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(54) **COMPOSITIONS FOR CATALYTIC GASIFICATION OF A PETROLEUM COKE**

(75) Inventor: **Yasuo Ohtsuka**, Miyagi (JP)

Correspondence Address:  
**MCDONNELL BOEHNEN HULBERT & BERG-HOFF LLP**  
**300 S. WACKER DRIVE, SUITE 3100**  
**CHICAGO, IL 60606 (US)**

(73) Assignee: **GREATPOINT ENERGY, INC.**,  
Chicago, IL (US)

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(57) **ABSTRACT**

The present invention relates to particulate compositions of a lower ash type petroleum coke containing at least two preselected components (alkali metal and iron) that exhibit an efficient, enhanced-yielding gasification to value added gaseous products, particularly when used in a steady-state integrated gasification process. The compositions of the present invention are particularly useful for catalytic gasification of petroleum coke at moderate temperatures ranging from about 450° C. to about 900° C. Advantageously, the compositions can be readily incorporated into fluidized bed gasification units, and can result in a cost-effective, high-yielding production of methane gas from petroleum coke.

## COMPOSITIONS FOR CATALYTIC GASIFICATION OF A PETROLEUM COKE

### CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Ser. No. 60/978,586 (filed Oct. 9, 2007), the disclosure of which is incorporated by reference herein for all purposes as if fully set forth.

[0002] This application is related to commonly owned U.S. application Ser. No. \_\_\_\_\_, (filed concurrently herewith), entitled "COMPOSITIONS FOR CATALYTIC GASIFICATION OF A PETROLEUM COKE".

### FIELD OF THE INVENTION

[0003] The present invention relates particulate compositions of a crude oil resid-based petroleum coke containing at least two preselected catalytic components, which composition exhibits an efficient, enhanced-yielding gasification to value-added gaseous products, particularly when used in a steady-state integrated gasification process. More particularly, this invention concerns compositions of a petroleum coke loaded with a mixture of (i) an alkali metal component, and (ii) an iron component.

[0004] The present invention further relates to processes wherein these particulate compositions, in the presence of steam, exhibit gasification activity, and thereby form value-added gaseous products including methane and one or more of hydrogen, carbon monoxide and other higher hydrocarbons.

### BACKRGOUND OF THE INVENTION

[0005] In view of numerous factors such as higher energy prices and environmental concerns, the production of value-added gaseous products from lower-fuel-value carbon sources, such as petroleum coke and coal, is receiving renewed attention. The catalytic gasification of such materials to produce methane and other value-added gases is disclosed, for example, in U.S. Pat. No. 3,828,474, U.S. Pat. No. 3,958,957, U.S. Pat. No. 3998607, U.S. Pat. No. 4,057,512, U.S. Pat. No. 4,092,125, U.S. Pat. No. 4,094,650, U.S. Pat. No. 4,204,843, U.S. Pat. No. 4,468,231 and GB1599932.

[0006] More recent developments to such technology directed specifically to methane as a predominant gaseous product are disclosed in commonly owned US2007/0000177A1, US2007/0083072A1, U.S. application Ser. No. 11/421511 (filed 1 Jun. 2006 and entitled "Catalytic Steam Gasification Process with Recovery and Recycle of Alkali Metal Compounds"), and U.S. application Ser. No. 11/832809 (filed 2 Aug. 2007 and entitled "Catalyst-Loaded Coal Compositions, Processes for Preparing Same, and Integrated Processes for Preparation of Methane from Coal").

[0007] Petroleum coke is a generally solid carbonaceous residue derived from delayed coking or fluid coking a carbon source such as a crude oil resid. Petroleum coke in general has a poorer gasification reactivity, particularly at moderate temperatures, than does bituminous coal due, for example, to its highly crystalline carbon and elevated levels of organic sulfur derived from heavy-gravity oil. Use of catalysts is necessary for improving the lower reactivity of petroleum cokes.

[0008] One advantageous catalytic process for gasifying petroleum cokes to methane and other value-added gaseous products is disclosed in the above-mentioned US2007/

0083072A1. This publication discloses the use of alkali metals to catalyze the gasification reaction. While the process disclosed in this publication is generally quite effective, it would be desirable to find alternative catalyst systems with potentially improved gasification activity.

