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㉖ **A method for producing a methane-lean synthesis gas from petroleum coke.**

㉗ A methane-lean synthesis gas is produced from the steam gasification of petroleum coke in a fluidized bed at temperatures of between 650 and 790°C and pressures of between 1.75 and 14 kg/cm² using a potassium or sodium salt to catalyze the steam-gasification reaction. The synthesis gas produced contains less than about 3 volume % methane and less than 40% volume of steam. Because of its low methane content the gas may be used to produce methanol or a high purity product gas containing substantially only hydrogen and carbon dioxide which, in turn, may be scrubbed to produce a gas containing at least 95 volume % hydrogen. If the methane lean gas produced from the gasification reactor contains nitrogen, e.g. when air is used to combust the coke to maintain the temperature of the fluidized bed, then the methane lean gas may be used to produce high purity ammonia.

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A METHOD FOR PRODUCING A METHANE-LEAN SYNTHESIS GAS
FROM PETROLEUM COKE

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10 In the processing of crude oil by refineries
a relatively large amount of petroleum coke is
produced, particularly during the cracking process
which is necessary in order to increase the gas
fraction derived from crude oil. Although it is
possible to use such petroleum coke in certain
technologies, for example, producing electrodes, if the
15 coke has either a relatively high ash content or sulfur
content, uses for the coke are diminished and disposal
thereof presents problems because of possible
pollution.

20 In addition, most refineries also require
relatively large amounts of hydrogen during the
refining process, for example, when the higher boiling
fractions of crude oil are cracked in the presence of
hydrogen, i.e. hydrocracking. It would therefore be
desirable if petroleum coke, either delayed or fluid,
25 such as that produced in a petroleum refinery could be
the starting material for the production of a synthesis
gas useful in producing a hydrogen-containing gas of
high purity, i.e. comprising 95 volume % or more
hydrogen, high purity methanol, or ammonia.

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Certain prior art workers have reacted
petroleum coke with steam to gasify the coke.
However, most of these prior art workers have produced
gases containing relatively large amounts of methane.
35 Methane containing gases are not, in general, useful in

producing a hydrogen containing gas of high purity since, inter alia, methane can only be removed by relatively complicated methods thereby making it uneconomical to produce a relatively hydrogen pure gas from a methane rich gas.

Exemplary of prior art which produces high methane content gases from petroleum coke is United States Patent 3,689,240 (Aldridge et al.). This patent discloses a method for producing a methane rich gas by steam gasifying petroleum coke in the presence of cesium carbonate at pressures in excess of 14 kg/cm^2 . In Table II of this Patent it is disclosed that under certain conditions, which are not specifically stated, but which do include a pressure of 0 psig there is produced a gas containing 1.7 volume % of methane. However, when the pressure is raised to 10.5 kg/cm^2 the gas thus produced from the steam gasification of petroleum coke contains 15.6 volume % methane. In this regard it is noted that it is, from a practical standpoint, virtually impossible to operate a fluidized bed at zero pressure due to the pressure drop which inevitably occurs because of the processing equipment used to produce a commercial gas. Such processing equipment includes cyclones, waste heat boilers, scrubbers, etc. which are necessary to produce a gas which is sufficiently particle free to be useful. If a pressure less than about 1.75 kg/cm^2 is used there is not sufficient pressure to move the gas through the fluidized reactor. In this regard, it is noted that if the data contained in Table II is extrapolated then, even when operating at pressures as low as 7 kg/cm^2 there would be produced a gas containing about 8 volume % methane and even at pressures as low as 1.75 kg/cm^2 there would be produced a gas containing about 6 volume %

methane which is undesirable in a gas intended to be used to produce relatively pure hydrogen or high purity methanol. It thus can be seen that this patent teaches it is virtually impossible using a cesium catalyst to produce a methane lean gas (i.e. one containing less than about 3 volume %) from the steam gasification of petroleum coke using a fluidized bed in a fluidized reactor.

