RESERVE COPY.

PATENT SPECIFICATION

668,941

Date of Application and filing Complete Specification: Feb. 7, 1950.

No. 3162/50.

Application made in United States of America on Dec. 1 1949.

Complete Specification Published: March 26, 1952.

3497

Index at acceptance:—**Classes 55(i),** B(4f: 11: 13); **and 55(ii),** H1o.

COMPLETE SPECIFICATION

Improvements in or relating to Gasification of Carbonaceous Solids

We, STANDARD OIL DEVELOPMENT COMPANY, a corporation duly organized and existing under the laws of the State of Delaware, United States of America, having an office at Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the production of gases from solid carbonaceous material, and specifically to the production of gas mixtures containing carbon monoxide and hydrogen, such as water gas, from such carbonaceous materials as coke and coals.

It has long been known that solid fuel materials, such as coke, coal, and the like, may be converted into more valuable gases which can more easily be handled and more efficiently utilized for a greater variety of purposes. One of the most widely practiced gas-generating conversions is the so-called water-gas process in which solid fuels, such as coal or coke of any origin, are reacted with steam at temperatures of about 1400° to 2000° F. to produce water gas mixtures of carbon monoxide and hydrogen in varying proportions, depending mainly on the time of contact, conversion temperatures, and steam feed rate. The overall water gas reaction being endothermic, heat must be supplied; this is usually accomplished by the combustion of a portion of the carbonaceous feed with an oxidizing gas, such as oxygen, at about 1600°—2400° F. The combustion reaction may be carried out either simultaneously with the water gas reaction or alternately in a make-and-blow fashion.

The water gas process permits the production of gas mixtures of varying composition and B.Th.U content. The process as such, therefore, is suited not only for the production of fuel gases but also for the production of gases for hydrogenation processes and particularly for the catalytic synthesis of hydrocarbons and oxygenated organic compounds from CO and H_2, which process requires H_2:CO ratios, depending on the products desired and reaction conditions to be maintained, varying within limits of about 0.5 to 2.5 or more volumes of H_2 per volume of CO.

The technical utilization of the water gas process, particularly for hydrogenation and for production of synthesis gas, has been impeded by difficulties encountered particularly in heat supply, continuity of operation, and limitations in temperature imposed by low ash fusion or softening points. The problem of continuity of operation has been satisfactorily solved heretofore by the application of the fluid solids technique wherein the carbonaceous charge is reacted in the form of a dense turbulent mass of finely divided solids fluidized by the gaseous reactants and products. Heat is generated either by partial combustion of carbonaceous materials within the gas generator in a so-called single-vessel system or a continuous circulation of suspended solid carbonaceous material to a separate heater in which heat is generated by combustion of the carbonaceous constituents of the residue, and recirculation of the highly heated fluidizable combustion residue to the gas generation zone to supply the heat required therein in a so-called two-vessel system.

The single-vessel system would as such be more desirable than the two-vessel system because the latter requires the circulation of tremendous quantities of solids between the two vessels, a factor which presents serious problems of design and equipment maintenance. However, single-vessel operation involves the disadvantage of product gas dilution with nitrogen and carbon dioxide when air is used as the combustion-supporting gas. Since technically pure oxygen has become available at relatively low cost, nitrogen dilution may be eliminated by the use of oxygen in a commercially feasible opera-

[*Price*

tion. However, carbon dioxide formation remains a problem seriously affecting the practicability of the otherwise preferable single-vessel system. Recent investigations have shown, for example, that in a gasification operation employing 2300 lbs. of powdered coal, 1700 cu. ft. of oxygen and 2000 lbs. of steam per hour to produce 70,000 cu. ft. of water gas, the product gas contains about 16% of CO_2. This carbon dioxide represents a total loss as far as the output of hydrogen or synthesis gas is concerned. The significance of this loss will be appreciated when it is borne in mind that the present methods of synthesis gas production account for about 60% of the cost of synthetic fuel production. Although CO_2 formation may be reduced to a certain extent by adjusting operation conditions, this can be done only at the expense of generator capacity.

