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(54) Title: IN SITU RECOVERY OF HYDROCARBONS FROM A KEROGEN-CONTAINING FORMATION

(57) Abstract: The present invention provides a method for the in-situ pyrolysis of hydrocarbons in a subterranean kerogen-containing formation, comprising: providing heat to at least a portion of the kerogen-containing formation such that at least a part of the heated portion reaches the pyrolysis temperature of kerogen, yielding pyrolysis products; and collecting pyrolysis products from the subterranean formation; wherein the subterranean formation is selected to comprise kerogen with a vitrinite reflectance of 0.2 to 3.0 %. Further, the invention provides a method for synthesis gas production after the collection of pyrolysis products by allowing the kerogen-containing formation to react with a synthesis gas generating fluid.

IN SITU RECOVERY OF HYDROCARBONS FROM A KEROGEN-
CONTAINING FORMATION

The present invention relates to a method for the
production of hydrocarbons from a kerogen-containing
formation.

Hydrocarbon containing materials obtained from
subterranean formations are often used as energy
resources, as feedstocks, and as consumer products.
Concerns over depletion of available hydrocarbon
resources have led to development of processes for more
efficient recovery, processing and/or use of available
hydrocarbon resources. In situ processes can be used to
remove hydrocarbon materials from subterranean
formations.

Such an in situ process by application of heat to oil
shale formations is described in US-A 2923535 and
US-A-4886118. Heat is applied to the oil shale formation
to pyrolyze kerogen within the oil shale formation. The
heat also fractures the formation to increase
permeability of the formation. The increased permeability
may allow pyrolysis product to travel to a production
well where the fluid is removed from the oil shale
formation. In the process of US-A-2923535, for example,
an oxygen-containing gaseous medium is introduced to a
permeable stratum, preferably while still hot from a
preheating step, to initiate combustion.

Kerogen is composed of organic matter, which has been
transformed due to a maturation process. Hydrocarbon
containing formations that include kerogen include, but
are not limited to, coal containing formations and oil
shale containing formations. The maturation process may
include two stages: a biochemical stage and a geochemical

stage. The biochemical stage typically involves
degradation of organic material by both aerobic and
anaerobic mechanisms. The geochemical stage typically
involves conversion of organic matter due to temperature
changes and significant pressures. During maturation, oil
and gas may be produced as organic matter of kerogen is
transformed.

For example, kerogen can be classified into four
distinct groups: type I, type II, type III, and type IV.
The types depend upon precursor materials of the kerogen.
The precursor materials transform over time into
macerals, which are microscopic structures that have
different structures and properties based on the
precursor materials from which they are derived. Oil
shale may be described as a kerogen type I or type II and
may primarily contain macerals from the liptinite group.
Liptinites are derived from plants, specifically the
lipid rich and resinous parts. The concentration of
hydrogen within liptinite may be as high as 9%. In
addition, liptinite has a relatively high H/C ratio and a
relatively low O/C ratio. A type I kerogen may also be
further classified as an alginite, since type I kerogen
may consist primarily of alga bodies. Type I kerogen may
result from deposits made in lacustrine environments.
Type II kerogen may develop from organic matter that was
deposited in marine environments.

Type III kerogen may generally include vitrinite
macerals. Vitrinite is derived from cell walls and/or
woody tissues (e.g., stems, branches, leaves and roots of
plants). Type III kerogen may be present in most humic
coals. Type III kerogen may develop from organic matter
that was deposited in swamps. Type IV kerogen includes
the inertinite maceral group. This group is composed of
plant material such as leaves, bark and stems that has
undergone oxidation during the early peat stages of

burial diagenesis. It is chemically similar to vitrinite
but has a high carbon and low hydrogen content. Thus, it
is considered inert.

As kerogen undergoes maturation, composition of
kerogen usually changes. For example, rank stages of
coal-containing formations include the following
classifications, which are listed in order of increasing
rank and maturity for type III kerogen: wood, peat,
lignite, sub-bituminous coal, high volatile bituminous
coal, medium volatile bituminous coal, low volatile
bituminous coal, semi-anthracite, and anthracite. In
addition, as rank increases, kerogen tends to exhibit an
increase in aromatic nature.

It has been found that it is possible to assess the
quality of fluids produced from certain formations by
vitrinite reflectance. Properties that may be used to
assess the hydrocarbon-containing material include but
are not limited to: an amount of hydrocarbon liquids that
will tend to be produced from the hydrocarbon-containing
material, an API gravity of the produced hydrocarbon
liquids, an amount of hydrocarbon gas that will tend to
be produced from the hydrocarbon-containing material,
and/or an amount of carbon dioxide that will tend to be
produced from the hydrocarbon containing material.

Accordingly, the present invention provides a method
for the in-situ pyrolysis of hydrocarbons in a
subterranean kerogen-containing formation, comprising:

providing heat from a heat source to at least a
portion of the kerogen-containing formation such that at
least a part of the heated portion reaches the pyrolysis
temperature of kerogen, yielding pyrolysis products; and

collecting pyrolysis products from the subterranean
formation;

wherein the subterranean formation comprises kerogen
with a vitrinite reflectance of 0.2 to 3.0%.

"Pyrolysis" is generally defined as the breaking of chemical bonds due to the application of heat in the absence of oxygen. For example, pyrolysis may include transforming a compound into one or more other substances by heat alone, i.e., without oxidation. As used herein "pyrolysis product" refers to a fluid produced during pyrolysis of a kerogen-containing formation.

Vitrinite reflectance (Ro) is the percentage of light reflected from the surface of polished vitrinite. It is a standard measurement used to classify organic source rock. Standards are followed for the preparation of samples. The sample is crushed to a particular size then embedded in a mounting medium, the surface is cut and polished and viewed under a microscope using reflected light. Reflectance is measured, and standards indicate the method to be used, viz., ASTM D2798. It has been found that an increase in vitrinite reflectance of the kerogen-containing material may coincide with a substantial reordering of a structure of the hydrocarbon containing material. Materials with a high vitrinite reflectance may have mirror-like properties and their thermal conductivity may increase. Excellent results have been obtained with kerogen-containing formations with a vitrinite reflectance of at least 0.25%, even better with formations having a vitrinite reflectance of at least 0.4%, most preferably at least 0.5% The upper limit is suitably 3.0%, more preferably 2.0%, most preferably 1.2%.

It is advantageous to select a kerogen-containing formation for treatment based on kerogen with a hydrogen content within the formation. For example, an advantageous kerogen for treatment has a hydrogen content greater than 2 wt%, preferably greater than 3 wt%, or more preferably greater than 4 wt% when measured on a dry, ash-free basis. In addition, the selected section

suitably includes kerogen with an elemental hydrogen to
carbon ratio that falls within a range from 0.5 to 2, and
in many instances from 0.70 to 1.65.

Hydrogen within the formation may neutralise radicals
in the generated hydrocarbon fluids. In this manner,
hydrogen present in the formation may substantially
inhibit reaction of hydrocarbon fragments by transforming
the hydrocarbon fragments into relatively short chain
hydrocarbon fluids. These hydrocarbon fluids may enter a
vapour phase and may be produced from the formation. The
increase in the hydrocarbon fluids in the vapour phase
may significantly reduce a potential for coking within
the selected section of the formation. It is believed
that if too little hydrogen is present in the formation,
then the amount and quality of the produced fluids will
be negatively affected. If too little hydrogen is
naturally present, then in some embodiments hydrogen or
other reducing fluids may be added to the formation.

When heating a portion of a hydrocarbon containing
formation, oxygen within the portion may form carbon
dioxide. It may be desirable to reduce the production of
carbon dioxide and other oxides. In addition, an amount
of carbon dioxide produced from a formation may vary
depending on, for example, an oxygen content of a treated
portion of the hydrocarbon containing formation. Hence,
it is preferable to select and treat a portion of the
formation having kerogen with an elemental oxygen weight
percentage of less than 20 wt%, preferably 15 wt%, and
more preferably 10%. In addition, certain embodiments may
include selecting and processing kerogen having an
elemental oxygen to carbon ratio of less than 0.15.
Alternatively, at least some of the kerogen- containing
material in a portion of a formation selected for
treatment may have an elemental oxygen to carbon ratio of
0.03 to 0.12. In this manner, production of carbon

dioxide and other oxides from an in situ conversion
process of hydrocarbon containing material may be
reduced.

