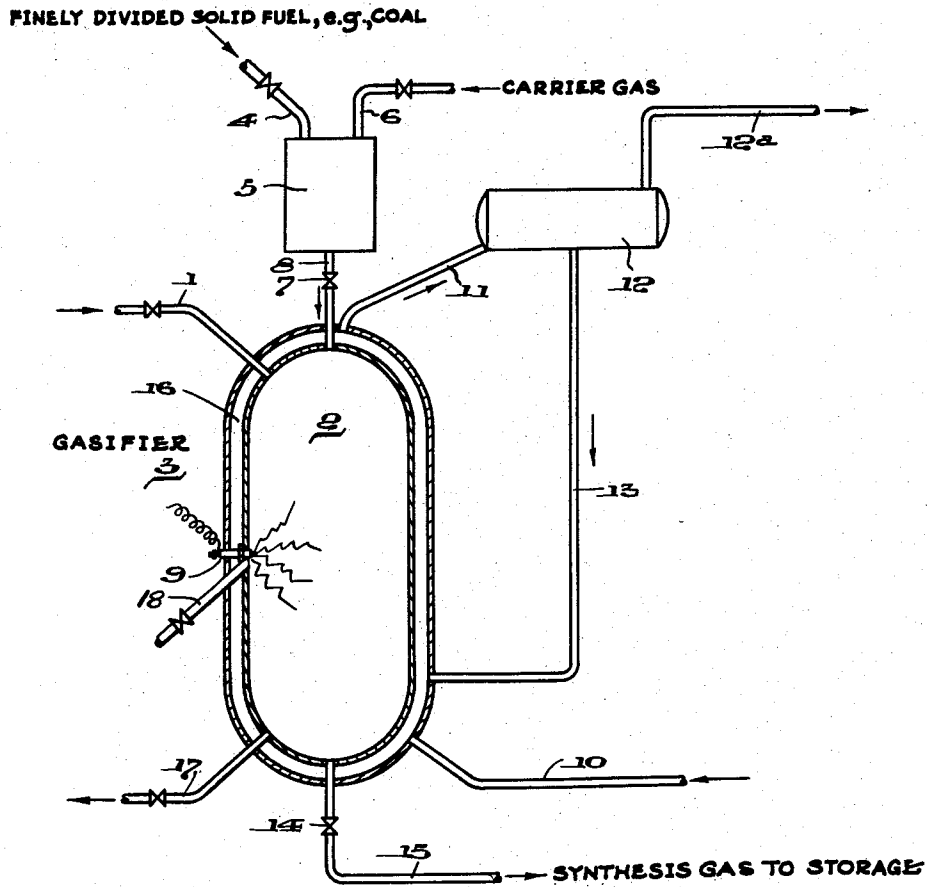


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PROCESS FOR THE GASIFICATION OF CARBONACEOUS
SOLID FUEL AT CONSTANT VOLUME
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PROCESS FOR THE GASIFICATION OF CARBONACEOUS SOLID FUEL AT CONSTANT VOLUME

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This invention relates in general to a process for the gasification of carbonaceous solid fuel at constant volume. More specifically it is directed to a process for the gasification of finely-divided carbonaceous solid fuel such as for example, coal, in suspension with oxygen-containing gas to produce gases containing primarily carbon monoxide and hydrogen, wherein the volume of the product gases is maintained constant during the concomitant pressure increase as a result of the gasification reaction.

In the known process for the gasification of carbonaceous materials such as, for example finely-divided coal, the coal is injected together with oxygen and steam or carbon dioxide into the gasifier and reacted at substantially constant pressure. Due to the volume increase occurring during the reaction, the produced gas supplies work which reduces the reaction temperature.

For example, gasification of finely-divided carbonaceous material to produce reaction products comprising carbon monoxide and hydrogen has been carried out in the past by injecting finely-divided solid or liquid carbonaceous material suspended in oxygen-containing gas into the cylinder of an internal combustion chamber, and thereafter exploding the suspension therein. This process is quite unlike the instant process, however, as will be hereinafter described in detail, inasmuch as product gases force or move the piston away from the cylinder head as these gases are formed. As a result, the temperature within the cylinder tends to decrease as a result of the work carried out by these product gases in moving the cylinder away from the piston head. This temperature decrease in such process is of course very undesirable since it is lost to the synthesis gas making process and so increases the cost of making the gas, as more fuel must be used to replace the heat lost to the gas making process, inasmuch as the gasification of carbonaceous material such as coal to CO and H₂ requires high temperatures to achieve a rapid reaction between carbon and an endothermically reacting gas such as steam.

