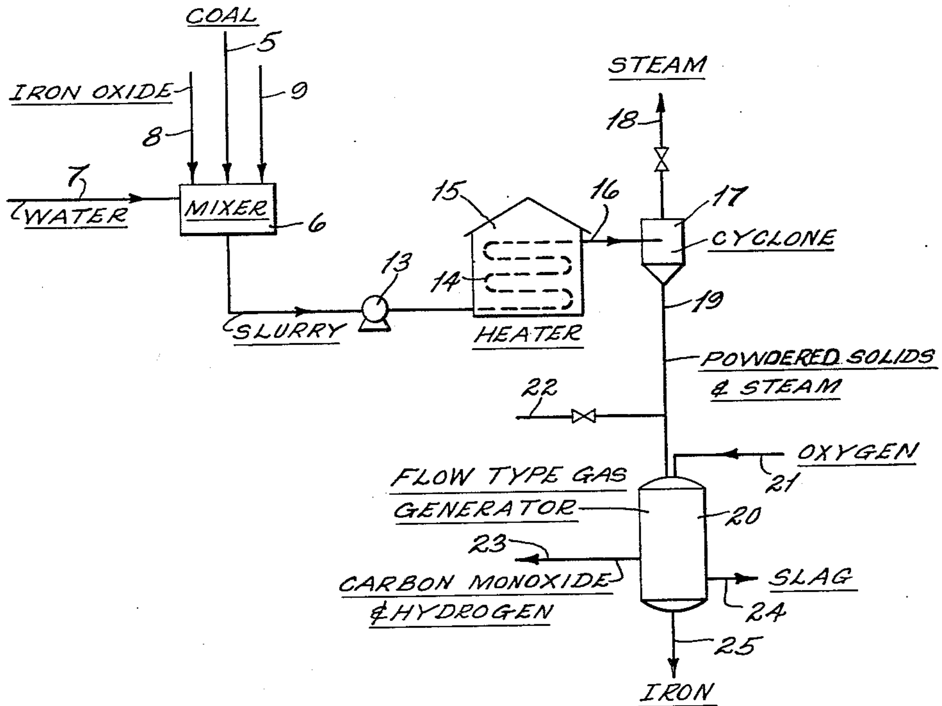
Feb. 15, 1955 H. V. REES ET AL 2,702,240

REDUCTION OF METAL OXIDES

Filed Feb. 8, 1951



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United States Patent Office

2,702,240

Patented Feb. 15, 1955

2,702,240

REDUCTION OF METAL OXIDES

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Application February 8, 1951, Serial No. 210,068

7 Claims. (Cl. 75—26)

This invention relates to a process for the reduction of a metal oxide with a carbonaceous fuel and the simultaneous production of carbon monoxide and hydrogen. In one of its more specific aspects, this invention relates to a process for the simultaneous reduction of an iron oxide to metallic iron and the partial oxidation of a solid carbonaceous fuel to carbon monoxide and hydrogen. Hydrocarbon gas, oil, coke, and various coals including lignite, anthracite, and bituminous coals are suitable as fuels for the process of this invention.

In the process of the present invention, a reducible metal oxide in powdered form is dispersed in an oxygen-containing gas and interacted with oxygen and a carbonaceous fuel at a temperature above 2,000° F. The particles of solid reactants are dispersed in gaseous reactants and reaction products in the reaction zone. Reduction of the metal oxide releases oxygen for oxidation of carbon from the fuel. Free oxygen is added in an amount sufficient to supply the necessary heat for the reaction with the simultaneous production of carbon monoxide. The reduction product of the metal oxide, e. g., the metal, is removed from the generator, generally in molten form. Gaseous products of reaction comprising carbon monoxide and hydrogen are also formed and may be recovered for fuel or as feed gas for chemical processes.

The present invention is particularly suited to the production of pig iron from iron ore and coal and the simultaneous gasification of coal by reaction with steam and oxygen to produce carbon monoxide and hydrogen. A flow-type gas generator of the type employed for the gasification of coal with steam and oxygen is used in the present process. Such a generator is disclosed on the co-pending application of Du Bois Eastman, Serial No. 105,985, filed July 21, 1949.

