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(12) Patent:

(54) GENERATION OF CARBON MONOXIDE AND HYDROGEN FROM A LIQUID HYDROCARBON

(54)

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- Abstract Image
- Claims Image
- Disclosures Image
- Drawings Image

This invention relates to the production of a gas mixture containing carbon monoxide and hydrogen from a liquid hydrocarbon.

Petroleum commonly contains small quantities of heavy metals. The most common heavy metals contained in petroleum are vanadium, nickel, iron, chromium and molybdenum. These heavy metals presumably occur in petroleum as compounds. The exact chemical compositions of the heavy metal compounds are somewhat in doubt. It is generally agreed that the metals are present, at least in part, in the form of oil-soluble metallo-organic compounds. Crude oils containing heavy metal constituents, and some heavy distillates from such crudes, have been found unsatisfactory for many purposes because of the nature of the ash from these fuels.

In particular, the naturally occurring compounds of vanadium and nickel contained in petroleum oils, upon oxidation, apparently yield very corrosive or erosive ash. The extent to which compounds of these metals are present in petroleum may vary from about 1 to about 1000 parts per million by weight based upon the weight of the metal, per se. In general, petroleum oils containing even minor amounts of vanadium and nickel are troublesome when used as fuel. The ash from these fuels is corrosive or erosive to both refractories and to alloy metals. Of the heavy metal contaminants in petroleum fuels, vanadium and nickel appear to be the most detrimental to high temperature refractories, particularly aluminum oxide refractories.

A number of attempts have been made to treat ash-containing liquid hydrocarbon fuels for removal or reduction of ash-forming constituents. These attempts have been

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generally unsuccessful. The heavy metal constituents of crude oils may be concentrated, to some extent, by means of distillation, the heavy metal constituents largely remaining in the distillation residues. Nevertheless, the metals or
5 their compounds are also present in many distillate products, particularly in heavy fractions, such as products of vacuum distillation. The presence of the metals in the distillates may be due either to actual vaporization of the metal compounds or to physical carryover or entrainment. These metals
10 have also been found in such stocks as propane-deasphalted oil and solvent-refined distillate.

Recently, partial oxidation of hydrocarbons with oxygen to carbon monoxide and hydrogen has been developed commercially; the process is disclosed in U.S. 2,582,938 to
15 duBois Eastman and Leon P. Gaucher. In this process, a hydrocarbon, for example, fuel oil, is reacted with steam and air, oxygen, or oxygen-enriched air in a closed, compact reaction zone at a temperature in the range of about 2,000 to about 3,200°F. The reaction zone is free from packing and catalyst
20 and has nearly minimum internal surface. The reaction may be conducted at atmospheric pressure or at an elevated pressure which may be as high as several hundred pounds per square inch. The reaction temperature, suitably about 2,600°F., is autogenously maintained. Preheating of the reactants is generally
25 desirable. The amount of uncombined oxygen supplied to the reaction zone is limited so that near-maximum yields of carbon monoxide and hydrogen are obtained. The product consists essentially of carbon monoxide and hydrogen and contains relatively small amounts of unconverted hydrocarbon and
30 carbon dioxide.

Air, oxygen-enriched air, or substantially pure oxygen may be employed in the process. Oxygen may be obtained by the rectification of air. Commercial oxygen plants are available capable of delivering large amounts of high purity oxygen. Commercial oxygen, so produced, usually contains in excess of 95 mol per cent oxygen. Substantially pure oxygen, e.g., commercial oxygen, is generally preferred for generation of carbon monoxide and hydrogen.

