GASIFICATION OF FUELS AND DECOMPOSITION OF GASES

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Filed July 31, 1956, Ser. No. 601,245

Claims priority, application Germany Aug. 11, 1955

1 Claim. (Cl. 48—216)

The present invention relates to an improved process for the gasification of fuels and decomposition of gases. In the process of gasifying fuels carried out in a molten slag bath which is circulated by the kinetic energy of the gasifying agents and, if desired, the fuel introduced into the slag bath, it is known that the slag promotes and accelerates the gasification reaction not only as heat transfer agent but also as reaction medium, since the fuel and gasifying agents alternatively react with substrates of the slag, thus creating a broader basis for the gasification reaction.

In accordance with the invention, it has been found that in the gasification of fuels and decomposition of gases by means of a slag bath recirculated by the kinetic energy of gasifying agents and/or the substances to be reacted introduced into the slag bath, the constituents of the slag bath can be more fully utilized for the performance of the reaction by using said constituents as carrier for the gasifying agents and/or for decomposing the gases or vapors.

The gasification and decomposition reaction according to the invention as well as the advantages of the new process will become clearer from the following description.

By contacting at high temperature liquid slag containing iron oxide and a fuel containing carbon, the iron oxide is reacted according to the equations:

\[ 3\text{Fe}_{2}O_{3} + C = 2\text{Fe}_{3}O_{4} + \text{CO} \] (1)
\[ 2\text{Fe}_{3}O_{4} + 2\text{C} = 6\text{FeO} + 2\text{CO} \] (2)

If the carbon present in a larger proportion the ferrous oxide is converted to iron by complete reduction:

\[ \text{FeO} + \text{C} = \text{Fe} + \text{CO} \] (3)

By the interaction of oxygen, for instance atmospheric oxygen, the reduction steps of iron oxide may occur at high temperatures in the reversed order, i.e., according to the following equations:

\[ 6\text{FeO} + 3\text{O}_{2} = 6\text{FeO}_{3} \] (4)
\[ 6\text{FeO} + 3\text{O}_{2} = 2\text{Fe}_{3}O_{4} \] (5)
\[ 2\text{Fe}_{3}O_{4} + \frac{1}{2}\text{O}_{2} = 3\text{Fe}_{2}O_{3} \] (6)

In this way, the iron oxide can be used again in the gasification of the carbon contained in fuels to form CO. In general, the gasification of fuels will not be conducted as far as to completely reduce the iron oxide to metallic iron, but will be carried out to obtain a slag between FeO and FeO.

Upon introducing steam into the reduced slag, the following reactions between the iron oxides and steam may occur:

\[ \text{FeO} + \text{H}_{2}O = \text{FeO} + \text{H}_{2} \] (7)
\[ 3\text{FeO} + \text{H}_{2}O = 2\text{Fe}_{2}O_{3} + \text{H}_{2} \] (8)
\[ 2\text{FeO} + \text{H}_{2}O = 3\text{FeO}_{2} + \text{H}_{2} \] (9)

If the Reactions 1–3 are combined with Reactions 7–9,

\[ \text{CO} + \text{H}_{2}O = \text{CO}_{2} + \text{H}_{2} \] (10)

5 proceeds as side reaction.

Methane may be reacted, for instance, with iron oxide at high temperature according to the following equation:

\[ 3\text{Fe}_{2}O_{3} + CH_{4} = 2\text{Fe}_{2}O_{4} + \text{CO} + 3\text{H}_{2} \]
\[ 2\text{Fe}_{3}O_{4} + 2\text{CH}_{4} = 6\text{FeO} + 2\text{CO} + 4\text{H}_{2} \]

The resultant ferrous oxide may be reoxidized with oxygen, for instance atmospheric oxygen, to iron oxide, principally similar to the reaction of methane proceeds the process using higher hydrocarbons, but the reaction process involves certain difficulties. If care is taken that the times of contact between the hydrocarbons and iron oxides are short and the gaseous products are rapidly discharged from the influent sphere of the iron oxide with subsequent rapid cooling, the reaction taking place between the fuels, which are initially split into lower hydrocarbons by heating, and the iron oxide proceeds only incompletely and gases result the calorific value of which may be adjusted within wide limits. If the times of contact are very short and the gases are rapidly cooled, unsaturated hydrocarbons are obtained besides small amounts of carbon monoxide and hydrogen.

