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(54) PRODUCTION OF SYNTHESIS GAS

(54)

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PRODUCTION OF SYNTHESIS GAS
(D#70,579-F)

BACKGROUND OF THE INVENTION

Field of the Invention: This invention relates to the production of synthesis gas. More particularly, it relates to improvements in the partial oxidation process for generating hydrogen and carbon monoxide or for producing fuel gas.

Description of the Prior Art: Synthesis gas, a mixture of carbon monoxide and hydrogen, is commonly made by the partial oxidation of a carbonaceous feed by means of a gaseous oxidant such as 95 mole percent oxygen or oxygen-enriched air (45% O₂ or more). The raw synthesis gas leaving the reaction zone at a temperature in the range of about 2000 to 3200°F. comprises principally CO and H₂, together with minor amounts of H₂O, CO₂, CH₄, H₂S, and free unconverted carbon or soot. Further, when the oxidant contains air, the product gas may be diluted with about 50 mole percent of nitrogen. For a more complete description of the synthesis gas process, refer to U. S. Patent 2,809,104 issued to Dale M. Strasser et al.

Depending upon the operating conditions, about .01 to 10% by weight (basis carbon in the feed) of unconverted carbon soot may be found in the effluent stream of raw synthesis gas from the reaction zone. Normally, about one to three percent of unconverted carbon is desirable in the effluent gas stream in order to sequester the vanadium and nickel compounds and other ash forming impurities in oil feed which are corrosive or erosive to the refractory lining of the reaction zone. In conventional processes for manufacturing synthesis gas the carbon yield is commonly controlled by regulating the free oxygen supplied to the reaction zone. However there are limitations to this scheme for free oxygen reacts exothermically and when the temperature in the reaction zone gets too high the refractory lining deteriorates

SUMMARY OF THE INVENTION

By the process of our invention, a liquid or solid oxygen containing organic material comprising from about 5 to 60% by weight of oxygen is blended with a carbonaceous fuel to comprise the feedstock for a synthesis gas generator. For a given soot yield, the effect of adding such oxygenated organic additives in the feedstock is to lower the temperature in the reaction zone and to reduce the free oxygen consumption, for example about 24%. When about 1 to 80 weight percent of an oxygenated hydrocarbon liquid such as isobutyraldehyde or sorghum molasses is mixed with a liquid hydrocarbon fuel, the normal soot yield of the effluent gas from the reaction zone may be reduced up to about 90% with no significant change in reaction temperature. The oxygenated hydrocarbonaceous organic material is supplied in an amount sufficient to provide a minimum of 0.5 wt. % of combined oxygen in the feedstock. Furthermore, it has been unexpectedly found that when the generator is operated to produce an effluent gas having a low yield of unconverted carbon (about 0.3 wt. % or less, basis carbon in the fuel), the life of the refractory lining of the reaction zone is improved when a heavy fuel oil feed containing an oxygenated organic additive is reacted at a temperature in the range of about 1700°F. to 2800°F. and a pressure in the range of about 50 to 250 atmospheres.

Finally, by this process the amount of CH_4 in the generator effluent gas may be controlled so as to produce a high Btu fuel gas containing a high percentage of methane at a given level of soot production.

It is therefore a principal object of the present invention to improve the economy and efficiency of the continuous partial oxidation process for producing large

volumes of synthesis gas comprising principally hydrogen and carbon monoxide and containing controlled amounts of unreacted carbon and methane.

Another object of the invention is to reduce the soot yield in a synthesis gas process without resorting to an increased consumption of free gaseous oxygen or to higher reaction temperatures.

A further object of the invention is to make a high Btu fuel gas or a reducing gas.

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DESCRIPTION OF THE INVENTION

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The present invention involves improvements in the partial oxidation process for generating hydrogen and CO (synthesis gas), or improvements in the manufacture of reducing gas or in the production of a high Btu fuel gas. About 1 to 80% by weight of either a liquid or a solid oxygenated hydrocarbonaceous organic additive is blended with a carboniferous fuel to comprise a feedstock for a synthesis gas generator having a minimum of 0.5 wt. % of combined oxygen. This permits gas production at a lower temperature in the reaction zone and with a reduced free oxygen/fuel ratio for a particular CH_4 /soot ratio.