Another patent which teaches producing a methane rich gas from the steam gasification of a carbonaceous material in the presence of a catalyst is United States Patent 2,682,459. In all of the examples of this patent, regardless of the catalyst used, the minimum amount of methane formed in the gas was 12.4 volume %. A gas containing this much methane is not useful to produce a gas containing at least 95 volume % hydrogen.

A further patent which discloses the steam gasification of a carbonaceous material is U.S. Patent 3,615,299. The patentees apparently attempted to develop a method to produce a hydrogen rich gas from the steam gasification of coke derived from coal. However, the Patentees did not succeed in obtaining a gas containing less than about 3 volume % methane and, in order to produce a hydrogen rich gas, the patentees found it necessary to use a large excess of steam so that the resulting gas contained more than 60 volume % steam. A gas containing more than about 3 volume % methane and more than 60 volume % steam is highly undesirable if a gas containing at least 95 volume % hydrogen is desired as the end product.

From the foregoing it is readily apparent that

problems exist in achieving production of a methane-lean synthesis gas from petroleum coke, derived from either delayed or fluid coking processes.

5 The present invention permits the production of a methane-lean synthesis gas (one containing, say, less than about 3 volume % methane) by the steam-gasification of petroleum coke in a fluidized bed in the presence of a potassium or sodium salt, utilizing low temperatures and pressures, and minimum amounts
10 of steam with high steam conversion rates.

This is by conducting the steam gasification reaction of petroleum coke under delicate and critical conditions in order to produce a
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methane-lean synthesis gas in an economic manner.

The process involves using a fluidized reactor (a fluidized gasification zone) within which is formed a fluidized mixture or bed of petroleum coke and a gasification catalyst which may be a potassium salt, a sodium salt, or mixtures thereof. The use of such catalysts allows the production of a methane lean synthesis gas when certain operating pressures and temperatures are used and when certain amounts of steam are used. The process also includes heating the reaction mixture of steam and carbon to the correct temperature by oxidizing a portion of the carbon in the petroleum coke using an oxygen containing gas such as air or, preferably, oxygen.

Both temperature and pressure are critical in the present invention if the desired results are to be obtained, such results including the following: (1.) high steam conversion, generally greater than 30 and preferably 40 volume % of the steam reacts with the carbon contained in the petroleum coke, (2.) the gasification rate of the carbon contained in the petroleum coke is from 5 to 25 weight % per hour, (3.) the gas produced from the steam gasification reaction contains less than about 40 volume % steam, and preferably less than about 30 volume % steam, prior to the time when the steam is separated from the synthesis gas, (4.) the overall process converts over 90 weight % of the carbon in the petroleum coke to a synthesis gas and (5.) the synthesis gas contains less than about 3 volume % of methane and preferably less than about 2 volume percent methane on a nitrogen and steam free basis. In order to obtain the foregoing results the parameters under which the reaction takes place must be

carefully controlled.

The pressure at which the gasification reaction takes place in the present invention is sufficient to overcome the pressure drop in the fluidized gasification zone (a minimum of about 1.75 kg/cm² gauge, hereinafter kg/cm², and preferably a minimum of about 3.5 kg/cm² but less than about 14 kg/cm²)

Therefore, in general, it may be said that the desired results discussed above are obtained when operating at pressures of between about 1.75 or 3.5 kg/cm² and 14 kg/cm² but, preferably, the pressures used will be between about 3.5 kg/cm² and 10.5 kg/cm². We have found that excellent results occur when the preferred pressures are utilized.

The temperature, at which the gasification reaction takes place, is also critical. In general, we have found that temperatures between about 650°C and about 790°C will produce good results but it is preferable if the temperature is at least 700°C and, more preferably, at least 730°C. The preferred temperature range is between about 700°C and more preferably 730°C and 760°C.

