

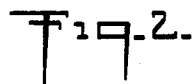
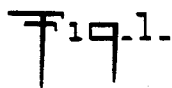
June 28, 1960

H. V. REES ET AL

2,942,959

PROCESS FOR THE PRODUCTION OF FUEL GAS

Filed Dec. 6, 1957



1

2,942,959

PROCESS FOR THE PRODUCTION OF FUEL GAS

Harry V. Rees, Chappaqua, Clifford G. Ludeman, Scarsdale, and Frederick Burton Sellers, Tarrytown, N.Y., assignors to Texaco Development Corporation, New York, N.Y., a corporation of Delaware

Filed Dec. 6, 1957, Ser. No. 701,126

3 Claims. (Cl. 48—197)

This invention relates to a method and apparatus for the production of fuel gas of high calorific value. More particularly, it is directed to a method which comprises contacting a gaseous mixture of carbon monoxide, hydrogen and water vapor with a carbonaceous solid at a pressure in excess of about 700 pounds per square inch gauge at a temperature to effect reaction of said carbon monoxide, hydrogen, water vapor and carbonaceous solid to form a product gas comprising methane. Advantageously a carbonaceous fuel may be converted to a fuel gas of high calorific value by subjecting the carbonaceous fuel to partial combustion with an oxygen-containing gas at a pressure in excess of 700 pounds per square inch gauge to produce a synthesis gas comprising carbon monoxide and hydrogen. Steam is admixed with said synthesis gas and the mixture contacted with a carbonaceous solid at substantially the pressure of the synthesis gas generation step forming a fuel gas of high calorific value.

Many processes have been employed for the gasification of carbonaceous fuels. The simpler and cheaper methods have been characterized by the production of gas of low heating value. Methods for the production of higher heating value fuels have been complicated and expensive. It is known that carbon monoxide and hydrogen may be generated by the partial combustion of carbonaceous fuels. However, such mixtures are unsuited for general fuel uses because of the relatively low heating values of hydrogen and carbon monoxide which have gross heating values of 323 to 321 B.t.u.'s per cubic foot respectively. It is also known that carbon monoxide and hydrogen may be reacted to form methane, which has a gross heating value of 1,009 B.t.u.'s per cubic foot, and heavier hydrocarbons, which have substantially higher heating values. The methanization of carbon monoxide and hydrogen mixtures is most effectively carried out at temperatures considerably below the temperatures effective for rapid and efficient partial oxidation. In the past, it has been observed that the cooling of synthesis gas mixtures from gas generation temperatures to lower temperatures at which methanization is substantial has resulted in the production of carbon deposits. We have found that contrary to the teachings of the prior art, the temperature of synthesis gas mixtures may be reduced without the production of carbon but with a net consumption of carbon by admixing steam with said synthesis gas and contacting the aforesaid mixture with a carbonaceous solid at a pressure in excess of about 700 pounds per square inch gauge. Gaseous mixtures of carbon monoxide and hydrogen may be produced readily by the partial oxidation of gaseous, liquid, or solid carbonaceous fuels. Liquid or solid carbonaceous fuels for example, coal, lignite, oil shale and the like, residual oils, fuel oils, shale oils, tar oils, gas oils, kerosene and gasoline boiling range hydrocarbons and the like may be used depending upon their relative availability and cost. The partial oxidation of solid carbonaceous fuels is described in detail in the copending application of duBois Eastman and Leon

2

P. Gaucher, Serial No. 490,214, filed February 24, 1955, now U.S. Patent 2,864,677. In the operation of a coal-fired synthesis gas generator the reaction temperature is maintained within the range of about 2000 to 3500° F. Partial oxidation of coal has heretofore usually been conducted at pressures within the range of about 100 to about 600 pounds per square inch gauge. However, the synthesis gas generation process may be conducted advantageously at higher pressures and we prefer to effect synthesis gas generation at pressures within the range of about 700 to 4500 pounds per square inch gauge. Although pressure per se has only little effect on the synthesis gas generation process, the generation of synthesis gas at the pressure of utilization is a convenient method of providing synthesis gas at high temperature and high pressure without extensive compression and reheating facilities.