In accordance with the present invention, carbon dioxide formation is considerably reduced and even substantially eliminated in water gas generators wherein a mass of finely divided carbonaceous solids in the form of a dense turbulent fluidized bed having a well defined upper level is gasified at an elevated temperature with steam and oxygen, by incorporating in the mass of carbonaceous solids an operative amount of a halide which at the reaction conditions yields halogen and/or a volatile halogen compound.

Alkali metal halides, such as the chlorides, bromides, and fluorides of sodium, potassium, lithium, rubidium, and cesium, or mixtures of such halides are particularly suitable for the purposes of the invention, but alkaline earth metal halides, such as those of barium, calcium, and magnesium, may also be used. Sodium chloride, because of its ready availability and low cost, is the preferred addition agent. Proportions of about 0.01—5%, preferably about 0.05—1%, by weight of alkali metal halide based on the amount of carbon in the solids supplied to the generator, are suitable to depress CO_2 formation from about 15—20% to less than about 5% of the product gas.

While it is not intended to limit the present invention by any theory of the reaction mechanism involved, it is believed that the effect of the addition of halides may be explained as follows. Alkali metal halides, such as NaCl, react with steam in the presence of oxygen at the gas generation temperatures of about 1800°—2000° F., to yield free halogen and/or hydrogen halide and alkali metal oxide and carbonate. Small amounts of halogen or volatile halogen compounds are known to suppress the formation of CO_2 in favor of an exclusive formation of CO in the combustion of carbonaceous materials. Since CO_2 formation in the water gas generator is largely due to a complete combustion of carbon to CO_2, the halogen or halogen halide supplied by the alkali metal halide will act to suppress CO_2 formation in the water gas reaction.

It will be appreciated from the foregoing that the addition of halides in accordance with the invention has nothing in common, regarding its purpose and effect, with the known addition of such agents catalyzing the water gas reaction as alkali metal carbonates, nickel, heavy metal oxides or sulfides, etc., or mixtures thereof which have no inhibiting effect on the formation of CO_2. It is, however, a particular advantage of the present invention that such catalytic agents as alkali metal oxides or carbonates are formed as the solid residue of the liberation of halogen or hydrogen halide. As a result of this secondary catalytic effect, the gasification temperature may be substantially reduced and the CO content of the product gas considerably increased. The latter effect is due mainly to an acceleration of the reaction

$$C + CO_2 \rightarrow 2CO$$

which may be very appreciable at Na_2CO_3 concentrations as low as 0.01%, as has been shown by other researchers.

In accordance with the preferred embodiment of the invention, the alkali metal halide to be added is introduced into the gas generator by the injection of, or the impregnation of the carbonaceous charge with natural brines containing the desired halide, for example sea water. The alkali metal oxide or carbonate remaining on the gasification residue may be recovered as the corresponding hydroxide or carbonate by an aqueous extraction of the gasification residue. The aqueous extract may be used as a scrubbing solution to remove any excess halogen from the product gases, if desirable. The halide salt content of the used scrubbing solution may be reutilized in the process as a carrier of alkali metal halide to be added to the generator in accordance with the basic principle of the invention. In some cases, it may also be desirable to pass a certain quantity of halogen with the gas produced to a synthesis stage in order to promote a selectivity more favorable to certain desired products, increased unsaturation of synthetic products, or to control the

H_2/CO consumption ratio of the synthesis reaction.

The fluidized solids technique employed according to the invention is beneficial because of its superior characteristics of gas-solids and solids-solids contact and its improved heat transfer characteristics, which greatly enhance the inhibiting and catalytic effects of the addition agents of the invention. The fluidized system employed is illustrated in the accompanying drawing, the single figure of which depicts schematically an expanded flow plan of the process.

Referring now to the drawing, the system shown consists essentially of a conventional fluid-type water gas generator 10 and metal halide recovering equipment 30 and 40, the functions and cooperation of which will be forthwith described using the gasification of a low temperature coke in the presence of NaCl as an example. It should be understood, however, that the system may be operated in a similar manner for the gasification of other carbonaceous solids, such as various coals, in the presence of other suitable halides.