Electrical heaters may be used to heat the
subterranean formation by radiation and/or conduction. An
electrical heater may resistively heat an element.
Examples of electrical heating elements are described in
US-A-2548360, US-A-4716960, US-A-5060287, and
US-A-5065818. US-A-6023554 describes an electrical
heating element that is positioned within a casing. The
heating element generates radiant energy that heats the
casing. A granular solid fill material can be placed
between the casing and the formation. The casing may
conductively heat the fill material, which in turn
conductively heats the formation. It may be advantageous
to employ uncased well bores for the heat sources.

US-A-4570715 describes an electrical heating element.
The heating element has an electrically conductive core,
a surrounding layer of insulating material, and a
surrounding metallic sheath. The conductive core has a
relatively low resistance at high temperatures. The
insulating material has electrical resistance,
compressive strength and heat conductivity properties
that are relatively high at high temperatures. The
insulating layer inhibits arcing from the core to the
metallic sheath. The metallic sheath has tensile strength
and creep resistance properties that are relatively high
at high temperatures.

Combustion of a fuel can also be used to heat a
formation. In certain instances, combusting a fuel to
heat a formation is more economical than using
electricity to heat a formation. Several different types
of heaters use fuel combustion as a heat source that
heats a formation. The combustion can take place in the
formation, in a well and/or near the surface. Combustion

in the formation can be a fire-flood. An oxidant is then
pumped into the formation. The oxidant is ignited to
advance a fire front towards a production well. Oxidant
pumped into the formation flows through the formation
along fracture lines and other high permeability paths in
the formation. In such instances the fire front does not
flow uniformly through the formation.

A flameless combustor can be used to combust a fuel
within a well. US-A-5255742, US-A-5404952, US-A-5862858,
and US-A-5899269 describe flameless combustors. Flameless
combustion is accomplished by preheating a fuel and
combustion air to a temperature above an auto-ignition
temperature of the mixture. The fuel and combustion air
are suitably mixed in a heating zone to combust.

Heat can also be supplied to a formation from a
surface heater. The surface heater produces combustion
gases that are circulated through well bores to heat the
formation. Alternately, a surface burner is used to heat
a heat transfer fluid that is passed through a well bore
to heat the formation. Examples of fired heaters, or
surface burners that may be used to heat a subterranean
formation, are illustrated in US-A-6056057 and
US-A-6079499.

The kerogen-containing formation may be oil shale.
Preferably the kerogen-containing formation is a coal-
containing formation. One important parameter for the
feasibility of the present method is the thermal
conductivity of the subterranean formation. Prior
literature indicated that certain hydrocarbon containing
formations, such as coal, exhibited relatively low values
for thermal conductivity and thermal diffusivity when
heated. For example, in Government report No. 8364 by
J.M. Singer and R.P. Tye, entitled "Thermal, Mechanical
and Physical Properties of Selected Bituminous Coals and
Cokes", US Department of the Interior, Bureau of

Mines (1979) the authors report the thermal conductivity
and thermal diffusivity for four bituminous coals. The
report includes graphs of thermal conductivity and
diffusivity that show relatively low values up to about
400 °C (e.g., thermal conductivity is about 0.2W/m °C) or
below, and thermal diffusivity is about 1.7 10-3 cm^2/s).
This government report states that "coals and cokes are
excellent thermal insulators". This finding has been
confirmed in "The Thermal and Structural Properties of a
Hanna Basin Coal", Trans. ASME, Vol. 106, p. 266. June
1984, reporting thermal conductivities for high volatile
bituminous coal of about 0.3-0.4 W/m.K, up to 400 °C.
These reported values for thermal conductivities of coal
containing material tend to discourage the use of in situ
heating for coal.

It was found that thermal conductivities of the coals
used were higher than reported values for thermal
conductivities of coal-containing material. It is
believed that the difference may be at least partially
accounted for if it is assumed that the reported values
do not take the confined nature of the coal in an in situ
location into consideration.

Coal is often mined and used as a fuel within an
electricity generating power plant. Most coal that is
used as a fuel to generate electricity is mined. A
significant number of coal containing formations are,
however, not suitable for economical mining. For example,
mining coal from steeply dipped coal seams, from thin
coal seams, and/or from deep coal seams may not be
economically feasible.

The kerogen-containing formation or the portion
thereof which is subjected to the in situ heat treatment
may have a width of for example at least 0.5 m, or at
least 1.5 m, or at least 2.4 m, or even at least 3.0 m.
The width may be up to 100 m, or up to 1000 m, or even up

to 2000 m, or more. The kerogen-containing formation or
the portion thereof which is subjected to the in situ
heat treatment may have a layer thickness of, for
example, at least 1 m, more typically in the range of
from 4 m to 100 m, more typically from 6 m to 60 m. The
overburden of the kerogen-containing formation may have a
thickness of, for example, at least 10 m, more typically
in the range of from 20 m to 800 m or to 1000 m or more.

Thin coal seams may include coal layers having a
thickness of less than about 10 m. Deep coal seams
include coal seams that are at, or extend to, depths of
greater than 760 m below surface level. The energy
conversion efficiency of burning coal to generate
electricity is relatively low, as compared to fuels such
as natural gas. Also, burning coal to generate
electricity often generates significant amounts of carbon
dioxide, oxides of sulphur, and oxides of nitrogen and
particulates that are released into the atmosphere.

A heat source may be used to heat the subterranean
formation. Suitably the heat sources are applied to the
formation via one or more well bores. The pyrolysis
products are suitable recovered via a production well.
The number of heat sources may vary. Advantageously more
than one heat source per production well is applied.
Advantageously, the number of heat sources per production
well ranges from 1 to 16. For example, in one embodiment,
an in situ conversion process for hydrocarbon containing
material includes heating at least a portion of a
hydrocarbon containing formation with an array of heat
sources disposed within the formation. In some
embodiments, the array of heat sources is positioned
substantially equidistant from a production well. Certain
patterns (e.g., triangular arrays) are being used.

The spacing between heat sources may typically be
within the range of from 5 m to 20 m, preferably from 8 m

to 15 m. Positioning of equidistant heat sources, in a triangular pattern, is preferred, as it tends to provide more uniform heating to the coldest spot of the formation in comparison to other patterns such as hexagons. In addition, a triangular pattern tends to provide faster heating to a predetermined temperature in comparison to other patterns such as hexagons. In addition, the in situ conversion process for hydrocarbon containing material may include heating at least a portion of the formation with heat sources disposed substantially parallel to a lateral boundary of the hydrocarbon containing material. Regardless of the arrangement of or distance between the heat sources, in an embodiment, a ratio of heat sources to production wells disposed within a formation is greater than 8.

Certain embodiments also include allowing heat to transfer from one or more of the heat sources to a selected section of the heated portion. In an embodiment, the selected section is disposed between one or more heat sources. For example, the in situ conversion process can also include allowing heat to transfer from one or more heat sources to a selected section of the formation such that heat from one or more of the heat sources pyrolyzes at least some hydrocarbon containing material within the selected section. In this manner, the in situ conversion process includes heating at least a portion of a kerogen-containing formation above a pyrolysis temperature of hydrocarbon containing material in the formation. Suitably a pyrolysis temperature includes a temperature of at least 250 °C, preferably 270 °C. Advantageously, the temperature is at least 305 °C. Heat may be allowed to transfer from one or more of the heat sources to the selected section substantially by conduction. The pyrolysis temperature can be as high as 900 °C, but preferably does not exceed 400 °C. In a further

embodiment, the portion may be heated such that an
average temperature of the selected section may be less
than 375 °C, such that the pyrolysis is carried out from
270 to 375 °C.

