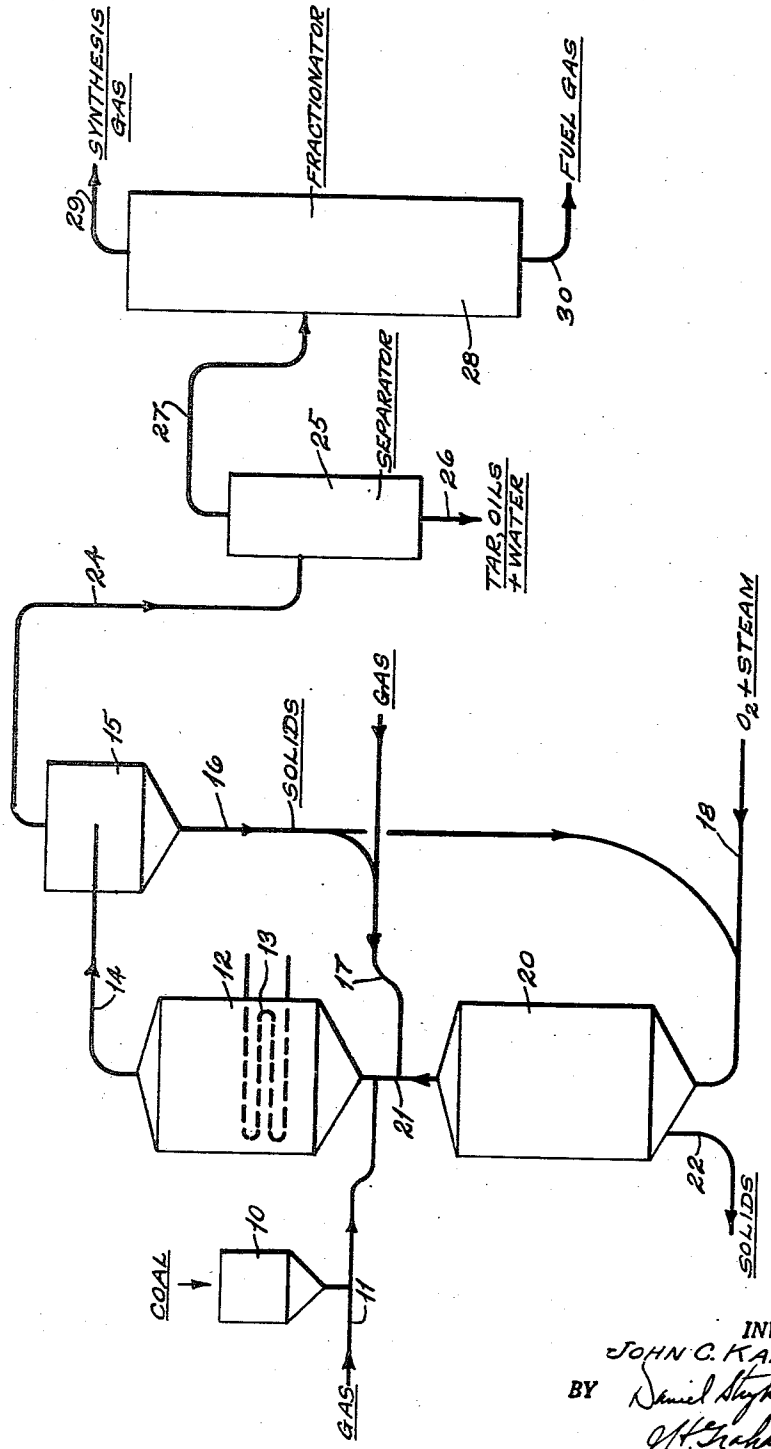
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GASIFICATION OF CARBONACEOUS SOLIDS
TO HYDROGEN-RICH GAS AND FUEL GAS
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GASIFICATION OF CARBONACEOUS SOLIDS TO HYDROGEN-RICH GAS AND FUEL GAS

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This invention relates to a process for the gasification of solid carbonaceous materials. The process of this invention is particularly applicable to the gasification of coals including anthracite, bituminous coals and lignite, to produce a gas rich in hydrogen and a fuel gas of relatively high heating value.

