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(54) Title: METHOD AND APPARATUS FOR GASIFICATION OF ORGANIC MATERIALS

(57) Abstract

A process and apparatus for gasification of organic materials (typically incorporated in domestic and industrial wastes, including auto shredder residues) to produce useful synthesis gas (with a major content CO & H₂) with effectively non-toxic ash residue by means of at least one continuously operated burner, preferably stoichiometrically balanced (1:2 for natural gas/oxygen) at least at startup and shut down (optionally with some excess of oxygen, usually under steady-state conditions, such as at a ratio of 1:4 or higher, especially if the charge has well over 18 % water content), directed into a primary single stage reaction zone (through an opening in common with the effluent product gas discharged therefrom such as to assure intimate contact therebetween), which zone contains a tumbling charge in a rotating barrel-shaped horizontal reactor thus heated to from about 650 to about 800 °C (below the incipient fusion temperature of the charge) and controlled to remain in such temperature range (by adjustment of the burner volume and fuel-to-oxygen ratio for any given charge) resulting in thermally cracking and gasifying the organic materials in the charge and reacting the complex hydrocarbons and gas evolved (1) normally with the CO₂ and H₂O derived from burner combustion of a fuel and oxygen-containing gas at a high flame temperature, typically 2500 to 3000 °C, (2) with excess oxygen, and/or (3) partially with H₂O or CO₂ otherwise added to or, present in, the charge.

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METHOD AND APPARATUS FOR GASIFICATION OF ORGANIC MATERIALS

RELATED APPLICATIONS

This application is a division and continuation-in-part of application Serial
No. 08/158,195, filed November 24, 1993 (due to be issued as Patent No. 5,425,792 on June 20, 1995), which in turn
was a File Wrapper Continuation of then co-pending parent Application Serial No. 07/879,608, filed May 7, 1992 (the contents of which are incorporated herein by reference).

FIELD OF THE INVENTION

The present invention relates to a method and 10 apparatus for producing reducing gases having a high content of hydrogen and carbon monoxide, commonly known as synthesis gas (or syngas), from solid organic resi-More particularly the invention relates to a method and apparatus for gasifying industrial and 15 domestic wastes of several types, including the nonmetallic residues of automobile scrap, known as Auto Shredder Residues (ASR) also called "fluff", tire chips, residues from the petrochemical, polymer and plastics industries, and in general wastes of organic compounds 20 (including even liquids such as used motor oil), to produce a gas having a high content of hydrogen and carbon monoxide (typically more than 50%, or even well over 65% on a dry basis) which can be utilized as raw material in other industrial processes, for example, to 25 reduce iron ores to metallic iron in the ironmaking processes known as Direct Reduction processes, or to be utilized as a source of energy to run an internal combustion engine or to produce steam and/or electricity. In its broader aspects the disclosed method can be used 30 for devolatilization of coal or of other such non-waste complex molecular sources of carbon and/or hydrogen.

BACKGROUND OF THE INVENTION

In these days, and primarily in the industrialized countries, there is a deep concern about the safe disposal of domestic and industrial wastes which have acquired great ecological importance. These wastes often include a substantial proportion of organic content.

Many such wastes often contain toxic substances and are nonbiodegradable. They cannot therefore simply be disposed of in landfills due to contamination problems of air and water. Another alternative to dispose of these wastes is incineration. Normal and simple incineration however is not permitted if the product gases are not duly cleaned because it causes air pollution with toxic chemicals for example, chlorine compounds and nitrogen oxides. In some countries, environmental laws and regulations have been passed which prohibit burial or incineration of these types of wastes. Therefore these alternatives for disposal of such wastes are now subject to many restrictions.

A thorough description of the problems which the shredding industry is facing regarding disposal of fluff and some suggestions for utilization of the energy content of fluff, is found in a paper by M.R. Wolman, 25 W.S. Hubble, I.G. Most and S.L. Natof, presented at the National Waste Processing Conference in Denver, Colorado held on 14 June, 1986, and published by ASME in the proceedings of said conference. This paper reports an investigation funded by the U.S. Department of Energy to 30 develop a viable process to utilize the energy content of fluff. However, the process therein suggested is aimed to carry out a total incineration of the wastes. utilizing the heat from said incineration for steam production, while the present invention is addressed to 35 producing from organic materials a high quality gas as an energy source.

It has also been proposed in the past to carry out a controlled combustion of the organic wastes and to utilize the heat or other values (such as process gases) released by such combustion. Such prior art processes typically gasify organic materials by one of two processes: pyrolysis, that is, thermal decomposition of the materials by indirect heating; or partial combustion of the materials with air or oxygen.

Energy consumption is one of the most important costs in ironmaking. Typical direct reduction processes consume from 2.5 to 3.5 Gigacalories (109 calories) per metric ton of product, known as sponge iron or direct reduced iron (DRI). Therefore, many processes have been proposed which utilize all types of available energy sources, such as coal, coke, liquid fuels, natural gas, reducing gases from biomass, nuclear energy and solar energy. Most of such proposals have not met practical success, sometimes because the materials and means needed are not yet available or because the relative costs for using such other energy sources are higher than for traditional fossil fuels.

Utilization of organic wastes as a source of energy for the ironmaking industry offers great economic advantages and solves environmental problems in those countries where large quantities of automobiles are scrapped or other wastes with high organic material content are generated. Metallic scrap is recycled for steelmaking. The nonmetallic residues of automobiles (fluff), however, had not been utilized to produce reducing gases useful in the production of iron or in other industrial processes.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to provide a process and apparatus for producing reducing gases, also known as synthesis gas, preferably from low cost carbon/hydrogen sources such as garbage, or other organic containing wastes, and with an

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adaptability to accommodate a wide range of different kinds of charges (wet and dry), and which syngas is strongly reducing and thus can be utilized as raw materials in chemical processes and also as fuel.

It is a further object to practice the method with a simplified low cost apparatus.

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Other objects of the invention will be described hereinbelow or will be evident to those readers skilled in the art.

The present invention comprises a process wherein gasification of organic materials is carried out by thermal cracking of complex hydrocarbons and reaction of the gases evolved from such hot materials (preferably at 650°C to 800°C) with carbon dioxide and water

(normally generated by combustion, preferably stoichiometric, at least initially, of a fuel and oxygen from at least one continuous burner at high flame temperature, typically at 2500 to 3000°C). For methane (CH₄), the stoichiometric ratio of the burner fuel-to-oxygen would

be 1:2 (thus natural gas, normally being largely methane, has about the same ratio). The heat produced by the combustion of the fuel etc. is transferred to the gasifiable materials not only by convection, but also by direct radiation from the flame and by tumbling contact

25 with the glowing interior refractory lining of a rotary reactor. The burner(s) inside the reactor is balanced in positioning and capacity in such a way that it is capable of delivering the necessary heat for thermally decomposing the materials and also for carrying out the

30 endothermic gaseous reactions of complex hydrocarbons with the water and carbon dioxide, as well as providing necessary amounts of $\rm H_2O$ and $\rm CO_2$ reactants for such reactions.

