# United States Patent [19]

# McKenzie et al.

- [54] PROCESS FOR PRODUCTION OF LOW BTU GAS
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- [52] U.S. Cl..... 60/39.02; 60/39.46 R; 60/39.12;
  - 48/203; 423/415 Int. Cl.<sup>2</sup>...... F02C 3/00

## [56] References Cited UNITED STATES PATENTS

1,921,711	8/1933	Wangemann 48/206
3,252,773	5/1966	Solomon et al 48/202
3,533,739	10/1970	Pelczarski 423/650 X
3,567,412	3/1971	LeFrancois et al 252/373 X
3,704,587	12/1972	Krieb et al 60/39.18 B X
3,708,270	1/1973	Birk et al 48/209 X

# [11] **3,916,617**

## [45] Nov. 4, 1975

3,710,737	1/1973	Birk 110/7 R
3,745,109	7/1973	Heredy et al 48/211 X
3,770,399	11/1973	Chong 48/210 X

Primary Examiner-S. Leon Bashore

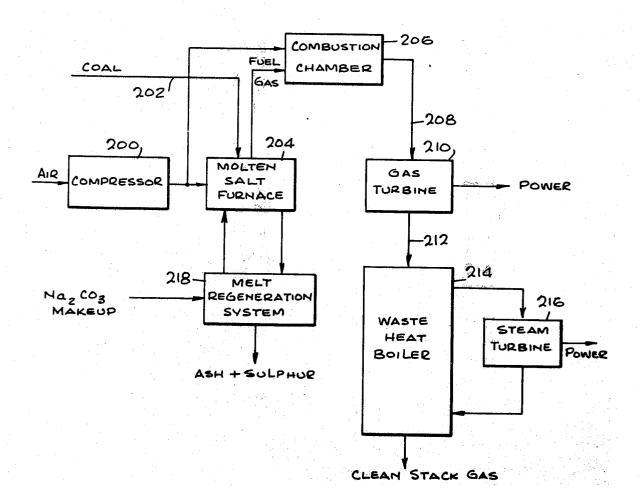
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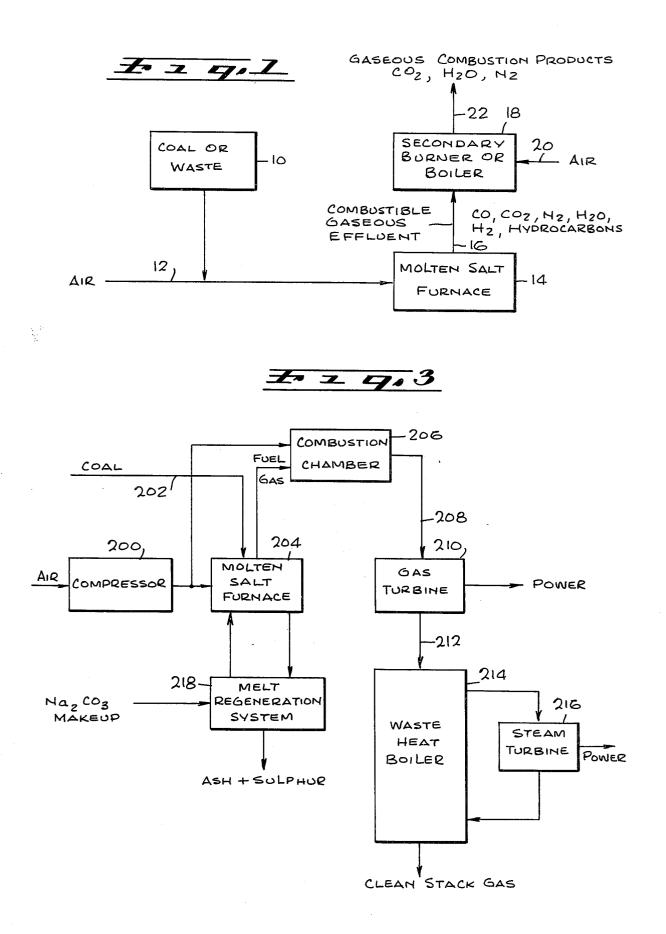
#### ABSTRACT