Two desiderata have been stated for an ideal gasification process. In addition to yielding a usable city gas at high thermal efficiency, it should be capable of modification to produce a hydrogen-rich gas, such as gas suitable for synthesis of hydrocarbons, and a fuel gas of high heating value suitable for transportation considerable distances by pipeline. Numerous processes have been devised for the gasification of carbonaceous materials for the production of hydrogen, Fischer-Tropsch synthesis feed gas, city gas, and the like, but most of these processes suffer from inflexibility and many are either too complex or too expensive in operation to find practical application.

The process of the present invention is capable of producing a hydrogen-rich synthesis gas having, for example, a hydrogen-to-carbon monoxide ratio of approximately 2:1 and a pipeline gas having a heating value of 800 to 1000 B. t. u.'s per cubic foot. This process is capable of converting 80 per cent of the heating value of the feed coal to the desired gaseous products after supplying all the power required for operation.

An important object of this invention is to provide a novel process for the gasification of solid carbonaceous materials to produce both a hydrogen-rich gas and a fuel gas of high heating value.

Another object is to provide such a process which is adaptable to production of various types of gases from various solid carbonaceous fuels.

Still another object of this invention is to provide an improved process for the production of a hydrogen-rich gas from a solid carbonaceous fuel.

A further object is to provide an improved process for the production of fuel gases of high heating value from a solid carbonaceous fuel.

Other objects and advantages will be apparent from the following detailed description taken in connection with the accompanying drawing.

The drawing is a diagrammatic view illustrating a preferred example of the process of the present invention as applied to the gasification of coal to produce synthesis gas and pipeline gas simultaneously.

The present invention is applicable to the gasification of solid carbonaceous material in the

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form of particles of relatively small sizes such as slack coal, coke breeze, and the like. The gasification is preferably carried out in a fluid bed type reactor, particularly where the feed material has a tendency to agglomerate or cake. Agglomerating coals or caking coals may be successfully used in the process of the present invention.

In accordance with this invention, the carbonaceous feed material is gasified by reaction with oxygen and steam, the tars, oils and water separated from the resulting product gas and the gas separated into fractions, one of which is rich in hydrogen and another rich in hyrocarbons. The separation may be carried out by low temperature fractionation of the Linde-Frankl type.

With reference to the drawing, solid carbonaceous material in particle form, for example, coal, is supplied to a feed hopper 11 from which it is fed into a stream of carrier gas in line 11. The carrier gas stream may be a gas produced in the system or a selected fraction of such gas and may comprise hydrocarbons, carbon monoxide, hydrogen, or other innocuous gas, e. g., a recycle gas stream, and is supplied to line 11 at a rate sufficient to entrain the particles of coal. The coal is fed through lines 11 and 21 into a carbonization zone 12 wherein it is fluidized and distilled by the action of hot gases passing upwardly through a bed of the coal particles. The coal particles are preferably less than 40 to 60 mesh in size, 40 to 50 per cent thereof being 200 mesh or smaller. The fluidizing gas stream is introduced at a rate such that its rate of flow in the carbonization zone 12 is on the order of about 0.5 to about 3.0 feet per second.

The hot gases, and in some cases the exothermic energy of conversions occurring in the carbonization zone 12, distill volatilizable constituents from the coal, the fluidizing action of the gases insuring excellent contact between the gas and the coal particles. The hot gases are obtained from a gasification zone in which solid carbonaceous particles are reacted with oxygen and steam under conditions such that a mixture of hydrogen and carbon monoxide is produced.

The temperature of the carbonization zone is maintained within the range of from about 1,000 to about 1,500° F. the pressure, within the range of from about 100 to about 800 pounds per square inch gauge. The temperature may be controlled by a cooling coil 13 disposed in the fluidized bed of carbonaceous particles in the carbonization zone. Alternatively, the temperature may be controlled by circulating the solids between car-

bonization zone 12 and a cooler connected therewith. Under these conditions, particularly at the higher pressures, some hydrogenation and methane formation takes place within the carbonization zone. Methane may be formed by the interaction of hydrogen and carbon monoxide. The carbonization zone may be operated under conditions either more or less favorable to the production of methane, depending upon the requirements for fuel gas from the system. Methane formation is desirable for the production of high heating value fuel gas but undesirable where synthesis gas is the desired product.