In operation, fresh coke ground to a particle size passing 4 mesh with a major proportion passing 60 mesh per linear inch is fed from a feed hopper, preferably a lock hopper 1, into a standpipe or other conveying means 3 into generator 10. The coke may be preheated to temperatures of about 400°—800° F. in hopper 1 by means of product gases passed therethrough via lines 6 and 8, or in any other conventional means. Sea water is introduced through line 5 into standpipe 3 in amounts sufficient to introduce into the coke about 0.05—1% by weight of NaCl, based on the amount of carbon in the coke supplied to the generator. About 25—100 gals. of sea water per ton of coke passing through standpipe 3 are normally adequate for this purpose. If the coke is preheated as described, the sea water evaporates quickly in the standpipe and the steam so generated acts as an aerating agent.

Simultaneously, a mixture of steam and O_2 in a ratio of about 700—1800 lbs. of steam per 1000 cu. ft. of O_2 is supplied from lines 12 and 14, respectively, through a distributing device such as grid 16. About 1000—1500 cu. ft. of oxygen and about 700—2400 lbs. of steam per ton of coke are normally sufficient to support the water gas reaction in the presence of NaCl at temperatures of about 1700°—1800° F. In the absence of NaCl, the steam and oxygen consumption are somewhat higher for the production of a gas of comparable composition, and the process is much more sensitive to variations in the concentration of these reactants than one employing the alkali halide additive. Reactor 10 should be so designed that at the solids and gas feed rates involved a linear superficial gas velocity of about 0.5—1.5 ft. per second is maintained in reactor 10, at which its contents are converted into a highly turbulent fluidized mass M_{10} having an upper interface L_{10} and an apparent density of about 20—40 lbs. per cu. ft.

A dilute solids-in-gas suspension is withdrawn overhead from level L_{10} and passed through a gas-solids separator, such as cyclone 18, from which separated fines may be returned to mass M_{10} via dip-pipe 20. Product gas substantially free of solids is withdrawn through line 22. This gas, at the conditions specified, may have a composition about as follows:

	Vol. %
H_2	40 to 45
CO	40 to 59
CO_2	<5
Total Cl (Free and Combined)	<0.5
N_2	1 to 4
Other Impurities	0 to 5

Any desired portion of the product gas may be heat exchanged with fresh coke in hopper 1 via lines 6 and 8 as above described. The total gas effluent in line 22 may then be further cooled in heat exchange with feed gases and/or other media in a heat exchange and cooling system 24 to be passed through line 26 to a scrubber 30 at a temperature of about 60° to 200° F.

Returning now to generator 10, solid gasification residue is withdrawn through line 35 and passed to an extractor 40. Sea water may be supplied through line 42 to extractor 40 in amounts adequate to extract the soda content of the ash. All or part of the sea water to be supplied to line 5 may be used for this purpose. Extracted ash may be discarded via line 44. Enriched sea water is passed through line 46 to scrubber 30 wherein it is used to remove chlorine and its compounds from the product gas in a manner obvious to those skilled in the art. Sea water which may now contain NaCl somewhat above its normal concentration may be returned via line 48 to feed line 5. The product gas recovered from scrubber 30 through line 50 is now substantially free of halogen and is ready as a feed gas to a conventional hydrocarbon synthesis or other hydrogenation unit, if desired after further desulfurization by conventional means. However, scrubber 30 may also be so operated that a substantial proportion of the sulfur content of the product gas is absorbed therein.

What we claim is:—

1. A process for the production of gas mixtures containing carbon monoxide and hydrogen which comprises passing a gas mixture containing steam and oxygen upwardly through a mass of finely divided carbonaceous material maintained in a gasification zone at an elevated temperature and in the form of a dense turbulent fluidized bed having a well defined upper level, wherein there is incorporated in said mass a halide yielding elemental halogen and/or volatile halogen compounds under the prevailing reaction conditions, said halide being employed in an amount sufficient to inhibit the formation of CO_2 in favour of CO formation.