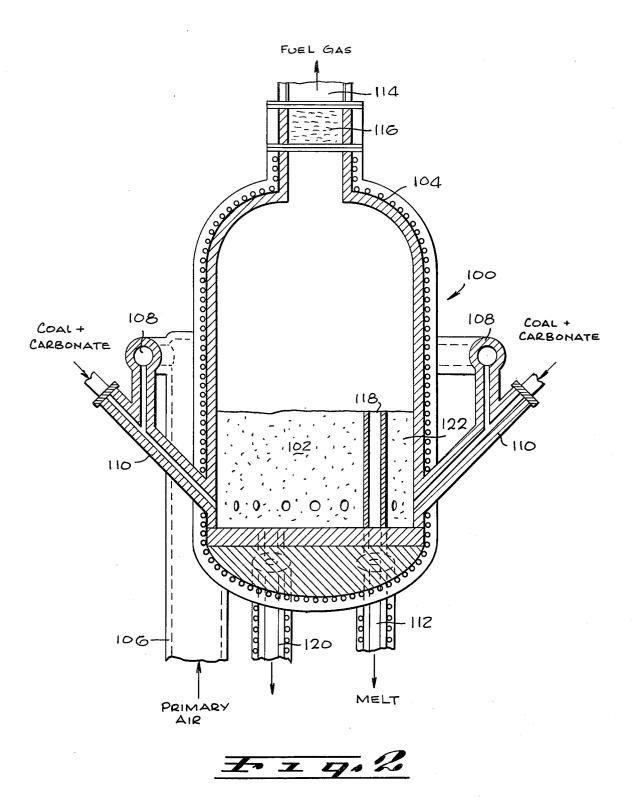
[57]

A process for partial oxidation and complete gasification of a carbonaceous material to produce a combustible gas containing a substantial proportion of carbon monoxide, by introducing the carbonaceous material and air as a preferred source of oxygen into a molten salt containing an alkali metal carbonate and preferably also an alkali metal sulfide, the system being operated preferably above atmospheric pressure, up to about 20 atmospheres. The air is employed in a proportion to provide less than about 60% of the amount of oxygen stoichiometrically required for complete oxidation of the carbonaceous material. Sulfur and ash introduced with the fuel are retained in the molten salt. The gaseous effluent, containing a weight ratio of carbon monoxide to carbon dioxide substantially greater than 1, is a low BTU gas. This gas can be reacted or combusted outside the molten salt in a second reaction zone, such as a conventional boiler, to recover the heat value of such gaseous effluent.

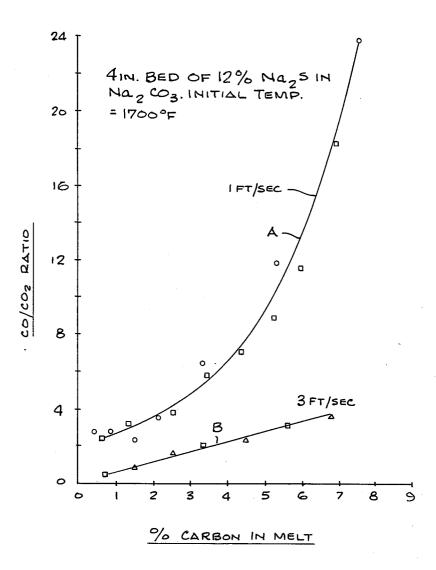
#### 4 Claims, 4 Drawing Figures







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## **PROCESS FOR PRODUCTION OF LOW BTU GAS**

#### BACKGROUND OF THE INVENTION

This invention relates to a process for the production <sup>5</sup> of low BTU gas by the combustion and gasification of carbonaceous materials, particularly solid sulfur-bearing carbonaceous fuel. The invention particularly relates to a molten salt process for the combustion and gasification of carbonaceous materials, particularly <sup>10</sup> coal, under conditions to obtain partial oxidation and production of a combustible gaseous effluent containing a high ratio of carbon monoxide to carbon dioxide, and, when employing air as the source of oxygen, obtaining a low BTU gaseous effluent of the above type <sup>15</sup> which contains nitrogen, such gas being adapted for complete combustion in a secondary reaction zone.

The combustion of carbonaceous material such as solid carbonaceous fuel by reaction with a source of oxygen such as air, oxygen-enriched air, or pure oxygen is <sup>20</sup> well known. In such a process, it is known to carry out the reaction employing an amount of air or oxygen equal to or greater than that required for complete combustion, whereby the gaseous effluent contains carbon dioxide with little if any carbon monoxide. It is <sup>25</sup> known also to carry out the gasification or partial oxidation of solid carbonaceous materials or fuels employing a limited quantity of oxygen or air so as to produce some carbon monoxide together with carbon dioxide.