### SUMMARY OF THE INVENTION

[0009] The present invention is directed to the gasification of a petroleum coke derived from a crude oil resid, for example, by coking processes used for upgrading heavy-gravity residual crude oil, which petroleum coke contains ash but as a minor component, typically about 1.0 wt % or less, and more typically about 0.5 wt % or less, based on the weight of the coke. Typically the ash in such lower-ash cokes predominantly comprises metals such as nickel and vanadium.

[0010] In this context, the present invention is directed to particulate compositions of such petroleum coke containing at least two preselected components that exhibit an efficient, enhanced-yielding gasification to value-added gaseous products. More particularly, the present invention is a particulate composition having a particle distribution size suitable for gasification in a fluidized bed zone, comprising an intimate mixture of (A) a petroleum coke derived from crude oil comprising ash in an amount of about 1.0 wt % or less, based on the weight of the petroleum coke, and (B) a gasification catalyst which under suitable conditions of temperature and pressure and in the presence of steam exhibits gasification activity whereby value added gaseous products are formed, wherein:

[0011] (a) the gasification catalyst comprises (i) a first component which is a source of at least one alkali metal, and (ii) a second component which is a source of iron; and

[0012] (b) the gasification catalyst is present in an amount sufficient to provide, in the particulate composition, a ratio of alkali metal atoms to carbon atoms in the range of from about 0.01 to about 0.1, and a ratio of iron atoms to carbon atoms in the range of from about 0.01 to about 0.1.

[0013] The compositions of the present invention are particularly useful for catalytic gasification of petroleum coke at moderate temperatures, such as disclosed in US2007/0083072A1. Advantageously, compositions and process according to the invention can be readily incorporated into fluidized bed gasification units, and can result in a more cost-effective, high-yielding production of methane gas.

[0014] In this context, the present invention also provides a process for converting petroleum coke to methane, comprising the steps of:

[0015] (1) combining a petroleum coke and a catalyst having steam gasification activity to produce a particulate composition having a particle distribution size suitable for gasification in a fluidized bed zone,

[0016] (2) reacting the particulate composition in a fluidized bed zone in the presence of steam to form gaseous products including methane and one or more of hydrogen, carbon monoxide and other higher hydrocarbons, and

[0017] (3) recovering methane from the gaseous products,

[0018] wherein the particulate composition is as set forth herein.

### DETAILED DESCRIPTION THE PREFERRED EMBODIMENTS

[0019] All publications, patent applications, patents and other references mentioned herein, if not otherwise indicated,

are explicitly incorporated by reference herein in their entirety for all purposes as if fully set forth.

[0020] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs. In case of conflict, the present specification, including definitions, will control.

[0021] Except where expressly noted, trademarks are shown in upper case.

[0022] Although methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, suitable methods and materials are described herein.

[0023] Unless stated otherwise, all percentages, parts, ratios, etc., are by weight.

[0024] When an amount, concentration, or other value or parameter is given as either a range, preferred range or a list of upper preferable values and lower preferable values, this is to be understood as specifically disclosing all ranges formed from any pair of any upper range limit or preferred value and any lower range limit or preferred value, regardless of whether ranges are separately disclosed. Where a range of numerical values is recited herein, unless otherwise stated, the range is intended to include the endpoints thereof, and all integers and fractions within the range. It is not intended that the scope of the invention be limited to the specific values recited when defining a range.

[0025] When the term "about" is used in describing a value or an end-point of a range, the disclosure should be understood to include the specific value or end-point referred to.

[0026] As used herein, the terms "comprises," "comprising," "includes," "including," "has," "having" or any other variation thereof, are intended to cover a non-exclusive inclusion. For example, a process, method, article, or apparatus that comprises a list of elements is not necessarily limited to only those elements but may include other elements not expressly listed or inherent to such process, method, article, or apparatus. Further, unless expressly stated to the contrary, "or" refers to an inclusive or and not to an exclusive or. For example, a condition A or B is satisfied by any one of the following: A is true (or present) and B is false (or not present), A is false (or not present) and B is true (or present), and both A and B are true (or present).