The spacing between heat sources can be selected to
increase an area of the selected section. In this manner,
spacing between heat sources is selected to increase the
effectiveness of the heat sources, thereby increasing the
economic viability of a selected in situ conversion
process for kerogen-containing material.

The portion of the kerogen-containing formation may
be heated at a heating rate in a range from 0.1 °C/day to
50 °C/day. Suitably, the selected portion of the kerogen-
containing formation is heated at a heating rate in a
range of 0.1 °C/day to 10 °C/day. For example, a majority
of hydrocarbons may be produced from a formation at a
heating rate within a range of about 0.1 °C/day to about
10 °C/day. Especially in the pyrolysis temperature range,
the heating rate is low. Hence, a kerogen-containing
formation is advantageously heated at a rate of from 0.1
to 1 °C/day, in particular less than 0.7 °C/day through
the pyrolysis temperature range. The pyrolysis
temperature range suitably includes a range of
temperatures as described above, i.e. from 270-400 °C.
Below the pyrolysis temperatures the heating rate is less
influential, and can be up to 50 °C/day, preferably from
3 to 10 °C/day. For example, the heated portion may be
heated at such a rate for a time greater than 50% of the
time needed to span the temperature range, more than 75%
of the time needed to span the temperature range, or more
than 90% of the time needed to span the temperature
range.

The rate at which a kerogen-containing formation is
heated can affect the quantity and quality of the
pyrolysis products produced from the hydrocarbon

containing formation. For example, heating at high
heating rates, as is the case when a Fischer Assay is
conducted, may produce a larger quantity of fluids from a
hydrocarbon containing formation. The products of such a
process, however, may be of a significantly lower quality
than when heating using heating rates less than about
10 °C/day. Heating at a rate of temperature increase less
than approximately 10 °C/day may allow pyrolysis to occur
within a pyrolysis temperature range in which production
of coke and tars may be reduced. In addition, a rate of
temperature increase of less than about 3 °C/day may
further increase the quality of the produced fluids by
further reducing production of tars within a hydrocarbon
containing formation.

     In some embodiments, controlling temperature within a
kerogen-containing formation involves controlling a
heating rate within the formation. For example,
controlling heating rate such that the heating rate is
less than approximately 3 °C/day provides better control
of a temperature within the kerogen-containing formation.

     An in situ pyrolysis process according to the present
invention can include monitoring a rate of temperature
increase at a production well. A temperature within a
portion of a kerogen-containing formation, however, can
be measured at various locations within the portion of
the kerogen-containing formation. For example, a method
for treating a portion of a hydrocarbon containing
formation includes monitoring a temperature of the
portion at a midpoint between two adjacent heat sources.
The temperature can be monitored over time. In this
manner, a rate of temperature increase may also be
monitored. A rate of temperature increase can affect a
composition of pyrolysis products produced from the
formation. As such, a rate of temperature increase may be
monitored, altered and/or controlled, for example, to

alter a composition of pyrolysis products produced from
the formation. The temperature of the portion can, e.g.,
be monitored through a test well disposed in the
formation. For example, the test well is positioned in a
formation between a first heat source and a second heat
source. Certain systems and methods include controlling
the heat from the first heat source and/or the second
heat source to raise the monitored temperature at the
test well at a rate of less than about a selected amount
per day. In addition or alternatively, a temperature of
the portion is monitored at a production well. In this
manner, the in situ process according to the present
invention includes controlling the heat from the first
heat source and/or the second heat source to raise the
monitored temperature at the production well at a rate of
less than a selected amount per day.

The pressure within a selected section of a heated
portion of the kerogen-containing formation may vary
depending on, for example, depth, distance from a heat
source, a richness of the hydrocarbon containing material
within the hydrocarbon containing formation, and/or a
distance from a producer well.

It has been found that the product quality of the
pyrolysis products can be further improved by maintaining
an elevated pressure in the kerogen-containing formation.

The pressure can be controlled during pyrolysis and
during the production of the pyrolysis products from the
formation. Although the pressure can be atmospheric,
suitably, a pressure of at least 1.4 bar (0.14 MPa),
preferably 1.5 bar (0.15 MPa) is applied, more typically
at least 1.6 bar, in particular at least 1.8 bar. In
particular, when the pyrolysis temperature is at least
300 °C, a pressure of at least 1.6 bar is suitably
applied. The upper limit of the pressure may be
determined by the structure and the weight of the

overburden. Frequently, under practical conditions, the
pressure is less than 70 bar, more frequently less than
60 bar or even less than 50 bar. The pressure may
advantageously be controlled within a range of from 2 bar
to 18 bar or 20 bar, or alternatively within a range of
from 20 bar to 36 bar.

In coal formations, the pressure is suitably
controlled within a range of 1.4 bar absolute to 36 bar
absolute (0.14 - 3.6 MPa). Preferably, the pressure is at
least 1.5 bar (0.15 MPa). For example, the process may
include controlling a pressure within a majority of a
selected section of a heated portion of the formation.
The controlled pressure is preferably above 2 bar
absolute (0.2 MPa) during pyrolysis. An in situ
conversion process for kerogen-containing formation
includes preferably raising and maintaining the pressure
in the formation within a range to 20 bars absolute
(2 MPa). Control of the pressure in the formation can
occur at the production well or at the heat sources.
Pressure within a formation can be determined at a number
of different locations, which may include but may not be
limited to, at a well head and at varying depths within a
well bore. In some embodiments pressure is measured at a
producer well. In alternate embodiments pressure may be
measured at a heater well. Also, test wells can be
employed, similar to the test wells described above for
temperature measurements.

A valve may be configured to maintain, alter, and/or
control a pressure within a heated portion of a hydro-
carbon containing formation. For example, a heat source
disposed within a hydrocarbon containing formation may be
coupled to a valve. The valve may be configured to
release fluid from the formation through the heater
source. In addition, a pressure valve may be coupled to a
production well, which may be disposed within the

hydrocarbon containing formation. In some embodiments,
fluids released by the valves may be collected and
transported to a surface unit for further processing
and/or treatment.

5   The pyrolysis products include molecular hydrogen. It
has surprisingly been found that controlling formation
conditions to control the pressure of hydrogen in the
produced fluid results in improved qualities of the
produced fluids. Therefore, it is advantageous to control

10   formation conditions such that the partial pressure of
hydrogen in the pyrolysis products product is greater
than about 0.5 bar absolute (0.5 MPa), as measured at a
production well.

       It is possible to provide a reducing agent to at

15   least a portion of the formation. A reducing agent
provided to a portion of the formation during heating may
increase production of selected pyrolysis products. A
reducing agent may include, but is not limited to,
molecular hydrogen. Pyrolysis of the kerogen-containing

20   formation is believed to result in hydrocarbon fragments.
Such hydrocarbon fragments may react with each other and
other compounds present in the formation. Reaction of
these hydrocarbon fragments can increase production of
olefinic and aromatic compounds. A reducing agent

25   provided to the formation may react with these
hydrocarbon fragments to form selected products and/or
inhibit the production of non-selected products such as
olefins and aromatics. Molecular hydrogen is generated in
the pyrolysis reaction. It is also possible to add

30   hydrogen. Such hydrogen may be generated by reaction of
hot carbon with steam. Molecular hydrogen may also be
generated by cracking an injected hydrocarbon fluid. The
reducing agent can also be provided from at least part of
the pyrolysis product produced in a first portion of a

35   hydrocarbon-containing formation to a second portion of

the formation. For example, molecular hydrogen generated
in a first portion of the formation is provided to a
second portion of the formation.

In another embodiment, a pressure within a heated
portion of the formation is sufficient to increase vapour
phase transport of the pyrolysis products within the
formation. The increased vapour phase transport will be
due, in part, to generation of hydrogen within a portion
of the hydrocarbon containing formation. It is believed
that the generated components may include a double bond
and/or a radical. H_2 in the pyrolysis products may reduce
the double bond of the generated pyrolysis products,
thereby reducing a potential for polymerisation of the
generated pyrolysis products. In addition, hydrogen may
also neutralize radicals in the generated pyrolysis
products. Therefore, hydrogen is believed to
substantially inhibit the generated pyrolysis products
from reacting with each other and/or with other compounds
in the formation. In this manner, relatively short chain
fluids may enter the vapour phase and may be produced
from the formation.