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Oxygenated hydrocarbonaceous organic additives suitable for the process of our invention contain about 5 to 60 percent by weight of combined oxygen, e.g., isobutyraldehyde and molasses. Other suitable materials include: starch and other carbohydrates, saw dust, wood flour and other cellulosic materials, sludge derived from acid refining petroleum products, organic acids, alcohols, aldehydes, ketones, sewer sludge and organic waste products that have some fuel value and which contain combined oxygen, and waste liquor from paper making processes containing organic solids such as hexose, pentose and lignin.

Further, fuel oil which has been pretreated with oxygen or air to introduce oxygen into the oil molecule may also be used.

10 Most carboniferous fuels used in the regular partial oxidation process are suitable for the process of our invention including: hydrocarbon oil, petroleum coke, tar, and mixtures thereof; also, slurries of petroleum coke in other fluids, such as water or oil, e.g., a mixture of 25 parts by weight water, 25 parts molasses and 50 parts dry, powdered petroleum coke. Ordinarily, with only water as the slurring medium, the water/coke ratio is about 1/1 or higher. However, in the embodiment of our invention using molasses as part of the slurring medium for coke, the water/fuel ratio may be reduced to about 1/3. Molasses is soluble in 840 Bunker Fuel to the extent of about 25 or more weight percent of molasses. Adding molasses to slurries of coke in oil assures better conversion of the coke to synthesis gas without increasing the feed rate of free oxygen.

20 The use of oxygen-containing organic additives in the feedstock to a synthesis gas generator effects a cost saving by permitting the system to operate with less free oxygen. The system may be operated with a free oxygen/carbon atomic ratio in the range of about 0.500 to 1.20, a steam/fuel wt. ratio in the range of about 0.2 to 1.00, and a pressure in the range of about 50 to 250 atmospheres. By lowering the free oxygen rate, the temperature in the reaction zone may be decreased until methane production becomes appreciable without making an intolerable amount of soot. The methane concentration in the product gas is usually in equilibrium with H_2 , H_2O , CO , and CO_2 , and is a function of temperature and pressure. Further, methane concentration increases as the reaction pressure increases and decreases as the reaction temperature increases.

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By operating the generator at high pressures (about 50 to 250 atmospheres) and at comparatively lower temperatures (about 1700 to 2500°F.), the methane concentration of the synthesis gas may be controlled at about ten mole percent or more. Since the gross heating value for methane is about 1010 Btu/CF while that for CO and H₂ is about 321 and 324 Btu/CF respectively, it follows that synthesis gas with a high methane content is attractive for use as a fuel gas.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 The following examples are offered as a better understanding of the present invention, but the invention is not to be construed as limited thereto.

Example I

The feasibility of using isobutyraldehyde (IBA) as part of the feedstock for a synthesis gas generator may be demonstrated by the data shown in Table I, runs 2 and 3.

20 Straight California Reduced Crude (CRC) comprises the feedstock for control run 1, whereas the feedstock for runs 2 and 3 are comprised of California Reduced Crude mixed respectively with 48.9 and 73.2 weight percent of IBA. IBA is comprised of about 22 weight percent of combined oxygen.

30 For a given soot yield, addition of IBA to the liquid hydrocarbon fuel permits operation of the synthesis gas generator at a substantially reduced free oxygen to fuel ratio and at a lower reaction temperature; however, the concentration of methane in the product gas is increased. For example, a comparison of the data for run 1 (0 wt. % IBA in the feed) with run 2 (48.9 wt. % IBA in the feed) shows that for both runs by adding IBA to the feedstock and by maintaining a carbon yield in the feed of about 1.2 weight percent and a steam/fuel weight ratio of about

0.37, the free oxygen charged to the generator drops over 19% (7529 SCFH for run 1 compared with 6103 SCFH for run 2), the free oxygen consumption (expressed as SCF/MSCF $H_2 + CO$) is reduced from 240.2 for run 1 to 232.8 for run 2, and the methane composition of the product gas in mole percent is increased from 0.30 in run 1 to 2.24 in run 2. The temperature in the reaction zone is also lowered from about 2485°F. in run 1 to about 2326°F. in run 2 due to the oxygenated organic additives undergoing endothermic reaction and to the reduction in the amount of free oxygen undergoing exothermic reaction.

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By increasing the amount of oxygenated organic additive in the feedstock, such as to 73.2 weight percent IBA in run 3, the soot yield is decreased further to 0.34 wt. %. Further, the CH_4 /soot mole ratio increases as the weight percent of IBA additive charged with the fuel increases. In comparison with control run 1, the low soot yield in run 3 is achieved with a lower free oxygen consumption and at a lower reaction temperature. It is believed that the oxygen content of the IBA (22 wt. % oxygen), and not its volatility, affected the soot yield.