In addition to the temperature and pressure the amount of steam used is also critical. In general, the amount of steam introduced into the gasifier will be between about 0.2 and about 1 part per weight of steam per hour per one part by weight of carbon in the fluid bed of the gasifier retort. Preferably, the amount of steam introduced into the gasifier is between about 0.3 and about 0.8 parts by weight of steam per hour per one part by weight of carbon.

In the method of the present invention the

temperature of the gasification reaction is maintained by introducing an oxygen containing gas into the gasification zone or retort to oxidize a portion of the carbon contained in the petroleum coke thereby raising the temperature. Since it is desirable to utilize as little carbon as possible in the oxidation reaction, only that amount of oxygen is introduced to maintain the reaction temperature in the gasifier zone to between 650°C and 790°C. If it is desired to produce a substantially pure hydrogen gas or methanol then the oxygen containing gas should be substantially pure oxygen instead of, e.g. air, since the presence of nitrogen in this situation is undesirable. On the other hand, if it is desired to produce ammonia high purity air, for example, may be used as the oxygen containing gas since, in this situation, the presence of nitrogen is not undesirable.

The method of the present invention also includes the use of a specific type of a gasification catalyst, which may be either a potassium or sodium salt ^{or both}. The prior art, enumerated above, indicates that other gasification catalysts, such as cesium salts, are not operable in the present invention because the use of such cesium salts in a fluidized reactor for the steam-gasification reaction produces a gas containing too much methane. It therefore may properly be said that ^{not} all gasification catalysts will work in the method of the present invention. Hence, using either a salt of potassium or a salt of sodium as a gasification catalyst is critical. Exemplary of such salts are the carbonate, the sulfide, the sulfate, the hydroxide and the oxide salts of potassium or sodium or any mixture of the foregoing salts.

The particular amount of catalyst used is not

very critical and may range between about 1 weight %
and about 50 weight % based upon the total weight of
the petroleum coke and the catalyst in the gasifier. A
more preferred range is between about 5 weight % and
5 about 50 weight %.

10 The catalyst may be added to the petroleum
coke in any convenient manner. For example, prior to
the introduction of the coke into the gasification
retort or zone the catalyst may be added as a solid and
a mixture of petroleum coke and catalyst formed.
However, it is not necessary to mix the catalyst and
the petroleum coke prior to the introduction of the two
15 into the gasification zone or retort because fluidizing
the two will form a mixture in the gasification retort
itself. In addition to adding the catalyst as a solid
to the coke prior to the introduction thereof into the
fluidized gasification zone, the catalyst may also be
20 added to the petroleum coke as an aqueous slurry or
solution, depending upon the solubility of the
particular catalyst in water. In this latter event,
fluidizing the catalyst and coke in the fluidized
reactor also forms a fluidized mixture of the two.

25 The synthesis gas (i.e. the gas produced by
the reaction between steam and carbon after removal of
the excess steam) produced by the process of the
present invention will in general contain about from
about 40 to about 50 volume % hydrogen, from about 10
30 to about 25 volume % carbon monoxide, from about 30 to
about 50 volume % carbon dioxide and from about 0.5 to
about 1.7 volume % methane, it being understood that
the foregoing percentages are on a steam, and if used,
nitrogen free basis. Such a synthesis gas is ideal for
35 producing methanol or a high purity product gas

containing substantially only hydrogen and carbon dioxide.

5 Surprisingly, the instant method produces more carbon dioxide than would be expected based on the amount of oxygen used in the process. As is known in the art, the oxygen reacts with the carbon to produce carbon dioxide. It would be expected that the carbon dioxide thus produced would be reduced by the carbon to 10 produce carbon monoxide. In other words, it would be expected that there would be less carbon dioxide in the synthesis gas than the amount of oxygen used. Apparently what is occurring is that whatever carbon dioxide is reduced by the carbon is more than 15 compensated for by the carbon monoxide being converted back to carbon dioxide because of the catalysis of the shift reaction. This relatively high production of carbon dioxide is highly desirable since the reaction is exothermic and maximizes heat release thereby 20 minimizing the amount of oxygen necessary to raise the temperature to 650°C to 790°C.