Increasing an amount of pyrolysis products in the
vapour phase significantly reduces the potential for
coking within the selected section of the formation. Also
vapour phase transport increases the hydrocarbon recovery
efficiency. A coking reaction may occur in the liquid
phase. Since many of the generated components are
transformed into short chain hydrocarbons and may enter
the vapour phase, coking tendency within the selected
section is decreased. Since coking may also reduce a
permeability of a formation, increasing an amount of
pyrolysis fluids in the vapour phase also increases the
permeability of the formation.

The mass of at least a portion of the formation will
be reduced due to the production of pyrolysis products

from the formation. As such, a permeability and porosity
of at least a portion of the formation will increase. In
addition, removing water during the heating may also
increase the permeability and porosity of at least a
5   portion of the formation.

In certain embodiments the permeability of at least a
portion of a kerogen-containing formation will increase
to greater than 0.01 or 0.1, or even 1 Darcy. In certain
embodiments a substantially uniform increase of the
10   permeability of at least a portion of the kerogen-
containing formation is obtained. Also the porosity of at
least a portion of the kerogen-containing formation can
be substantially uniformly increased.

Heating of a kerogen-containing formation to a
15   pyrolysis temperature range can occur before substantial
permeability has been generated within the hydrocarbon
containing formation. An initial lack of permeability may
prevent the transport of generated fluids from a
pyrolysis zone within the formation. In this manner, as
20   heat is initially transferred from a heat source to the
kerogen-containing formation, a fluid pressure within the
kerogen-containing formation may increase proximate to a
heat source. Such an increase in fluid pressure may be
caused by, for example, generation of fluids during
25   pyrolysis of at least some hydrocarbon containing
material in the formation. The increased fluid pressure
may be released, monitored, altered, and/or controlled
through such a heat source. For example, the heat source
may include a valve as described in above embodiments.
30   Such a valve may be configured to control a flow rate of
fluids out of and into the heat source. In addition, heat
source may include an open hole configuration through
which pressure may be released.

Alternatively, pressure generated by expansion of
35   pyrolysis fluids or other fluids generated in the

formation may be allowed to increase although an open
path to the production well or any other pressure sink
may not yet exist in the formation. In addition, a fluid
pressure may be allowed to increase to a lithostatic

5   pressure. Fractures in the hydrocarbon containing
formation may form when the fluid pressure equals or
exceeds the lithostatic pressure. For example, fractures
may form from a heat source to a production well. The
generation of fractures within the heated portion may

10   reduce pressure within the portion due to the production
of pyrolysis products through a production well. To
maintain a selected pressure within the heated portion, a
back pressure may be maintained at the production well.

Fluid pressure within a hydrocarbon containing

15   formation may vary depending upon, for example, thermal
expansion of hydrocarbon containing material, generation
of pyrolysis fluids, and withdrawal of generated fluids
from the formation. For example, as fluids are generated
within the formation a fluid pressure within the pores

20   may increase. Removal of generated fluids from the
formation may decrease a fluid pressure within the
formation.

The process according to the invention allows for
altering and/or controlling production of olefins. For

25   example, the process may include heating the portion at a
temperature rate to produce pyrolysis products having an
olefin content of less than about 10 % by weight of a
condensable component of the pyrolysis products. The
reduction of olefin production reduces substantially the

30   tendency for coating of a pipe surface by such olefins,
thereby reducing difficulty associated with producing
hydrocarbons through such piping. Reducing olefin
production also tends to inhibit polymerisation of
hydrocarbons during pyrolysis, thereby enhancing the

quality of produced fluids (e.g., by lowering the carbon number distribution, increasing API gravity, etc.).

In some embodiments, however, the portion may be heated at a temperature rate to selectively increase the olefin content of a condensable component of the hydrocarbon fluids. For example, olefins may be separated from such a condensable component and may be used to produce additional products.

In certain embodiments, after pyrolysis of a portion of the formation, synthesis gas may be produced from hydrocarbon containing material remaining within the formation. Pyrolysis of the portion may produce a relatively high, substantially uniform permeability throughout the portion. Such a relatively high, substantially uniform permeability may allow generation of synthesis gas without production of significant amounts of hydrocarbon fluids in the synthesis gas. The portion may also have a large surface area and/or surface area/volume. The large surface area may allow synthesis gas producing reactions to be substantially at equilibrium conditions during synthesis gas generation. The relatively high, substantially uniform permeability may result in a relatively high recovery efficiency of synthesis gas, as compared to synthesis gas generation in a hydrocarbon containing formation that has not been so treated.

Synthesis gas may be produced from the formation prior to or subsequent to producing a pyrolysis product from the formation. Synthesis gas is generally defined as a mixture of hydrogen and carbon monoxide. Additional components of synthesis gas may include water, carbon dioxide, methane and other gases. For example, synthesis gas generation may be commenced before and/or after pyrolysis product production decreases to an uneconomical level. In this manner, heat provided to pyrolyze may also

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be used to generate synthesis gas. For example, if a portion of the formation is at a temperature of 270 °C to 375 °C after pyrolysis, then less additional heat is generally required to heat such portion to a temperature sufficient to support synthesis gas generation.

Pyrolysis of at least some hydrocarbon containing material can in some embodiments convert about 20 %wt or more of carbon initially available. Synthesis gas generation may convert at least an additional 10 %w and typically up to an additional 70 %wt of carbon initially available. In this manner, in situ production of synthesis gas from a hydrocarbon containing formation may allow conversion of larger amounts of carbon initially available.

The synthesis gas may be generated in a wide temperature range, such as between 400 °C and 1200 °C, more typically between 600 °C and 1000 °C. At a relatively low synthesis gas generation temperature a synthesis gas tends to be produced which has a high H_2 to CO ratio. A relatively high formation temperature may produce a synthesis gas having a H_2 to CO ratio that approaches 1, and the stream may include mostly, and in some cases substantially only, H_2 and CO. At a formation temperature of about 700 °C, the formation may produce a synthesis gas having a H_2 to CO ratio of 2. Typically synthesis gas may be generated which has a H_2 to CO mole ratio in the range of from 1:4 to 8:1, more typically in the range of from 1:2 to 4:1, in particular in the range of from 1:1 to 2.5:1. Certain embodiments may include blending a first synthesis gas with a second synthesis gas to produce synthesis gas of a desired composition. The first and the second synthesis gases may be produced from different portions of the formation.

Heat sources for synthesis gas production may include any of the heat sources as described in any of the

embodiments set forth herein. Alternatively, heating may include transferring heat from heat transfer fluid (e.g., steam or combustion products from a burner) flowing within a plurality of well bores within the formation.

A synthesis gas generating fluid (e.g., liquid water, steam, carbon dioxide, and mixtures thereof or mixtures with air, oxygen and hydrocarbons) may be provided to the formation. For example, the synthesis gas generating fluid mixture may include steam and oxygen. In an embodiment, a synthesis gas generating fluid may include aqueous fluid produced by pyrolysis of at least some hydrocarbon containing material within one or more other portions of the formation. Providing the synthesis gas generating fluid may alternatively include raising a water table of the formation to allow water to flow into it. Synthesis gas generating fluid may also be provided through at least one injection well bore. The synthesis gas generating fluid will generally react with carbon in the formation to form H_2, water, CO_2, and/or CO. A portion of the carbon dioxide may react with carbon in the formation to generate carbon monoxide. Hydrocarbons such as ethane may be added to a synthesis gas generating fluid. When introduced into the formation, the hydrocarbons may crack to form hydrogen and/or methane. The presence of methane in produced synthesis gas may increase the heating value of the produced synthesis gas.

Synthesis gas generating reactions are typically endothermic reactions. In an embodiment, an oxidant may be added to a synthesis gas generating fluid. The oxidant may include, but is not limited to, air, oxygen enriched air, oxygen, hydrogen peroxide, other oxidising fluids, or combinations thereof. The oxidant may react with carbon within the formation to exothermically generate heat. Reaction of an oxidant with carbon in the formation may result in production of CO_2 and/or CO. Introduction

of an oxidant to react with carbon in the formation may economically allow raising the formation temperature high enough to result in generation of significant quantities of H_2 and CO from carbon within the formation.