[0027] Use of "a" or "an" are employed to describe elements and components of the invention. This is done merely for convenience and to give a general sense of the invention. This description should be read to include one or at least one and the singular also includes the plural unless it is obvious that it is meant otherwise.

[0028] The materials, methods, and examples herein are illustrative only and, except as specifically stated, are not intended to be limiting.

#### Petroleum Coke

[0029] As indicated previously, the petroleum coke utilized in the present invention is derived from a crude oil, for example, by coking processes used for upgrading heavy-gravity residual crude oil, which petroleum coke contains ash but as a minor component, typically about 1.0 wt % or less, and more typically about 0.5 wt % or less, based on the weight of the coke. Typically the ash in such lower-ash cokes predominantly comprises metals such as nickel and vanadium. The petroleum coke preferably comprises at least about 70 wt % carbon, and alternatively at least about 80 wt % carbon,

based on the weight of the petroleum coke. Typically, the petroleum coke comprises less than about 20 wt % percent inorganic compounds, based on the weight of the petroleum coke.

[0030] The petroleum coke is utilized in particulate form as a fine powder having a particle size distribution suitable for gasification in a fluidized bed zone, which size also facilitates efficient catalyst loading. The ground coke (and resulting composition) has a particle size preferably ranging from about 25 microns, or from about 45 microns, to about 2500 microns, or to about 500 microns. Petroleum coke can be ground by any methods known to the art.

#### Catalyst Component

[0031] Particulate compositions according to the present invention are based on the above-described petroleum coke, and contain (i) an amount of an alkali metal component, as alkali metal and/or a compound containing alkali metal, sufficient to provide, in the composition, a ratio of alkali metal atoms to carbon atoms in the range of from about 0.01 to about 0.1, or in a range from about 0.01 to about 0.08, or in a range from about 0.01 to about 0.05; and (ii) an amount of iron component, as iron metal and/or a compound containing iron, sufficient to provide, in the composition, a ratio of iron atoms to carbon atoms in the range of from about 0.01 to about 0.1, or in a range from about 0.01 to about 0.08, or in a range from about 0.01 to about 0.05.

[0032] The alkali metal component is typically loaded to achieve an alkali metal content of from about 3 to about 10 times more than the ash content of the petroleum coke, on a mass basis.

[0033] The ratio of alkali metal atoms to iron atoms can range from about 1:5, or about 1:3, or about 1:2, to about 5:1, or about 3:1, or about 2:1.

[0034] Suitable alkali metals are lithium, sodium, potassium, rubidium and cesium, and potassium is preferred.

#### Methods of Making the Particulate Compositions

[0035] Particulate compositions in accordance with the present invention can be prepared by a process comprising the steps of: (a) grinding a petroleum coke, and (b) soaking the ground coke in a catalyst-containing solution for a contact time and at a temperature so as to provide ample opportunity to achieve substantial and uniform catalyst loading. The soaked catalyst-loaded coke can be recovered and used as such or, more preferably, can be further processed prior to gasification as disclosed in US2007/0083072A1.

[0036] The finely ground coke is soaked as a slurry in a catalyst-rich solution, preferably of a salt of a catalysts. The solution is in an aqueous medium. Depending upon the solubility of the source compounds, other liquids such as ethanol may be used. Where the desired source is insoluble in water and alcohols, a slurry mixture is useful, for example, a mixture of an aqueous potassium hydroxide and iron hydroxide powder.

[0037] Suitable alkali metal catalyst salts include, but are not limited to, carbonate, hydroxide, acetate, halide and nitrate salts. In preferred embodiments, carbonate or hydroxide salts are used and, more preferably, carbonate salts are used. In a particularly preferred embodiment, potassium carbonate is used.

[0038] Suitable iron salts include, but are not limited to, hydroxide, acetate, halide and nitrate salts. In preferred embodiments, nitrate and acetate salts are used.