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It was unexpectedly found that although the soot production for run 3 was unusually low, there was no evidence of damage to the refractory lining the reaction zone after extended generator operation. Consequently, the amount of unconverted carbon in the effluent stream from the reaction zone may be kept low thereby making it possible to simplify or to eliminate at a substantial cost savings the carbon recovery unit now part of the conventional synthesis gas purification system.

TABLE I
Synthesis Gas Generation

	Run No.					
	1	2	3	4	5	6
Fuel Change						
Process Fuel, lbs/hr	629.5	622.4	629.8	435.4	442.3	451.7
Gravity ° API	14.4	29.4	38	6.1	5.0	4.4
Composition - % by weight						
California Reduced Crude (CRC) or Vacuum Residuum (VR)	CRC 100	CRC 51.1	CRC 26.8	VR 100	VR 95.0	VR 93.0
Isobutyralsdehyde (IBA) or Sorghum Molasses (M)	IBA 0	IBA 48.9	IBA 73.2	M 0.0	M 5.0	M 7.0
Oxygen in Fuel Supplied by IBA or M, wt. %	0	11.3	16.5	0	2.6	4.3
Process Water Charge						
Process Water, lbs/hr	233.8	236.8	236.3	233.2	223.8	235.0
Oxygen Charge						
Free Oxygen Flow, SCFH	7529	6103	5696	5355	4751	4482
Generator Operation						
Reaction Zone Temperature, °F.	2485	2326	2394	2075	1947	1785
Pressure, psig	1000	1000	1014	1035	1040	1040
Dry Product Gas Flow, SCFH, forced	33505	28384	27902	22719	21184	21620
Composition of Product Gas, mole %						
H ₂	48.62	47.37	48.77	46.49	45.92	45.72
CO	44.93	44.96	43.37	44.38	40.37	40.55
CO ₂	5.68	5.18	5.73	8.30	10.04	9.71
CH ₄	0.30	2.24	1.94	0.40	3.33	3.67
H ₂ S	0.34	0.13	0.07	0.23	0.24	0.25
N ₂	0.02	0.02	0.02	0.12	0.02	0.02
A	0.08	0.08	0.08	0.08	0.08	0.08
Performance						
Free oxygen/Fuel Ratio, SCF/lb	12.0	9.8	9.10	12.3	10.7	9.9
Steam/Fuel Ratio, lb/lb	0.37	0.38	0.37	0.53	0.50	0.52
Oxygen/Carbon Ratio, atom/atom	0.87	0.811	0.797	0.881	0.804	0.748
Free Oxygen Consumption, SCF/MSCF H ₂ + CO	240.20	232.8	221.5	259.4	259.9	240.3
Unconverted Carbon(soot yield) wt.%	1.2	1.2	0.34	0.82	3.71	2.69
H ₂ + CO, SCFH	31340	26210	25710	20640	18270	18650
Hydrogen/Carbon Ratio, atom/atom	2.04	2.37	2.53	2.03	2.21	2.12
CH ₄ /Soot Ratio, mole/mole	0.48	3.5	11.1	0.91	1.60	2.46

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Example II

The use of sorghum molasses as an oxygenated organic additive to the feedstock for a synthesis gas generator may be demonstrated by the data shown in Table I, runs 5 and 6. Straight Vacuum Residuum (VR) comprises the feedstock for control run 4, whereas the feedstock for runs 5 and 6 are comprised of Vacuum Residuum mixed respectively with 5 and 7 weight percent of sorghum molasses. Sorghum molasses contains about 40 weight percent of combined oxygen.

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The effects of charging a synthesis gas generator with a feedstock comprising a liquid hydrocarbon fuel, e.g. heavy fuel oil or vacuum residuum mixed with molasses are similar to those described in Example I for IBA. The methane concentration in the effluent gas from the generator increases as the temperature in the reaction zone decreases and the CH_4 /soot ratio increases as the weight percent of molasses charged in the feedstock increases. For example by maintaining a CH_4 concentration in the product gas of about 3.33 to 3.67 mole % and a steam/fuel weight ratio of about 0.50 - 0.52, when 5 wt. % of molasses in the feedstock of run 5 is increased to 7 wt. % in run 6 then the soot yield of 3.71 wt. % in run 5 is reduced to 2.69 wt. % in run 6, although the free oxygen flow in run 6 (4482 SCFH) is less than the free oxygen flow in run 5 (4751 SCFH). Further, the data for runs 4, 5 and 6 demonstrate that both the oxygen/fuel ratio and the free oxygen consumption decrease as the amount of molasses in the feedstock increases.