Synthesis gas generation may be via a batch process or a continuous process, as is further described herein. Synthesis gas may be produced from one or more producer wells that include one or more heat sources. Such heat sources may operate to promote production of the synthesis gas with a desired composition.

Certain embodiments may include monitoring a composition of the produced synthesis gas, and then controlling heating and/or controlling input of the synthesis gas generating fluid to maintain the composition of the produced synthesis gas within a desired range. For example, a desired composition of the produced synthesis gas may have a ratio of hydrogen to carbon monoxide of about 2:1.

Certain embodiments may include blending a first synthesis gas with a second synthesis gas to produce synthesis gas of a desired composition. The first and the second synthesis gases may be produced from different portions of the formation.

Synthesis gases described herein may be converted to heavier condensable hydrocarbons. For example, a Fischer-Tropsch hydrocarbon synthesis process may be configured to convert synthesis gas to branched and non-branched hydrocarbons, in particular to paraffins. Paraffins produced from the Fischer-Tropsch process may be configured to produce other products such as diesel, jet fuel, and naphtha products. The produced synthesis gas may also be used in a catalytic methanation process to produce methane. Alternatively, the produced synthesis gas may be used for production of methanol, gasoline and diesel fuel, ammonia, and middle distillates. Produced

synthesis gas may be used to heat the formation as a combustion fuel. Hydrogen in produced synthesis gas may be used to upgrade oil.

Synthesis gas may also be used for other purposes. Synthesis gas may be combusted as fuel. Synthesis gas may also be used for synthesising a wide range of organic and/or inorganic compounds such as hydrocarbons and ammonia. Synthesis gas may be used to generate electricity, either by reducing the pressure of the synthesis gas in turbines, and/or using the temperature of the synthesis gas to make steam (and then run turbines). Synthesis gas may also be used in an energy generation unit such as a molten carbonate fuel cell, a solid oxide fuel cell, or other type of fuel cell.

In an embodiment, a portion of a formation that has been pyrolysed and/or subjected to synthesis gas generation may be allowed to cool or may be cooled to form a cooled, spent portion within the formation. For example, a heated portion of a formation may be allowed to cool by transference of heat to adjacent portion of the formation. The transference of heat may occur naturally or may be forced by the introduction of heat transfer fluids through the heated portion and into a cooler portion of the formation. Alternatively, introducing water to the first portion of the formation may cool the first portion. Water introduced into the first portion may be removed from the formation as steam. The removed water may be injected into a hot portion of the formation to create synthesis gas.

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

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Fig.1 shows a cross-sectional view of an in situ
experimental field test system;

Fig. 2 illustrates the location of heat sources,
production wells, and temperature observation wells used
in the experimental field test system;

Fig. 3 illustrates a plot of cumulative volume of
liquid hydrocarbons produced as a function of time
(m^3/day); and

Fig. 4 illustrates a plot of cumulative volume of gas
produced in standard cubic feet, produced as a function
of time (in days) for the same in situ experiment.

Example 1

A series of experiments was conducted to determine
the effects of vitrinite reflectance on properties of
fluids produced from such kerogen-containing formations.
The series of experiments included Fischer Assay and
Rock-Eval pyrolysis. The series of experiments were
conducted on cubes of coals to determine source rock
properties of each coal and to assess potential oil and
gas production from each coal.

Rock-Eval pyrolysis is a petroleum exploration tool
developed to assess the generative potential and thermal
maturity of prospective source rocks. A ground sample may
be pyrolysed in a helium atmosphere. The sample is
initially heated and held at a temperature of 300 °C for
5 minutes, releasing hydrocarbons. The sample is further
heated at a rate of 25 °C/min to a final temperature of
600 °C, generating further hydrocarbons. Any CO_2
generated is measured by thermal conductivity detection.
The results are presented as percentage of oil based on
the sample on a dry and ash-free basis.

Seven coals of different ranks were treated in a
laboratory to simulate an in situ conversion process. The
different coal samples were heated relatively fast to
250 °C, and subsequently at a rate of about 2 °C/day to

600 °C and at a pressure ("p") indicated in Table I. The products were cooled and the condensed phase was collected as oil.

Table I

Coal	1	2	3	4	5	6	7	8	9
VR	0.29	0.40	0.44	0.51	0.59	0.75	1.28	3.1	5.7
p,MPa	0.45	0.1	0.45	0.1	0.1	0.45	0.45	-	-
FA	6.14	14.54	12.27	16.95	18.25	26.87	11.84	0.43	0.33
RE	2.50	5.99	5.00	6.67	9.28	10.53	4.79	-	-
ICP	2.42	9.58	9.02	10.89	15.26	23.14	9.09		
P/A	0.14	0.30	0.34	0.45	0.56	0.84	0.55	-	-
C/A	0.14	0.45	0.23	0.21	0.22	0.59	0.63	-	-
API,°	23	28	30	34	34	36	33	-	-

VR is vitrinite reflectance in %;

FA is Fischer Assay, the oil yield based on a dry and ash-free basis, expressed in gal/ton (4.2×10^{-3} l/kg);

RE is Rock-Eval pyrolysis test, %wt of oil based on the dry and ash-free sample;

ICP is the oil yield obtained in the laboratory experiments to simulate an in situ conversion process, expressed in gal/ton, based on a dry and ash-free basis;

P/A is the ratio paraffins over aromatics in the oil;

C/A is the ratio of cyclic alkanes over aromatics in the oil; and

API is the API gravity in °.

The results clearly show that the vitrinite reflectance has an influence on the oil yield and the properties of the hydrocarbons produced. The more advantageous range appears to be from 0.4-1.2%, the optimal appears to be around a vitrinite reflectance of 0.7-0.9%.

Example 2

A cube of Fruitland high volatile B bituminous coal having a vitrinite reflectance of 0.71%, was heated at about 2 °C/day. Table II shows yield fractions of products generated by heating this cube at 2 °C/day to about 450 °C. In addition, Table II shows yield fractions of products generated by a fluidized bed gasification process of two different blocks of a similar type of coal. The two different blocks of coal include Utah high volatile bituminous and Illinois No. 6 high volatile Bituminous. The yield data for the fluidized bed gasification process was obtained by Jacobs, Jones and Eddinger, as presented in, "Hydrogenation of COED Process Coal-Derived Oil", Industrial and Engineering Chemistry, Process Design and Development. Vol. 10, No. 4, pp. 558-562, 1971. The yield fractions are defined as: naphtha (initial boiling point to 166 °C), jet fuel (166 °C to 249 °C), diesel (249 °C to 370 °C), and bottoms (boiling point greater than 370 °C).

Table II

	Coal cube	Fluidized Bed-Utah	Fluidized Bed-Ill.
Char.	74.7	56.7	57.1
CO_2	2.6	4.6	2.5
Gas	9.7	10.5	10.7
Water	6.8	4.6	6.1
Naphtha	1.6	0.0	0.2
Jet	2.0	1.0	2.4
Diesel	2.2	6.2	5.0
Bottoms	0.4	16.4	15.0

The fluidized bed processes for which yield fractions are displayed in Table I are indicative of yield fractions which may be obtained from a process involving

rapid heating and pyrolysis at an elevated temperature. A
rapid heating rate may include greater than approximately
20 °C/day. An elevated temperature for pyrolysis may be
450 °C. In contrast, yield fractions obtained from
heating the coal cube are indicative of a process
involving slow heating and lower temperature pyrolysis.
The API gravity of the total oil produced from the coal
cube was about 37°. In contrast, the API gravity of the
total oil produced from the fluidized bed-Utah coal was
about -3.5°, and the API gravity of the total oil
produced from the fluidized bed Illinois coal was about
-13.1°. In this manner, slowly heating the coal cube
produced a better product having a higher API gravity
than product produced from coal that was rapidly heated.