It is apparent that the process of this invention, which provides a source of both fuel gas and synthesis gas, is an improvement over those processes of the prior art wherein one of these product gases is produced and wherein neither can be produced at high thermal efficiency.

The gases from the carbonization zone 12 are discharged through line 14 into a separator 15 to effect removal of solid materials from the gases produced in the gasification apparatus. The solids removed from the gas stream are passed through line 16 into either or both of lines 17 and 18. Normally, a portion of the solids or char from line 16 are passed into line 18 to supply the gasification zone and the remainder recycled through lines 17 and 21 to the carbonization zone. A stream of a suitable carrier gas is introduced through line 17 at a rate of flow sufficient to entrain the solids from line 16 and transport them into line 21. The rate of recycle of solids to the carbonization zone depends upon several operating factors like temperature control and the gas velocity in said zone. Generally, where the coal is of the coking or caking type, it is desirable to recirculate about 10 parts of char per part of coal fed to the process to prevent agglomeration of coal particles in the carbonization zone.

Oxygen and steam are introduced through line 18 for reaction with the solid particles from line 16. The particles of solid from line 16 are admixed with oxygen and steam in line 18 and passed into reaction zone 20. Preferably, the oxygen admixed with the steam is in the form of an oxygen concentrate containing at least 95 per cent oxygen by volume. Oxygen produced by conventional processes, such as the Linde-Frankl process, is suitable for the gasification. The steam and oxygen react with the solid particles in the gasification zone 20 to produce a mixture of hydrogen and carbon monoxide, as well as carbon dioxide and water vapor depending on the residence time of the gases in the gasification zone.

Preferably the gasification reaction is conducted at a temperature in the range of from about 1400° F. to about 2100° F. and at a pressure corresponding to that in the carbonization zone; of course, the gasification temperature is not lower than the carbonization temperature.

The gases produced in the gasification zone are discarged through line 21 into the carbonization zone 12. Solids are withdrawn from the gasification zone to line 22. These solids may be used as fuel or may be passed to a separate gasification unit for complete carbon cleanup, leaving ash and slag as a residue. Withdrawal of a stream of solids through line 22 provides a method for eliminating ash from the gasification system.

The products from the gasification apparatus, after separation of solids therefrom, are passed through line 24 into a separator 25 wherein tar, oil and water, together with any entrained solids passing through separator 15, are removed from the gases. The resulting gas stream is then passed through line 27 into a separation unit 28 wherein a hydrogen-rich fraction comprising chiefly carbon monoxide and hydrogen, is separated from a fuel gas fraction comprising chiefly methane. The hydrogen-rich stream is discharged from the separation unit through line 29 and fuel gas through line 30. Preferably, the separation unit 28 is of the low temperature type wherein at least a portion of the gas stream is condensed to liquid form and fractionally distilled under pressure. The gasification apparatus may be operated at a pressure such that little, if any, additional compression is required for liquefaction to effect low temperature fractionation.

A gasification and carbonization unit of the type described herein is operated with coking coal at a pressure of 600 pounds per square inch gauge. A temperature of about 1200° F. is maintained in the carbonization zone by cooling coils which are used for the generation of steam. About 10 parts of coke per part of fresh feed is recycled to the carbonization zone to prevent agglomeration of the fresh coal feed. A portion of the product gas is returned to the carbonization zone at 900° F. as a carrier gas for the fresh coal and recycled coke. The gasification zone is operated at 1600° F. The gases have a residence time of about 18 seconds in the gasification zone. All of the gas from the gasification zone is passed into the carbonization zone. Approximately 1515 pounds of oxygen and 2170 pounds of steam are used per ton of coal.