The use of ash-forming hydrocarbons, particularly those containing vanadium and nickel, as fuels for the production of carbon monoxide and hydrogen by partial oxidation with oxygen has resulted in operational difficulties. The reaction zone in which the partial oxidation takes place generally comprises a steel pressure vessel provided with a high temperature refractory lining, for example, aluminum oxide. Ash from the fuel apparently combines with the refractory to form a composite having a lower melting point than that of the original refractory. The result of this combination is that the refractory melts away in a relatively short time (often a matter of a few hours) at usual operating temperatures of the order of 2500 to 2800°F. This results in overheating of the pressure vessel, a particularly dangerous condition when the gas generator is operated at elevated pressure. Since the low cost and the high Btu content of heavy fuel oils and residua make them particularly attractive as fuels for the production of carbon monoxide and hydrogen by partial oxidation, it is most desirable to devise a method for preventing attack on the refractories employed as linings for the gas generators. The present invention provides a method for the production of carbon monoxide and

hydrogen from ash-containing hydrocarbons by partial oxidation with free oxygen in which the ash is sequestered with carbon, protecting the refractory lining of the gas generator.

In accordance with this invention, a hydrocarbon
5 fuel containing mineral ash-forming constituents which are detrimental to the life of the refractory lining of the synthesis gas generator are introduced into the reaction zone of the gas generator together with sufficient free oxygen to react exothermically with the fuel to autogenously maintain a
10 temperature in the range of about 2200°F. to about 3200°F. and to convert not less than about 90 per cent and not more than 99.5 per cent of the carbon contained in the fuel to carbon oxides. The extent of conversion of the carbon may be varied within this range depending upon the amounts of heavy
15 metals contained in the fuel. The quantity of unconverted carbon should be at least 50 times and preferably 100 times the combined weights of the nickel and vanadium contained in the fuels on the basis of the weight of the metal content of the metal-containing constituents present in the fuel. The
20 unconverted carbon from the hydrocarbon is liberated as free carbon. Under these conditions of limited carbon conversion, the ash-forming constituents of the fuel, particularly the ash resulting from the heavy metal constituents, are associated with the carbon and the composite is liberated as
25 a carbonaceous solid in particle form. The carbonaceous solid particles containing the heavy metals are substantially harmless to the refractory lining of the gas generator.

In a specific embodiment of the process of the present invention, oil containing mineral ash-forming constituents including nickel and vanadium is admixed with steam
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and fed into a compact, unpacked reaction zone. The reaction zone is free from packing and catalyst and has an internal surface area to volume of not more than 1.5 times the surface of a sphere equal in volume to the volume of the reaction zone. An oxygen-rich gas containing in excess of about 95 per cent oxygen by volume is introduced into the reaction zone into intimate admixture with the oil and steam. The generator may be operated at atmospheric or superatmospheric pressure. Preferably the generator is operated at a pressure within the range of from about 100 to about 600 pounds per square inch gauge. The temperature within the gas generator is autogenously maintained within the range of 2500 to 2900°F.

The quantity of free oxygen supplied to the gas generator is limited so that the conversion of carbon to carbon oxides is limited to 90 to 99.5 per cent of the carbon content of the oil fed to the gas generator. From about 1.8 to about 1.9 mols of free oxygen are supplied to the gas generator for each million Btu's gross heating value of the oil feed to the gas generator.

The amount of unconverted carbon released as a carbonaceous solid in the generator is at least 50 times by weight the combined weights of the nickel and vanadium contained in the oil, based on the weight of the free metal content of the nickel and vanadium compounds in the fuel. Free carbon released in the gas generator is entrained in the gaseous products of reaction. Ash from the fuel, particularly the heavy metal constituents, is substantially completely retained in the carbonaceous residue. The hot gases from the generator containing entrained carbon are contacted with water in a gas scrubbing and quenching operation in which the gases

are rapidly cooled to a temperature below the reaction temperature. The carbonaceous solid is removed from the gas stream in the scrubbing operation. The product gas is a mixture of carbon monoxide and hydrogen useful as feed gas for synthesis of hydrocarbons, methanol synthesis, or as a source of hydrogen for the synthesis of ammonia or for other purposes.