2. A process according to Claim 1, wherein said halide is employed in an amount of from 0.01—5% by weight, preferably 0.05 to 1%, based on the amount of carbon present in the carbonaceous material in the gasification zone.

3. A process according to Claim 1 or 2, wherein said halide is an alkali metal halide, preferably sodium chloride.

4. A process according to any one of Claims 1—3, wherein said halide is added to said material prior to the gasification reaction.

5. A process according to Claim 4, wherein said halide is added in the form of a natural halide brine, preferably sea water.

6. A process according to any one of Claims 1—5, wherein solid gasification residue withdrawn from the gasification zone is extracted with an aqueous medium to form a solution containing the cation of said halide.

7. A process according to Claim 6, wherein the product gas mixture is scrubbed with said solution to remove therefrom at least a substantial portion of its halogen content.

8. A process according to Claim 7, wherein the halide dissolved by the scrubbing solution is reused in the process.

9. A process according to Claims 1 or 2, wherein said halide is an alkaline earth meatl halide.

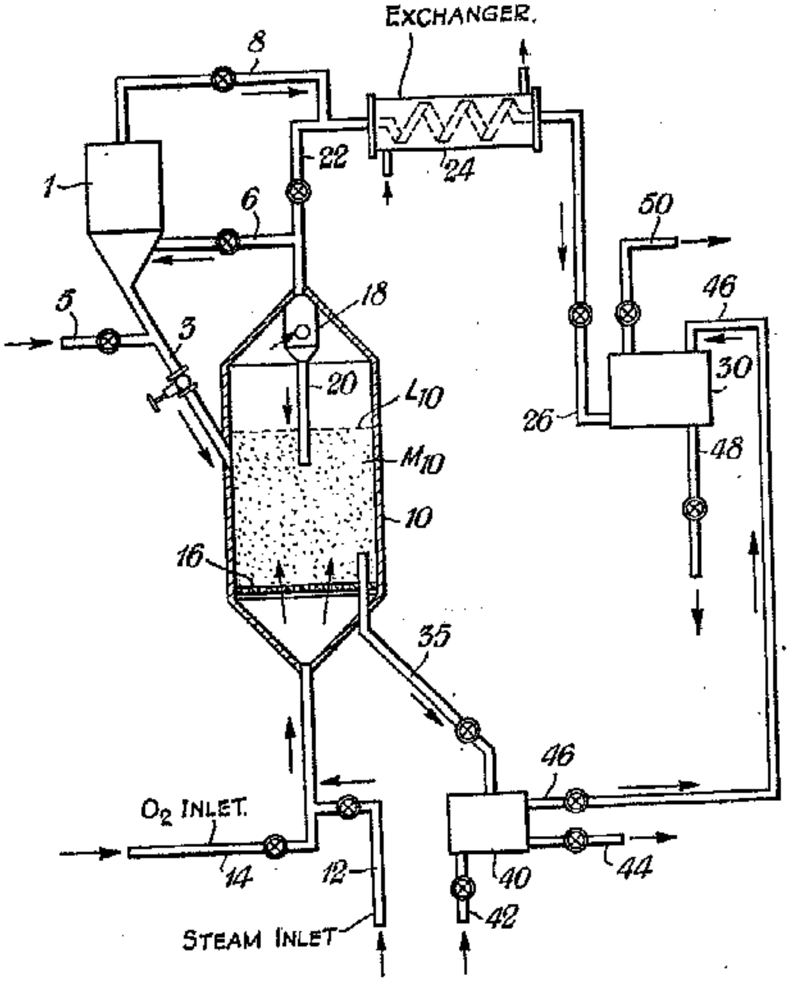
10. A process according to Claim 9, wherein said halide is a halide of barium, calcium or magnesium.

D. YOUNG & CO.,
29, Southampton Buildings,
Chancery Lane, London, W.C.2,
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—11/52.
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which copies may be obtained.

668,941 COMPLETE SPECIFICATION 1 SHEET

This Drawing is a reproduction of the Original on a reduced scale



H.M.S.O. (M.F.P.)