The product gases are withdrawn from the carbonization zone, cooled, cleaned and separated by low temperature fractional distillation into a hydrogen-rich gas suitable as synthesis gas feed and a pipeline gas of high heating value. The yields per ton of coal are approximately as follows:

24,400 cubic feet of synthesis gas of the following analysis:

	Per cent by volume
Hydrogen	66
Carbon monoxide	33
Nitrogen	1

13,100 cubic feet of pipeline gas having a heating value of 914 B. t. u.'s per cubic foot and the following analysis:

	Per cent by volume
Carbon Monoxide	19.6
Methane	77.8
Illuminants	2.6

In addition, about 200 pounds of tar and light oil having a heating value of 3,300,000 B. t. u.'s, are recovered. About 80 per cent of the heating value of the coal is recovered in the form of the various products.

In another modification of the operation of the present process, the carbonization zone is operated at 1250° F. and the gasification zone at 1650° F. The contact or residence time of the gases in the gasification zone is limited to about 4 seconds so that the water gas shift reaction is substantially complete but the producer gas reaction is incomplete. About 745 pounds of oxygen and 2760 pounds of steam are used per ton of coal. Under these conditions, the following yields are obtained per ton of coal:

25,600 cubic feet of synthesis gas of the following analysis:

	Per cent by volume
Hydrogen	65.8

Carbon monoxide	32.9
Nitrogen	1.3

13,100 cubic feet of fuel gas having a heating value of 1,022 B. t. u.'s per cubic foot and the following analysis:

	Per cent by volume
Carbon monoxide	3.2
Methane	94.5
Illuminants	2.3

About 87 percent of the heating value of the coal is recovered in the form of various products.

In the second modification, the residence time of the reactants in the reaction zone is considerably less than in the first. This limits the extent to which the producer gas reaction

$$(CO_2+C\rightarrow 2CO)$$

takes place. This reaction may be effectively limited by maintaining a contact time, or reaction time, of less than about 5 seconds. It will be noted that by so limiting the reaction time, as determined by rate of throughput, the oxygen requirement for the second modification is less than half that of the former; comparable yields of synthesis gas are obtained, the heating value of the fuel gas is considerably improved, and the efficiency of the operation measurably increased. To obtain these important advantages of my invention the contact time between reactant gas and carbon in the reaction zone is limited to less than 5 seconds. This may be accomplished by flow of the reactant gases through the gasification zone at a rate such that the contact time therein is less than 5 seconds. The preferred range of contact time is from 2 to 5 seconds.

From the foregoing specific examples illustrating the operation of the present invention, it will be evident that the process of this invention is adaptable to varying product requirements. The flexibility of the process is an important advantage over processes of the prior art which produce only a single product.

In carrying out the process of the present invention, it has been found desirable to operate the gasification zone with an oxygen feed rate of from about 0.25 to about 1.0 pound and a steam feed rate of from about 1.5 to about 1.0 pounds per pound of carbon reacted. In the preferred case, as illustrated by the second example, where the contact time is from about 2 to about 5 seconds, the oxygen feed rate is within the range of from about 0.25 to about 0.50 pound and the steam feed rate is within the range of from about 1.50 to about 1.25 pounds per pound of carbon reacted. It will be evident from the foregoing examples and explanation that as the contact time is decreased, the oxygen requirement is decreased and the steam requirement is increased.

Obviously many modifications and variations of the invention, as hereinbefore 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.

I claim:

1. A process for the gasification of a solid carbonaceous material containing volatilizable constituents which comprises introducing said solid carbonaceous material into a carbonization zone into direct contact with hot gases comprising carbon monoxide and hydrogen at a temperature within the range of from 1,000° F. to 1,500° F. and a pressure within the range of 100 to 800 pounds per square inch gauge whereby volatilizable constituents are volatilized and methane is formed; introducing the resulting carbonaceous residue from the carbonization zone into a gasification zone, reacting said residue with a mixture of oxygen and steam at a temperature within the range of from 1,400° F. to 2,100° F., to produce carbon monoxide and hydrogen as principal reaction products; passing the resulting gases from the gasification zone to the carbonization zone as the source of hot gases; discharging product gases from the carbonization zone; separating entrained solids and readily liquefiable constituents therefrom; and subjecting the residual gaseous product comprising carbon monoxide, hydrogen and methane to liquefaction and fractional distillation to obtain a methane-rich fuel gas and a synthesis gas comprising carbon monoxide and hydrogen in substantial proportions adapted for Fischer-Tropsch synthesis.