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The effectiveness of isobutyraldehyde as an oxygenated organic additive in comparison with sorghum molasses may be shown from the data in Table I by means of a semi-log plot showing "weight percent oxygen in the fuel" (supplied by the isobutyraldehyde or by the molasses) as the abscissa

and " CH_4 /soot molecular ratio" as the ordinate. The resulting straight lines show that the CH_4 /soot ratio for each feedstock increases exponentially with the oxygen content in the fuel. The runs made with molasses vacuum residuum feedstock at a slightly higher steam/fuel ratio show a greater CH_4 /soot ratio for any fixed amount of oxygen in the feed.

Example III

10 To demonstrate further the relationship between soot yield vs. combined oxygen in the fuel, Straight California Reduced Crude is fed to a synthesis gas generator at 1000 psig and with a 0.38 steam/fuel weight ratio to produce a soot yield of about 3.0 wt. % (basis carbon in the feed) and 0.46 mole % of methane. When isobutyraldehyde is charged with the CRC in an amount so that the combined oxygen in the feedstock is about 7 wt. %, the soot yield in the product gas drops ten-fold to about 0.30 wt. %. Similarly, straight Vacuum Residuum is fed to a synthesis gas generator operating at 1000 psig with a 0.55 steam/fuel wt. ratio to produce a soot yield of about 3.0 wt. % and 0.71 mole % of methane. When sorghum
20 molasses is charged with the vacuum residuum in an amount so that the combined oxygen in the feedstock is about 4.5 wt. % of oxygen, the soot yield drops about ten-fold to about 0.30 wt. % of carbon in the feed. Accordingly under the conditions described, molasses was more effective than IBA in reducing the soot yield.

Example IV

30 Fuel gas may be produced by the process of our invention in a synthesis gas generator operating with a H_2O to fuel ratio of 0.4, a pressure of about 1640 psig, a temperature of about 1800°F., and with a feedstock comprised of a 50/50 mixture by weight of heavy fuel oil and IBA. The approximate composition of the product gas in mole % follows: CO_2 - 4.6,

CO - 36.1, H₂ - 34.0, CH₄ - 10.0 and H₂O - 6.2. The gross heating value of the product gas is about 386 Btu/CF and if desired may be raised by increasing the concentration of high Btu methane. For example, the CO₂ may be scrubbed out of the product gas and the CO and CH₄ may then be removed as 480/Btu/CF heating gas. The remaining pure H₂ may be used for ammonia synthesis or hydrotreating. Alternately, if the CO is shifted first to CO₂ and H₂, the pure CH₄ may be then obtained as one stream and pure hydrogen as a second stream, after scrubbing out CO₂. Or, liquid nitrogen may be used for cryogenic cooling in a nitrogen wash system in which said product gas is separated into one stream comprising essentially methane with some nitrogen and CO, and a second stream comprising hydrogen and nitrogen, which may be used as feedstock for ammonia synthesis. Ordinary nitrogen wash plants do not salvage the nitrogen-methane mixture because there is insufficient methane to be worthwhile (only about .2 to .4% of the raw synthesis gas). Now, however, with 10 mole % or more of methane in the synthesis gas, the nitrogen-methane mixture becomes valuable as a fuel gas.

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In summary, the addition of oxygenated organic additives to the feedstock of a synthesis gas generator as described in the above examples resulted in product gas with unusually low soot yields, requiring a reduction in the free oxygen feed rate to maintain a desired soot yield. The lower oxygen rate resulted in a lower generator temperature and higher methane content of the synthesis gas. Furthermore, fuel gas may be produced with a methane concentration of about 10 mole % or more. Thus, the effect of adding oxygenated organic materials to the generator feedstock is to trade off

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lower reaction temperature and lower oxygen consumption for more methane at a given level of soot production and fixed steam/fuel ratio.