Other oxides likewise react in a manner similar to iron oxide. In some cases it may be advantageous to use pure oxide melts to carry out the process of the invention. For this purpose, naturally occurring minerals or synthetically produced oxides may be used; alternatively, the oxides are produced from the fuels by the action of oxygen, for instance atmospheric oxygen, at high temperatures. Impurities of such oxides are mostly negligible, since they usually react neutral in the melt. Because of the ready availability and low cost, slag of solid fuels which always contains oxides reacting with the fuels to be reacted and gasifying agents, will generally be used. Besides, slags which are obtained for instance by smelting ores may be suitable for the purpose of the invention. By adapting the process of the invention the gasification of solid fuels yielding slag can be accomplished most simply. In case reactive oxides are present in the slag formed from solid fuels or in foreign slags at low concentration only, this deficiency can be cured by adding reactive oxides. If the melting point and/or the viscosity of the slag are too high, substances conventionally used for reducing same may be added to adjust said properties within desired limits. By continuing the reaction of the oxides with fuel, carbides result for instance according to the equation:

\[ \text{CaO} + 3\text{C} = \text{CaC}_{2} + \text{CO} \]

Calcium carbide reacts with steam at high temperatures:

\[ \text{CaC}_{2} + 3\text{H}_{2}O = 2\text{CO} + 3\text{H}_{2} \]
\[ \text{CaC}_{2} + 5\text{H}_{2}O = 2\text{CO} + 5\text{H}_{2} \]

At low temperatures, say about 100° to 300° C, steam is converted to acetylene via calcium carbide:

\[ \text{CaC}_{2} + \text{H}_{2}O = \text{CaO} + \text{C}_{2}\text{H}_{2} \]

Thus the invention offers the possibility of producing acetylene by the action of steam, by allowing the continuously freshly formed slag to run off and cooling same to 100–300° C. The reacted slag may be returned to the slag bath. The advantage of this process consists for instance in that the slag may contain other substances, for instance silicate acid and calcium oxide, which substances reduce the melting point and viscosity of the slag.

The process of the invention may be carried out continuously or discontinuously.

In the discontinuous performance, the slag is heated to high temperature with simultaneous oxidation of the
oxides contained in the slag. Thereupon, heating is stopped and the substances to be gasified or reacted are introduced into the slag containing oxygen. While the slag is reduced and cooled down, reaction of the slag proceeds in the desired direction. The reaction products are removed. Thereupon the slag is blown hot again and the aforesaid process is repeated.

In the continuous performance of the process, the slag circulates between two or more compartments which are divided from one another by gas-tight partitions. As a rule, the oxidation process is conducted in one compartment while the slag is simultaneously heated up therein, and the reduction processes proceed in the second or in the other compartments. The resulting gaseous or vaporous products are led off from the compartments separately.

The intimate mixing of the slag with the substances reacting therewith is achieved by the kinetic energy of said substances. The substances to be reacted with the slag are blown into the slag bath at high velocity, whereby an intimate contact is effected between the reactants, and the kinetic energy of said substances is transferred for the most part to the slag which foams up like a boiling fluid and is set into a vivacious and turbulent motion.

The substances reacting with the slag or with constituents of the slag may be introduced into the slag bath through the bottom or the boundary side walls of the slag bath or through inlet means positioned above the surface level of the slag bath. The arrangement of the inlet means is so chosen that the slag is set into a substantially circulating motion.

In the continuous process, the kinetic flux transferred by the manner of introducing the substances reacting with the slag is adjusted in such a manner that the slag is caused to flow between the individual compartments at appropriate velocities. Besides, care is taken that the processes taking place in the individual compartments proceed completely and that residues of gaseous reaction products are not carried along with the slag into the other reaction chamber.

It is of advantage to preheat to high temperature the slag, especially the gaseous reactants, such as air, oxygen, oxygen-enriched air, steam, carbon dioxide, and hydrocarbons. Preheating is preferably carried out by heat exchange with the produced gases which leave the reaction chamber at high temperature.

In the gasification of ash-containing fuels, fresh ash is continuously formed and may be removed in known manner either continuously or discontinuously. Any resultant by-products for instance metals formed by reduction of metal oxides contained in the slag, are discharged in liquid form.