[0039] The total amount of catalyst loaded is controlled by controlling the concentration of catalyst components in the solution, as well as the contact time, temperature and method, as can be readily determined by those of ordinary skill in the relevant art based on the characteristics of the starting petroleum coke.

#### Catalytic Gasification

[0040] The particulate compositions of the present invention are particularly useful in integrated gasification processes for converting petroleum coke to combustible gases, such as methane.

[0041] Generally, the particulate compositions of the present invention provide a suitable feedstream of catalyst-containing petroleum coke to any steam gasification process. Generally, such steam gasification processes provide a means for introducing dry particulate feed into a fluidized bed zone in a gasification reactor. Coke and superheated steam are reacted while in contact with the catalyst having steam gasification activity, to form a raw product gas, comprised of unreacted steam, methane, carbon dioxide, hydrogen, and carbon monoxide, and a particulate residue, or char having catalyst values incorporated therewith. A purge of the char is withdrawn from the gasification reactor. A raw product effluent stream is cooled to condense unreacted steam to form a sour water stream and a stream of cooled raw product gas from which methane and other components such as syngas are recovered.

[0042] The particulate compositions of the present invention are particularly useful for gasification at moderate temperatures of at least about 450° C., or of at least about 600° C., or above, to about 900° C., or to about 750° C., or to about 700° C.; and at pressures of at least about 50 psig, or at least about 200 psig, or at least about 400 psig, to about 1000 psig, or to about 700 psig, or to about 600 psig.

[0043] A preferred process is described in US2007/0083072A1, and reference can be had to that publication for further process details.

#### EXAMPLES

##### Petroleum Coke Sample Preparation

[0044] Where the as-received petroleum coke was found to be too damp (i.e. not free-flowing) to be jaw-crushed, it was necessary to first air-dry it in a mechanical-convection oven at 35° C. for an extended period of time. Stage-crushing was performed carefully so as not to generate excessive fines and to maximize the amount of material having particle sizes ranging from about 0.85 to about 1.4 mm.

[0045] Analyses of the petroleum coke samples provided results as follows: 8.9 percent by weight volatile matter and 0.38 percent by weight ash (proximate analysis); metal components in the ash of vanadium 170 mg/kg and nickel 220 mg/kg; carbon 86.3 percent, hydrogen 3.6 percent, nitrogen 1.8 percent, sulfur 6.0 percent and oxygen 2.3 percent (ultimate analysis); and a BET surface area of 2 to 3 m<sup>2</sup>/g. The atomic ratio of hydrogen to carbon was 0.20, and sulfur to carbon 0.026.

[0046] Compounds of potassium (nitrate, acetate, hydroxide and carbonate) and iron (nitrate, acetate and hydroxide) were used as catalyst precursors in a liquid medium. Prese-

lected amounts were contacted with the petroleum coke by mixing with a rotary evaporator at room temperature or at 0° C. if a water/ethanol solution was used. After separation from the liquid, the wet solid particles were subjected to reduced pressure thereby drying them for gasification.

[0047] Catalysts of about 1 and about 5 mass % of potassium were made, as well as catalysts of about 3 mass % iron. Binary catalysts of combinations of the above were also made.

##### Petroleum Coke Gasification

[0048] Gasification was carried out in a high-pressure apparatus that included a quartz reactor. About 100 mg of the sample was first charged into a platinum cell held in the reactor and then gasified. Typical gasification conditions were as follows: total pressure, 1.0 MPa; partial pressure of H<sub>2</sub>O, 0.21 MPa, in an atmosphere of high purity argon; temperatures, 750° C. to 900° C.; and reaction times, 2 to 3 hr. Product gas after the removal of H<sub>2</sub>O and H<sub>2</sub>S was analyzed on-line with a high-speed micro GC attached with a thermal conductivity detector. In order to determine the amount of H<sub>2</sub> produced precisely, argon gas was used as the carrier gas of GC. Coke conversion was estimated by using the weight change before and after gasification and expressed in percent by weight on a catalyst-free basis.

