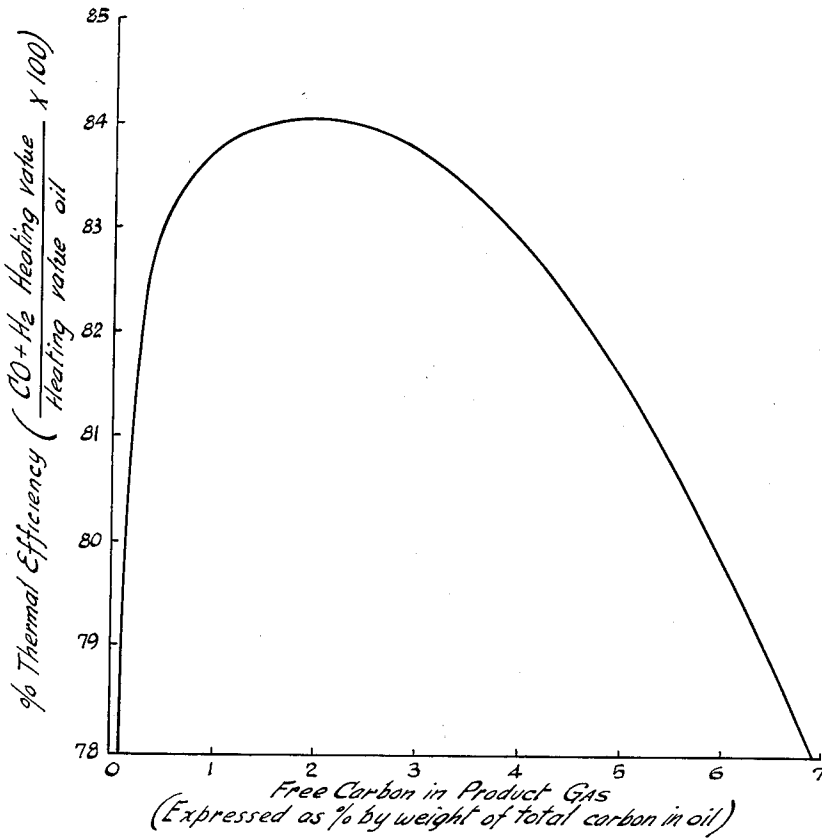


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GENERATION OF CARBON MONOXIDE AND HYDROGEN
FROM A LIQUID HYDROCARBON
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1

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GENERATION OF CARBON MONOXIDE AND HYDROGEN FROM A LIQUID HYDROCARBON

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This invention relates to the production of a gas mixture containing carbon monoxide and hydrogen from a liquid hydrocarbon by partial combustion in a gas generator.

As the result of extensive research and numerous experiments I have found that it is beneficial to operate a gas generator under such conditions that a small critical amount of free carbon is deliberately produced along with the gases.

In the first place, I have found that the life of a gas generating combustion chamber is greatly lengthened when operating in such a way as to produce 0.5 to 10% of free carbon expressed as percent by weight of the total carbon in the oil. This advantage is particularly notable when the oil happens to be one containing compounds of heavy metals which generally have a corrosive or erosive effect on ordinarily refractory materials.

In the second place, within the broad range 0.5 to 10%, there is a narrower range of 0.5 to 5% within which there is obtained the additional advantage of optimum thermal efficiency of the gas generating operation. The best thermal efficiency actually is obtained at a value of about 2% free carbon.

The single figure of the drawing is a graph showing the critical relationship between free carbon production and thermal efficiency in a gas generation process operating with partial combustion of fuel oil.

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 molybdenum 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 1,000 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 generally unsuccessful. The heavy metal con-

2

stituents 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 of 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 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 du Bois 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 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 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 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 percent 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 2,500 to 2,800° 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 B.t.u. 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 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 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 auto-
 genously maintain a temperature in the range of about
 2,200° F. to about 3,200° F. and to convert not less
 than about 90 percent and not more than 99.5 percent
 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
 metals contained in the fuel. The quantity of uncon-
 verted carbon should be at least 50 times and preferably
 100 times the combined weights of the nickel and vana-
 dium contained in the fuels on the basis of the weight
 of the metal content of the metal-containing constituents
 present in the fuel. The 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 a carbo-
 naceous 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
 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 percent oxygen by vol-
 ume 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 gener-
 ator is autogenously maintained within the range of
 2,500 to 2,900° F.

The quantity of free oxygen supplied to the gas gener-
 ator is limited so that the conversion of carbon to car-
 bon oxides is limited to 95 to 99.5 percent of the carbon
 content of the oil feed 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 B.t.u.'s gross heating value
 of the oil feed to the gas generator.