It has been found by the present inventor that improved yields of synthesis gas (CO+H₂) from coal can be obtained with the heat available and heretofore lost to the CO and H₂ gas making process by conducting the reaction at constant volume. When the gasification of coal to synthesis gas is conducted in an apparatus at constant volume, the gases cannot expand and higher reaction temperatures are obtained, since the specific heat of the reaction products at constant volume is smaller than at constant pressure and thus higher temperatures can be obtained at constant volume with better and more rapid utilization of the carbon by reaction with steam. Consequently, the same carbon utilization as obtained in gasification at constant pressure can be obtained with smaller amounts of oxygen if the gasification reaction is carried out at constant volume.

It is therefore a primary object of this invention to provide an improved process, particularly from an economic standpoint, for the gasification of solid carbonaceous material such as, for example, coal to produce

gases comprising primarily carbon monoxide and hydrogen.

Additional objects and advantages will be apparent as the invention is hereinafter described in more detail.

The instant process, in its broader aspects, comprises reacting finely-divided solid carbonaceous fuel in suspension with free oxygen-containing gas to produce gases containing primarily carbon monoxide and hydrogen, while maintaining the volume of the product gases constant during the concomitant pressure increase as a result of the reaction.

The terminology "exploded" or "exploding" is used herein to designate the rapid and sometimes violent incomplete combustion of the finely-divided carbonaceous solid fuel. The terms "exploding" and "burning" may be understood as synonymous in so far as they indicate combustion generally, but differing in rate or speed with "exploding" designating the more rapid or faster reaction.

Advantageously the finely-divided carbonaceous solid fuel is in suspension in free oxygen-containing gas which is in admixture with an endothermically reacting gas selected from the group consisting of steam, carbon dioxide, and mixtures thereof.

Finely-divided carbonaceous solid fuels which can be utilized herein are bituminous coal, anthracite, brown coal, lignite or lignitic coal, peat, coke, charcoal, wood, etc.

Examples of free oxygen-containing gas advantageous for use in this invention are oxygen, oxygen-enriched air and other gases or vapors containing a higher concentration of oxygen than is contained in atmospheric air. Although essentially pure oxygen is most advantageous, even atmospheric air is within the scope of this invention and could be utilized in some instances, if desired.

Calculations show that less oxygen in relation to coal is required for gasification at constant volume rather than constant pressure, in accordance with this invention, to obtain the same temperature as at essentially constant pressure in accordance with prior art processes, since the specific heat of gases at constant volume is smaller than at constant pressure. Therefore, the endothermic steam-carbon reaction proceeds further at constant volume in accordance with the instant invention than in the conventional constant pressure process, before the system reaches the temperature at a sufficient rate.

The accompanying drawing is illustrative of one arrangement of apparatus for carrying out the instant invention.

Referring now to the drawing, the gasifier 3 comprises a rigid, non-expandable, pressure vessel and reaction chamber 2 and a jacket 16 surrounding or encompassing the walls of this reaction chamber 2 and spaced therefrom for cooling the walls of the reaction chamber. Cooling liquid such as water is fed through line 10 into the annular zone located between this jacket 16 and the walls of the reaction chamber where a substantial portion of this liquid is converted by the heat of reaction into a gaseous medium such as steam. Water is advantageously employed as the cooling liquid inasmuch as the steam, if desired, can afterwards be utilized in the gasification reaction. The gaseous medium developed leaves the jacket 16 through line 11 and passes to the collector vessel 12. If water is employed as the cooling liquid, excess steam is vented from the collector vessel 12 through line 12a. Water carried up with the developed steam into the collector vessel 12 is returned to the jacket 16 through line 13. Make-up water is fed into the cooling jacket through line 10.

The cooling jacket prevents overheating of the gasifier walls and maintains its walls at a sufficiently low temperature to prevent attack by oxygen as well as sulfur

compounds formed by the reaction. Temperatures between about 200 and 500° F. or higher are advantageous. At such temperatures the steam used as reactant does not condense and in the cooling jacket steam can be generated under sufficient pressure for use in the reaction, as conveying gas, etc. The gasifier 3 is also provided with means 8 for feeding coal, oxygen, and steam into the reaction chamber 2, with means 9 for exploding the suspension in the reaction chamber, and with means 15 for the removal of product gases and unreacted solid carbonaceous material and ash from the reaction chamber as hereinafter described.