The following specific examples illustrate the effect of the limited carbon conversion on the life of a typical high temperature gas generator refractory. In each of the following examples the fuel oil was a San Ardo crude oil of the following composition and physical properties:

	Gravity	12.8° API
	Viscosity	650 S.F. at 122°F.
15	Flash	235°F.
	Pour Point	50°F.
	Conradson Carbon	9.6
	Gross Heating Value	18,450 Btu/lb.
	Ultimate Analysis	
20	Carbon	85.5 wt. per cent
	Hydrogen	11.0 " " "
	Nitrogen	1.0 " " "
	Sulfur	1.9 " " "
	Oxygen	0.6 " " "
25	Ash: Vanadium	68 ppm.
	Nickel	56 "
	Iron	57 "

The oil was atomized with steam and mixed with oxygen of 99.9 per cent purity in a flow-type gas generator of the type disclosed in U. S. patent 2,582,938. In each of the examples

the generator was provided with 2 1/2 inches of high purity alundum (aluminum oxide) lining surrounded by insulating firebrick.

	<u>Example 1</u>	<u>Example 2</u>
	<u>High Carbon Conversion</u>	<u>Moderate Carbon Conversion</u>
5		
10		
Feed Rates		
Oxygen CF/hr	5,186	12,187
Oil lbs/hr	401.5	954
Water lbs/hr	224.1	258
Dry Gas Production CF/hr	20,195	47,915
15		
Soot Production		
lbs/hr	1.50	15.47
Weight % of carbon fed	0.44	1.89
20		
Operating Conditions		
Temperature °F.	2,600	2,850
Pressure psig.	373	341
Preheat temp. °F.		
Oil-steam	710	740
Oxygen	67	70
Mols O ₂ /MM Btu of oil fed	1.847	1.824
25		
Product Gas Analysis-		
Dry Basis-mol%		
CO	47.0	49.06
CO ₂	5.5	3.71
H ₂ S	0.1	0.44
COS	-	0.02
30		
H ₂	47.0	46.51
N ₂	0.3	0.22
CH ₄	0.1	0.04
	<u>Total</u>	<u>100.00</u>
	100.00	100.00

35 After 186 hours of operation under operating conditions of high carbon conversion, representative data for which are shown in Example 1, the alundum lining of the generator was examined and was found to be so badly deteriorated as to preclude further operation of the generator. The lining was replaced and after about 673 hours of operation

40 under conditions of moderate carbon conversion, some of the data for which are shown in Example 2, the lining was examined and was found to be in excellent condition. Operations

continued with the same generator under similar conditions of moderate carbon conversion until a total operating time of about 3091 hours had been accumulated. During this period a number of heavy fuel oils was fed to the generator.

5 Some of the fuel oils contained larger amounts of vanadium and nickel than the amounts contained in the San Ardo crude. At the end of this period, inspection of the lining of the generator showed that it was in excellent condition.

10 It will be evident from the foregoing that limiting the extent of carbon conversion in a synthesis gas generator wherein mineral ash-forming constituents are contained in the fuel so that sufficient free carbon is released to sequester the ash, results in long life of the refractory lining of the generator and satisfactory operation over long periods of
15 time.

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
20 the appended claims.

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

1. In a process for the generation of carbon monoxide and hydrogen from an ash-forming hydrocarbon liquid wherein said hydrocarbon is subjected to reaction with steam and a gas containing free oxygen, the improvement which comprises introducing said reactants into a reaction zone, supplying said oxygen-containing gas to said reaction zone in an amount such that at least 0.5 per cent and not more than 10 per cent of the carbon contained in said hydrocarbon is uncombined and is liberated as a carbonaceous solid together with ash from said hydrocarbon while autogenously maintaining the reaction zone at a temperature in the range of 2000°F. and higher, and withdrawing from the reaction zone an effluent stream of gas comprising carbon monoxide and hydrogen together with said carbonaceous solid containing ash from said hydrocarbon.