Some carbonaceous materials require the addition of steam for the production of hydrogen and carbon monoxide by reaction with oxygen at temperatures within the range of about 2000 to 3500° F. Other carbonaceous materials contain water in sufficient quantities or even in excess of that required. Anthracite coal is an example of the former, requiring a considerable quantity of steam, for example, about 30 percent by weight. Lignite is an example of the latter, often containing more water than required for reaction. Water in excess of the normal requirements is not detrimental in the process of this invention. However, water in the gas generator feed affects the generator temperature and oxygen requirements. While water may supply a part of the oxygen requirements of the system thereby increasing the hydrogen production, water is an endothermic reactant and lowers the reaction temperature. Advantage may be taken of this characteristic to effect reaction temperature control by regulation of the water content of the feed.

Advantageously particles of solid carbonaceous materials are admixed with a liquid to form a suspension or slurry of particles in a vaporizable liquid for example, water. The aforesaid suspension is passed as a continuous stream through an externally heated tubular zone under turbulent flow conditions. The slurry is heated in the heating zone to an elevated temperature sufficient to vaporize the liquid thereby forming a suspension of solid particles in vapor and preheating the solid particles. The dispersion of solid particles in vapor is then admixed with an oxygen-containing gas in an unobstructed partial oxidation zone autogenously maintained at a temperature within the range of about 2000 to about 3500° F. and at a pressure of above about 700 pounds per square inch gauge.

A preferred method of effecting the partial oxidation of heavy hydrocarbon oils is disclosed in the copending application of Dale M. Strasser, Serial No. 523,641, filed July 21, 1955, and now abandoned. The partial oxidation of hydrocarbon oils is usually effected at a temperature within the range of about 1800 to about 3500° F. and at a pressure within the range of about 20 to about 3000 pounds per square inch gauge. However, as in the case of carbonaceous solids, the partial oxidation of oils may be effected advantageously at pressures in excess of 700 pounds per square inch gauge and as high as 4500 pounds per square inch gauge if desired. Oil is readily introduced into a gas generator in the form of a dispersion in steam. In accordance with one method of introducing oil feed, the oil is mixed with about 10 to about 200 weight percent of water. The mixture so formed is passed to a tubular heating zone under turbulent flow conditions to effect substantially complete vaporization of the water forming a dispersion of minute particles of oil in steam. The oil-steam dispersion in admixture with oxygen is introduced into a partial ox-

dation zone maintained at an autogenous temperature within the range of about 1800 to 3500° F.

Product gases from the partial oxidation of solid carbonaceous fuels or of liquid hydrocarbons may have compositions falling within the range of about 25 to about 70 percent of hydrogen, 25 to 70 percent carbon monoxide, 1 to 20 percent carbon dioxide, 3 to 10 percent water vapor, less than about 0.5 percent methane, and from about 0 to about 5 percent of other gases. Effluent gas is withdrawn from the gas generator at substantially the temperature and pressure of the gas generator and passed in admixture with water or steam to a methanization zone wherein the aforesaid mixture is contacted with a carbonaceous solid at a reduced temperature. The carbonaceous solid present may be that produced in situ upon cooling or may be from an external source.

In the methanization zone the hydrogen, carbon monoxide, water vapor, and carbonaceous solid react with one another to produce substantial quantities of methane. Methanized gas, after removal of carbon dioxide and water vapor, is readily produced having heating values in excess of 430 B.t.u.'s per standard cubic foot and in excess of 550 B.t.u.'s per standard cubic foot under preferred operating conditions. Carbon dioxide may be readily removed from gaseous mixtures by methods well known in the art, for example, by scrubbing with caustic or ethanolamine solutions. Most of the water vapor is removed by condensation upon cooling to atmospheric temperatures and further drying is usually neither necessary nor desirable when the product gas is intended for fuel use.