Prior to starting the gasification reaction, the rigid, non-expandable, pressure vessel and reaction chamber 2 is advantageously heated to an elevated temperature, e.g., 410° F., by passing steam through line 10 into the annular zone located between the jacket 16 and the wall of the reaction chamber 2, or by any other suitable heating means. The heated reaction chamber is then advantageously purged with steam, added through valved line 1 and vented through valved line 17. After the two steam valves are closed in valved lines 1 and 17 respectively, finely-divided carbonaceous solid fuel, e.g., bituminous coal, is blown at a relatively high velocity from feed vessel 5 with carrier gas such as, for example, free oxygen-containing gas, steam, etc., into the reaction chamber 2 through valved line 8. This feed vessel 5 had been previously charged with a weighed amount of finely-divided carbonaceous solid fuel through valved line 4, and with carrier gas through valved line 6 to pressurize the carbonaceous solid fuel therein to the desired extent.

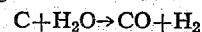
As soon as the desired pressure is reached in the reaction chamber 2, which pressure is advantageously within the range of approximately 2 to 20 atmospheres or higher, desirably approximately 3-10 atmospheres pressure, valve 7 in line 8 is closed. The reaction mixture suspension within the reaction chamber is then ignited by means of a spark plug 9 operatively connected with a source of electric current to start the reaction that produces gas consisting primarily of carbon monoxide and hydrogen. Any suitable igniting or exploding means such as an electric resistance heater, injection of self igniting chemicals such as metal alkyls, etc., a torch device, or any other suitable igniting or exploding means could be employed for exploding the suspension instead of this spark plug. The reaction begins before the suspension of finely-divided carbonaceous solid fuel such as coal has had time to settle to the bottom of the reaction chamber 2. Usually after 0.1-5 seconds, and in most cases after 0.5-2 seconds, the reaction is terminated, that is, the temperature drops to a point where further reaction occurs very slowly.

At the high temperature resulting from the initial reaction, viz., the incomplete combustion of carbonaceous solid fuel such as coal with oxygen, a very rapid reaction of endothermically reacting gas such as steam with the coal is observed. As a result of the reaction, the pressure may be as much as ten times or more higher than the initial pressure in the reaction chamber. As the cooling proceeds, the pressure decreases. After a suitable time for instance, 5 seconds to 5 minutes, especially 10 to 60 seconds, the gas mixture is cooled sufficiently to be depressured through valve 14 into the synthesis gas main 15 without danger of corroding valves. Advantageously the synthesis gas pressure is above atmospheric pressure, for instance, between 5 to 50 atmospheres or higher, especially 10 to 25 atmospheres. The synthesis gas remaining at this pressure in reaction chamber 2 can be either vented into an atmospheric pressure main and compressed, or this synthesis gas can be purged from reaction chamber 2 by additional steam supplied to this reaction chamber. When large gasifiers are employed, displacement of the synthesis gas can be achieved by spraying water into reaction chamber 2. The water is converted into steam which pushes or forces the syn-

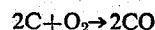
thesis gas from the gasifier into the gas main. After closing valve 14, excess steam can be vented through valved line 17 and the entire gasification cycle is advantageously repeated.

Instead of simultaneous addition of finely-divided carbonaceous solid fuel, such as coal, and oxygen-containing gas, such as oxygen, into the steam filled reaction chamber, the reactants can be added in different sequences. For instance, the reaction chamber of the gasifier can be filled with oxygen under pressure and the heated coal dust blown into the reaction chamber with steam, or other suitable carrier gas under pressure; or the coal can be blown with a suitable inert gas into the reaction chamber containing steam and oxygen; or the gasifier can be charged with fine coal and oxygen; or oxygen and steam can be blown into the gasifier preferably at high velocity and thereby bring the coal in the gasifier into suspension. Further the exploding of the reaction mixture suspension need not be done at the end of the charging cycle. For example, the coal can be passed into the reaction chamber of the gasifier that is filled with oxygen and, if desired, steam. Igniting or exploding can be initiated as soon as only small amounts of coal have entered the reaction vessel. In this case, a relatively higher charging pressure is required for the carrier gas that feeds the coal into the reaction chamber than is necessary in those instances previously described.

In accordance with this invention, the gasification of a finely-divided carbonaceous solid fuel such as coal to produce synthesis gas may be represented stoichiometrically by the following reaction:



Inasmuch as the above reaction is endothermic, as is the reaction of carbon dioxide with hot carbon to produce more carbon monoxide, sufficient oxygen and coal are added to the reaction chamber to result in the following reaction:



This latter exothermic reaction liberates sufficient heat to maintain the endothermic reactions.