Another feature of the present invention is

that a high quality gas is obtained in a single stage or
primary reaction zone. This results in a commercially
desirable, simple, low cost, low maintenance, apparatus

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having relatively few exposed or moving parts. Prior art processes typically are more complex, often requiring require two stages (with the bulk of the CO and H₂ gas being produced in the second stage). Complex gases

5 within the reaction zone reacts by dissociation according to their thermal/chemical equilibrium composition and become substantially stable simple hydrocarbon-derived gases at lower temperatures [resulting in a stable synthesis gas containing primarily hydrogen (H₂) and

10 carbon monoxide (CO) {at the very least 50%, or 60% on a dry basis}; and secondarily, carbon dioxide (CO₂), water (H₂O), and nitrogen (N₂); and lesser amounts of residual hydrocarbons, including methane (CH₄), ethane (C₂H₆), ethylene (C₂H₄), and acetylene (C₂H₂)].

Since one of the advantages of this invention 15 is to supply a high quality process gas at a cost competitive with traditional process gases (such as reformed natural gas), it may be necessary in practicing the invention in one of its broader aspects and under 20 certain market conditions and with certain kinds of "fluff" or other waste materials to use an excess of oxygen stoichiometrically in the burner or to the reactor to reduce the amount of fuel (e.g. natural gas) used in the burner relative to the amount of organic waste 25 gasified. If the cost of natural gas or other standard fuel is too high, the syngas itself can be used in the burner. However, essentially the same thing can be accomplished preferably and more efficiently, by reducing the fuel supplied to the burner to result in a relatively 30 more substantial stoichiometric excess of oxygen. is essentially the same result (since the oxygen will react in the reaction zone with the disassociated molecules which are the syngas precursors {which however most advantageously are already in a highly reactive 35 state, and which also avoid cost of extra handling of withdrawing, cleaning, and recycling essentially the same "fuel"). The net result of this alternative will be that

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(1) the same amount of garbage will be processed, (2) but at less cost (the syngas effluent precursor normally being less costly than natural gas); however, (3) with

less net syngas product. Less syngas can be

advantageous, if it is to be used only as a medium grade fuel (since in essence the natural gas saved is a better fuel). On the other hand, if the product is to be used as a reducing gas, the conversion of natural gas into $\rm H_2$ and $\rm CO$ has value which to some degree may have to be

10 balanced into deciding how to adjust the burner feed ratio.

An excess of oxygen is also needed when the charge has more than on the order of 15% water content. In practicing the process according to the present invention in a process demonstration plant (rated at up to 4,000 pounds organic feed per hour), the primary process burner was initially restricted, for safety reasons, to operating near the theoretical stoichiometric balance (1:2) between fuel and oxygen in order to eliminate the potential for run-away temperatures and/or atmospheric conditions which could lead to damaging

atmospheric conditions which could lead to damaging and/or explosive conditions in the hearth of the gasification apparatus. This works well in gasifying Automobile Shredder Residue (ASR). Such ASR materials almost uniformly contain between 8 and 15 percent

moisture (H₂O). At such moisture levels the 1:2 fuel-to-oxygen ratio for the primary burner works very efficiently. However, certain feed materials other than ASR, including Municipal Solid Waste (MSW), Recycled

Card-board Residue (RCR), and blends of each with tire chips, are found normally to contain between 25% to 50% free water (H₂O). Such larger water content results in less gasifi-cation efficiency, when compared with gasifying feed materials, such as ASR, which contain less

35 water. To improve the gasification efficiency when gasifying feed materials with excessive levels of moisture $({\rm H}_2{\rm O})$ it is necessary to reduce the total water

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 $(H_2^{\circ}0_{(g)})$ content in the gasification reactor. As predrying of feed material, such as MSW, would not be economically feasible. The total water introduced into the gasification reactor preferably is lowered by

5 reducing the amount of fuel fed to the primary process burner relative to the oxygen. How this can be accomplished is exemplified as follows:

-For Firing 1:2 Ratio: Primary Process Burner:CH₄+2O₂ ->CO₂+2H₂O

10 Here, 45% of the molecular weight of the combustion product is water.

-Firing 1:4 Ratio: Primary Process Burner: CH₄+4O₂-->CO₂+2H₂O+2O₂

Here, only 25% of the molecular weight of the combustion product is water.

The decrease in water introduced via the primary process burner operating with a 1:4 fuel-to-oxygen ratio amounts to a reduction in total weight of water in the hearth of the gasification reactor of about 30%; assuming the MSW feed material used in this example contained 35% water.

Higher levels of water contained in the source feed, gasification efficiency losses can be offset by reducing the injected fuel relative to injected oxygen in the primary process burner, provided that the temperature of the atmosphere inside the gasification reactor is retained in the preferred range i.e., 650°C to 800°C (or more preferably, 700°C to 750°C).

CO₂ can be added to the reactor with much the

30 same effect that excessive moisture in the charge would
have (serving to be a potentially low cost substitute for
natural gas, especially since CO₂ is an unwanted byproduct in both the syngas process and in the Direct
Reduction of iron process discussed below {which latter

35 process advantageously is integrated to use syngas}).

The CO₂ can be added to the burner so long as the flame
and temperature range is adequately maintained, or can be

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added directly to the reactor, with a compensating in the burner feed ratio (again so as to maintain the proper temperature range).

In determining the burner ratio for a given 5 charge, not so much excess oxygen should be used as to result in substantial insufficient gasification (by over production of H2O & CO at the expense of H2 & CO) nor to result in excessive temperatures above the preferred If as much as CO₂ is present in the syngas 10 product (on a dry basis) that is too much (and in fact would soon result in the temperature rising unacceptably and fuse the residual ash in the reactor. Nor should the modification be so as to result in the need for the prior art's separate two-stage processing (at two significantly 15 different temperatures, with the second stage being in the absence of the solid burden). The limit for excess oxygen for some ASR charges for example might be up to 10% more oxygen relative to the molar content of the Excessive oxygen, especially during transition, 20 can make control of the process difficult and is safer, if minimized. Alternatively, as economics may dictate, a portion of the previously generated synthesis gas may replace an equivalent amount of natural gas in the burner, up to 100 percent replacement.

In operation, the process for gasification in the preferred apparatus is started over a 4 hour period by heating the internal atmosphere and refractories of the gasification apparatus up to about 650°C to 800°C prior to introduction of a charge of organic feed material into the hearth area of the apparatus. The heating of the internal atmosphere and the refractories of the apparatus is accomplished by one or more process burners which are operated at a fuel-to-oxygen ratio of 1:2; thus, generating a sufficient volume of burner product gases which are essentially void of uncombusted fuel and free oxygen; i.e. CO₂ and H₂O. During the heat-up period the hot product gases (CO₂ and H₂O) from the

primary process burner pass into and then out of the hearth of the gasification apparatus and through the connecting ducts and gas cleaning system for a period of several hours; thus, preheating the apparatus and completely purging free oxygen (air) from the entire gasification reactor as well as the product gas management system.