We have found that important operating variables of the methanization process include pressure, terminal reaction temperature, and the ratio of mols of water per atom of carbon contained in the synthesis gas-steam feed to the methanization zone. We have found that pressure exerts a marked effect upon the extent of methanization which may be obtained. At temperatures within the range of about 1000 to 1700° F., very little methanization of synthesis gas mixtures may be obtained at pressures near atmospheric. However, as pressure is increased, the amount of methane which may be produced in synthesis gas rises rapidly, up to a pressure of about 700 pounds per square inch gauge. Further increase in pressure above 700 pounds per square inch gauge has relatively little effect upon the total amount of methane produced. It is therefore preferred to effect the methanization process at a pressure in excess of about 700 pounds per square inch gauge and pressures within the range of about 700 to about 4500 pounds per square inch gauge or higher are suitable.

Another important operating variable of the methanization process is the reaction temperature. Temperatures in the methanization step of this process may vary from the high temperature at which the synthesis gas is produced to the final or terminal temperature of the reaction zone, that is, the temperature of the reactants when they are separated from the carbonaceous solid as set forth hereinbefore. Synthesis gas may be produced at temperatures within the range of about 1800 to about 3500° F. Although reaction velocities are greatest at high temperatures, the production of substantial quantities of methane requires effecting methanization at substantially lower temperatures. Since low temperatures favor compositions having high calorific values but reaction velocities are greatest at high temperatures, most efficient utilization of reactor volume is achieved by reducing the temperature gradually as the gases undergoing conversion pass through the reactor. In this manner, maximum rate is maintained as the gas composition changes until the final composition is reached. Reduction of the methanization temperature from the high temperature of the feed to the relatively low terminal reaction temperature may be effected by one or more of numerous means. Water or steam introduced into the methanizer feed as

a reactant may be employed as coolant as desired. Additionally, the water vapor present in the methanizer is an endothermic reactant in that reaction of water vapor with carbon monoxide and with carbon tends to absorb heat. The steam or water introduced into the methanizer may readily be employed to control reaction temperatures by control of the rate of steam or water added responsive to temperature measurements. A temperature gradient may be established in the bed of carbonaceous solid by introducing steam incrementally throughout the length of the reaction bed. The cooling capacity of the water or steam employed may be varied by control of the preheat of the water or steam employed. Obviously, heat exchange of the synthesis gas feed with other processing streams, and the use of cooling coils disposed within the bed of carbonaceous solids may be used for temperature control and the recovery of useful heat. Some reduction in temperature is effected by radiation of heat from the walls of the methanization zone. Terminal temperatures within the range of about 1000 to 1700° F. may be employed in the process of this invention to produce substantial quantities of methane. However, we prefer to employ terminal temperatures within the range of about 1300 to about 1500° F. At terminal reaction temperatures within the range of 1000 to 1700° F., we employ reaction times within the range of about 5 to 1500 seconds, preferably within the range of about 25 to 500 seconds.

We have found that by maintaining a ratio of mols of water to atoms of carbon in the methanizer feed above about 0.7 that the production of carbon deposits may be prevented in our process. We prefer to employ ratios of mols of water to atoms of carbon in excess of about 0.7 and preferably in excess of about 0.9 in order to effect consumption of carbonaceous solid. Ratios of mols of water to atoms of carbon up to about 2.0 may be employed with good results to effect the consumption of substantial amounts of carbonaceous solid.

In the process of our invention the methanization reaction is effected in the presence of a bed of carbonaceous solid. Various carbonaceous solids are suitable, for example petroleum coke, coal, lignite and coke oven coke. When fuels are employed containing volatilizable constituents, for example, coal or lignite, the volatile constituents are distilled from the methanization zone and appear in the product gas contributing to the heating value of the gas produced. Petroleum coke is a preferred carbonaceous solid because of the negligible ash content. Since the carbonaceous solid is continuously consumed in our process, it is necessary to add carbonaceous solid to the methanization zone as make-up for that consumed. It is preferred to maintain the carbonaceous solid in the form of a fixed bed so that a temperature gradient may be established to permit reduction in the temperature of the reactants to the desired terminal temperature.