The flow-type generator is characterized by the reaction of a gaseous dispersion of solid fuel in powder form with oxygen and steam in an unpacked and unobstructed reaction zone. It is important that the reaction zone be compact, presenting a relatively small amount of surface in comparison with its volume and that it be designed to minimize heat losses by radiation. It is preferable to arrange the inlet and outlet of the reaction zone relative to one another such that the reactants and reaction products flow substantially uniformly through the reaction zone, for example, as by introducing the reactants at or near one end and withdrawing reaction products at or near the other.

The reaction zone preferably is generally cylindrical in shape with an internal surface area not greater than about one and one-half times the surface of a sphere of equal volume. Openings and "black body" surfaces are kept at a minimum to prevent loss of radiant heat from the reaction space. Free transfer of heat by radiation is achieved in this type reaction vessel so that the entire reaction zone operates essentially at a single uniform temperature. The quantity of solid fuel supplied to the generator is just sufficient to react with the steam and oxygen present therein so that the fuel is almost completely consumed. In this way, the flow-type generator distinguishes materially from gasifiers employing a stationary, moving, or dense phase fluidized bed of solid fuel.

For most successful operation of a generator of this type for the production of carbon monoxide, the temperature throughout the generator must be maintained within the range of from about 2,000° F. to about 3,000° F., or higher. Practical considerations, especially apparatus limitations, usually limit the maximum operating temperature to about 2,600° F. At these temperatures, the slag from the fuel and metal oxide, if present, are molten and fluid.

In a co-pending application of Du Bois Eastman and Leon P. Gaucher, Serial No. 49,626, filed September 16, 1948, a novel process for heating and pulverizing carbonaceous solids is disclosed. In accordance with the method disclosed in said application, particles of a solid carbonaceous material, particularly coal, are admixed with a liquid to form a suspension and the suspension passed as a continuous stream in turbulent flow through a heating zone comprising an externally heated conduit. The slurry is heated in the heating zone to an elevated temperature sufficient to vaporize the liquid, thereby suspending the solid particles in vapor and preheating the solid. The heating and turbulent flow at relatively high velocity through the heating zone results in appreciable disintegration of the solid particles. Particles having average diameters less than 40 microns, and even less than one micron, may be economically produced by this method. This novel step of heating and pulverizing solid carbonaceous material is preferably employed in connection with the present process. Either the fuel or the metal oxide, or both, may be supplied to the generator by this means.

In accordance with one embodiment of the present invention, a reducible metal oxide, e. g., iron oxide, is admixed with coal and water to form a slurry. The slurry is passed through a tubular heating zone as a continuous stream. The slurry is heated in the heating zone to a temperature at least sufficient to vaporize the water. Vaporization of the water to steam results in a great increase in volume which in turn greatly increases the velocity in flow of the stream. The solid particles are suspended in the stream of steam and are subjected to the disintegrating action of both the vaporization and the highly turbulent flow of the confined stream of steam. The mixture of powdered solids is passed into admixture with oxygen in a flow-type generator maintained at a temperature above about 2,000° F. All of the steam may be passed to the generator or part or all of the steam may be separated from the dispersion.

Oxygen from the metal oxide enters into reaction with a portion of the carbon from the fuel to produce carbon oxides. Additional oxygen is supplied in uncombined form in an oxygen-containing gas stream, preferably with a high concentration of free oxygen, to provide the amount necessary to maintain the reaction temperature. The total oxygen supplied to the reactor, as both free and available combined oxygen, relative to the carbon in the fuel may be expressed as the O/C ratio where O represents pound atoms of oxygen, and C, the pound atoms of carbon. Generally, the total oxygen necessary to supply the heat requirements of the process will be considerably in excess of the amount theoretically required to convert all of the carbon to carbon monoxide. The total O/C ratios may vary from about 1.05 to about 2.0, depending upon the relative amounts of fuel and metal oxide supplied to the generator.

Suitable metal oxides include the oxides of iron, copper, vanadium and barium. The reduction product may be reconverted to the desired metal oxide or utilized as a product of the process. Barium peroxide, for example, is readily converted to barium oxide and is easily reconverted to the peroxide.