The process of the invention has been described generally and by examples with reference to oxygenated organic additives, hydrocarbon feedstocks, effluent gas streams, and various other materials of particular composition for purposes of clarity and illustration only. From the foregoing it would be apparent to those skilled in the art that the various
10 modifications of the process, the materials, and the amounts of the materials disclosed herein can be made without departure from the spirit of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for producing synthesis gas comprising principally hydrogen and carbon monoxide which comprises reacting with free oxygen in the reaction zone of a synthesis gas generator a feedstock comprising a mixture of carboniferous fuel and oxygenated hydrocarbonaceous organic material supplied in an amount sufficient to provide a minimum of 0.5 wt. percent of combined oxygen in said feedstock at a temperature in the range of about 1700°F. to 2800°F., a pressure in the range of about 50 to 250 atmospheres, a steam/fuel wt. ratio in the range of about 0.2-1.0 and a free oxygen/carbon atomic ratio in the range of about 0.500-1.20, and said oxygenated hydrocarbonaceous organic material comprises from about 5 to 60 wt. percent of combined oxygen.

2. A process as defined in Claim 1 wherein said oxygenated hydrocarbonaceous organic material is present in the feedstock in the amount of about 5 to 80 wt. percent.

3. A process as defined in Claim 1 wherein the oxygenated hydrocarbonaceous organic material comprises from about 1.0 to 20 wt. percent of molasses and the carboniferous fuel comprises heavy fuel oil.

4. A process as defined in Claim 1 wherein the oxygenated hydrocarbonaceous organic material comprises from about 20 to 80 wt. percent of isobutyraldehyde and the carboniferous fuel comprises heavy fuel oil.

5. A process as defined in Claim 1 wherein said feedstock comprises a mixture of about 15-40 parts by weight

of water, 5-40 parts by weight of molasses, and 45-55 parts by weight of dry powdered petroleum coke.

6. A process for producing synthesis gas and fuel gas comprising,

(1) reacting with free oxygen in the reaction zone of a synthesis gas generator a feedstock comprising a mixture of carboniferous fuel and oxygenated hydrocarbonaceous organic material supplied in an amount sufficient to provide a minimum of 0.5 wt. percent of combined oxygen in said feedstock at a temperature in the range of about 1700°F. to 2500°F., a pressure in the range of about 50 to 250 atmospheres, a steam/fuel wt. ratio in the range of about 0.2-1.0 and a free oxygen/carbon atomic ratio in the range of about 0.50-1.00, to produce a gaseous mixture comprising principally carbon monoxide and hydrogen, and containing methane in the amount of about 10 mole percent or more;

(2) subjecting the gaseous mixture from (1) to water gas shift reaction with steam at a temperature in the range of about 350 to 1050°F. to produce H_2 and CO_2 ;

(3) removing carbon dioxide from the shifted gas stream from (2);

(4) contacting the remaining gas from (3) with liquid N_2 in a nitrogen wash operation;

(5) recovering a first gaseous mixture comprising CH_4 and containing some N_2 and unconverted CO from (4);
and

(6) recovering a second gaseous mixture comprising H_2 and N_2 from (4).

7. A process as defined in Claim 6 wherein the oxygenated carbonaceous organic material of (1) comprises about 20 to 80 wt. percent of isobutyraldehyde and the carboniferous fuel in (1) comprises heavy fuel oil.

8. A process as defined in Claim 6 wherein the oxygenated carbonaceous organic material of (1) comprises from about 1.0 to 20 wt. percent of molasses and the carboniferous fuel comprises heavy fuel oil.

9. In the process for producing synthesis gas by the partial oxidation of a carboniferous fuel with free oxygen in the reaction zone of a free-flow synthesis gas generator the improvement comprising introducing said carboniferous fuel into said reaction zone in admixture with about 5 to 90 wt. percent of oxygenated hydrocarbonaceous organic material containing from about 3 to 60 wt. percent of combined oxygen; and reacting said reactants at a temperature in the range of about 1700°F. to 2800°F., a pressure in the range of about 1 to 250 atmospheres, and a free oxygen/carbon atomic ratio in the range of about 0.500-1.20.

10. The process of Claim 9 wherein said oxygenated hydrocarbonaceous organic material is selected from the group consisting of isobutyraldehyde, molasses, starch, sawdust, wood flour, carbohydrates, cellulosic materials, sludge derived from acid refining petroleum products, organic acids, alcohols, aldehydes, ketones, sewer sludge and organic waste products having some fuel value and containing combined oxygen, waste liquor from paper making processes containing hexose, pentose, or lignin, and oxygenated fuel oil.

11. The process of Claim 9 wherein said carboniferous fuel is a liquid hydrocarbon fuel, and H_2O is introduced into said reaction zone in the ratio of about 0.2-1 parts by weight of H_2O to 1 part by weight of hydrocarbon fuel.