However, prior art combustion reactions generally <sup>30</sup> have been carried out in a single stage to obtain substantially complete oxidation of the carbonaceous materials or fuel, so that only a minor amount of carbon monoxide is present in the effluent gas. In many cases, carbonaceous materials or fuels often contain impuri-<sup>35</sup> ties such as sulfur, and hence during gasification and combustion thereof undesirable acidic pollutants such as oxides of sulfur are formed.

The use of molten salts in the combustion and gasification of carbonaceous materials is known. Thus, U.S. 40 Pat. No. 3,710,737 to Birk, directed to a method for producing heat, discloses carrying out the combustion of carbonaceous materials in a molten salt medium in the form of an alkali metal carbonate melt containing a minor amount of alkali metal sulfate or sulfide. In such 45 combustion reaction, the combustion of the oxygen and carbon occurs indirectly, as described in the above patent, and the alkali metal carbonate, such as sodium carbonate, provides a compatible salt medium at practical operating temperatures, retains heat for conduct- 50 ing the combustion reaction, and also reacts with and neutralizes acidic or undesirable pollutants such as sulfur-containing gases which are formed during combustion of carbonaceous materials, e.g. coal, containing impurities such as sulfur and sulfur-bearing com- 55 pounds. A similar reaction in such molten salt medium is disclosed in U.S. Pat. No. 3,708,270 to Birk et al, directed to a method of pyrolyzing carbonaceous material. A carbonaceous feed is thermally decomposed in a pyrolysis zone by heating it in the absence of oxygen to 60 form char and a gaseous effluent. An optional steam input for gasification of the char material may also be utilized. In a heat generation zone, carbon and oxygen are reacted to form carbon dioxide to provide heat for the pyrolytic decomposition reaction.

In both of the above patents the reaction in the alkali melt is carried out to maximize heat generation so that the reaction product principally contains CO<sub>2</sub>, and also 2

 $N_2$  where air is the source of oxygen. Thus, in these patents, particularly U.S. Pat. No. 3,710,737, it is noted that carbon monoxide formation is undesirable, and although provision is made for a separate furnace or burner to combust any carbon monoxide present, carbon monoxide is stated to be a minor product of the reaction.

The above patents point out that an excess of carbon is used, i.e., an amount of oxygen less than that stoichiometrically required for complete oxidation of the carbonaceous material is present in the melt, so that under steady-state operating conditions the sulfur present in the melt is maintained substantially all in the sulfide form. These conditions are employed in these patents not for purposes of obtaining incomplete combus-

tion and formation of carbon monoxide, but in a manner so that substantially complete combustion of the char or coal to  $CO_2$  is achieved with as little production of CO as possible. Thereby a maximum amount of heat is obtained from the char or coal, most of this heat being generated in the molten salt.

According to the present invention, CO is obtained as the major product from the partial combustion and gasification process occurring in the molten salt. Subsequent heat generation is attained by combustion of the CO to  $CO_2$ , carried out in a boiler separate from the molten salt.

U.S. Pat. No. 3,567,412 to Lefrancois et al describes a process for the production of synthesis gas in which a
two-zone furnace is utilized for the gasification of carbonaceous materials, in one zone of which steam and a carbonaceous material are added to an alkali metal carbonate melt. The resulting char is transferred to the second melt-containing zone where it is catalytically
combusted to provide heat for the gasification reaction by maintaining at least a critical minimum concentration of 0.4 weight percent sodium sulfate.

U.S. Pat. No. 3,567,377 to Lefrancois et al, is directed to absorption of sulfur from liquid and solid carbonaceous materials by contacting such material with a molten salt. There is envisioned either a two-step process of gasification (steam plus carbonaceous material) plus combustion or a two step process involving sulfate reduction and pyrolysis, plus an oxidation step in which heat is produced by an exothermic oxidation of a carbonaceous material.

U.S. Pat. No. 3,252,773 to Solomon et al discloses a carbon-containing solid material and steam brought into contact with a melt comprising an alkali metal compound under conditions such that a hydrogen-rich gas is formed along with a resultant char. As an adjunct, heat may be supplied for the gasification reaction by combusting the resultant char with air, a requirement of the system being that any heat generation occur as the direct combustion of carbon by the reaction of carbon and oxygen to form carbon dioxide.