When the refractories and atmosphere inside the hearth of the gasification apparatus reach a temperature level sufficient to ensure autothermal ignition (above 10 650°C) of organic gases with any residual free oxygen (air) which may remain in the hearth, a charge of organic feed material is fed into the gasification apparatus. The solid organic feed materials are quickly elevated in 15 temperature above their melting and boiling temperatures and become organic vapors (gas) which at the autothermal temperature ignites with the last vestige of free oxygen (air) that may remain in the hearth area of the gasification apparatus. The hearth area of the 20 gasification apparatus quickly becomes void of free oxygen, and the heterogeneous mixture of organic vapors which evolve from the organic feed material enter into the. hearth area atmosphere and makes contact with the high temperature flame from the primary process burner 25 and with the flame products of combustion (CO_2 and H_2O). The process of gasification by both exothermic and endothermic reactions result in the reformation and/or dissociation of complex molecular bonds, and stable production of synthesis gas is achieved.

As the synthesis gas product passes from the gasification apparatus through the connecting ducts and gas cleaning devices, said synthesis gas pushes the residual startup gases (CO₂ and H₂O) forward through the system until the entire gas management system is safely devoid of startup gas and free oxygen (air); and the potential for generating an explosive mixture of synthesis gas and oxygen is eliminated.

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With the steady state gasification process established and the preferred atmospheric temperature in the gasification apparatus being in the range of 650°C to 800°C, and with organic vapors from the organic feed 5 material coming into direct contact with the flame from the primary process burner (which is operating with a 1:2 ratio of fuel-to-oxygen), the total energy input that is necessary to maintain the proper thermal balance to offset endothermic gasification reactions and systems 10 heat losses can be determined. Once the optimum energy input requirement is determined, the base rate of oxygen injection through said burner can be established. example: assume one ton per hour of organic material is fed to the gasification apparatus (generating $\frac{1}{2}$ ton of 15 ash); 3 million Btu/hour is required to balance the thermal heat losses; the primary process burner is operating with a 2:1 ratio of fuel as natural gas and oxygen; and further, assume natural gas has a HHV of 1000 Btu/scf; then 3000 scf/h of natural gas and two times 20 that amount (6000 scf/h) of oxygen will be required for stoichiometric combustion. Thus, this example identifies the base rate of oxygen injection.

Once the base oxygen rate is known, fuel to the primary process burner can be slowly decreased while the oxygen injection rate remains at the optimum level as determined above. At the same time, evolving organic vapors are pulled into the vortex of the high velocity flame; thus, replacing the withdrawn fuel (natural gas in this example). The organic vapors rather than natural gas then react with free oxygen contained in the burner flame and the resulting exothermic reactions act to sustain the process atmospheric temperature in the hearth of the gasification apparatus.

Direct combustion between the organic feed

35 material and oxygen injected through the primary burner should not occur due to the ready availability of organic

vapors which mix in the vortex of the primary process burner flame.

As the gasification process is transmuted from one primary burner fuel-to-oxygen ratio to a leaner fuel ratio, oxygen injection remains approximately at the same level as first established by the 1:2 fuel-to-oxygen ratio to the primary process burner. The hearth bed material and atmospheric temperature inside the gasification apparatus remains approximately the same as when operating the primary process burner with a 1:2 fuel-to-oxygen ratio; however, organic vapors contained in the synthesis gas are further reformed to carbon oxides and hydrogen and the hydrocarbon content of organic gases will be reduced toward zero.

15 The higher ratio of oxygen relative to fuel injected through the primary process burner does not result in a significant increase in the volume percentage of carbon dioxide in the resulting synthesis gas. The example given below was taken from actual operating data 20 and reflects the relative effect the primary process burner firing ratio has on the resulting synthesis gas.

Typical Synthesis Gas Produced By

25 Primary Process Burner:

	Analysis	1:2 Ratio	1:4 Ratio
30	H ₂ CO CO ₂ N ₂	35.96 33.57 13.20 6.01	36.60 34.16 13.90 5.98
35	N_{2}^{T} CH_{4} $C_{2}H_{4}$ $C_{2}H_{6}$ $C_{2}H_{2}$ $C_{6}H_{6}$	6.80 2.60 0.55 0.67 0.64	6.09 2.06 0.37 0.40
40	Total HHV	100.00	100.00

In the above example, it is apparent that the percentage of hydrocarbon gases are reduced; thus, a 6.8%

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loss in heating value. By further reducing the fuel injection ratio relative to the oxygen injection ratio, the hydrocarbon gases can be ultimately reduced to near zero; and the HHV of the synthesis gas will decrease accordingly to reflect the higher relative percent of H₂ (325 BtU/ft²) and CO (323 BtU/ft³) contained in the resulting synthesis gas.

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Regarding the rotary reactor disclosed in the present invention, it comprises some unique character-10 istics, namely: it has a continuously operating burner, it has a common opening serving both the burner input and the product effluent output (assuring intimate intermixing of the two) , and the rotary reactor is disposed substantially horizontally with respect to its 15 axis of rotation, while known rotary reactors are inclined so that the materials tumbling inside are caused to move from their charge end to their discharge end. the rotary reactor of the present invention solids move from the charge end to the discharge end of the reactor 20 by the tumbling action of the rotating vessel, and by the volumetric displacement of reacted solid ash in the bed by unreacted material and inert solids contained in the feed material. The center of the reactor has a bulged shape to give the bed an adequate volume and burden 25 retention time and to conform to the shape of the burner flame.

The process could be carried out in other apparatus such as a generally cylindrical horizontal stationary reactor having internal slightly-angled rotating paddles for tumbling the burden. The latter has some drawbacks such as possible obstruction of the preferred single flame within the reactor chamber and the engineering problems of the paddles and supporting moving parts being within the high temperature regions of the reactor.

Another important feature of the present invention is the unique structure of the high temperature

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seals which minimize seepage of outside air into the rotary reactor.

Because the primary process burner is driven by oxygen and fuel (natural gas, syngas, fuel oil, coal, etc.) the nitrogen content of the resulting product gas is normally limited to the nitrogen contained in the organic feed materials; thus, the nitrogen content of the product gas is normally less than ten percent by volume.

A significant aspect of this invention is the
mixing of the evolved complex hydrocarbon gases and entrained soot-laden dust particles exiting the reactor
into and through the high temperature CO₂ and H₂O laden
recirculating vortex created in the reactor's atmosphere
by the counter-current burner gas stream(s). The flame
of the primary process burner preferably enters the
reactor from a counter-current direction relative to the
movement of the burden material. The dust-laden gases
generated by this process preferably pass out of the
gasification reactor past the burner in a co-current
direction relative to the movement of the bed of burden
(ash plus gasifying materials).

