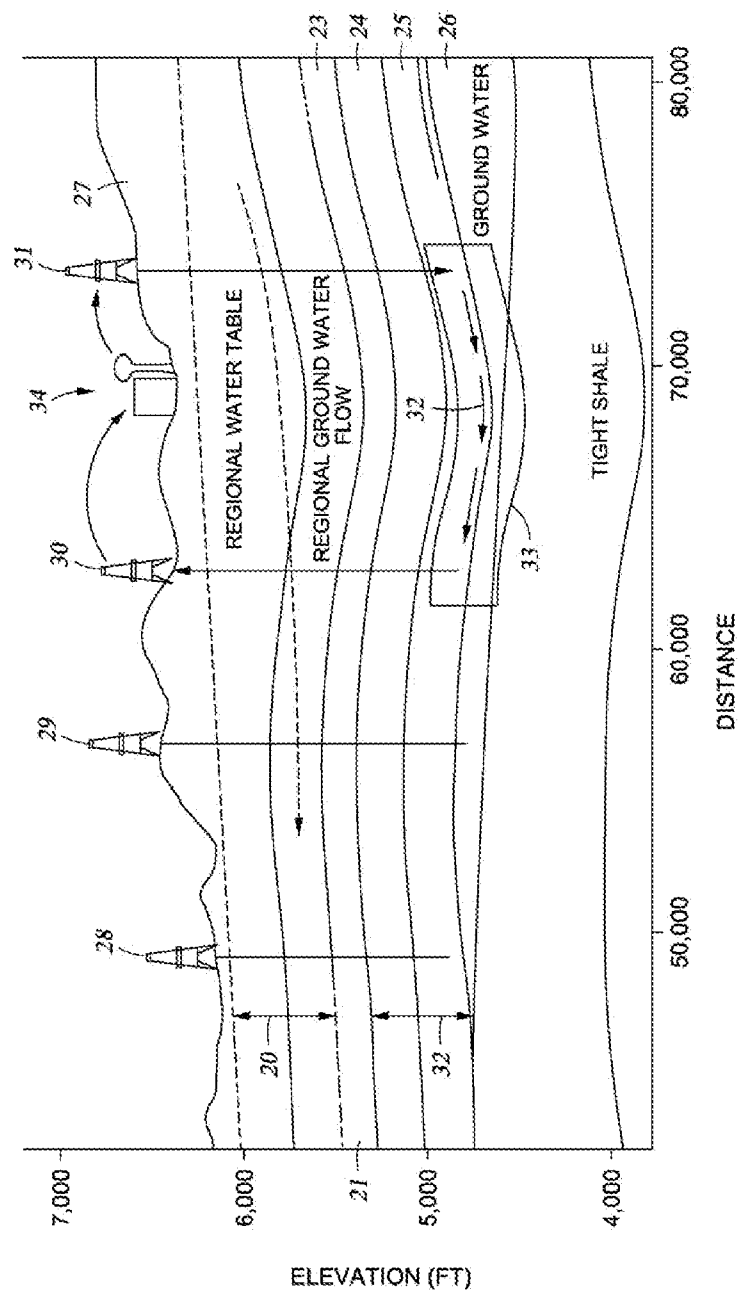
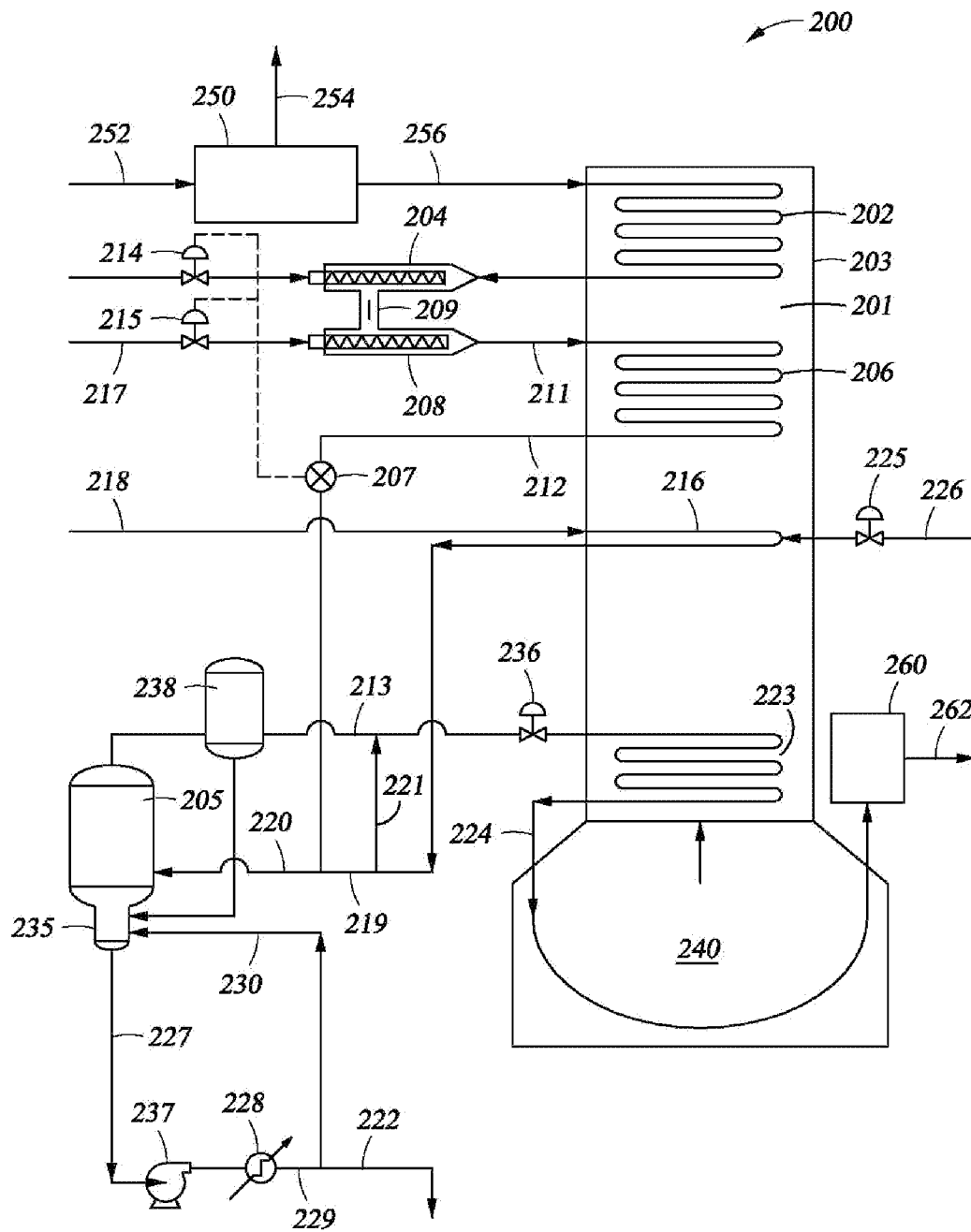


