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**PROCESS FOR THE PRODUCTION OF FUEL GAS
LOW IN CARBON MONOXIDE**

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This invention relates to improved gaseous fuels applicable for industrial and residential use by both municipal and long distance distribution, and more particularly to a process by which crude fuel gases having a relatively high content of carbon monoxide and other impurities may be treated to remove substantially all of these impurities.

By subjecting carbon-containing solid fuels such as coal to oxygen and steam treatment under pressure, gaseous fuel products may be recovered which are useful for industrial or residential purposes in areas where natural fuel gases are not readily available. These pressure-formed gaseous fuels are particularly useful in various thermal synthesis operations. Usually, upon reducing the undesirable carbon dioxide present to a content of only about 2% by scrubbing techniques, the heating value of the resulting fuel gas is between 3700 and 4500 kcal./m.³(N.T.P.), depending on the particular solid fuel charged.

The carbon monoxide content of these pressure-formed fuel gases ordinarily ranges between about 18 and 32% which is considerably higher than that of coke-oven gas (6%) or municipal gas (10 to 15%), and the density of these gaseous (fuels), after scrubbing, is higher than that of coke-oven gas as well. This carbon monoxide content varies within said range of 18 to 32% depending on the quantity of steam used in the gas formation. Generally, the higher the rate of steam addition, the lower will be the carbon monoxide content.

Nevertheless, during pressure gasification of solid fuels, disadvantageously only a part of the steam present is actually converted, the remainder merely passing through the reaction zone unused. Moreover, where fresh steam is added to the reaction zone, the solid fuel ash does not sinter, but accumulates as a powder instead which can only be removed with difficulty from the ash sluice. Additionally, it is uneconomical and technically difficult to produce a pressure-formed gas fuel with a desirable carbon monoxide content of less than 18%.

It is an object of the invention to overcome the above disadvantages and to provide a process for the production of fuel gas low in carbon monoxide and substantially free from undesired impurities.

Other and further objects will become apparent from a study of the within specification.

It has been found, in accordance with the invention, that crude fuel gas, such as that obtained by gasification of solid fuels in the presence of oxygen and steam under pressure, having a high content of carbon monoxide, may be treated to remove the larger portion of the carbon monoxide and attendant impurities while utilizing otherwise unreacted steam present in the crude gases, leaving the pressure gasification reaction zone to enrich the quantity of combustible products in the final gas.

Accordingly, a crude fuel gas upon its exit from the pressure gasification zone is suitably cooled, for example, by water injection means to the extent necessary to separate out high boiling hydrocarbons which may be present. The somewhat cooled gas which is still under the same or perhaps slightly lower pressure as that which it leaves the pressure reaction zone is then reheated to about 250° to

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400° C. and conducted over a conversion catalyst wherein the unused steam present is utilized to produce a richer combustibles content. The converted gas thus obtained is thereafter cooled and purified in any known manner.

The process according to the invention advantageously may be carried out at temperatures which are as high as those technically attainable without the higher carbon monoxide content unfavorably influencing the final composition or the density of the final pure gas. In this way, any unused steam present in the crude gas will be efficiently and completely used, whereby an economy in overall steam requirements will be realized.

Specifically, in accordance with the invention, crude fuel gas, such as that leaving the pressure gasification reaction zone at a pressure of about 25 atmospheres and a temperature of from 400 to 700° C. and which contains 20 to 25% carbon monoxide with respect to dry gas as well as considerable amounts of unused steam, high boiling hydrocarbons and dust, may be favorably purified and enriched in combustibles content by first cooling to remove most of the thereby separatable materials such as high boiling hydrocarbons and dust and thereafter subjecting the cooled gases to catalytic conversion at higher temperatures.