Advantageously about 5-14 cubic feet of O_2 , especially about 7-10 cubic feet, is utilized in the gasification reaction of this invention per pound of carbonaceous solid fuel such as bituminous coal.

The synthesis gas yield per unit fuel from the first reaction is higher than from the second reaction. The contribution of the first reaction is increased as heat losses from the gasifier decrease. The heat loss decreases as the size of the gasifier vessel decreases. While satisfactory reaction is obtained in experimental gasifier units with a volume as small as 0.1-0.2 cubic foot, the oxygen consumption in such units may exceed 350 cubic feet per 1000 cubic feet of synthesis gas. For commercial operation therefore larger gasifier vessels of a volume advantageously greater than 50 cubic feet, desirably greater than 200 cubic feet, are employed. Two or more of such units can be used in parallel with a staggered reaction cycle to obtain a more uniform synthesis gas stream for further continuous processing and purification steps.

A small or limited amount of a gaseous material selected from the group consisting of oxygen and combustible gas such as, for example, synthesis gas, methane, natural gas, producer gas, water gas, or materials known as combustion catalysts, etc., can be advantageously admixed with the suspension in the reaction chamber, advantageously at high velocity, immediately prior to exploding the suspension to effect gasification. It has been found that the addition of this gaseous material will facilitate the igniting or exploding, especially if added in the vicinity of or near the igniting means or device through after valved inlet pipe 18. The exact amount and composition of gas that is added to the reaction chamber will be determined by experience and judgment and will depend on the composition of the coal, the

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oxygen-coal ratio, the amount of steam employed, the pressure and, if needed, this amount can be determined by preliminary experiments.

The solid carbonaceous fuel that is utilized herein is finely divided so that it can readily be suspended and distributed in the gasifier. Advantageously a size is used such that 70% thereof will pass through a 200 mesh U.S. standard sieve, and desirably a size such that 100% will pass through a 200 mesh U.S. standard sieve.

Although the gasification reaction is advantageously carried out within the reaction chamber at superatmospheric pressure, it is to be understood that this gasification reaction could be initiated, if desired, under atmospheric pressure. The essential feature of this invention is that the volume of the product gases within the reaction chamber is maintained constant while the gasification reaction is being effected therein with the concomitant pressure increase resulting from this reaction.

The wall of the rigid, non-expansible gasifier vessel or reaction chamber of this invention are advantageously constructed of a material which exhibits excellent strength and durability so as to enable this material to withstand the relatively high and alternating pressure and the attack of reactants and reaction products produced within the chamber during the rapid and sometimes violent gasification reaction. Steel such as stainless steel, and other suitable metals are eminently adapted and can be employed, if desired.

The obtained synthesis gas can be readily purified and used in the synthesis of ammonia, methanol, and in Fischer-Tropsch type reactions, hydrogenation reactions, etc.

The following specific examples are given by way of illustration only and without limitation.

The coal utilized in these following examples is bituminous coal from the Sewickley Seam, Bunker Mine, Morgantown, West Virginia and shows in its ultimate analysis the following percentages of the indicated elements:

	Percent by weight
Carbon	74.94
Hydrogen	5.03
Oxygen	5.70
Sulphur	1.53
Nitrogen	1.59
Ash	11.21

Example 1

Finely-divided bituminous coal of the analysis set forth above and of a size such that 90% passes through a 200 mesh U.S. standard sieve is blown at high velocity with oxygen into a rigid, non-expansible steel pressure vessel or reaction chamber of 50 cubic feet volume at a temperature of 410° F. The gasifier, constructed as shown in the accompanying drawing and as hereinbefore described, contains steam which has been previously introduced therein. The pressure within the gasifier vessel or reaction chamber is raised to 3 atmospheres pressure. Approximately 9 cubic feet of oxygen and 0.2 pound of steam are utilized per pound of coal. This suspension of finely-divided coal in oxygen and steam is then exploded in the sealed pressure vessel by means of a spark plug 9 inserted through the wall of the gasifier vessel. After product gases within the reaction chamber have been permitted to cool down, the considerable pressure within the reaction chamber is released and the product gases are withdrawn.

Analysis of the synthesis gas obtained showed the following:

	Percent by volume
CO ₂	3.5
H ₂	33.9
CO	61.6
N ₂	0.8
H ₂ S	0.2

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Per thousand cubic feet of CO plus H₂ produced, 33 pounds of coal and 300 cubic feet of oxygen are consumed, and 6.6 pounds of steam are employed.

Good results are also obtained when finely-divided anthracite coal, brown coal, lignitic coal or lignite, peat, coke, charcoal or wood are utilized wholly or partly in place of the bituminous coal.