As noted before, the synthesis gas produced by the present invention is excellent for conversion into 25 a product gas (i.e. a gas containing primarily hydrogen and carbon dioxide) by the well known water gas reaction wherein steam reacts with carbon monoxide, normally in the presence of an iron and/or chromium catalyst, to produce hydrogen and carbon dioxide. In 30 the present invention the synthesis gas when subjected to the water shift reaction produces a product gas of approximately 70% hydrogen and 30% carbon dioxide with minor amounts of methane and carbon monoxide depending upon the respective amounts of hydrogen, carbon 35 monoxide and carbon dioxide in the initial synthesis

gas.

5 The carbon dioxide is easily removed from the product gas by scrubbing the gas with either a chemical or a physical solvent by means well known in the art. The thus produced gas contains over 95 volume % hydrogen with trace amounts of carbon monoxide, carbon dioxide and a small amount of methane. Inasmuch as methane cannot be removed from the product gas in an economical manner, it is very undesirable to have
10 methane in the initial synthesis gas.

15 The gas produced by the present invention is also excellent for conversion into methanol by the reaction of hydrogen with carbon monoxide and/or carbon dioxide in the presence of certain catalysts such as zinc oxide.

20 The particular reactor used for the gasification reaction is not critical and can be any of a well known number of reactors having differing sizes, shapes and configurations. However, in the preferred exemplary embodiment the particular type of reactor used was 10 metres long and had an internal diameter of
25 25 cm. In most of the preferred exemplary embodiment fluid coke was used although as shown in Examples 13-15 delayed coke may also be used with equally good effect. The particular type of petroleum coke used contained approximately 0.5 weight % ash and
30 about 2.5 weight % sulfur, although petroleum coke containing more or less ash and/or sulfur may be used to good effect. If the petroleum coke, either delayed or fluid, used herein contains relatively small amounts of sulfur then it is not necessary to remove the
35 hydrogen sulfide from the gas produced by the

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gasification reaction. As is known in the art, during the gasification most of the sulfur in the coke is converted to hydrogen sulfide which is contained in the effluent gas from the reactor. After the solids which are entrained in the effluent gas are removed and after removal of steam the hydrogen sulfide, if desired, may easily be removed by conventional methods. For example, dry purification methods may be used utilizing bog iron ore which comprises ferric hydroxide or oxide. The gas is passed through the iron ore which is spread as a thin layer in large flat boxes having perforations therein. The gas passes through the iron ore and the hydrogen sulfide reacts with the ferric hydroxide to form ferrous sulfide. In addition, the gas may be desulfurized with activated carbon, the hydrogen sulfide absorbed on the carbon being oxidized by catalytic oxidation with air to form sulfur.

Another method which is preferred in the present invention is the so-called "Stretford" method wherein the hydrogen sulfide is absorbed in a sodium vanadate-sodium carbonate solution and the resulting sulfur removed by filtration. Inasmuch as removal of hydrogen sulfide from a gas is well known in the art no detailed exemplification thereof will be given herein.

The process used in the Examples is as follows:

Petroleum coke and catalyst are mixed and introduced near the bottom of the reactor described above by a screw conveyor. Steam and oxygen are injected into the reactor below the point where the petroleum coke and catalyst are introduced into the reactor.

The steam and oxygen may be introduced separately into the reactor or as a mixture. In the preferred exemplary embodiment the steam and oxygen are introduced together at the bottom of the reactor through a gas distributor. The temperature at which the steam is injected into the reactor is not particularly critical but, in the preferred exemplary embodiment superheated steam at a temperature of 480 to 540°C was used.

The initial amount of fluid coke and catalyst fed to the bed was about 180 kg and the bed of petroleum coke and catalyst was fluidized to a bed depth of about 5 metres and at a fluidizing velocity of about 0.3 to 0.6m per second. Under such conditions, the amount of oxygen necessary to maintain a temperature of between about 650°C and 790°C was between about 14 kg per hour and 23 kg per hour. In all of the examples, coke and catalyst were continuously fed to the fluidized reactor so that the weight concentration of the catalyst, based on the weight of the solids in the reactor was substantially constant.