The amount of unconverted carbon released as a car-
 bonaceous 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 scrub-
 bing 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, and is then
 disposed of in a manner other than by burning it in the
 gas generator wherein its metal content would be re-
 leased and damage the generator. The product gas is
 a mixture of carbon monoxide and hydrogen useful as
 feed gas for synthesis of hydrocarbons, methanol syn-
 thesis, 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 ----- API --- 12.8°
 Viscosity ----- S.F. at 122° F --- 650

Flash ----- ° F --- 235
 Pour point ----- ° F --- 50
 Conradson carbon ----- 9.6
 Gross heating value ----- B.t.u./lb --- 18,450

Ultimate analysis:
 Carbon ----- Wt. percent --- 85.5
 Hydrogen ----- do --- 11.0
 Nitrogen ----- do --- 1.0
 Sulfur ----- do --- 1.9
 Oxygen ----- do --- 0.6
 Ash:
 Vanadium ----- p.p.m --- 68
 Nickel ----- do --- 56
 Iron ----- do --- 57

The oil was atomized with steam and mixed with oxygen
 of 99.9 percent 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 2½
 inches of high purity alundum (aluminum oxide) lining
 surrounded by insulating firebrick.

	Example 1— High Carbon Conversion	Example 2— Moderate Carbon Conversion
Feed Rates:		
Oxygen c.f./hr.-----	5,186	12,187
Oil, lbs./hr.-----	401.5	954
Water, lbs./hr.-----	224.1	258
Dry Gas Production, c.f./hr.-----	20,195	47,915
Soot Production:		
Lbs./hr.-----	1.50	15.47
Weight percent of carbon fed.-----	0.44	1.89
Operating Conditions:		
Temperature, ° F.-----	2,600	2,850
Pressure, p.s.i.g.-----	373	341
Preheat temp., ° F.:		
Oil-steam.-----	719	740
Oxygen.-----	67	70
Mols O ₂ /MM B.t.u. of oil fed.-----	1.847	1.824
Product Gas Analysis:		
Dry Basis, mol percent--		
CO.-----	47.0	49.06
CO ₂ .-----	5.5	3.71
H ₂ S.-----	0.1	0.44
CO ₂ S.-----		0.02
H ₂ .-----	47.0	46.51
N ₂ .-----	0.3	0.22
CH ₄ .-----	0.1	0.04
Total.-----	100.00	100.00

After 186 hours of operation under operating condi-
 tions 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 gen-
 erator. The lining was replaced and after about 673
 hours of operation 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 were fed to the generator.
 Some of the fuel oils contained larger amounts of vana-
 dium 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.

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 time.

The improved thermal efficiency from operating with
 deliberate free carbon production is clearly demonstrated
 by the single figure of the drawing, which is a graph based
 on a large number of gas generation runs, the individual

5

6

results of which actually lay on or close to the curve. Data for some of the runs are set forth in Table I below, the principal variable being the amount of carbon produced which varies inversely with the oxygen/oil ratio. All data were accumulated from runs in the same mullite lined autogenously heated synthesis gas generator using Bunker C fuel oil, oxygen and steam, and a generator pressure of 400-450 p.s.i.g.

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

TABLE I

	A	B	C	D	E	F	G	H
Oxygen, Standard Cu. ft./hr.....	6,804	6,707	7,266	6,240	7,612	5,879	7,520	35,200
Oil, lbs/hr.....	503	504.78	560.8	510.6	631.67	492.8	639	2,713
O ₂ /oil, Mol/million B.t.u.....	1.958	1.924	1.88	1.769	1.745	1.727	1.704	1.595
Water, lbs/hr.....	202.58	204.27	326	208	310	198.86	320.5	2,288
CO+H ₂ , Standard Cu. ft./hr.....	23,067	23,516	26,169	24,186	29,754	23,395	29,935	118,874
Generator Temperature, ° F.....	2,499	2,363	2,550	2,163	2,384	2,114	2,603	2,200
Free Carbon in product gas, percent by weight of total carbon in oil.....	0.13	0.24	1.06	2.15	2.83	2.84	4.18	4.5
Thermal efficiency, percent.....	81.16	82.30	83.7	83.90	83.39	84.04	82.60	82.4

The important advantages of improved refractory life (particularly for ceramic materials) and improved thermal efficiency discussed above increase the flexibility of the gas generation process. A wide variety of oils can be employed in the same generator, without having to analyze each oil carefully and make fine adjustments in the conditions of operation dependent upon the metals content or other composition variables.

This application is a continuation-in-part of my abandoned application Serial No. 487,451, filed February 10, 1955 for "Generation Of CO AND H₂ From An Ash-forming Hydrocarbon."

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. 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 catalyst and packing, the improvement which comprises introducing said reactants

the reaction zone gaseous products of reaction and said carbonaceous solid combined with ash from said hydrocarbon.

2. A process as defined in claim 1 wherein at least 90 percent but not more than about 99.5 percent of the carbon contained in said hydrocarbon is converted to carbon oxides and at least 0.5 percent of the carbon contained in said hydrocarbon is liberated as said carbonaceous solid.

3. A process as defined in claim 1 wherein the weight of the carbon liberated as a solid by said reaction is at least 100 times the combined weights of said nickel and vanadium.

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