Fig. 3

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*Fig. 4*

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/022918

A. CLASSIFICATION OF SUBJECT MATTER

INV. C10G45/46 B01J29/06 C10G45/00 B01J29/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

B01J C10G

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

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

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2008/048451 A2 (EXXONMOBIL UPSTREAM RES CO [US]; KAMINSKY ROBERT D [US]) 24 April 2008 (2008-04-24)	1-22
Y	see paragaraphs [0094], [0120], [0142], [0162]; see figure 5.	1-22
X	US 2008/207970 A1 (MEURER WILLIAM P [US] ET AL) 28 August 2008 (2008-08-28)	1-22
Y	see paragraphs [0246]-[0252], [0256], [0257]; ----- -/-	1-22



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

28 March 2012

Date of mailing of the international search report

04/04/2012

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Rumbo, Angel

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/022918

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WILLIAN A. SYMINGTON ET AL.: "ExxonMobil's Electrofrac Process for In Situ Oil Shale Conversion", AAPG Datapages/Search and Discovery AAPG Annual Convention, 21 April 2008 (2008-04-21), pages 1-14, XP002662337, SAN ANTONIO, TEXAS (US) Retrieved from the Internet: URL:http://www.searchanddiscovery.com/documents/2008/08131symington/ndx_symington.pdf [retrieved on 2011-10-28] see page 7 = "T=268°C"; see page 8 = "Stress is applied in axial direction" -----	1-22
Y	HUI TIAN ET AL.: "NEW INSIGHTS INTO THE VOLUME AND PRESSURE CHANGES DURING THE THERMAL CRACKING OF OIL TO GAS IN RESERVOIRS; IMPLICATIONS FOR THE IN-SITU ACCUMULATION OF GAS CRACKED FROM OILS", AAPG BULLETIN, vol. 92, no. 2, 28 February 2008 (2008-02-28), pages 181-200, XP002662339, SEE PAGE 187, FIGURE 5; SEE TABLE 2 -----	1-22
Y	DANIEL A. NETZEL ET AL.: "N.M.R. STUDY OF US EASTERN AND WESTERN SHALE OILS PRODUCED BY PYROLYSIS AND HYDROLYSIS", FUEL, vol. 61, 30 November 1982 (1982-11-30), pages 1101-1109, XP002662340, see tables 1,4, 6,7,8 and 9; see page 1104 "Shale oil analytical data" and "Shale oil n.m.r. data" -----	1-22
Y	US 4 458 757 A (BOCK JAN [US] ET AL) 10 July 1984 (1984-07-10) see tables I-XI; see figure; see claim 1; see examples 1-12. -----	1-22
Y	WO 2005/045192 A1 (EXXONMOBIL UPSTREAM RES CO [US]; KAMINSKY ROBERT D [US]; SYMINGTON WIL) 19 May 2005 (2005-05-19) see claims 1-23; see figures see page 7, lines 8-16. ----- -/--	1-22