Hot gases containing entrained solid fines (mostly unreacted petroleum coke but also some catalyst and ash) exit the top of the reactor and pass through an external first stage cyclone for removal of a portion of the entrained solids. The solids collected in this cyclone were reinjected near the bottom of the bed via an external dipleg. The hot gases leaving the first cyclone were then fed to a second cyclone providing a higher inlet gas velocity to effect more efficient fines removal. The fines from the second cyclone were withdrawn and fed back into the reactor to

be further gasified. In this manner over 90 weight % of the unreacted petroleum coke is recycled into the reactor thus allowing at least 90 weight % conversion of the carbon contained in the petroleum coke.

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The hot gases leaving the cyclone, which is essentially synthesis gas and steam, the amount of steam in said gas being between about 20 and 25 volume %, were conveyed to a venturi-type scrubber which contacts the hot gas with a recirculating water stream. A gravity separator de-entrained the water from the gas and heat was removed by a heat exchanger in the circulating water system. Scrubbed solids and condensed steam were purged from the scrubber system at a rate equal to the rate of production. The resulting synthesis gas, which contained from 40 volume % to 50 volume % hydrogen on a nitrogen free basis, with the steam and fines removed, was then used to produce a product gas by the water gas shift reaction and the carbon dioxide removed therefrom to produce a gas containing at least about 97 volume % hydrogen.

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During the process oxygen flow is controlled based upon the temperature desired and the petroleum coke feed rate is controlled to maintain a constant bed level of approximately 5 metres. In the preferred exemplary embodiments the amount of petroleum coke fed to the reactor, per hour, was between about 14 kg and 27 kg depending on the amount of steam used and the gasification rate of the carbon.

Examples 1 to 5

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In these examples fluid petroleum coke was used in the method described above. The catalyst used

was potassium carbonate and the concentration of catalyst in the reactor was about 8 weight %. The carbon gasification rate in each of Examples 1 through 5 was about 15 to 20 weight % per hour, the steam conversion rate was about 40% and the steam rate was about 0.45 parts by weight per hour per one part by weight of carbon in the reactor. The amount of hydrogen in the gas produced, on a steam and nitrogen free basis was between about 40 volume % and 50 volume %. The temperatures used, the pressure used,

and the amount of methane formed, in volume %, is given below in Table 1 for each example:

| <u>Example</u> | <u>Temp. (°C.)</u> | <u>Press. kg/cm²</u> | <u>Methane</u> |
|----------------|--------------------|---------------------------------|----------------|
| 1 | 730 | 3.5 | 1.01 |
| 2 | 752 | 4.2 | 1.22 |
| 3 | 738 | 4.2 | 1.39 |
| 4 | 753 | 5.25 | 1.41 |
| 5 | 750 | 3.5 | 1.04 |

From the above examples, it is readily evident that a methane lean gas is produced at relatively low pressures of 3.5 to 5.25 kg/cm² which is unexpected in view of the prior art, specifically U.S. Patent 3,689,240 (Aldridge et al.) where one skilled in the art would expect to produce a gas containing at least 6 to 8 volume % methane.

Example 6

In this example, the same conditions were used as in the preceding examples except the steam rate was 0.32 parts by weight per hour per one part by weight of carbon in the reactor, the steam conversion was about

38%, the carbon gasification rate was about 7 weight % per hour, and the concentration of catalyst in the reactor was about 20 weight %. Under these conditions, the volume % of methane in the thus produced gas was about 1.10 at a temperature of 680°C and a pressure of 2.2 kg/cm².