2. A process as defined in claim 1 wherein said solid carbonaceous material is coal.

3. A process as defined in claim 1 wherein a fluidized bed of particles of solid carbonaceous material is maintained in each of said carbonization and gasification zones.

4. A process for the gasification of a solid carbonaceous material containing volatilizable constituents which comprises introducing said solid carbonaceous material into a carbonization zone into direct contact with hot gases comprising carbon monoxide and hydrogen at a temperature within the range of from 1,000° F. to 1,500° F. and a pressure within the range of 100 to 800 pounds per square inch gauge whereby volatilizable constituents are volatilized and methane is formed; introducing resulting carbonaceous residue from the carbonization zone into a gasification zone; reacting said residue with a mixture of oxygen and steam in said gasification zone at a temperature within the range of from about 1,400° F. to about 2,100° F. with a time of contact between said gases and said carbonaceous residue within the range of from about 2 to about 5 seconds to produce carbon monoxide and hydrogen as the principal reaction products; passing the resulting gases from the gasification zone to the carbonization zone as the source of said hot gases; discharging product gases from the carbonization zone; separating entrained solids and readily liquefiable constituents therefrom; and subjecting the residual gaseous product comprising carbon monoxide, hydrogen, and methane to liquefaction and fractional distillation to obtain a methane-rich fuel gas and a synthesis gas comprising carbon monoxide and hydrogen in substantial proportions adapted for Fischer-Tropsch synthesis.

5. A process for the gasification of a solid carbonaceous material containing volatilizable constituents which comprises introducing said solid carbonaceous material into a carbonization zone into direct contact with hot gases comprising carbon monoxide and hydrogen at a temperature within the range of 1,000° F. to 1,500° F. and a pressure within the range of 100 to 800 pounds per square inch gauge whereby volatilizable constituents are volatilized and methane is formed; introducing resulting carbonaceous residue from the carbonization zone into a gasification zone; effecting reaction of the carbonaceous residue in said gasification zone by contacting said residue with a mixture of oxygen and steam wherein from about 0.25 to about 0.5 pound of oxygen and from about 1.5 to about 1.25 pounds of steam are supplied per pound of carbon reacted; main-

taining the temperature of said gasification zone within the range of 1,400° F. to 2,100° F. thereby producing carbon monoxide and hydrogen; passing the resulting gases from the gasification zone to the carbonization zone as the source of said hot gases; discharging product gases from the carbonization zone; separating entrained solids and readily liquefiable constituents therefrom; and subjecting the residual gaseous product comprising carbon monoxide, hydrogen and methane to liquefaction and fractional distillation to obtain a methane-rich fuel gas and a synthesis gas comprising carbon monoxide and hydrogen in substantial proportions adapted for Fischer-Tropsch synthesis.

6. A process for the gasification of a solid carbonaceous material containing volatilizable constituents which comprises introducing said solid carbonaceous material into a carbonization zone into direct contact with hot gases comprising carbon monoxide and hydrogen at a temperature within the range of 1,000° F. to 1,500° F. and a pressure within the range of 100 to 800 pounds per square inch gauge whereby volatilizable constituents are volatilized and methane is formed; introducing resulting carbonaceous residue from the carbonization zone into a gasification zone; effecting reaction of the carbonaceous residue in said gasification zone by contacting said residue with a mixture of oxygen and steam wherein from about 0.25 to about 0.5 pound of oxygen and from about 1.5 to about 1.25 pounds of steam are supplied per pound of carbon reacted; supplying said mixture of oxygen and steam at a rate such that a contact time of from 2 to 5 seconds is obtained; maintaining the temperature of said gasification zone within the range of 1,400° F. to 2,100° F. thereby producing carbon monoxide and hydrogen; passing the resulting gases from the gasification zone to the carbonization zone as the source of said hot gases; discharging product gases from the carbonization zone; separating entrained solids and readily liquefiable constituents from said product gases; and subjecting the residual gaseous product comprising carbon monoxide, hydrogen and methane to liquefaction and fractional distillation to obtain a methane-rich fuel gas and a synthesis gas comprising carbon monoxide and hydrogen in substantial proportions adapted for Fischer-Tropsch synthesis.

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