Example 2

A finely-divided bituminous coal of the type utilized in Example 1 and of a size such that 95% passes through a 200 mesh U.S. standard sieve is suspended in oxygen-enriched air containing 48% by volume oxygen, and steam and is gasified by being exploded utilizing the procedure and the rigid non-expansible gasifying apparatus of Example 1. The pressure within the reaction chamber is 5 atmospheres pressure prior to exploding the suspension. A small amount of product synthesis gas and oxygen is admixed therewith through line 18 at a relatively high velocity immediately prior to the exploding near the ignition point 9. 9.3 cubic feet of oxygen and 0.15 pound of steam per pound of coal are utilized in the gasification and there is about 85% carbon utilization in this gasification reaction. Synthesis gas of the following analysis is obtained:

	Percent by volume
CO ₂	2.7
H ₂	26.3
CO	46.6
N ₂	24.2
H ₂ S	0.2

After conversion of carbon monoxide into H₂+CO₂ with steam by the catalytic shift reaction, and CO₂ and H₂S removal, the gas is suitable for the production of synthetic ammonia.

Example 3

The finely-divided coal of Example 1 is suspended in oxygen and steam and is gasified by exploding, utilizing the procedure and the rigid, non-expansible gasifying apparatus substantially identical to that of Example 1 except that the gasifier vessel or reaction chamber has a volume of 200 cubic feet. This gasifier vessel is at a temperature of 435° F. at the time of the introduction of the reactants therein. The pressure within the reaction chamber 2 is 4 atmospheres pressure prior to exploding the suspension. Only 8 cubic feet of oxygen and 0.2 pound of steam per pound of coal are used in the gasification and there is about 90% carbon utilization in the gasification reaction. Synthesis gas of the following analysis is obtained:

	Percent by volume
CO ₂	3.1
H ₂	35.2
CO	60.8
N ₂	0.7
H ₂ S	0.2

Per thousands cubic feet of CO plus H₂ produced, 31 pounds of coal and 250 cubic feet of oxygen are consumed and 6.2 pounds of steam is employed.

Similar results are also obtained in this example when most of the steam is replaced by carbon dioxide as the endothermically reacting material. A synthesis gas with a higher content of CO and CO₂ is obtained.

Obviously many modifications and variations of the invention as above set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

What I claim is:

1. In a process of gasification of solid carbonaceous fuel in suspension with free oxygen and steam to form synthesis gas comprising primarily CO and H₂, which comprises reacting a suspension of said solid carbonaceous

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fuel in finely divided form in free oxygen in the presence of steam with the free oxygen in amount sufficient for combustion of only that part of the fuel required for supplying the heat for reaction of the remaining part of the fuel with the steam to form the synthesis gas comprising primarily CO and H₂, the improvement comprising igniting said suspension at an elevated temperature in a closed zone of constant volume so that an explosive combustion of said fuel takes place in said closed constant volume zone, and maintaining the volume of the exploded products constant in said closed zone during said explosion and thereafter to produce the synthesis gas comprising primarily CO and H₂ until completion of the synthesis gas reaction whereby the gases cannot expand and cool during the reaction and as a result the heat thereof is consumed in furthering the endothermic reaction of the steam and carbon.

2. The process of claim 1 wherein said carbonaceous fuel is so finely divided that at least 70% passes through a 200 mesh U.S. standard sieve.

3. The process of claim 1 wherein the free oxygen of said oxygen-containing gas is present to the extent of 5 to 14 cubic feet of oxygen per pound of coal.

4. The process of claim 1 wherein the initial elevated temperature is between 200 and 500° F.

5. A process in accordance with claim 1 wherein said carbonaceous fuel is coal.

6. A process in accordance with claim 5 wherein the coal is in suspension in free oxygen-containing gas which is in admixture with an endothermically-reacting gas selected from the group consisting of steam, carbon dioxide and mixtures thereof.

7. A process in accordance with claim 6 wherein the

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endothermically-reacting gas is steam in the ratio of .15 to .20 pound of steam per pound of coal.

8. A process in accordance with claim 1 wherein the pressure is increased within the closed zone prior to exploding the suspension therein to approximately 2-20 atmospheres pressure.

9. A process in accordance with claim 8 wherein the pressure is increased within the closed zone prior to exploding the suspension therein to approximately 3-10 atmospheres pressure.

10. A process in accordance with claim 9 wherein a small amount of at least one member of the group consisting of oxygen and combustible gas is added to the suspension within the closed zone, in the vicinity of the igniting means, immediately prior to exploding said suspension to facilitate exploding the suspension.

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