The experiment was repeated in a drum with his coal.
It appeared that production of condensable hydrocarbons
is substantially complete when the temperature reaches
about 390 °C. Methane starts to be produced from 270 °C.
Between 270 and 400 °C condensable hydrocarbons, methane
and hydrogen were produced. At temperatures above 400 °C
methane and hydrogen continued to be produced. Above
about 450°C methane concentration decreased.

Example 3

Hydrocarbon fluids were produced from a portion of a
coal-containing formation by an in situ experiment
conducted in a portion of a coal containing formation.
The coal is high volatile bituminous C coal with a
vitrinite reflectance of 0.54%. It was heated with
electrical heaters. FIG. 1 illustrates a cross-sectional
view of the in situ experimental field test system. As
shown in FIG. 1, the experimental field test system
included at least coal containing formation 3802 within
the ground and grout wall 3800. Coal containing
formation 3802 dipped at an angle of approximately 36°
with an intercepted thickness of approximately 4.9

meters. FIG. 2 illustrates a location of heat sources
3804a, 3804b, 3804c, production wells 3806a, 3806b, and
temperature observation wells 3803a, 3808b, 3808c, 3808d
used for within the experimental field test system. The
three heat sources were disposed in a triangular
configuration. Production well 3806a was located
proximate a center of the heat source pattern and
equidistant from each of the heat sources. A second
production well 3806b was located outside the heat source
pattern and spaced equidistant from the two closest heat
sources. Grout wall 3800 was formed around the heat
source pattern and the production wells. The grout wall
included pillars 1-24. Grout wall 3800 was configured to
inhibit an influx of water into the portion during the in
situ experiment. In addition, grout wall 3800 was
configured to substantially inhibit loss of generated
hydrocarbon fluids to an unheated portion of the
formation.

Temperatures were measured at various times during
the experiment at each of four temperature observation
wells 3808a, 3808b, 3808c, 3808d located within and
outside of the heat source pattern as illustrated in
FIG. 2. Temperatures at observation wells 3808a, 3808b,
and 3808c were relatively close to each other. A
temperature at temperature observation well 3808d was
significantly colder. This temperature observation well
was located outside of the heater well triangle
illustrated in FIG. 2. This data demonstrates that in
zones where there was little superposition of heat
temperatures were significantly lower. Temperature
profiles were relatively uniform at the heat sources.

FIG. 3 illustrates a plot of cumulative volume of
liquid hydrocarbons produced 3840 as a function of time
(m^3/day). FIG. 4 illustrates a plot of cumulative volume
of gas produced 3910 in standard cubic feet, produced as

a function of time (in days) for the same in situ
experiment. Both FIG. 3 and FIG. 4 show the results
during the pyrolysis stage only of the in situ
experiment. Relatively high quality products were

5   produced during treatment.

Two laboratory experiments on coal cubes from the
field experiment site were conducted. One experiment was
conducted at 1 bar absolute (0.1 MPa). The second
pressure was 8 bar (0.8 MPa). The laboratory carbon

10   number distribution is similar to that produced in the
field experiment also at 1 bar absolute. As pressure
increases, a range of carbon numbers of the hydrocarbon
fluids decreases. An increase in products having carbon
numbers less than 20 was observed when operating at

15   8 bars absolute. Increasing the pressure from 1 bar
absolute to 8 bars absolute also increased an API gravity
of the condensed hydrocarbon fluids. The API gravities of
condensed hydrocarbon fluids produced were approximately
23.1° and approximately 31.3°, respectively. Such an

20   increase in API gravity represents an increased
production of more valuable products.

Example 4

Table III illustrates fractions from a boiling point
separation of oils generated by a Fischer Assay and a

25   boiling point separation of oils from the coal cube
experiment described above. The field experiment was an
in situ conversion process (ICP) that was conducted at a
much slower heating rate to a lower final temperature
than the Fischer Assay. Table III shows the weight

30   percent of various boiling point cuts of oil produced
from a Fruitland high volatile bituminous B coal
(vitrinite reflectance 0.71%). Different boiling point
cuts may represent different hydrocarbon fluid
compositions. The boiling point cuts illustrated include

35   naphtha (initial boiling point to 166 °C), jet fuel

(166 °C to 249 °C), diesel (249 °C to 370 °C), and
bottoms (boiling point greater than 370 °C). The ICP
liquid was a substantially more valuable product. The API
gravity of the ICP liquid was significantly greater than
the API gravity of the Fischer Assay liquid. The ICP
liquid also included significantly less bottoms that the
Fischer Assay liquid.

Table III

	ICP	Fischer Assay
Naphtha	25.7	8.4
Jet fuel	32.5	17.2
Diesel	34.9	35.4
Bottoms	6.8	39.0
API gravity, °	37	17

It was further found that decreasing the heating rate
of the portion decreases production of olefins.

Example 5

An experiment was conducted on the formation treated
according to the in situ conversion process to measure
the uniform permeability of the formation after
pyrolysis. After heating a portion of the coal containing
formation, a ten minute pulse of CO_2 was injected into
the formation at first production well 3806a and produced
at well 3804a, as shown in FIG. 2. The CO_2 tracer test
was repeated from production well 3806a to well 3804b and
from production well 3806a to well 3804c. As described
above, each of the three different heat sources were
located equidistant from the production well. The CO_2 was
injected at a rate of 4.08 m^3/hr. The CO_2 reached each of
the three different heat sources at approximately the
same time. The yield of CO_2 from each of the three
different wells was also approximately equal over time.

Such approximately equivalent transfer of a tracer pulse
of CO_2 through the formation and yield of CO_2 from the
formation indicated that the formation was substantially
uniformly permeable. Steady state gas permeability

5   measurements were made between various wells inside the
triangle of heater wells. The post treatment
permeabilities ranged from 4.5 darcy to 39 darcy, with an
average of about 20 darcy. The initial permeabilities had
averaged at about 50 millidarcy. The fact that the first

10   CO_2 arrival only occurred approximately 18 minutes after
start of the CO_2 pulse indicates that preferential paths
had not been created between well 3806a and 3804a, 3804b,
and 3804c.

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C L A I M S

1. A method for the in-situ pyrolysis of hydrocarbons in a subterranean kerogen-containing formation, comprising:
    providing heat to at least a portion of the kerogen-containing formation such that at least a part of the heated portion reaches the pyrolysis temperature of kerogen, yielding pyrolysis products; and
    collecting pyrolysis products from the subterranean formation;
    wherein the subterranean formation is selected to comprise kerogen with a vitrinite reflectance of 0.2 to 3.0%.

2. Method according to claim 1, in which the kerogen-containing formation is a coal-containing formation.

3. Method according to claim 1 or 2, in which the pressure is suitably controlled within a range of 1.4-36, preferably 2-20 bars absolute.

4. Method according to any one of claims 1 to 3, in which the pyrolysis temperature ranges from 270-400 °C, preferably from 275-375 °C.

5. Method according to any one of claims 1 to 4, in which the kerogen-containing formation is heated by one or more heat sources and the pyrolysis products are collected via one or more production wells.

6. Method according to claim 5, in which the number of heat sources ranges from 1 to 16, preferably from 8 to 16, per production well.