In the preferred embodiment the reactor rotates on a horizontal axis. On the charge end of the reactor the feed tube to the burden serves the following
25 purposes: (1) as a raw material feed input, and (2) as an atmospheric seal.

Raw material/feed is force-fed by appropriate means such as by a method of extrusion into the gasification reactor by an auger which is of standard commercial design; however, the diameter, length, and taper of the extrusion tube from the auger into the reactor, and the exact position and clearance between the extrusion tube and the rotating reactor have been determined by practice and provide a support for the rotating slip-seal design on the feed-end of the reactor. Solid feed material in the auger serves as part of the atmospheric seal on the feed-end of the reactor. The auger can also

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serve a shredding function for oversized pieces of feed material.

Another method for feeding raw material into the reactor involves a hydraulic ram system in which two sets of hydraulic rams act to compact and force feed the material through a specially designed feed tube.

The nature of the carbonaceous feed material consumed in this process is such that some of the feed material has extremely low melting and volatilization temperatures; for example, plastics, rubber, and oil/grease. Therefore, it is important that the temperature of the feed material be controlled to prevent premature reactions before the material reaches the inside of the gasification reactor. The design of the feed extrusion tube and the receiving shaft, or tube through which the feed material is injected and through which the atmospheric seal must be maintained are important parts of the design of this invention.

The process temperature must be controlled to

20 prevent ash materials in the bed from reaching their
temperatures for incipient fusion; thus, preventing the
formation of agglomerates in the bed and on the wall of
the reactor. The critical ash fusion temperature has
been determined by practice for various types of raw feed

25 material(s). In the ideal practice of the art of this
process it is important to maintain the highest possible
bed temperature; however, the temperature of the bed
should remain below the point of incipient fusion of the
ash (hence the preferred 650-800°C range).

Non-reactive dust particles which become airborne pass out of the gasification reactor with the product gas into the hot gas discharge hood and then through hot ducts into a cyclone, venturi, or other appropriately adapted commercial equipment. The gas then passes through a packed-bed column where the acids are scrubbed from the gas and the wash water is adjusted to a

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Ph'of about seven (7). The clean gas is then moved by compressor via pipeline to storage for use.

The design of the hot gas discharge hood is another important aspect of this invention. The hot gas discharge hood provides the port support structure for the process burner.

Secondary air/oxygen injector(s) may advantageously be located in the hot gas discharge hood and/or the hot cyclone for the purpose of adding air and/or oxygen to control the temperature of the product gas as it exits the hot gas discharge hood and/or to aid in "finishing" the gasification of any residual hydrocarbons or soot. In practice of this process it is important to maintain the temperature of the product gas at a sufficiently high level until the gas reaches the gas scrubber in order to avoid condensation of any remaining higher molecular weight gases exiting through the hood. The added residence time of the product gas in the hot gas discharge hood and the hot ducts and cyclone leading 20 to the gas scrubber is such as to increase reaction efficiencies between gases and the carbonaceous portion of the dust.

By controlled additions of air and/or oxygen to the hot gas discharge hood, both the temperature and 25 pressure in the discharge hood can be better managed. It has been found that by raising the temperature of the product gas to about 700°C by the injection of about 5 percent by volume of oxygen, the residual complex hydrocarbon gases are predominantly decomposed into 30 carbon monoxide and hydrogen. Ideally, such additions are minimized in order to maintain the quality of the synthesis gas. However, the differing types of burden require adjustments to give the required flexibility to the process. Where the type of burden is not 35 standardized, such flexibility can be accomplished by adjusting the amount of air and/or oxygen additions. The amount of air and/or oxygen added in the hot gas

discharge duct must also be controlled in view of the BTU requirements of the product gas being produced. For example: if the content of nitrogen in the product gas is not critical relative to the end use of the gas, air can be used exclusively to control the temperature and pressure in the hot gas discharge hood. However, if the content of nitrogen in the process gas must be maintained at a low level in order to meet the required BTU specifications for the gas, oxygen can be used instead of air.

Because the synthesis gas produced by this process is naturally high in particulate matter and acid gases, the sensible energy of the gas cannot be easily utilized by heat exchangers. On the other hand, the gas can be controlled to contain between about 1335 Kcal/m³ and 3557 Kcal/m³ (150 and 400 BTU/cubic foot) and can be easily scrubbed of particulate matter and acids.

Ash discharged directly from the reactor and from the hot cyclone is very low in leachable metals.

This ash does not require further treatment to be disposed of in an environmentally safe manner.

disposed of in an environmentally safe manner. Dust remaining in the product gas following the hot cyclone can be removed in a wet venturi scrubber and recovered from the wash water as a sludge. Such sludge may be relatively high in leachable metals and therefore may

require treatment for environmentally safe disposal.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a partially schematic diagram of a preferred embodiment of the present invention useful for gasifying organic wastes to yield a synthesis gas and showing a number of exemplary end uses for such gas;

Figure 2 shows a partially schematic vertical cross section in more detail of a rotary reactor of the type illustrated in Figure 1; and

Figure 3 shows a cross section of a rotary high temperature seal for the charge end of the reactor shown in Figure 2.

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DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

A preferred embodiment of the invention as applied to the gasification of fluff will be described with reference to the appended drawings wherein common elements are designated by the same numerals in all the figures for easier reference. Referring to Figure 1, showing a partially schematic diagram of the general process and apparatus, numeral 10 designates a charging hopper wherefrom fluff is introduced into the gasification reactor 18 by an auger feeder 20 having an auger 14 (shown in Figure 2) driven by a motor 12.

Reactor 18 is of the rotary type and is provided with riding rings 22 and 24 which rest and roll on support rolls 26 and 28. Motor 30 causes reactor 18 to rotate about its horizontal axis by means of a suitable transmission device 32, for example of the type of chain and sprocket ring 34, in a manner known in the art.

into a gas collecting hood 36 having at its upper portion an emergency stack 38, through which the product gases can flow by safety valve 40, and a lower discharge section for collection of the solid residues or ash resulting from gasification of the fluff. Rotary

valve(s) 42 is provided for regulation of solids discharge and contributes to prevent combustible gas from leaking to the outer atmosphere. Screw-type conveyor 44 driven by motor 46 cools the ash and transfers it into receiving bin 48 for disposal.

A burner 49 is positioned generally horizontally through hood 36 with its nozzle 50 reaching the interior of reactor 18 in the manner shown and described with reference to Figure 2. Fuel gas and oxygen are fed to burner 49 through conduits 52 and 54.

35 From hood 36, the gases produced by reactor 18 are transferred through take off conduit 58 into a hot cyclone 60. The solid fine particles of fluff or soot 61

which may be entrained by the gases from reactor 18 are separated and are collected, cooled, and discharged into receiving bin 48.

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A secondary burner 64, fed with oxygen/air
5 and/or fuel gas, is positioned upstream of cyclone 60 for optional addition of air or oxygen to gasify any hydrocarbons or soot in the form of fine particles or gases which may reach that point.