Example 7

In this example, the method described above was utilized. The catalyst used is potassium carbonate and its concentration in the reactor was between about 40 and 45 weight %. The steam space velocity is about 0.24 parts by weight of steam per one part by weight of carbon contained in the fluid coke. The temperatures was 700°C and the pressure was 2.95 kg/cm². Steam conversion was approximately 55%. The gasification rate of the carbon is approximately 15 weight % per hour. The synthesis gas thus produced, when unreacted steam is excluded from the gas, contains about 1.4 volume % methane which means that the hydrogen containing gas produced from such a synthesis gas will contain in excess of about 98 volume % hydrogen.

Example 8

This example used conditions approximating those of example 6 except the reactor temperature was held at 730°C and the catalyst used was sodium carbonate. Under conditions approximating example 6, it was found the gasification rates and steam conversion rates are approximately the same as in example 6 but the synthesis gas contains between about 1.3 volume % to 1.7 volume % methane.

In all of the preceding examples, a sufficient

amount of unreacted coke is recycled to the reactor so that 95% of the carbon is converted to a synthesis gas, including the oxygen-carbon reaction.

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Examples 9 through 12

In these examples, the method described in examples 1 through 5 was utilized except the reactor was operated at lower temperature and pressure, but at higher catalyst concentrations to determine the effect of these variables on the methane content of the gas. The results are presented below in Table 2.

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Table 2

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| | <u>Examples</u> | | | |
|---|-----------------|-----------|-----------|-----------|
| | <u>9</u> | <u>10</u> | <u>11</u> | <u>12</u> |
| Temp. (°C) | 657 | 676 | 700 | 700 |
| 20 Press. (kg/cm ²) | 2.5 | 2.2 | 2.7 | 2.95 |
| Steam Rate | | | | |
| kg/hr/kg Coke | 0.29 | 0.29 | 0.33 | 0.41 |
| Wt% K ₂ CO ₃ | 22 | 19 | 22 | 45 |
| Steam Conv. % | 36 | 38 | 47 | 52 |
| 25 Gas'n. Rate | | | | |
| wt%/hr | 8.1 | 7.0 | 9.3 | 10.8 |
| Gas Analysis, mole %, dry, air free | | | | |
| 30 H ₂ | 46.4 | 48.0 | 48.9 | 49.5 |
| CO | 8.4 | 10.9 | 13.6 | 12.6 |
| CO ₂ | 43.8 | 39.7 | 36.1 | 36.3 |
| CH ₄ | 1.4 | 1.1 | 1.2 | 1.4 |

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As can be seen from the data presented in

Table 2 above, a methane-lean gas is produced at temperatures of from 657°C to 700°C and pressures of from 2.2 to 2.95 kg/cm² regardless of the catalyst concentration, which varied from 19 wt% to 45 wt% in the fluidized bed. In addition, the data also show that the gasification temperature can be lowered while maintaining high steam conversions and good gasification rates by increasing the catalyst concentration.

Examples 13 through 15

In these examples, the method described in examples 1 through 5 was utilized except delayed coke containing 9.1% volatile matter was used in lieu of fluid coke containing approximately 10% volatile matter. The catalyst used was potassium carbonate and the concentration of catalyst in the reactor was between 4.7 and 9.9 weight percent. The carbon gasification rates were between about 7.4 and 10.6 weight percent per hour. The steam conversion was between about 21 and 30 percent at steam rates of between 0.45 and 0.53 kg of steam per hour per kg of carbon. The amount of hydrogen in the gas produced, on a steam and nitrogen-free basis, was about 48 volume percent. The amount of methane formed, as shown below in Table 3, for each example while operating the reactor at 3.5 kg/cm² and 730°C to 760°C, is comparable to the quantity of methane formed from fluid coke at essentially the same operating conditions (see examples 1 and 5).