[0049] The conversion of petroleum coke without any catalyst was only about 25 percent at 750° C.; however, it increased with increased temperature and reached about 95 percent at 900° C. Petroleum coke treated with an iron salt (3%) exhibited almost no catalytic effects, irrespective of the temperature. By contrast, potassium compounds promoted the steam gasification even at low loading of 1 percent by weight and the conversion was about 40 percent at 750° C. and about 95 percent at 850° C.

[0050] Gasification of petroleum coke using binary combinations of iron and potassium compounds (1% K/3% Fe) was studied. Petroleum coke overall conversion, after 2 hours at 750° C., without any catalysts was only about 15 percent, which was almost unchanged with iron compounds alone (3%), whereas conversion increased up to about 40-45 percent when a potassium-containing catalyst (5%) was used. An increase in conversion to more than 95% was observed with the use of binary compositions (5% K/3% Fe). A temperature of about 900° C. was required to obtain a conversion that high for uncatalyzed coke, meaning that the binary catalysts demonstrated a lowering of more than 150° C. in gasification temperature.

[0051] The rates of methane formation for the binary catalysts at 750° C. were found to be very high (and highest) under the conditions at the start of the gasification (where the molar ratio of coke/H<sub>2</sub>O was highest), but decreased rapidly as the time increased (and the molar ratio of coke/H<sub>2</sub>O decreased).

##### What is claimed:

1. A particulate composition having a particle distribution size suitable for gasification in a fluidized bed zone, comprising an intimate mixture of (A) a petroleum coke derived from crude oil comprising ash in an amount of about 1.0 wt % or less, based on the weight of the petroleum coke, and (B) a gasification catalyst which under suitable conditions of temperature and pressure and in the presence of steam exhibits gasification activity whereby value added gaseous products are formed, wherein:

- (a) the gasification catalyst comprises (i) a first component which is a source of at least one alkali metal, and (ii) a second component which is a source of iron; and
- (b) the gasification catalyst is present in an amount sufficient to provide, in the particulate composition, a ratio of alkali metal atoms to carbon atoms in the range of from about 0.01 to about 0.1, and a ratio of iron atoms to carbon atoms in the range of from about 0.01 to about 0.1.
2. The particulate composition according to claim 1, wherein the alkali metal is potassium.
3. The particulate composition according to claim 1, wherein the source of alkali metal is an alkali metal salt selected from the group consisting of carbonate, hydroxide, acetate, halide and nitrate salts.
4. The particulate composition according to claim 1, wherein the source of alkali metal is potassium carbonate.
5. The particulate composition according to claim 1, wherein the source of iron is an iron salt selected from the group consisting of hydroxide, acetate, halide and nitrate salts.
6. The particulate composition according to claim 1, wherein the source of iron is iron acetate or iron nitrate.
7. The particulate composition according to claim 1, wherein the alkali metal is potassium; the source of alkali metal is an alkali metal salt selected from the group consisting of carbonate, hydroxide, acetate, halide and nitrate salts; and the source of iron is an iron salt selected from the group consisting of hydroxide, acetate, halide and nitrate salts.
8. The particulate composition according to claim 1, wherein the source of alkali metal is potassium carbonate, and the source of iron is iron acetate or iron nitrate.
9. The particulate composition according to claim 1, wherein the gasification catalyst is present in an amount sufficient to provide in the particulate composition a molar ratio of alkali metal atoms to carbon atoms in the range of from about 0.01 to about 0.08.
10. The particulate composition according to claim 1, wherein the gasification catalyst is present in an amount sufficient to provide in the particulate composition a molar ratio of iron atoms to carbon atoms in the range of from about 0.01 to about 0.08.
11. The particulate composition according to claim 1, having a particle size ranging from about 25 microns to about 2500 microns.
12. A process for converting petroleum coke to methane, comprising the steps of:
- (1) combining a petroleum coke and a catalyst having steam gasification activity to produce a particulate composition having a particle distribution size suitable for gasification in a fluidized bed zone,
  - (2) reacting the particulate composition in a fluidized bed zone in the presence of steam to form gaseous products including methane and one or more of hydrogen, carbon monoxide and other higher hydrocarbons, and
  - (3) recovering methane from the gaseous products, wherein the particulate composition is as set forth in claim 1.

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