The cooling operation may be carried out by suitable water injection cooling means, and for greater efficiency and economy may employ exit water from cooling apparatus conventionally applied at a subsequent stage in the process. This first cooling step by which the temperature of the gas is lowered to about 200° or slightly less separates high boiling products and dust including tars and oil droplets from the crude gas, all of which may be removed therefrom as for example by suitable cyclone means. Still under pressure, the crude gas may be cooled even further to about 160 to 190°, as for example, by passage through heat exchange means to remove additional vaporous hydrocarbon impurities.

The cooled crude gas which still contains under pressure 40–60% by volume of steam and other impurities is then reheated, as for example, via suitable heat exchange means, by the hot pure gases emanating from the subsequent conversion reaction zone, to a temperature of from about 250° to 400° C. These hot gases are then conducted over a conversion catalyst in said conversion reaction zone to convert a substantial part of the carbon monoxide present with a stoichiometric quantity of the unused steam present to carbon dioxide and hydrogen. In this way, little or no steam is wasted in the overall process and the quantity of gas liquors from which water must be recovered is decreased, thereby decreasing the cost of such water recovery.

During the conversion step, the gas increases its temperature by about 100° C. due to the heat of reaction. Surprisingly, this conversion takes place at conditions almost completely corresponding to those of equilibrium, in spite of the impurities contained in the crude gas, such as carbon dioxide, hydrogen sulfide, organic sulfur compounds, ammonia, hydrocyanic acid, resin forming impurities, and the like, which are recognized catalyst poisons.

The process of the invention gives conversion yields which are from 80 to 95% of the theoretical. The preponderant amount of resin formers and organic sulfur compounds are removed in the conversion zone through hydrogenation or conversion into easily separable hydrogen sulfide. It should be noted that not only the scrubbed pure gas but also the oils and petroleum fractions yielded upon cooling contain considerably less organically bound sulfur than in similar procedures without conversion.

The catalytic conversion of the greater part of the carbon monoxide present with the unused steam may be carried out with suitable conversion catalysts such as a

mixture of iron oxide and chromium oxide. However, other less expensive materials may be advantageously used such as active hydrated iron oxides as used for the removal of hydrogen sulfide from carbonisation gases, bog iron ore or similar iron oxide hydrates. All of these materials may be employed separately as well as in mixture with each other. By suitable work-up procedures, they may be reduced to the desired particle size, dried and without further pretreatment employed directly in the process. These catalysts before use, nevertheless, may be essentially increased in their activity by heating at 300 to 350° C. with already converted gas to effect reduction, since such gas still contains about 20 to 40 g./m.³ (N.T.P.) of steam.

In place of iron oxide type catalysts, metals of the 6th group of the periodic system, particularly molybdenum and tungsten, in the form of their oxides and sulfides, and metals of the 8th group of the periodic system, such as cobalt and nickel, may be used with equally good results. Carrier substances for these catalyst materials include mineral products, such as alumina, silica gel, and the like. These catalysts advantageously may be readily converted at lower temperatures (250°–300° C.) than the iron oxide type catalysts require.

The activity of the catalyst which strongly diminishes after prolonged operation, can be renewed once again by regeneration at normal reaction temperature with air or oxygen containing inert gases and/or steam and subsequent reduction with converted gas low in steam content. Conventional pressure resistant means employed for pressure gasification of solid fuels in accordance with the invention may be used for this regeneration step.

After leaving the conversion zone, the converted gas may be precooled through heat exchange means, releasing the major part of its heat to the gas entering the conversion reaction zone and its residual heat through heat exchange means to a waste heat boiler for the production of steam. Thereafter, direct or indirect cooling means may be employed for final cooling of the gas freed from carbon dioxide and hydrogen sulfide, as for example, by suitable conventional scrubbing techniques. Upon drying, the purified gas may be used as a synthesis gas, or directly as an industrial or residential gas via long range or local distribution.