The raw product gas flows through conduit 70 into a wet venturi scrubber 72 where entrained dust 10 particles are removed. More preferably the raw product gas may be cooled, for example to 150°C, and passed through a bag house (with subsequent vitrifi-cation of the collected materials). The bag filter will even 15 remove with collected dust the trace amounts (well under 1%) of the solidified more refractory hydrocarbon gases such as toluene, xylene, cumene, etc. that may survive in the product gas. The product gas then passes through packed bed tower 74 where acids (together with any 20 benzene (C₆H₆) passing the bag filter) are removed by water wash. Emergency pressure control valve 76 is provided at purge line 78 to relieve excess pressure in the system should upset conditions occur. Solids collected by scrubber 72 are sent into sludge tank 80 25 forming a sludge 82.

Clean and cool product gas flows to compressor 84 through pipe 86, connected to a flare stack 98 provided with valve 100 for disposal of excess gas surges.

The product gas can be utilized for a variety
of purposes. For example, the high quality clean product
gas can produce mechanical power as a fuel for an internal combustion engine 88, or can be stored in tank 90 for
later use (e.g. to be burned for its heat content), or
used to produce electricity in a gas turbine generator
35 92, or to produce steam in boiler 94 or to be used as a
reducing gas in a direct reduction process 96.

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Referring now to the more detailed drawing of the gasification reactor 18 shown in Figure 2, the bed of material 102 to be gasified is formed in the reactor 18, and solids are caused to move from the charge end 103 to the discharge end 35 by tumbling action induced by rotation of reactor 18 and by the volumetric displacement of reacted solid ash in the bed 102 by unreacted and inert solids contained in the feed material delivered by auger feeder 20. The tumbling and mixing action of hot reacted and inert ash with fresh unreacted solids in the feed material greatly increases the rate of heat transfer in the bed 102 and thus enhances the rate and completeness of gasification of the raw feed material.

The depth of bed 102, and the retention time for feed material in reactor 18, are determined by the diameter and length of the reaction zone and are also relative to the length, diameter, and the angle of the slope of reactor 18 leading to discharge end 35.

A horizontal rotation axis is preferred among
other reasons because the seals 120 and 122, located at
the periphery of reactor 18 generally at its charge end
103 and discharge end 35, do not have to withstand
excessive thrust or strain due to uneven distribution of
the center of gravity of reactor 18. This also applies
to the support rolls 26 and 28, which are of a simpler
design and easier to maintain if reactor 18 rotates
horizontally.

In one of the preferred embodiments, the shape of reactor 18 is an important feature of this invention because the hot volatile gases which evolve from the bed of material 102 must be brought immediately into contact with the extremely hot products of combustion (CO₂ + H₂O) from burner 49, in order to more directly absorb the high temperature energy of the flame via the endothermic reactions of complex gases to form gases of simpler compounds. The shape and length of the flame from burner 49 is such that volatile gases which evolve from the bed

102, and over the entire length of reactor 18, react with the high temperature products of the combustion from burner 49.

Reactor 18 is provided with refractory lining 5 108 in the manner known in the art. Refractory lining 108 contributes to a uniform and efficient heating of bed 102 because the exposed portion of refractory lining 108 receives heat from the flame by radiation and also by convection. The lining 108 includes a typical 10 intermediate insulation layer 107 (shown in Figure 3) as a thermal protection to the metallic shell 109 of the reactor 18. Uniform and efficient absorption of the high temperature energy from burner 49 by bed 102 also depends upon the rotation speed of reactor 18 and is necessary to 15 prevent overheating of areas of bed 102 which are exposed directly to the heat of the flame, as well as to prevent overheating refractory lining 108. If uncontrolled overheating of bed 102 and/or refractory lining 108 should occur, fusion and/or melting and agglomeration of 20 ash-to-ash and/or ash-to-refractory lining 108 could result in damage to refractory lining 108.

It has been found that the process can be adequately controlled by monitoring the heat in the reactor and making adjustments to keep the process

25 operating within the preferred temperature range. This can be accomplished by two thermocouples, one positioned in the widest part of the reactor and the other in the throat of the discharge of the reactor. Two or more such on-board thermocouples are positioned to project through reactor wall and the refractory and are exposed to direct temperature of residue and atmospheric gases within the reactor.

A second burner 51 has been shown in dashed lines to illustrate an alternative embodiment having a plurality of burners. However, in the preferred embodiment only a single burner 49 is used.

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Adjustable positioning of nozzle 50 of burner 49, shown in solid and dotted lines, inside reactor 18 is an important feature for optimal operation of the process. The preferred position of nozzle 50 will be such that an effective reaction between the gases evolved from bed 102 and the oxidants produced by the flame of burner 49 is accomplished. The flame causes a vortex near the discharge end 35 of reactor 18 and the gases evolving from bed 102 must pass by or through the influence zone of the flame. This arrangement results in the production of a high quality gas in a single reaction zone.

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The discharge end 35 of reactor 18 is provided with a foraminous cylinder 110 for screening of fine and coarse solid particles of ash discharged from reactor 18.

The fine particles 116 and coarse particles 118 are collected through conduits 112 and 114, respectively, for disposal or further processing.

Burner 49 in this preferred embodiment is operated stoichiometrically to minimize the direct oxidation of the material in bed 102 inside reactor 18.

Seals 120 and 122 are provided to substantially prevent uncontrolled introduction of atmospheric air into reactor 18. The design of seals 120 and 122 will be better appreciated with reference to Figure 3. The design of reactor 18, (shape, length and horizontal axis rotation), results in minimal thermal expansion, both axial and radial. Seals 120 and 122 are specifically designed to absorb both axial and radial expansion, as well as normal machine irregularities, without damage while maintaining a secure seal.

The seals comprise a static U-shaped ring 130 seen in cross section supported by annular disk plate 132 which closes off the end of the reactor space 138 and in turn is attached by flange 134 to the outer housing structure of the auger feeder 20. A fixed packing 136 is provided to ensure that no gas leaks from space 138 which

communicates with the interior of reactor 18 through annular space 140.

Two independent annular rings 142 and 144, made of stainless steel, are forced to contact the static U5 shaped ring 130, by a plurality of springs 146. Rings 142 and 144 are fastened to supporting annular plate 148 to form an effective seal between ring 142 and plate 148 by conventional fasteners 150. Supporting plate 148 is securely attached to member 152 which forms part of or is fixed to the outer shell of reactor 18.

Springs 146 maintain the sealing surfaces of rings 142 and 144 against the surface of static ring 130, in spite of temperature deformations or wear.

EXAMPLE NO. 1

A pilot plant incorporating the present invention was operated during many trial runs. The rotating kiln reactor is on the order of 4.3 meters long by 2.4 meters wide (14 x 8 feet) at its widest point and is shaped generally and has accessory equipment as

20 illustrated in Figure 1. The following data was obtained: Auto shredder waste from a shredder plant was fed to a rotary reactor as described in the present specification.