The slag bath is placed in one or more bodies lined with heat-insulating material which is resistant to the slag. If slag-resistant material is not available, the walls of the body are cooled in known manner to form therein a solid layer of slag crust which prevents an excessive dissipation of heat by the cooling means. It may be of advantage to use bodies lined with refractory material and to additionally provide a layer of slag crust on the walls by cooling.

The heat dissipated through the walls and by the slag running off, as well as the sensible heat of the produced gaseous or/vaporous products as far as not used to preheat the gasifying agents or reactants, is preferably utilized to a substantial extent, for instance, for producing high-pressure steam.

In accordance with the invention, the slag or constituents contained therein are used as gasifying agent which carries only that substance (for instance, oxygen for the gasification or reaction of substances) with which the desired gaseous or vaporous reaction products are produced. It is however within the scope of the invention to employ gaseous or vaporous gasifying or reaction agents if gas mixtures of predetermined composition are to be obtained. In the latter case, gasification or reaction of the substances is not effected by the slag alone.

In some cases where foreign substances in the slag are not desired, the said substances can be removed during the process immediately, for instance, by vaporizing them at high temperature, e.g. alkalis, or reducing them to metals which separate from the slag because of their higher specific gravity and are obtained as by-product, e.g. iron.

The gasification or decomposition reactions according to the invention may be carried out at atmospheric pressure, but superatmospheric pressures may also be applied if these involve advantages. As is known, the equilibrium position of a number of reactions is influenced by only by the temperature but also by the pressure applied, so that the application of a higher or lower pressure than the atmospheric pressure is helpful in specific cases.

The execution of the process of the invention shall be more fully explained by way of two specific examples which are given to illustrate the invention without restricting the same in any way.

In the process described in Example 1, the slag containing iron oxide is used as oxygen-transmitting agent for producing water gas, while Example 2 describes the production and use of calcium carbide containing slag for producing carbon monoxide and acetylene.

**Example 1**

Open-burning coal having an ash-content of about 17.2% is used to produce water gas being free of oxygen, the slag serving as gasifying agent. The slag of the coal contains 20% of iron oxide. Between a combustion chamber and a gasification chamber, a slag bath which is common to both chambers is recirculated by the kinetic force of air introduced into the combustion chamber. The slag bath was produced by burning coal and melting slag, and heated to a temperature of 1700° C. Upon introducing 1 kg of coal per 75 kg of the circulating slag contained in the gasification chamber, 1.652 Nm³ of water gas are obtained in the hot slag by destructive distillation of the coal and gasification of the resulting fuel residue by reduction of about 50% of the iron oxide contained in the slag to ferrous oxide. The water gas obtained has the following composition:

<table>
<thead>
<tr>
<th>Percent</th>
<th>CO₂</th>
<th>CO</th>
<th>H₂</th>
<th>N₂</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>5.0</td>
<td>68.3</td>
<td>25.6</td>
<td>1.1</td>
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During the destructive distillation and gasification process, the slag has cooled to 1560° C, and enters at this temperature the combustion chamber. By blowing into the combustion chamber 3.53 Nm³ of air heated to 800° C and 0.13 kg of coal, referred to 1 kg, each of coal introduced into the gasification chamber, the iron oxides previously reduced in the slag are reoxidized and the coal is burnt, whereby the slag is heated up again to a temperature of 1700° C. The slag runs off through an overflow provided in the combustion chamber at the rate fresh slag is formed by the gasification and combustion of coal. After the slag heated to 1700° C. has entered the gasification chamber, the aforesaid process is repeated.

The produced water gas, the sensible heat of which may be utilized to generate steam, is lead off from the gasification chamber. After cooling and purifying in known manner, the gas may be utilized for any desired application. The hot flue gas formed in the combustion chamber is used for the air oxidation of the coal introduced into the gasification chamber, the air used for generating steam may be applied for other purposes, for instance for drying coal.

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This example describes the production of carbon monoxide and acetylene from fine-grained or powdery coke of Rhenish brown coal having an ash-content of about 15%. The accompanying diagrammatic drawing shows in side elevation an apparatus which may be used to carry out the process of this example.