The purified gas obtained in accordance with the process of the invention normally contains only about 4 to 8% carbon monoxide and its density is ordinarily below that of coke oven gas. However, if desired, for specific purposes, the gas may be made to have a higher carbon monoxide content than 8% and a higher density as well by effecting a less complete transformation in the conversion zone or by mixing non-converted gas with the purified converted gas.

It will be seen that the process in accordance with the invention whereby a purified gas low in carbon monoxide may be produced may be readily adapted without difficulty to conventional apparatus for pressure gasification of solid fuels by merely leading the crude gas from the conventional apparatus through heat exchange means for cooling and thereafter heating the gas and conversion reactor means for reducing the carbon monoxide content of the gas. These additional means are conveniently positioned adjacent the pressure gasification zone, for example, between the waste heat steam boiler and the crude gas reactor condensers.

The invention is further illustrated by the following examples but it is to be understood that it is not to be limited thereby.

EXAMPLE 1

Conventional Production of Fuel Gas

A low coking mineral coal was gasified under an operational pressure of 23 atmospheres pressure with oxygen

and steam. The composition of the gas, after cooling and after scrubbing in the conventional manner was:

	Crude gas after cooling to 25°, percent	Scrubbed pure gas, percent
CO ₂	29.7	2.0
C ₂ H ₄	0.5	0.7
CO.....	17.0	24.1
H ₂	40.1	56.9
CH ₄	10.6	15.0
N ₂	0.9	1.3
H ₂ S.....	1.2	0

Upper heating value..... 3,970 kcal./m.³ pure gas (N.T.P.).
Density with reference to air..... 0.49.
Content of organically bound sulfur. 150 mg./m.³ pure gas (N.T.P.).

Consumption of gasification agents:

	For crude gas	For pure gas
Oxygen.....	0.16 m. ³ /m. ³ crude gas (N.T.P.).	0.22 m. ³ /m. ³ pure gas (N.T.P.).
Fresh steam.....	0.95 kg./m. ³ crude gas (N.T.P.).	1.33 kg./m. ³ pure gas (N.T.P.).

EXAMPLE 2

Purified Fuel Gas Low in Carbon Monoxide Content

The same coal as used in Example 1 was gasified under an operational pressure of 23 atmospheres pressure according to the conventional hot passage technique, whereinafter a gas with a high carbon monoxide content was produced. The following content values were obtained:

	Crude gas composition after cooling to 190°, percent	Crude gas cooled to 20°, percent	Pure gas upon cooling a portion of the crude gas to 25° and scrubbing out of CO ₂ and H ₂ S, percent
CO ₂	11.5	26.7	2.0
C ₂ H ₄	0.2	0.5	0.7
CO.....	9.7	22.6	30.8
H ₂	16.5	38.3	52.3
CH ₄	4.0	9.3	12.6
N ₂	0.5	1.2	1.6
H ₂ S.....	0.6	1.4	-----
Steam.....	57.0	-----	-----

Oil and petroleum fractions content..... 15 g./m.³ crude gas (N.T.P.).
Having an organically bound sulfur content of. 1.5%.

A quantity of the wet crude gas after cooling to 190° was heated to 350° and conducted over a conversion catalyst comprising a mixture of iron oxide and chromium oxide. The rate of flow volume was 600 l. gas/h.l. catalyst (N.T.P.).

After the cooling, the gas had the following composition:

	Crude conversion gas, percent	Scrubbed pure conversion gas, percent
CO ₂	38.3	2.0
C ₂ H ₄	0.4	0.6
CO.....	3.0	4.8
H ₂	48.1	78.3
CH ₄	7.8	12.7
N ₂	1.0	1.6
H ₂ S.....	1.4	-----

Upper heating value..... 3,850 kcal./m.³ pure conversion gas (N.T.P.).
Density/air..... 0.22.
Organically bound sulfur..... 40 mg./m.³ pure conversion gas (N.T.P.).
Organically bound sulfur in the oil and petroleum fractions. 0.6%.