An advantage of the process of this invention is that carbonaceous solids and heavy fuel oils may be efficiently converted to fuel gases of high calorific value.

Another advantage of this process is that gases comprising carbon monoxide and hydrogen produced by partial combustion may be methanized without the deposition of carbon.

Another advantage of the process of this invention is that the high sensible heat resultant from the high temperature partial oxidation of carbonaceous fuels may be efficiently utilized to convert steam and carbonaceous solids to gas of high calorific value.

Figure 1 diagrammatically illustrates an embodiment of the process of this invention.

Figure 2 is a graphical representation of the effect of pressure upon the heating value of gases produced according to the process of this invention.

Although Figure 1 illustrates one embodiment of apparatus in which the process of this invention may be practiced it is not intended to limit the invention to the particular apparatus or materials described.

5

Referring to Figure 1, coal from an external source, not shown, is introduced through line 2 into mixer 3. Water from an external source not shown, is admitted to the mixer through line 4 in an amount sufficient to form a fluid slurry of coal particles in water. Slurry is withdrawn from mixer 3 through line 5 and is forced under pressure by pump 7 to a heating coil 8 in heater 9. The slurry in heating coil 8 is heated to a temperature at least sufficient to vaporize the water contained therein. The resultant dispersion of coal in steam is discharged through line 10 to gas generator 12. Synthesis gas generator 12 may comprise a pressure vessel provided with an internal refractory lining enclosing an essentially unobstructed reaction space. A suitable gas generator for the partial combustion of solid fuels is described in the copending application of duBois Eastman, Serial No. 525,240, filed July 29, 1955, now U.S. Patent 2,871,114.

Oxygen for the reaction is supplied from an external source, not shown, through line 13 and is passed at a rate controlled by valve 14 to gas generator 12. In gas generator 12 the coal, oxygen, and steam are reacted at a temperature within the range of about 2000 to 3500° F., preferably in the range of about 2200 to about 2800° F., to produce a gas comprising carbon monoxide and hydrogen. Effluent synthesis gas from generator 12 is discharged through line 15 to methanizer 24. Water, either in the form of liquid water from line 16 at a rate controlled by valve 17, or steam from line 19, heating coil 20 and lines 21 and 22 at a rate controlled by valve 23, or both water and steam are passed through line 18 and admixed with the synthesis gas in line 15 to form the gaseous feed mixture passed to methanizer 24. The temperature of the gas mixture entering methanizer 24 may be readily controlled by varying the quantity of water, steam, or both introduced through line 18 as well as varying the temperature of the steam by control of heating coil 20.

Metallurgical coke is introduced through valve 28 into lock hopper 27. Pressure in lock hopper 27 is then increased to the pressure of methanization zone 24, and the coke is introduced into the methanization zone 24 by opening valve 29. Coke, in the form of a dense bed, slowly gravitates from the top to the bottom of methanizer 24 as coke in the bottom of the methanizer is consumed by reaction with the carbon monoxide, hydrogen and water vapor present. Ash is withdrawn from the bottom of methanizer 24 by means of lock hopper 30 and valves 32 and 33. Optionally the reaction temperature in methanizer 24 may be gradually reduced by introducing steam into the coke bed at various levels. Steam for this purpose is introduced through lines 21, 34, and 34a, 34b, 34c and 34d at rates controlled by valves 35a, 35b, 35c and 35d. Reactants reaching the top of methanizer 24 reach a terminal temperature within the range of about 1300 to 1500° F. and are withdrawn through line 37, cooled in heat exchanger 38, and are passed through line 40 to water separator 45. Water is discharged through line 46. Separated gas is withdrawn from separator 45 through line 47 and passed to carbon dioxide and sulfur removal facility 48. Methods are well known which may be used for the removal of carbon dioxide and sulfur compounds from gaseous mixtures, for example, scrubbing with water, caustic or ethanolamine solutions. These scrubbing methods also remove much of the sulfur present in the gas treated, however if substantially complete sulfur removal is desired, the scrubbed gases may be further treated, for example, by contact with iron or an iron oxide such as luxmasse. Carbon dioxide and sulfur compounds separated from the gas are discharged continuously or intermittently through line 49 either during processing or during regeneration. Product gas having a heating value in excess of 500 B.t.u. per thousand standard cubic feet is discharged through line 50.