7. Method according to any one of claims 1 to 6, in which the kerogen has a vitrinite reflectance from 0.25 to 2.0%, preferably from 0.4 to 1.2%.
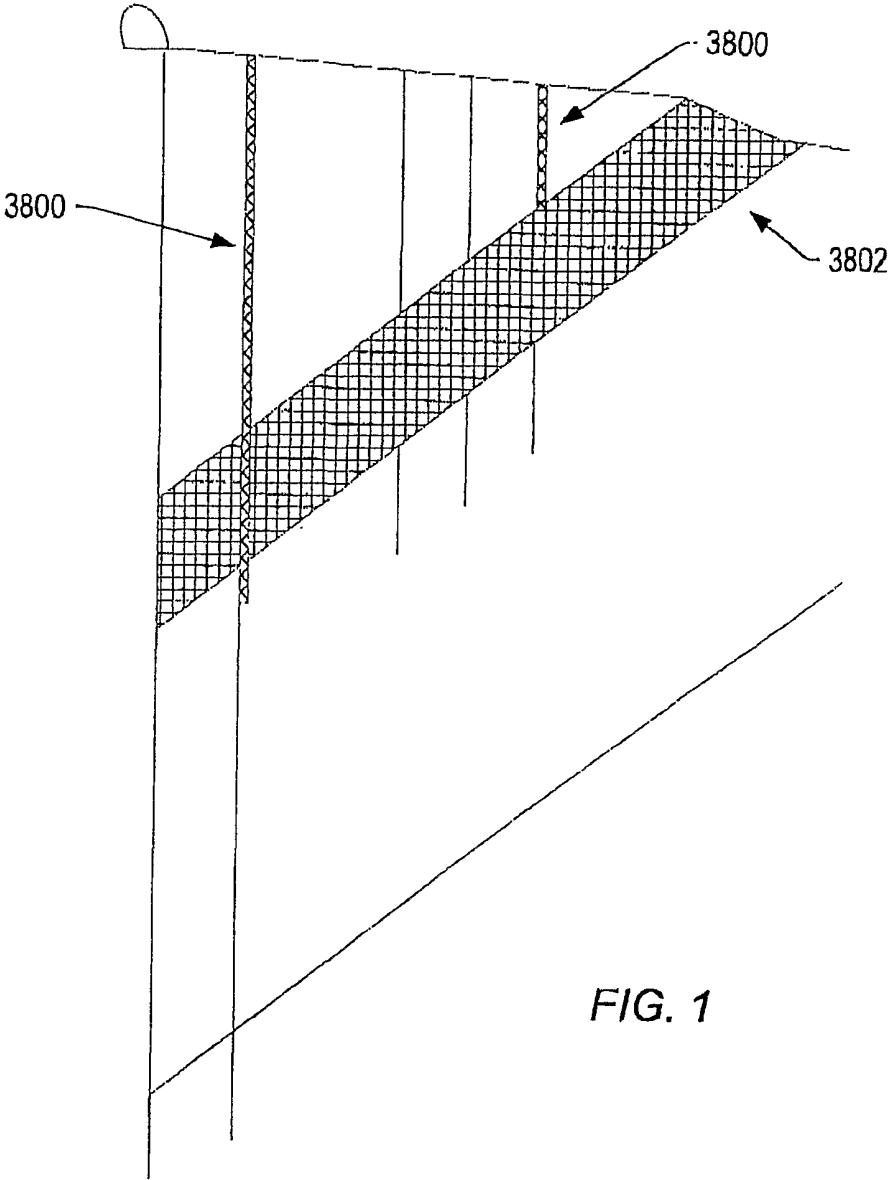
8. Method according to any one of claims 1 to 7, in which the kerogen has a hydrogen content greater than 2 wt%, preferably greater than 3 wt%,

9. Method according to any one of claims 1 to 8, in which the kerogen includes an elemental hydrogen to carbon ratio ranging from 0.5 to 2, preferably from 0.70 to 1.65.

10. Method according to any one of claims 1 to 9, in which the kerogen has an elemental oxygen weight percentage of less than 20 wt%, preferably less than 15 wt%.

11. Method according to any one of claims 1 to 10, in which the kerogen has an elemental oxygen to carbon ratio of 0.03 to 0.12.