Consumption of gasification agents:

	For unconverted crude gas	For pure gas
Oxygen-----	0.17 m. ³ /m. ³ unconverted gas (N.T.P.).	0.22 m. ³ /m. ³ pure gas (N.T.P.).
Fresh Steam-----	0.65 kg./m. ³ unconverted gas (N.T.P.).	0.87 kg./m. ³ pure gas (N.T.P.).

EXAMPLE 3

Purified Fuel Gas Low in Carbon Monoxide Content

After several weeks of operation, deposits formed by the polymerization of the high-boiling unsaturated hydrocarbons, during the heating of the crude gases to 350° in the heat exchangers, could be observed. Therefore, the conversion heater was charged with a cobalt-molybdenum oxide catalyst such as used for the refining of petroleum and crude gas heated only to 250° C. was passed at a flow volume rate of 400 m.³/h.m.³ catalyst (N.T.P.) over the catalyst.

The conversion of the crude gas took place in similar manner to that of Example 2, so that a pure gas of the same composition was obtained. After operating for several months in this way, no clogging occurred in the heat exchanger.

The pure gas obtained in Examples 2 and 3 has a lower CO content and a lower density than coke-oven gas. The content of organically bound sulfur was lower than that of coke-oven gas by 73%, that of the oil and petroleum fractions in Example 2 by 60% and in Example 3 by 71%. The steam consumption for gas low in carbon monoxide, which is obtained in accordance with the process of the invention, is lower by 0.46 kg./m.³ (N.T.P.), corresponding to 34%, than for a conventionally produced gas which contains about five times as much carbon monoxide.

EXAMPLE 4

Catalyst Regeneration

After a period of four months' operation, the activity of the iron oxide conversion catalyst had diminished so far that crude gas having a 22.0% CO content could only be converted to one having a CO content of 6.2%. The reactor was removed from operation, the gas pressure released and the coal tar oil adsorbed on the catalyst blown out with steam. Thereupon, the reactor was connected in a circulation system containing a gas blast apparatus and a gas heater. The entire system was filled with an inert gas mixture made up of a combustion gas consisting of nitrogen and carbon dioxide. This gas was conducted under normal pressure through the reactor and heated to 300°. The rate of flow volume amounted to 150 to 200 m.³/h.m.³ catalyst (N.T.P.). After reaching this temperature, so much air was fed into the system that the O₂ content of the entrance gas passing into the reactor amounted to 1-4%. The oxygen was consumed in the combustion of the resin and carbon deposits which blocked the catalyst, the excess of inert gas being carried out of the system. The addition of air was so controlled that the temperature in the catalyst was kept in the vicinity of the hottest point at about 450° to 550°. After 36 hours the regeneration was completed since the temperature peak had traversed the catalyst layer from top to bottom, essentially no more CO₂ formation was noted, and 0.3 to 0.6% of O₂ appeared in the exit gas from the reactor.

The system was then cooled to 350° C. with the above mentioned inert gas mixture and filled with converted gas which contained 3% CO and 48% H₂ and only 30 g./m.³ steam (N.T.P.). During the next three hours, the catalyst was reduced by recycling converted gas there-through at 350° C., consumed gas being continually replaced by fresh gas.

The reactor was disconnected from the recycling system and again connected to the conversion system and

placed in operation using wet crude gas at 23 atmospheres excess pressure.

The entering gas which contained 23.8% CO was converted by the regenerated catalyst to a CO value of 2.5%, i.e., the catalyst had regained its original activity.