2. The method according to Claim 1 wherein said gas containing free oxygen is essentially pure oxygen.

3. The method according to Claim 1 wherein said gas containing free oxygen is air.

4. The method according to Claim 1 wherein said gas containing free oxygen is oxygen-enriched air.

5. The method according to Claim 1 wherein the pressure within the reaction zone is at least 100 pounds per square inch gauge.

6. In a process for the production of carbon monoxide and hydrogen from an ash-forming liquid hydrocarbon wherein said hydrocarbon is subjected to reaction with steam and free oxygen at a temperature above about 2,000°F. in a closed, compact reaction zone free from catalyst and packing, the improvement which comprises introducing said reactants into said reaction zone in relative proportions such that at least 90 per cent but not more than about 99.5 per cent of the carbon contained in said hydrocarbon is converted to carbon oxides and at least 0.5 per cent of the carbon contained in said hydrocarbon is liberated as a carbonaceous solid in combination with ash from said hydrocarbon; and continuously removing from the reaction zone gaseous products of reaction, and said carbonaceous solid combined with ash from said hydrocarbon.

7. A process as defined in Claim 6 wherein said ash-forming liquid hydrocarbon contains vanadium and nickel and the weight of the carbon liberated as a solid by said reaction is at least 50 times the combined weights of the nickel and vanadium contained in said hydrocarbon feed to the reaction zone.

8. A process as defined in Claim 6 wherein the amount of free oxygen supplied to said reaction zone is within the range of from about 1.8 to 1.9 mols of free oxygen per million Btu's gross heating value of said liquid hydrocarbon.

9. A process as defined in Claim 6 wherein said ash-forming liquid hydrocarbon contains vanadium and nickel and the weight of carbon liberated as a solid by said reaction is at least 100 times the combined weights of the nickel and vanadium contained in said hydrocarbon feed to the reaction zone.

10. In a process for the production of carbon monoxide and hydrogen from an ash-forming liquid hydrocarbon containing vanadium and nickel wherein said hydrocarbon is subjected to a partial combustion reaction with steam and free oxygen at a temperature above 2,000°F. in a reaction zone free from fixed catalyst and packing, the improvement which comprises introducing said reactants into said reaction zone in relative proportions such that a portion of the carbon contained in said hydrocarbon is uncombined and is liberated as a carbonaceous solid together with ash from said hydrocarbon and the weight of the carbon liberated as a solid by said reaction is at least 50 times the combined weights of the nickel and vanadium contained in said liquid hydrocarbon supplied to the reaction zone, and continuously removing from the reaction zone gaseous products of reaction and said carbonaceous solid combined with ash from said hydrocarbon.

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11. In a process for the generation of carbon monoxide and hydrogen from a hydrocarbon liquid wherein said hydrocarbon liquid is subjected to reaction with steam and free oxygen, the improvement which comprises introducing said reactants into a reaction zone, supplying said oxygen to said reaction zone in an amount such that at least 0.5 per cent and not more than 10 per cent of the carbon contained in said hydrocarbon liquid is uncombined and is liberated as free carbon while autogenously maintaining the reaction zone at a temperature in the range of 2,000°F. and higher, and withdrawing from the reaction zone an effluent stream of gas comprising carbon monoxide and hydrogen together with said carbonaceous solid from said hydrocarbon.

12. In a process for the production of carbon monoxide and hydrogen from a hydrocarbon liquid wherein said hydrocarbon liquid is subjected to reaction with steam and oxygen at a temperature in the range of 2200°F. to 3200°F. and an elevated pressure of at least 100 pounds per square inch gauge in a reaction zone free from fixed catalyst and packing, the improvement which comprises introducing said reactants into said reaction zone in relative proportions such that a portion of the carbon content of said hydrocarbon liquid is liberated as solid carbon while autogenously maintaining the temperature in said reaction zone within the aforesaid range, said liberated carbon being equivalent to at least 0.5 per cent and not more than 10 per cent of the carbon contained in said hydrocarbon, and withdrawing from said reaction zone an effluent stream of gas comprising carbon monoxide and hydrogen together with said solid carbon from said hydrocarbon.