12. Method according to any one of claims 1 to 11, in which after pyrolysis products have been collected the kerogen-containing formation is allowed to react with a synthesis gas generating fluid.
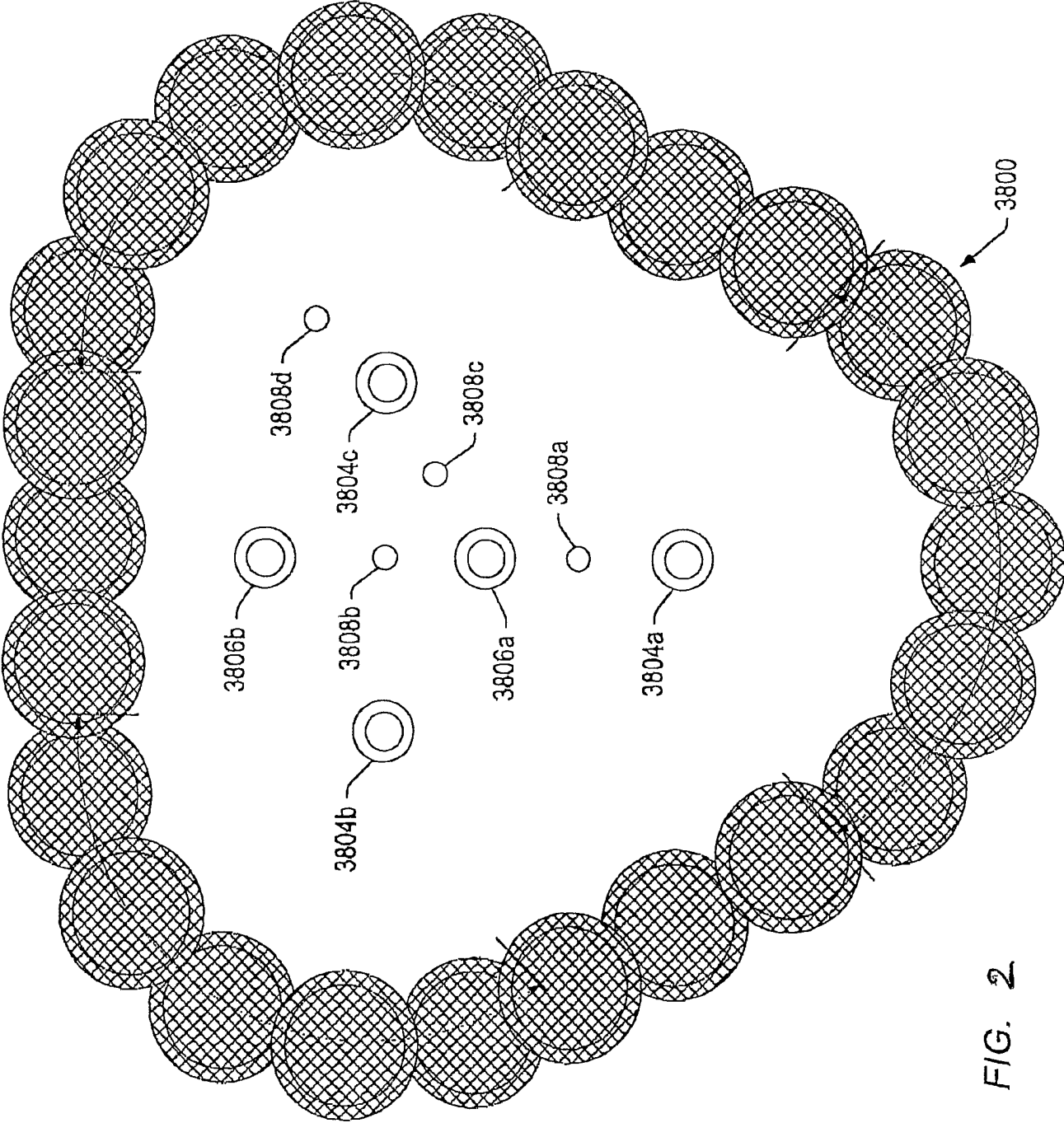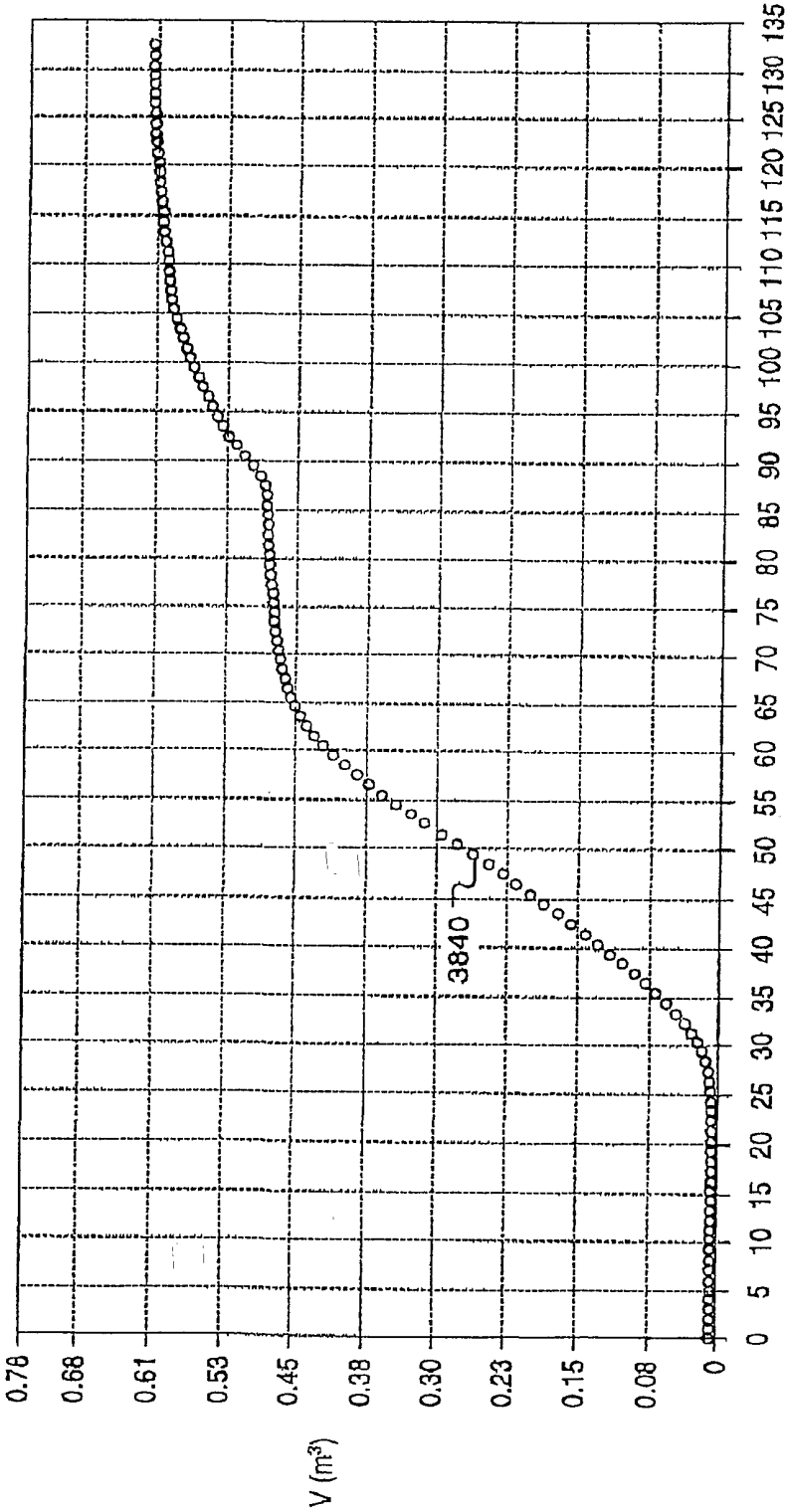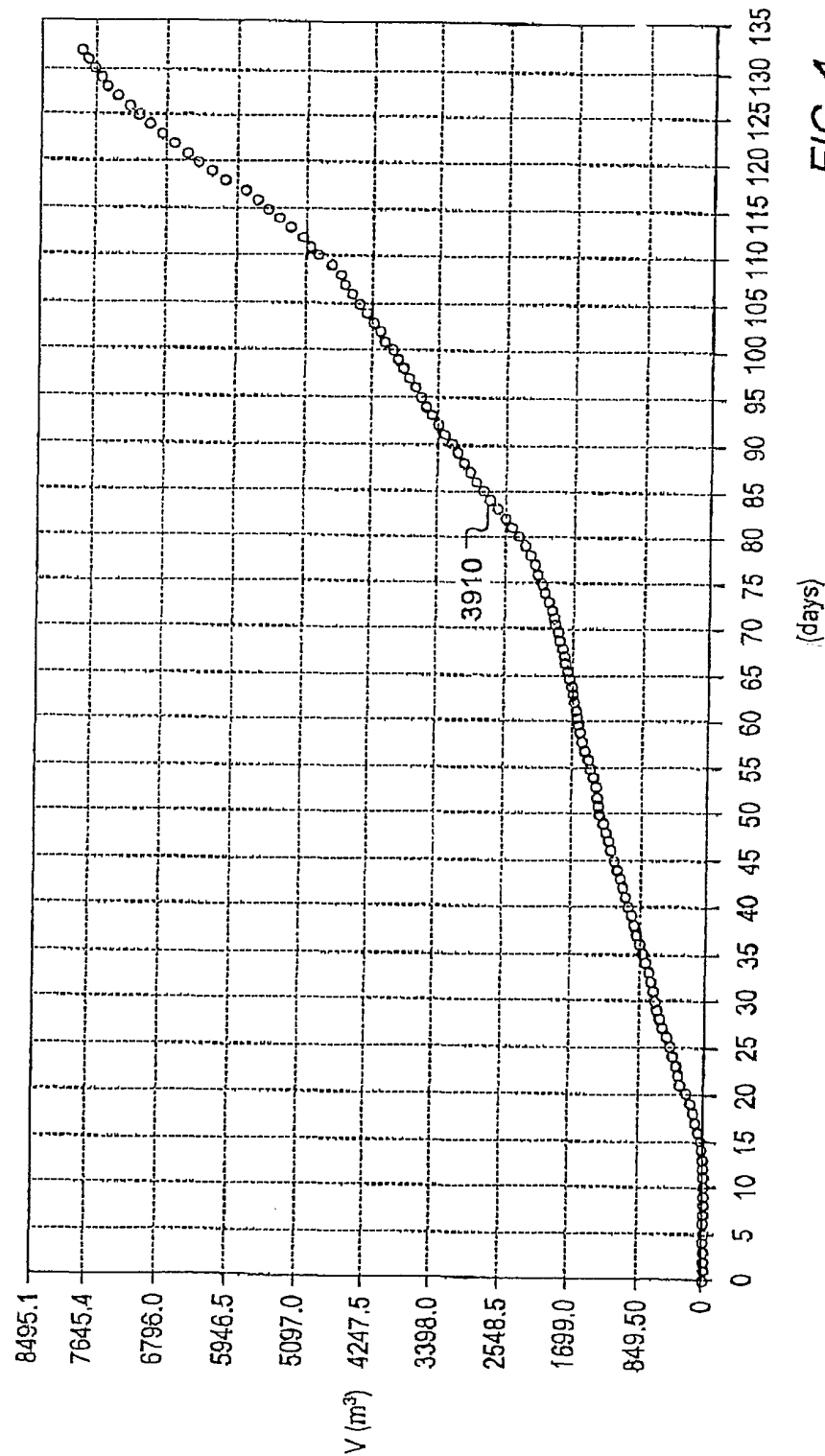
1/4

FIG. 1

FIG. 2

3 / 4

FIG. 3

4 / 4

FIG. 4

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7   E21B43/24

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)
IPC 7   E21B

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, WPI Data, TULSA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 397 732 A (HOOVER DAVID S ET AL) 9 August 1983 (1983-08-09) column 4, line 15-22	1
A	W. KALKREUTH, C. ROY, M. STELLER: "Conversion characteristics of selected Canadian coals based on hydrogenation and pyrolysis experiments" GEOLOGICAL SURVEY OF CANADA, PAPER 89-8, 1989, pages 108-114, XP001014535 the whole document	1

☐ Further documents are listed in the continuation of box C.   ☒ Patent family members are listed in annex.

° Special categories of cited documents :

'A' document defining the general state of the art which is not considered to be of particular relevance
'E' earlier document but published on or after the international filing date
'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
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'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
'&' document member of the same patent family

Date of the actual completion of the International search	Date of mailing of the international search report
13 August 2001	21/08/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Schouten, A

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

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