6

The invention will be more clearly understood with reference to the following example.

EXAMPLE

A cycle fuel oil having a gravity of 4.4° API, a flash of 300° F., a B. S. & W. of 0.2 weight percent and a carbon residue of 18.6 weight percent is reacted with steam and oxygen to produce a raw synthesis gas comprising carbon monoxide and hydrogen. A series of tests is made at the conditions and with the results shown in Table I, following:

Table I

Synthesis Gas Generation	Test 1	Test 2	Test 3
Steam and oil temperature, ° F.....	710	710	710
Oxygen temperature, ° F.....	80	80	80
Reaction temperature, ° F.....	2,600	2,690	2,780
Pressure, p.s.i.g.....	279	720	2,925
Charge and product rates, per pound of oil feed:			
Steam, pounds.....	.382	.382	.382
Oxygen, SCF.....	11.61	11.61	11.61
Synthesis gas, as produced, SCF.....	53.1	53.0	52.6
Analysis, volume percent:			
H ₂	42.1	42.0	41.0
CH ₄		.1	.5
H ₂ O.....	4.8	4.9	5.3
H ₂ S+CO ₂	.2	.2	.2
N ₂	.2	.2	.2
CO.....	51.0	51.1	51.0
CO ₂	1.6	1.6	1.6
Heating value, higher, after treatment for sulfur, CO ₂ and water removal, BTU/SCF.....	321	321	325

It will be noted that Tests 1, 2 and 3 are conducted at essentially the same conditions with the exception of the synthesis gas generation pressure which is respectively 279, 720 and 2,925 pounds per square inch gauge. It will be noted that the synthesis gas composition is substantially the same for all three tests. The heating values shown in Table I are obtained for comparison by treatment of the synthesis gas with an ethanolamine solution and iron-iron oxide for removal of sulfur and water is separated by condensation.

The synthesis gas of Tests 1, 2 and 3 is passed directly to a methanization reactor in admixture with steam and a carbonaceous solid for a contact time of about 150 seconds in each case with the results and at the conditions shown in Table II, following:

Table II

Methanization	Test 1A	Test 1B	Test 2A	Test 2B	Test 3
Water/carbon ratio.....	0.50	1.00	0.91	1.82	1.00
Terminal temperature, ° F.....	1,430	1,430	1,340	1,340	1,520
Pressure, p.s.i.g.....	279	279	720	720	2,925
Charge and product rates, per pound of synthesis gas generator oil feed:					
Water or steam added, pounds.....	.545	1.09	1.086	2.294	1.196
Coke consumed, pounds.....		0.235	0.046	0.499	0.153
Coke produced, pounds.....	0.046				
Raw product gas, SCF.....	53.1	71.9	59.3	88.9	62.0
Analysis:					
H ₂	28.3	28.9	17.6	18.0	15.2
CH ₄	9.4	9.8	15.2	15.9	17.0
H ₂ O.....	21.3	21.5	32.6	32.5	31.5
H ₂ S+CO ₂	0.2	0.2	0.2	0.1	0.2
N ₂	0.2	0.2	0.2	0.1	0.2
CO.....	21.8	21.4	9.7	9.5	12.1
CO ₂	18.8	18.1	24.5	23.8	23.8
Methanized fuel gas, treated for removal of CO ₂ , water and sulfur:					
SCF/pound of synthesis gas generator oil feed.....	31.9	43.6	25.7	39.1	27.9
Heating value, higher, BTU/SCF.....	426	430	559	566	577
Analysis:					
H ₂	47.1	47.6	40.7	40.8	33.8
CH ₄	15.6	16.2	35.2	36.1	37.8
H ₂ O.....	.1	.1			
H ₂ S+CO ₂					
N ₂	.4	.3	.5	.3	.4
CO.....	36.2	35.2	22.4	21.6	26.8
CO ₂	.6	.6	1.1	1.1	1.1