Typical analysis of the ASR material, (also called "fluff") which is the material remaining after metallic articles, such as auto bodies, appliances and sheet metal, are shredded and the metals are removed, is in weight percent as follows:

	Fiber	26.6%	Metals	3.3%
30	Fabric	1.9%	Foam	1.4%
	Paper	3.7%	Plastics	12.5%
	Glass	2.4%	Tar	3.6%
	Wood Splinters	1.4%	Wiring	1.3%
	Elastomers	3.3%	Dirt/Other	38.6%
35			TOTAL =	100.0%

It should be understood, however, that actual analyses vary in a wide range due to the nature and

origin of this material. Depending on the shredding process, fluff contains a variable weight percentage of noncombustible (ash). Bulk density of fluff is approximately 448 kg/m³ (28 lb/ft³). In general,

5 noncombustibles account for about 50% by weight and combustible or organic materials account for about 50%.

About 907 kg/hr (2000 lb/hr) of fluff were fed to the rotary furnace by means of the auger-type feeder after a period of heat-up of the reactor, so that its interior temperature reached above 650°C (1202°F). During stable operation, the temperature in the reactor was more or less homogeneous and near 700°C (1292°F). Although the temperature of the flame may reach about 3000°C (5432°F), the endothermic reactions between the gases evolved from the hot fluff and the oxidants (CO₂ and H₂O) produced by the burner cause the interior reactor temperature in the bed and adjacent internal atmosphere to stabilize at about 700°C (1292°F).

The reactor was set to rotate at about 1 r.p.m.

The burner was operated stoichiometrically using about

64.3 NCMH (2271 NCFH) of natural gas and 129 NCMH (4555

NCFH) of oxygen. A rate of 573 NCMH (20,235 NCFH) of

good quality synthesis gas was obtained.

Typical analysis of the synthesis gas produced 25 is:

		<pre>% Volume (dry basis)</pre>
	H ₂	33.50
	CŌ	34.00
	CH ₄	8.50
30	CO ₂	13.50
	N_2^-	5.50
	C ₂ H ₂	0.75
	C ₂ H ₄	3.50
	C_2H_6	<u>0.75</u>
35	2 0	TOTAL: 100.00

As can be readily observed, the product gas obtained contained 67.5% of reducing agents (H₂ and CO) and 13.5% of hydrocarbons which in some applications for this gas, for example, in the direct reduction of iron ores, may undergo reformation in the direct reduction process and produce more reducing components (H₂ + CO).

The heating value (HHV) of the product gas was about 3,417 Kcal/m³ (384 BTU/ft³), which corresponds to a medium BTU gas and may be used for example to fuel an internal combustion machine, and certainly can be burned to produce steam or for any other heating purpose. As a comparison, the gas effluents from blast furnaces have a heating value of about 801 TO 1068 Kcal/m³ (90 to 120 BTU/ft³) and even so are utilized for heating purposes in steel plants.

The amount of dry ash discharged from the reactor amounts to about 397 kg/hr (875 lb/hr) and additionally about 57 kg/hr (125 lbs/hr) were collected as sludge from the gas cleaning equipment.

The hot ashes collected directly from the

15 reactor discharge port and from the hot cyclone are very
low in "leachable" heavy metals, and consistently pass
the TCLP tests without treatment. These ashes contain
between eight and twelve percent recyclable metals,
including iron, copper, and aluminum. The hot ashes are

20 composed of iron oxides, silica, alumina, calcium oxide,
magnesium oxide, carbon, and lesser amounts of other
matter.

After removal of oversize metal pieces by screening, the remaining dry ash is environmentally safe for landfilling without further treatment. The toxicity analysis of the concentration of the eight RCRA metals in an extract obtained by TCLP tests is illustrated in the following table.

30	Metals	Regulatory Concentrations (mg/L)	*TCLP Test Results (mg/L)
	Silver	5.0	< 0.01
	Arsenic	5.0	< 0.05
35	Barium	100.0	5.30
	Cadmium	1.0	< 0.01
	Chromium	5.0	< 0.05
	Mercury	0.2	< 0.001
	Lead	5.0	< 0.02
40	Selenium	1.0	< 0.05

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* Toxicity Characteristics Leachate Procedure (per Resource Conservation & Recovery Act).

Dust solids collected from the gas scrubbing

5 system are recovered as sludge and have been analyzed for
the eight RCRA metals as illustrated in the following
table:

	Metals	Regulatory Concentrations	TCLP Test Results
10		(mg/L)	(mg/L)
	Silver	5.0	< 0.01
	Arsenic	5.0	0.06
	Barium	100.0	3.2
15	Cadmium	1.0	0.78
	Chromium	5.0	< 0.05
	Mercury	0.2	< 0.001
	Lead	5.0	4.87
	Selenium	1.0	< 0.07
20			

Several TCLP tests have been made and in each case the sludge materials have passed the test without additional treatment.

EXAMPLE NO. 2

25 The effectiveness of the seals which are described and claimed in this application, constituting an important feature of the present invention, can be seen comparing the results of two trial runs of the pilot plant (the first with a commercial seal installed and the other with a seal made as shown in Fig. 3).

		COMMERCIAL SEAL SCMH (SCFH)	FIGURE 3 SEAL SCMH (SCFH)
	Gases Produced		
	(except N ₂)	574 (20,279) 64%	606 (21,408) 94%
35	Nitrogen	333 (11,753) 36%	36 (1,263) 6%
	TOTAL Gas Produced	907 (32,032) 100%	642 (22,671) 100%

Although it has been found that about 3 percent
40 of the nitrogen content in the final product gas is
originated from the fluff material, it can be seen that
an important decrease in the nitrogen content of the
produced synthesis gas was made by the unique construction of the inventive seals, which contribute to gas
45 produced having a higher quality and value.

EXAMPLE NO. 3

In order to assess the suitability of the synthesis gases produced according to this invention for the chemical reduction of iron ores, the following material balance was carried out running a computer simulation program specifically devised for said purpose.

The basis for calculations was 1 metric ton of metallic iron produced.

Although the reducing gas produced according to
the present invention can be utilized by any of the known
direct reduction processes. The material balance was
calculated as applied to the HYL III process invented by
employees of one of the Co-assignees of this application.
Examples of this process are disclosed in U.S. patents
3,765,872; 4,584,016; 4,556,417 and 4,834,792.

For an understanding of this example, reference can be made to Figure 1 where one of the applications shown is the direct reduction of iron ores, and to Table I showing the material balance.

926 Kg (2042 lb.) of fluff are gasified in reactor 18.

95 NCM (3354 NCF) of natural gas are fed to burner 49 along with 190 NCM (6709 NCF) of oxygen.

Gasification of this amount of fluff produces 1,000 NCM

25 (35,310 NCF) of raw hot reducing gas (F₁) which after cleaning and cooling will reduce to 785 NCM (27,718 NCF) with the composition identified as F₂.