The reduction product of the metal oxide, i. e., either metal or a lower metal oxide, may be removed from the generator either as solid particles entrained in the product gases, or withdrawn separately in molten form. With an iron oxide, or iron ore, as the metal oxide, it is preferable to operate the generator at a temperature on the order of 2,500° F. or higher and to draw off both iron and slag in molten form, as in blast furnace operations.

The generator pressure may vary from atmospheric pressure to an elevated pressure on the order of 500 pounds per square inch gauge, or higher. Limitations imposed by structural materials and the high temperatures required, will determine the allowable operating pressure.

The quantity of liquid admixed with the solid to form a fluid slurry may vary considerably. A minimum of about 35 per cent liquid by volume is required, based upon the apparent volume of the granular solid. The slurry may be readily pumped with suitable equipment, for example, with a piston pump of the type commonly used for handling drilling mud in oil well drilling operations.

The solid feed material need be reduced only to a particle size such that it may be readily handled as a suspension or a slurry. It is preferable to use particles smaller than about ¼ inch in average diameter; particles of 100 mesh size and smaller are more readily handled as a slurry. In general, satisfactory slurry preparation may be obtained with a composite mixture of particles smaller than ¼ inch in size, the bulk of which comprises particles within the range of from about ¼ inch to 200 mesh.

The suspension is heated by passing it through an elongated externally heated zone of restricted cross-sectional area. The heating may be most effectively carried out in a pipe still type furnace such as those commonly used for heating liquid streams in the refining of petroleum. The suspension is fed into the heated tube at a rate sufficient to prevent settling out of the solid particles. The linear velocity of slurry at the inlet to the heating tube should generally be within the range of from about ½ to 10 feet per second, suitably about 1 foot per second. The velocity of gaseous dispersion of powdered coal and vapor, e. g., at the outlet of the tube, is within the range of from about 25 to about 2000 feet per second, suitably about 300 feet per second. Higher velocities may be used.

Pressure, in itself, is not critical in the heating step. The temperature and pressure relationships effecting vaporization are well known. The pressure may be coordinated with associated processes. Generally, it is desirable to maintain the pressure at a low value, particularly in that portion of the tubing in which the carrier liquid exists as a vapor to provide large vapor volume and high velocity.

The coarser particles of solid may be separated from the vaporous dispersion and returned to the slurry preparation step for further pulverization. Separation of the coarser particles may be accomplished, for example, by a classifier, forming no part of this invention. Optionally, powdered solid may be recycled to the slurry feed make-up step as an aid in the preparation of a fluid suspension. The recycled particles, being finer than the feed particles, serve as a filler or "weighting" material to more readily suspend the larger fixed particles.

A potassium salt, preferably potassium carbonate, may be added to the slurry to increase the rate of burning of solid carbonaceous fuel and fluxing of the ash and slag in the generator.

A portion of the free oxygen, preferably a minor amount, may be added to the slurry charged to the heating zone. Some reaction may take place between the oxygen or metal oxide and the solid carbonaceous fuel in the heating zone. This reaction increases the temperature in the heating zone and aids in the disintegration of the solid materials.

A flux may be used to reduce the fusion temperature of the slag or to render it more fluid. Lime is generally suitable as the flux, where one is indicated, although with some coals it may be desirable to add fluorite, silica or alumina to increase the quantity or fluidity of the slag. The addition of lime to the generator not only increases fluidity of the slag and decreases the fluxing temperature but also effects removal of at least a portion of the hydrogen sulfide from the product gas stream from feed materials containing sulfur. The amount of lime required as flux may be determined from the composition of the iron ore and coal ash as is known in the blast furnace art. In general, the most satisfactory fusion is obtained when the sum of the lime and magnesia in the feed is approximately equal in weight to the sum of the silica and alumina. The lime and magnesia may be added in the form of the carbonates, but should be converted to equivalent quantities of the oxides in determining the quantity of flux required.

Oxygen-enriched air or commercially pure oxygen may be used in the process. Commercially pure oxygen is preferred, especially for the generation of gases free from nitrogen, e. g., hydrocarbon synthesis feed gas. In the generation of gas for ammonia synthesis, it may be desirable to use oxygen-enriched air.