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Table 3

| Example | Temp. (°C) | Press. (kg/cm ²) | K ₂ CO ₃ (%) | Gasification Rate (wt % C/hr) | Steam Conv. (%) | Methane (vol %) |
|---------|---------------|---------------------------------|---------------------------------------|-------------------------------------|-----------------------|--------------------|
| 1 | 730 | 3.5 | 8 | 15-20 | 40 | 1.01 |
| 5 | 750 | 3.5 | 8 | 15-20 | 40 | 1.04 |
| 13 | 730 | 3.5 | 4.7 | 7.4 | 21.0 | 1.28 |
| 14 | 730 | 3.5 | 6.7 | 11.7 | 29.9 | 1.61 |
| 15 | 760 | 3.5 | 9.9 | 10.6 | 26.6 | 1.38 |

In the foregoing preferred exemplary embodiments certain pressures, catalyst concentrations, catalysts, steam rates, etc. were utilized, it being understood that such was solely for the purpose of exemplification and not to be considered as limiting the invention.

CLAIMS

- 5 1. A method for producing a synthesis gas by
steam-gasification of petroleum coke characterized in
producing a methane-lean synthesis gas by introducing
steam and oxygen or an an oxygen containing gas into a
reactor at a rate sufficient to fluidize and form a
10 fluidized mixture of petroleum coke and a gasification
catalyst which is a potassium salt, a sodium salt or a
mixture thereof, whereby to oxidize a sufficient amount
of the carbon in said coke to maintain the temperature in
the reactor at between about 650°C to about 790°C so that
15 the steam reacts with, and gasifies the coke, maintaining
the pressure in the reactor at between about 1.75 kg/cm²
and about 14 kg/cm²; the steam being fed into the fluid-
ized mixture in an amount of between about 0.2 and about
1 part by weight of steam per hour per one part by weight
20 of carbon in said fluidized mixture whereby the steam-
carbon gasification rate is between about 5 weight % and
about 25 weight % per hour based on the weight of the
carbon contained within the fluidized mixture.
- 25 2. A method according to claim 1 wherein the
temperature in the reactor is maintained at ^{between} /about 700°C
to about 760°C.
3. A method according to claim 1 or claim 2
30 wherein the pressure in the reactor is between about 3.5
and 14 kg/cm².
4. A method according to any one of the preceding
claims wherein the amount of catalyst in the fluidized
35 mixture of coke and catalyst is between about 1 weight %

and about 50 weight % based upon the total weight of the petroleum coke and catalyst.

5. A method according to claim 4 wherein the amount of catalyst is at least about 5 weight %.

6. A method according to any one of the preceding claims wherein said catalyst is a potassium salt or a mixture thereof.

10 7. A method according to any one of claims 1 to 5 wherein the catalyst is potassium carbonate, sodium carbonate, or a mixture thereof.

15 8. A method according to any one of the preceding claims wherein the said oxygen containing gas is used and is air.

20 9. A method according to any one of the preceding claims wherein the amount of steam fed to the fluidized mixture is between about 0.3 and about 0.8 parts by weight per hour per one part by weight of carbon in the mixture.

25 10. A method according to any one of the preceding claims wherein the pressure maintained in the reactor is between about 3.5 and about 10.5 kg/cm².

30 11. A method according to any one of the preceding claims wherein the amount of steam in the synthesis gas is less than about 40%.

35 12. A method according to any one of the preceding claims including the further steps of conveying the synthesis gas, unreacted steam and entrained particles of unreacted coke to a solids separation zone and separating at least a portion of said unreacted coke particles from

the synthesis gas and steam and continually recycling a sufficient amount of said separated coke particles to said fluidized mixture to gasify at least about 90 weight percent of the carbon contained in said petroleum coke based on the amount of said coke introduced into said fluidized mixture.

13. A method according to claim 12 including the further step of separating the steam from the produced synthesis gas to yield a synthesis gas consisting essentially of hydrogen, carbon monoxide, carbon dioxide and less than about 3 volume % methane.

14. A method according to any one of the preceding claims wherein the methane-lean synthesis gas contains less than about 2 volume % methane.

15. A method according to any one of the preceding claims wherein the petroleum coke is fluid coke.

16. A method according to any one of claims 1 to 14 wherein the petroleum coke is delayed coke.