The thus clean reducing gas then is combined with about 1,400 NCM (49,434 NCF) of recycled gas

30 effluent from the reduction reactor after being cooled by quench cooler 124 and divided as composition F₇.

The mixture of fresh reducing gas F_2 and recycled gas F_7 is then passed through a CO_2 removal unit 126, which can be of the type of packed bed absorption towers using alkanolamines resulting in 1,876 NCM (66,242 NCF) with the composition of F_3 , which clearly is a gas with high reductant potential, of the type normally used in

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Direct Reduction processes. By means of unit 126, 297 NCM (10,487 NCF) of ${\rm CO_2}$ are removed from the system as gas stream ${\rm F_{10}}$. The resulting gas stream ${\rm F_3}$ is then heated by heater 110 to about 950°C (1742°F) and is fed to the reduction reactor 104 as gas stream ${\rm F_4}$ to carry out the reduction reactions of hydrogen and carbon monoxide with iron oxides to produce metallic iron.

The gas stream effluent F_5 from said reduction reactor 104 has consequently an increased content of CO_2 and H_2O as a result of reactions of H_2 and CO with the oxygen of the iron ore, therefore the effluent gas F_5 is dewatered by cooling it in a direct contact water quench cooler 124 to give 1687 NCM (59,568 NCF) of a gas F_6 . From gas F_6 a purge F_8 of 287 NCM (10,134 NCF) is split out and removed from the system to eliminate inerts (e.g. N_2) from building up in the system and also for pressure control. The rest of the gas is recycled as described above as gas stream F_7 (being combined with F_2 , stripped of CO_2 , and then fed to the reduction reactor as gas stream F_3 having the composition shown in Table 1).

Optionally a cooling gas, preferably natural gas, can be circulated in the lower portion of the reactor in order to cool down the direct reduced iron (DRI) before discharging it.

To this end, about 50 NCM (1766 NCF) of natural gas F₉ are fed to a cooling gas loop and circulated through the lower portion of the reduction reactor 104. The gas stream effluent from the cooling zone of said reactor is cooled and cleaned at quench cooler 106 and 30 recirculated within said cooling loop.

TABLE 1

Material Balance of the HYL III D.R. Process (of Example 3) Using Synthesis Gas From Gasification of ASR Materials

	F1	F2	F3	\mathbb{F}_4	F.S.	F.	F7	FB	Fg	F10
H, & Vol.	28	35	44	44	33	40	40	40	0.4	
00	26	33	26	26	14	16	16	16	0.1	
	11	14	0	0	11	13	13	13	0.4	100
CH,	7	10	16	16	13	16	91	91	63.7	
N ₂	4	S	12	12	11	14	14	14	5.0	
C,H,	0								4.6	
$c_{ m cH_{10}}$	0								0.3	
н,о	24	3	2	2	18	1				
Flowrate (NCM) Ton Fe	1,000	785	1,876	1,876	2,023	1,687	1,400	287	50	297
Temperature (°C)	500	30	40	950	639	30	30	30	25	30

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WE CLAIM:

1. Method for gasifying organic materials in a primary reactor having a single reaction zone to produce a synthesis gas, said method comprising:

feeding a charge of waste organic materials into a charge end of said reactor and continuously tumbling said waste organic materials in said reactor so as to form a bed in said reactor and move said bed toward a discharge end of said reactor;

heating the waste organic materials 10 sufficiently to volatilize, thermally decompose, and otherwise gasify hydrocarbons contained in the organic materials resulting in evolved gases and residual ash, by means of at least one high temperature burner gas stream 15 above said bed formed by combustion with an oxygencontaining gas (1) of a fuel separate from said charge and suitable to produce CO2 and/or H2O and (2) with said evolved gases when there is an excess of said oxygencontaining gas, said fuel and said oxygen-containing gas 20 being in a ratio and at a volume such that the amount of said fuel is sufficient to keep the temperature of the bed and adjacent atmosphere within said primary reactor above 650°C and below the fusion temperature of the residual ash;

continuously operating said at least one high temperature burner gas stream at the discharge end to provide sufficient energy and oxidizing combustion products within said primary reactor to react with the evolved gases in said primary reactor to yield the synthesis gas; and

discharging said residual ash and synthesis gas at the discharge end countercurrent to the burner gas stream such that said burner gas stream makes good contact with said evolved gases.

2. Method according to claim 1, wherein said combustion is substantially stoichiometric.

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- '3. Method according to claim 1, wherein said oxidizing combustion products comprise H_2O and CO_2 .
- 4. Method according to claim 3, wherein said charge has a moisture content of about 15% to about 50% and the burner has a fuel-to-oxygen ratio in excess stoichiometric sufficient to maintain the temperature in said primary reactor above 650°C and below the fusion temperature of the residual ash.
- 5. Method according to claim 4, wherein the burner has a fuel-to-oxygen ratio about 1:4.
 - 6. Method according to claim 3, wherein said high temperature gas stream is generated with a flame at a temperature of from 2500 to 3000°C.
- 7. Method according to claim 3, wherein said

 15 synthesis gas produced is dewatered and stripped of CO₂

 and at least a portion of the latter is recycled through said burner or directly into said reactor.
- 8. Method according to claim 3, wherein said synthesis gas exits said primary reactor at a temperature above about 650°C and contains less than about two percent by volume of gases with molecular structure having more than two carbon atoms.
 - 9. Method according to claim 8, further comprising maintaining the temperature of said synthesis gas exiting said primary reactor above 650°C;

reactor; increasing the temperature of said synthesis gas in the secondary reactor by contacting said synthesis gas with a finishing secondary gas stream injected therein;

said finishing gas stream being chosen from the group consisting of the product of a combustion of a fuel with a secondary oxygen-containing gas and a secondary oxygen-containing gas only, which latter is injected into the effluent synthesis gas from the primary reactor at a rate of up to about 5 percent on a volume basis relative to such effluent synthesis gas; and

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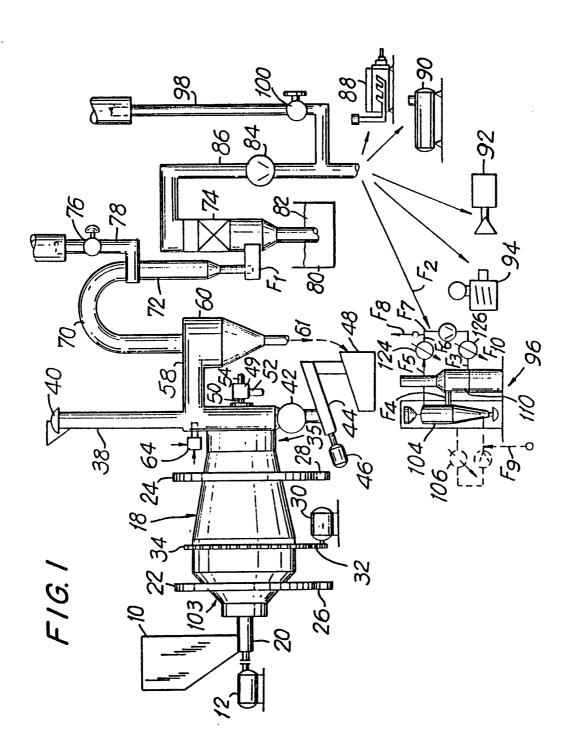
the temperature of said synthesis gas is raised on the order of up to 50°C, and at least a portion of any carbon particles and complex hydrocarbon gases in said synthesis gas effluent from said primary reactor are reacted and/or dissociated preferentially into CO and H2.