What is claimed is:

1. A process for directly producing purified low carbon monoxide content fuel gas of density lower than coke-oven gas from hot crude fuel gas high in carbon monoxide and attendant impurities obtained by pressure gasification of solid carbon-containing fuels with steam and oxygen which comprises cooling said hot crude gas including unused steam therein to a temperature of from about 160 to 200° C. under pressure to separate impurities such as high boiling hydrocarbon fractions, oils, tars and dust, removing said impurities from said crude gas and said unused steam, heating the cooled crude gas and said unused steam to a temperature between 250 and 400° C., conducting the heated crude gas and said unused steam over a conversion catalyst to convert the high carbon monoxide content and steam unused in the pressure gasification to carbon dioxide and hydrogen substantially removing resin-formers and sulphur compounds during said conversion, and thereafter recovering the purified lower carbon monoxide content fuel gas.
2. A process according to claim 1 wherein said cooling of the hot crude gas is carried out by injection of water thereinto, whereby the steam content of said crude gas is raised to an amount within the range of from about 40 to 60% by volume.
3. A process according to claim 1 wherein the hot crude gas to be cooled is under pressure and the cooling, heating and converting steps are carried out under the same pressure.
4. A process according to claim 1 wherein the cooling, heating, and converting steps are carried out under slightly lower pressure than the pressure of the starting hot crude gas.
5. A process according to claim 1 wherein the conversion catalyst is an activated iron oxide catalyst.
6. A process according to claim 1 wherein the conversion catalyst is an iron oxide hydrate.
7. A process according to claim 1 wherein the conversion catalyst is an oxide of a metal of the 6th group of the periodic system of elements.
8. A process according to claim 1 wherein the conversion catalyst is molybdenum oxide.
9. A process according to claim 1 wherein the conversion catalyst is tungsten oxide.
10. A process according to claim 1 wherein the conversion catalyst contains a metal of the 6th and the 8th group of the periodic system of elements.
11. A process according to claim 1 wherein the conversion catalyst contains metal oxides of metals of the 6th and the 8th group of the periodic system of elements.
12. A process according to claim 1 wherein the conversion catalyst is cobalt.
13. A process according to claim 1 wherein the conversion catalyst is nickel with an oxide of the 6th group of the periodic system of elements.
14. A process according to claim 1 wherein the heated crude gas and steam to be converted are conducted over catalyst containing an oxide of a metal of the 6th group of the periodic system of elements and thereafter over an iron oxide catalyst.
15. A process according to claim 1 wherein the catalyst is an iron oxide and the iron oxide, before contact with the crude gas and steam, is pretreated at 300 to 400° C. with already converted gas low in steam content.
16. A process according to claim 1 wherein the conversion catalyst may be regenerated by treatment with an inert gas containing about 1 to 4% oxygen at from about 300 to 600° C., and thereafter effecting reduction by treatment with already converted gas low in steam content.
17. A process according to claim 1 wherein the con-

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version catalyst may be regenerated by treatment with steam containing about 1 to 4% oxygen at from about 300 to 600° C., and thereafter effecting reduction by treatment with already converted gas low in steam content.

18. A process according to claim 1 wherein the hot crude fuel gas to be purified contains from about 20 to 25% carbon monoxide with respect to dry gas.

19. A process for directly producing purified low carbon monoxide content fuel gas of density lower than coke-oven gas from hot crude fuel gas high in carbon monoxide and attendant impurities, said impurities comprising organic and inorganic sulfur compounds, ammonia, hydrogen cyanide, resin-forming impurities, said fuel gas being obtained by pressure gasification of solid carbon-containing fuels with steam and oxygen, which comprises cooling the hot crude gas still under pressure and still containing unused steam in an amount of from 40 to 60%, obtained by pressure gasification, to a temperature of about 200° C. to separate impurities such as high boiling hydrocarbon fractions, oils, tars, and dust, remov-

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ing said impurities from said crude gas, heating the cooled crude gas still under pressure and still containing said steam to a temperature of at least 250° C., conducting the heated crude gas and said steam over a reducing catalyst whereby the carbon monoxide content and the contained steam are substantially stoichiometrically converted to carbon dioxide and hydrogen substantially removing resin-formers and sulfur compounds during said conversion, thereafter further cooling and scrubbing the converted gas and recovering the purified lower carbon monoxide content fuel gas.

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