The invention will be more readily understood from the accompanying drawings and the following detailed description of preferred modes of operation of the process. For convenience in the description of the process, as illustrated in the drawings, iron oxide is referred to as the reducible metal oxide. It is to be understood that while iron oxide is taken as a preferred example for the purpose of illustration, other metal oxides may be admixed with or substituted for iron oxide.

The figure is a diagrammatic elevational view showing a suitable arrangement of apparatus for carrying out a specific embodiment of the present invention.

With reference to the drawing, crushed coal is introduced through line **5** into a mixer **6**. Sufficient water to form a fluid dispersion is admitted to the mixer through line **7**. Iron oxide is supplied to the mixer through line **8**. Additive materials, e. g., a flux, oxidation catalyst, a deflocculating agent, wetting agent, etc., may be added to the mixer through line **9**. The resulting suspension of solid particles in water, or slurry, is passed through line **10** to a pump **13** from which it is passed through a tubular heater **14**. Heat may be supplied to the tubular heater **14** from any suitable source as, for example, by a furnace **15**.

The slurry is heated to a temperature at least sufficient to vaporize the water and the resulting dispersion of solid particles in steam passed at high velocity through the tubular heating coil **14**. The solid is subjected to the disintegrating action of vaporization and the highly turbulent flow resulting from high velocities. Venturis, nozzles, or orifices may be provided in the heater **14** to increase turbulence and provide more uniform suspension of solids therein.

The dispersion is discharged through line **16** into a cyclone separator **17**. Line **16** may be any desired length to take advantage of additional pulverizing action due to turbulent fluid flow of the suspension of solid particles in the steam. A portion of the steam is separated from the mixture of steam and powdered solid in the cyclone separator; the remaining steam and solids are passed into a flow-type generator, the amount of steam being regulated as required for the operation of the generator. Steam discharged from the separator **17** through line **18** may be fed to an engine as a source of power or may be passed in heat exchange with cooler streams in the process. Powdered solid particles pass through line **19** into a flow-type gas generator **20**. Oxygen is supplied through line **21**.

Powdered solid may be taken through line **22** for recycle to the mixer **6** as an aid in making up slurry.

A gaseous product comprising mainly carbon monoxide and hydrogen is discharged from the generator through line **23**. Molten slag is drawn off the generator through line **24**, while the molten iron is drawn off line **25**.

It will be understood that the cyclone separator **17** may be replaced by other types of separation equipment, and that, if desired, all of the steam may be separated from the powdered solid.

The following examples illustrate the application of the process to the reduction of iron ore to pig iron while at the same time producing carbon monoxide and hydrogen in good yields.

Iron ore from the Mesabi Range containing 90 weight per cent iron oxide and about 7.5 per cent silica by weight is used in the process. The coal employed is a bituminous coal having the following proximate analysis:

	Weight per cent
Moisture	4.3
Volatile matter	39.7
Fixed carbon	46.7
Ash	9.3

Limestone containing 96.8 weight per cent calcium carbonate and 1.6 per cent magnesium carbonate is used as flux.

These solid materials are mixed with sufficient water to form a fluid suspension and pumped through a heating coil where it is heated to 1,000° F. forming a dispersion of powdered solids in steam. Steam is separated from the powdered solids which are then charged to a flow type generator into admixture with oxygen of 95.3 volume per cent purity. The oxygen is preheated to 750° F.

The generator is operated at about 2,900° F. and 220 pounds per square inch gauge in all of the examples. Operating conditions and products follow:

Example	1	2	3	4	5
Coal, tons/hr	22	22	22	22	22
Iron ore, tons/hr	41.5	21.4	14.4	10.8	4.4
Limestone, tons/hr	7.9	5.8	5.1	4.8	4.1
Oxygen feed gas, std. cu. ft./hr	511,500	468,100	453,200	444,800	429,700
Coal/Iron ore (wt. ratio)	0.53	1.03	1.53	2.03	5.03
O/C ratio	1.8	1.4	1.3	1.2	1.1
Iron T./hr	27.8	14.5	9.7	7.4	3.2
Slag T./hr	8.6	6.2	5.4	5.0	4.3

The pig iron produced in the process contains about 95 weight per cent iron, and about 3 per cent solution.