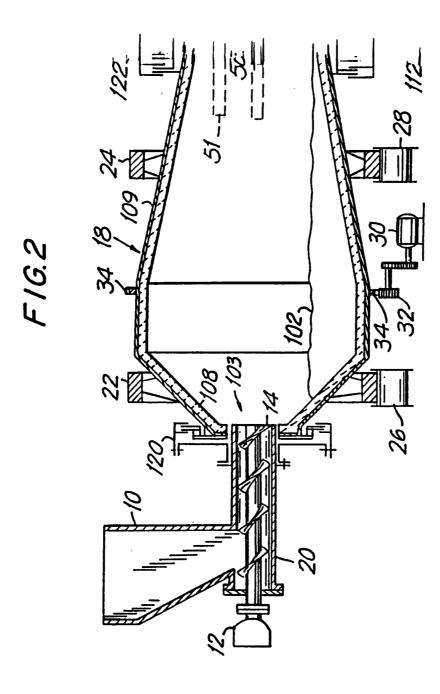
- Method according to claim 9, further comprising removing entrained particles remaining in said synthesis gas from said secondary reactor by subjecting said synthesis gas to cyclonic separation and wet scrubbing.
- 11. Method according to claim 9, wherein said finishing secondary gas stream is produced by combustion of a fuel with an oxygen-containing gas and is injected at a rate such that the temperature of said synthesis gas effluent from said primary reactor thereby is raised to 15 above 700°C, and at least a portion of any remaining free carbon or complex hydrocarbon gases in said synthesis gas are reacted and/or dissociated preferentially into CO and H₂.
- 12. Method according to claim 1, wherein the charge 20 containing organic materials is selected from the group consisting of automotive shredder residue (ASR); garbage; municipal waste; plastic wastes; tire chips; motor oil; and residues derived from petrochemical, polymer and plastics industries other than those previously listed.
- 13. Method according to claim 1, wherein said heating is accomplished by a plurality of burners positioned and directed into said primary reactor such that said oxidizing combustion products contact said evolved gases such that said resulting synthesis gas 30 contains less than two percent by volume of gases with a molecular structure having more than two carbon atoms.
 - Method according to claim 1, wherein said tumbling is accomplished by rotating said reactor about its horizontal axis; the charge containing organic materials is fed into said primary reactor at said charge end; and said residue is discharged from said primary

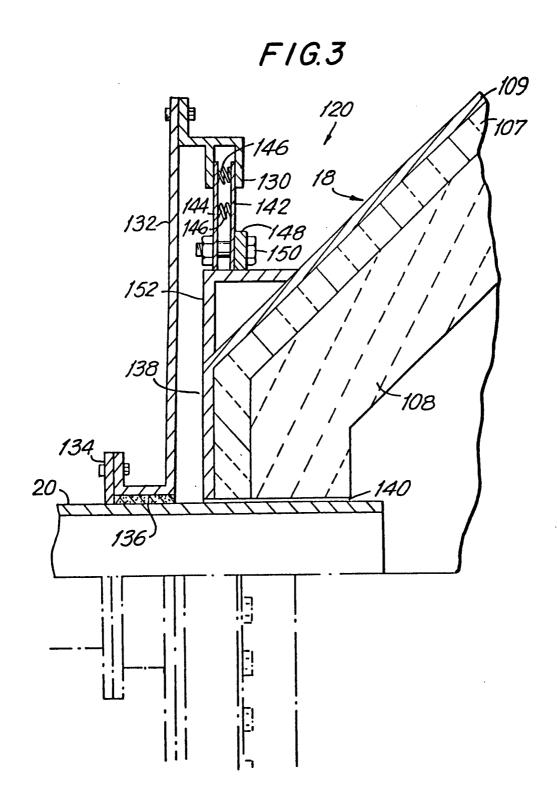
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reactor by volumetric displacement through an opening at said discharge end by means of said tumbling.

- 15. Method according to claim 1, wherein said fuel for said primary reactor is partially or wholly comprised of said synthesis gas.
 - 16. Method according to claim 1, wherein said fuel is selected from the group consisting of natural gas, synthesis gas, fuel oil, and coal.
- 17. Method according to claim 1, further comprising using the synthesis gas in the direct reduction of iron ore.
- 18. Method according to claim 12, wherein iron ore is reduced by a hydrogen and carbon monoxide containing reduction gas in a reducing zone and the resulting spent reducing gas is recirculated with dewatering and CO₂ removal prior to reintroduction into the reducing zone, said synthesis gas being itself dewatered and added to the recirculation loop at least prior to the CO₂ removal.
- 19. Method according to claim 1, wherein at least a portion of the CO₂ removed from the spent reducing gas is recycled through said burner or directly into said reactor.







INTERNATIONAL SEARCH REPORT

Ir utional Application No PCT/US 96/09628

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 C10J3/06 C10J3/14 C10J3/66 According to International Patent Classification (IPC) or to both national classification and IPC Minimum documentation searched (classification system followed by classification symbols) IPC 6 C10J Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practical, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT Relevant to claim No. Category * Citation of document, with indication, where appropriate, of the relevant passages 1-19 X EP,A,O 568 997 (PROLER ENVIRON. SERVICE) 10 November 1993 cited in the application see page 10-11; claims 1-21 1-3 GB,A,227 880 (HARALD NIELSEN) 19 February Α 1925 see page 1, line 11 - page 2, line 47 see page 3, line 43 - page 5, line 55 1.19 US,A,4 295 331 (REKANT) 20 October 1981 see column 6; claims 1-6 1-3,12Α GB,A,2 087 424 (FOSTER WHEELER POWER) 26 May 1982 see page 1, line 1-113 -/--Patent family members are listed in annex. Further documents are listed in the continuation of box C. Special categories of cited documents: "T" later document published after the international filing date or priority date and not in conflict with the application but sited to understand the principle or theory underlying the "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international "X" document of particular relevance; the claimed invention filing date cannot be considered novel or cannot be considered to "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docucitation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or ments, such combination being obvious to a person skilled other means in the art. document published prior to the international filing date but later than the priority date claimed "A" document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search 25.09.96 16 September 1996 Authorized officer Name and mailing address of the ISA European Patent Office, P.B. \$818 Patentiaan 2 NL - 2280 HV Ripwisk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Wendling, J-P Fax: (+31-70) 340-3016

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INTERNATIONAL SEARCH REPORT

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