The ash of the coke contains about 50% of calcium oxide and 15% of iron oxide. Into the slag bath 1 produced by melting the ash of the coke, there are introduced coke through pipes 2 and oxygen through pipes 3. Pull 8. The coke evolves carbon monoxide with liberation of heat. Another portion of the coke reacts with the calcium oxide with the formation of calcium carbide and carbon monoxide with heat absorption. Finally, coke reacts with the oxide in the slag under strongly reducing atmosphere in the slag bath with the formation of raw steel and carbon monoxide. Because of its high specific gravity, the raw steel deposits on the bottom of the slag bath and is discharged, continuously or discontinuously, through the tap hole 4. The calcium carbide formed from the calcium oxide of the ash runs off through overflow 5 together with the other ash constituents reacting neutral, for instance silicon oxide. The carbon monoxide gas and the constituents of the slag vaporizing up to a temperature of about 1800-1900° C., for instance alkalies, are lead from the reaction chamber 6 through pipe 7 to a conventional cooling and purifying plant.

The heat required for the endothermic reaction producing calcium carbide and in the reduction of iron oxide is supplied by the heat evolved in the exothermic reaction of coke gasified with oxygen.

The calcium carbide-containing slag which runs off is cooled and comminuted to small particles by the crusher mill 8. The slag drops into bunker 9 where it is cooled to about 100° C. by cooling means. The bucket wheel 10 feeds the slag to a conveyor mechanism of known construction which drops the slag into the bunker 12. Via bucket wheel 13 and conveyor screw 14, the slag is passed into the acetylene generator 15 wherein the slag is subjected in a fluidized state to the action of steam. The steam enters the fluidization bed beneath the grate 18 through pipe 17 and streams through the eddy in uniform distribution. The steam reacts in known manner with the calcium carbide of the slag to form acetylene which leaves the generator through pipe 19. Any slag droplets dragged along are separated in cyclone 20 and fall into bunker 21. The acetylene gas passes pipe 22 to a cooling and purifying plant (not shown in the drawing). Since the reaction in the acetylene generator proceeds exothermally, cooling means are provided to remove the heat of reaction or part thereof. Besides, the heat of reaction may be absorbed, wholly or in part, by an excess of steam or by introducing additional cold slag into the fluidization bed. The mixture of acetylene and water vapor and the fluidization bed reach a temperature of at most 300° C.

The slag reacted in the fluidization bed runs off into bunker 23; the slag collected in bunker 21 is likewise delivered to bunker 23 by means of the bucket wheel 24. The slag collected in bunker 23 is continuously removed by the bucket wheel 25 and part thereof pneumatically returned to the slag bath 1 through pipe 26. Only the excess formed by formation of fresh slag from the ash of the coke is removed from the cycle.

The proportion of calcium carbide contained in the slag introduced into the acetylene generator amounts to about 50%. The balance substantially consists of calcium oxide and siliceous acid reducing the viscosity of the slag. The temperature in the gasifier 6 is about 1700-1900° C.

By the process of this example, 1,420 Nm. 3 of carbon monoxide having a low content of carbon dioxide and hydrogen as well as 92 kg. of acetylene are obtained from one ton of brown coal coke and 670 Nm. 3 of oxygen. As by-products there are obtained about 16 kg. of raw steel by reduction of the iron oxide of the fuel ash, and 1.3 tons of steam (80 atm., 450° C.) by utilizing the waste heat.

In the same manner, water gas and acetylene may be produced from dry brown coal. If the process is carried out with fuel yielding ash which has a low content of lime only, any desired composition of the resulting slag can be adjusted by addition of lime.

A particular advantage of the process according to the invention for the production of acetylene consists in that high-percentage calcium carbide is not required. The melting point and the viscosity of the slag formed are reduced by the accompanying substances of the ash; this allows of carrying out the herein described process at temperatures lower than those to be applied in the manufacture of calcium carbide in the electric furnace.

It is of course within the scope of the invention to form a slag which is rich in calcium carbide and to carry out the production of acetylene in separate generators of known construction by introducing water.

I claim:

In a process of producing gas by the reaction of a carbonaceous fuel in a circular molten slag bath wherein a combustion agent and an excess of said fuel are tangentially introduced in said slag bath with sufficient velocity to create violent turbulence, said bath containing a reducible metal oxide as a donor for oxygen to form gaseous carbon oxide with the carbon of said excess of fuel, the improvement which comprises introducing in said slag bath calcium oxide as said donor, circulating said calcium oxide in the slag bath to effect the reduction of the oxide to the calcium carbide, withdrawing from said slag bath the produced gas and the calcium carbide, treating said carbide with steam in a separate reaction zone to reoxidize said calcium carbide whereby acetylene is also formed, and returning the thus obtained calcium oxide to the slag bath.

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