Gas produced in the process is cooled, washed with water and then contacted with an aqueous solution of ethanolamine containing about 25 weight per cent of amine. The purified gas has a net heating value of about 300 B. t. u.'s per cubic foot. The composition varies somewhat, depending upon operations, as shown below.

Example No	1	2	3	4	5
Gas produced (std. cu. ft./T. coal)	31,630	50,100	55,420	58,700	64,680
Gas Analysis, Vol. percent:					
Hydrogen	15.9	22.1	24.4	25.9	28.7
Water	.3	.3	.3	.3	.3
Carbon Monoxide	77.8	74.5	72.6	71.4	68.9
Carbon Dioxide	1.3	.3	.2	.1	.1
Nitrogen	4.7	2.8	2.5	2.3	2.0

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.

We claim:

1. A process for the simultaneous reduction of a reducible solid metal oxide and the production of carbon monoxide and hydrogen which comprises admixing said metal oxide in particle form and a particulate solid carbonaceous fuel with sufficient water to form a slurry, passing said slurry as a confined stream in turbulent flow through a tubular heating zone wherein said slurry is heated to a temperature at least sufficient to vaporize the water thereby forming a dispersion of said solid particles in steam and subjecting said particles to heating and the disintegrating action of the highly turbulent flow of the confined stream of steam resulting from vaporization of the water, dispersing the resulting mixture of finely divided metal oxide and solid carbonaceous fuel in an oxygen-containing gas in a reaction zone, effecting interaction of said solids and oxygen in the reaction zone at a temperature above about 2,000° F., and recovering the reduction product of the metal oxide and a gaseous product comprising carbon monoxide and hydrogen from the reaction zone.

2. A process as defined in claim 1 wherein said dispersion of solid particles in steam is heated to a temperature above about 600° F.

3. A process for the simultaneous reduction of a reducible solid metal oxide and the production of carbon monoxide and hydrogen which comprises admixing said metal oxide in particle form and a particulate solid carbonaceous fuel with sufficient water to form a slurry, passing said slurry as a confined stream in turbulent flow through a tubular heating zone wherein said slurry is heated to a temperature at least sufficient to vaporize the water thereby forming a dispersion of said solid particles in steam and subjecting said particles to heating and the disintegrating action of the highly turbulent flow of the confined stream of steam resulting from vaporization of the water, separating steam from said dispersion, dispersing the resulting mixture of finely divided metal oxide and solid carbonaceous fuel in an oxygen-containing gas in a reaction zone, effecting interaction of said solids and oxygen in the reaction zone at a temperature above about 2,000° F., and recovering the reduction product of the metal oxide and a gaseous product comprising carbon monoxide and hydrogen from the reaction zone.

4. A process for the simultaneous reduction of iron oxide to pig iron and the production of carbon monoxide and hydrogen which comprises admixing particles of iron oxide, limestone, and a solid carbonaceous fuel with sufficient water to form a slurry; passing said slurry as a confined stream in turbulent flow through a tubular heating zone wherein said slurry is heated to a temperature at least sufficient to vaporize the water thereby forming a dispersion of said solid particles in steam and subjecting said particles to heating and the disintegrating action of the highly turbulent flow of the confined stream of steam resulting from vaporization of the water; separating steam from the resulting dispersion; dispersing the resulting mixture of finely divided iron oxide, limestone, and solid carbonaceous fuel in an oxygen-containing gas in a reaction zone, effecting interaction of said solids and oxygen in the reaction zone at a temperature of at least 2,500° F., discharging gaseous products comprising carbon monoxide and hydrogen from the reaction zone, and withdrawing molten iron from the reaction zone.

5. A process as defined in claim 4 wherein from about 0.2 to about 2 pounds of iron oxide per pound of fuel is charged to the reaction zone.

6. A process as defined in claim 4 wherein potassium carbonate is admixed with said iron oxide, limestone and fuel to form said slurry.

7. A process as defined in claim 1 wherein free oxygen is added to the slurry charged to the heating zone.

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