Effluent product from Test 1 in Table I is employed

at water to carbon ratios of 0.50 and 1.00 identified as Test 1A and 1B respectively in Table II. Similarly the synthesis gas from Test 2, Table I, is employed at water to carbon ratios at 0.91 and 1.82 identified as Test 2A and 2B respectively in Table II. The effluent gas from Test 3, Table I, is employed in Test 3, Table II. It will be noted from the result in Test 1A, wherein the water to carbon ratio was below the critical level of 0.7, that carbon was not consumed but on the contrary there was a deposition of about 0.046 pound of carbon per pound of synthesis gas generator oil feed. Test 1B shows that when the water to carbon ratio is increased to a point above the critical value of 0.7, carbon is not produced but is consumed at the rate of 0.235 pound per pound of synthesis gas generator oil feed. The effect of pressure upon the methanization reaction and hence upon the heating value of the fuel gas produced is evident by comparison of the heating values of the methanized fuel gas from Tests 2A, 2B and 3 with Tests 1A and 1B. In the former the pressures are in excess of 720 pounds per square inch gauge and heating values in excess of 559 B.t.u.'s per standard cubic foot are obtained. In Tests 1A and 1B pressures less than 700 pounds per square inch gauge are employed and heating values of 430 B.t.u. per standard cubic foot or lower are obtained. The increase in heating value of the fuels produced by methanization is evident by comparison of the heating values of the methanized fuel gas in Table II with the corresponding heating values of the synthesis gas in Table I.

The heating values of the methanized fuel gas of Table II and the synthesis gas of Table I are plotted in Figure 2. Figure 2 clearly shows the effect of methanization and the relative effect of pressure upon the heating value of the methanized fuel gas. It is evident that heating value increases rapidly as pressure is increased up to a critical pressure of about 700 pounds per square inch and increase of pressure above this level has little effect upon the heating value of the fuel gas produced.

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

We claim:

1. A process for the manufacture of fuel gas which comprises subjecting a carbonaceous fuel to partial combustion with an oxygen-containing gas at a temperature within the range of about 1800 to 3500° F. and at a pressure in excess of about 700 pounds per square inch gauge forming a raw synthesis gas comprising mainly carbon monoxide and hydrogen, passing said raw synthesis gas together with sufficient steam to provide a gas mixture comprising in excess of 0.7 mol of water vapor per atom of carbon at an elevated pressure above 700 pounds per square inch gauge and a temperature above 1800° F. into contact with a fixed bed of solid carbon, passing said gas mixture through said bed and introducing steam into said bed along the path of flow of said gas and resulting reaction products, said added steam being supplied in relative proportions sufficient to remove heat of reaction and reduce the temperature of the gas stream to a terminal reaction temperature within the range of about 1,000 to 1,700° F. whereby a temperature gradient is maintained through said bed of carbonaceous solids effecting gradual cooling of said gaseous mixture and gaseous reaction products passing therethrough to said terminal reaction temperature effecting reaction of said carbon monoxide, hydrogen, water vapor and carbon to form a product gas comprising methane and having a higher heating value than said raw synthesis gas.

2. A process according to claim 1 wherein said bed of carbon is petroleum coke.

3. A process according to claim 1 wherein said terminal reaction temperature is within the range of about 1300 to 1500° F.

References Cited in the file of this patent

UNITED STATES PATENTS

2,609,283	Kalbach	Sept. 2, 1952
2,657,124	Gaucher	Oct. 27, 1953
2,687,950	Kalbach	Aug. 31, 1954

FOREIGN PATENTS

665,781	Great Britain	Jan. 30, 1952
683,719	Great Britain	Dec. 3, 1952
515,904	Canada	Aug. 23, 1955

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,942,959

June 28, 1960

Harry V. Rees et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, line 53, for "523,641" read -- 523,601 --;
line 54, strike out ", and now abandoned".

Signed and sealed this 14th day of November 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD

Commissioner of Patents

USCOMM-DC