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2012/022918

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	R MICHELS ET AL.: "EFFECTS OF PRESSURE ON ORGANIC MATTER MATURATION DURING CONFINED PYROLYSIS OF WOODFORD KEROGEN", ENERGY AND FUELS, vol. 8, 31 December 1994 (1994-12-31), pages 741-754, XP002662338, SEE PAGE 744, LEFT COLUMN, EXPERIMENTAL AND ANALYTICAL SECTION, LINES 1-19; SEE TABLES 1-3	1-22
Y	LEVENT BALLICE: "STEPWISE CHEMICAL DEMINERALIZATION OF GÖYNÜK (TURKEY) OIL SHALE AND PYROLYSIS OF DEMINERALIZATION PRODUCTS", IND. ENG. CHEM. RES., 1 May 2006 (2006-05-01), pages 906-912, XP002662341, see page 907= "Pyrolysis experiments" see tables 3-6; see figures 2-4	1-22
Y	K.DAS: "Solvent and Supercritical Fluid Extraction of Oil Shale: A Literature Survey", The National Energy Technology Laboratory (NETL), 31 December 1989 (1989-12-31), pages 1-24, XP002662342, U.S. DEPARTMENT OF ENERGY, VIRGINIA (US) Retrieved from the Internet: URL: http://www.netl.doe.gov/KMD/cds/disk22/G-CO2%20&%20Gas%20Injection/METC89_4092.pdf [retrieved on 2011-10-28] see tables 1-2; see point 1.4 "pyrolysis mechanism " lines 10-12= "440°C" ; see point 2.2 "Low temperature recovery"; see point 2.3 "Extraction of Eastern oil shale", last line "BTX"	1-22
Y	R.M.BALDWIN ET AL.: "PYROLYSIS OF OIL SHALE IN SUPERCRITICAL TOLUENE: REACTION MECHANISM AND ROLE OF HYDROGEN", FUEL PROCESSING TECHNOLOGY, vol. 13, 31 December 1986 (1986-12-31), pages 103-110, XP002662343, SEE TABLES 1-4	1-22
	----- -/--	

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2012/022918

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Mark T. Atwood: "Integration of Large Scale Retorting Operations with Laboratory Testing and Analyses.", Colorado Energy Research Institute 26th Oil Shale Symposium, 19 October 2006 (2006-10-19), XP002662344, COLORADO SCHOOL OF MINES, COLORADO (US) Retrieved from the Internet: URL:http://www.ceri-mines.org/documents/A14d-MarkAtwoodJB.pdf see tables 1,3; see "Diagnostic Measurements for Controlling process performance" -----	1-22
Y	EP 0 834 071 B1 (EXXON RESEARCH ENGINEERING CO [US] EXXONMOBIL RES & ENG CO [US]) 30 October 2002 (2002-10-30) the whole document -----	1-22
Y	WO 2008/021218 A2 (EXXONMOBIL RES & ENG CO [US]; FRANKLIN HOWARD D [US]; GEORGIU APOSTOL) 21 February 2008 (2008-02-21) the whole document -----	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2012/022918

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2008048451	A2	24-04-2008	
		AU 2007313391 A1	24-04-2008
		AU 2007313393 A1	24-04-2008
		CA 2663650 A1	24-04-2008
		CA 2664316 A1	24-04-2008
		CN 101553628 A	07-10-2009
		CN 101636554 A	27-01-2010
		US 2008087421 A1	17-04-2008
		US 2008087426 A1	17-04-2008
		US 2009101348 A1	23-04-2009
		US 2009107679 A1	30-04-2009
		US 2010089585 A1	15-04-2010
		WO 2008048451 A2	24-04-2008
		WO 2008048453 A2	24-04-2008
US 2008207970	A1	28-08-2008	
		AU 2007313388 A1	24-04-2008
		CA 2666296 A1	24-04-2008
		US 2008207970 A1	28-08-2008
		WO 2008048448 A2	24-04-2008
US 4458757	A	10-07-1984	NONE
WO 2005045192	A1	19-05-2005	
		AU 2004288130 A1	19-05-2005
		CA 2543963 A1	19-05-2005
		CN 1875168 A	06-12-2006
		EP 1689973 A1	16-08-2006
		IL 174966 A	29-04-2010
		US 2007023186 A1	01-02-2007
		US 2009038795 A1	12-02-2009
		WO 2005045192 A1	19-05-2005
		ZA 200603083 A	26-09-2007
EP 0834071	B1	30-10-2002	
		AU 696178 B2	03-09-1998
		AU 6248896 A	22-01-1997
		CA 2221034 A1	09-01-1997
		DE 69624569 D1	05-12-2002
		DE 69624569 T2	03-04-2003
		EP 0834071 A1	08-04-1998
		JP H11508363 A	21-07-1999
		NO 976049 A	18-02-1998
		US 5699269 A	16-12-1997
		WO 9701096 A1	09-01-1997
WO 2008021218	A2	21-02-2008	
		CA 2660502 A1	21-02-2008
		EP 2050038 A2	22-04-2009
		JP 2010500452 A	07-01-2010
		US 2008040051 A1	14-02-2008
		WO 2008021218 A2	21-02-2008