The Pelczarski et al U.S. Pat. Nos. 3,533,739 and 3,526,478 disclose the gasification of solid sulfur-bearing fuel wherein the fuel is injected into a molten iron bath maintained at a temperature above about 1400°C, and a limited quantity of oxygen or air is also injected into the bath. Carbon contained in the fuel is absorbed by the iron and preferentially reacts with the air or oxygen to form carbon monoxide which then passes up-<sup>65</sup> wardly through the iron bath. A molten layer of limebearing slag is maintained on the surface of the molten iron bath to function as a fluxing agent for the ash and to cause the sulfur absorbed by the molten iron to be

desorbed and to react with the lime to form calcium sulfide. A portion of the slag is continuously withdrawn thereby continuously removing sulfur from the iron bath. The mixture of gases from the combustion reaction including carbon monoxide can then be reacted 5 with oxygen to form carbon dioxide thereby generating additional heat.

## SUMMARY OF THE INVENTION

It is an object of the present invention to provide an 10 improved process for generating a low BTU gas from carbonaceous material. It is yet another object of the present invention to provide a process for heat generation from carbonaceous materials which obviates removal of pollutants formed in the combustion reaction. <sup>15</sup> A particular object of the invention is the provision of a process for partial oxidation of a carbonaceous material in a molten alkali metal salt medium for production of a gaseous effluent containing a high proportion of combustible gases, particularly carbon monoxide and 20 hydrogen, such gaseous effluent then being adapted for further and complete combustion in a secondary reaction zone or combustor, to utilize the heat value of the gas.

In accordance with the broad aspects of the present.<sup>25</sup> invention, a carbonaceous material such as coal or a combustible waste material is introduced, together with a source of oxygen, suitably and preferably air, into a reaction zone preferably maintained at above atmospheric pressure. Pressures from 1 to about 20 atmospheres are preferred, pressures between 5 to 10 atmospheres being particularly preferred. This reaction zone contains a molten salt mixture consisting essentially either only of an alkali metal carbonate or mixture of alkali metal carbonates, or preferably consisting essen-35 tially of a major portion of an alkali metal carbonate and a minor portion of an alkali metal sulfate or sulfide. The source of oxygen, preferably air, is employed in a proportion such as to provide an amount of oxygen 40 substantially below the amount stoichiometrically required for complete combustion of the carbonaceous material. Generally the air employed is used in a proportion to provide less than about 60 percent of the amount of oxygen stoichiometrically required for complete oxidation or combustion. Other reaction parameters are controlled so as to favor incomplete combustion of the carbonaceous material, and maximize production of CO, consistent with maintenance of the molten salt temperature at a desired value, as well as adequate throughput of coal or carbonaceous material in <sup>50</sup> CO<sub>2</sub> with the release of 68 kcal of heat. Thus, of the the most economical manner.

It is particularly preferred that at least 1 wt. percent of alkali metal sulfide, and up to 25 wt. percent, be present in the molten salt under steady-state conditions, the sulfide serving to catalyze the rate of partial 55 combustion of the carbonaceous material. Any sulfate initially present is converted to sulfide under steadystate conditions. In addition to the direct addition of sulfide to the melt, coal or other carbonaceous material containing sulfur can also serve as a source of the sulfide. The temperature of the molten salt is maintained between about 1400° and about 2000°F (about 760° to 1100°C), particularly between about 1,600° and about 1,800°F (about  $870^{\circ} - 980^{\circ}$ C) where coal is the carbonaceous material. The result is a gaseous effluent from <sup>65</sup> the gasification and combustion reactions which contains a substantially greater volume of CO than CO<sub>2</sub>, generally at least 5:1 and up to 20:1, and which also

contains other combustible gases such as hydrogen and hydrocarbons.

The sulfur and sulfur-bearing contaminants and ash present in the carbonaceous material or fuel, e.g., coal, are retained in the molten salt. The retention of the sulfur and ash from the fuel in the melt eliminates the requirement for a stack gas sulfur oxide removal system and an electrostatic precipitator. These materials can be removed from the reaction zone with a continuous stream of molten salt, the contaminants removed from such stream, and the regenerated stream of molten salt being returned to the reactor. Nitrogen oxide formation is negligible at the relatively low temperatures prevailing in the molten salt furnace.

The resulting combustible gaseous effluent from the salt furnace containing a substantial portion of combustible gases such as carbon monoxide and hydrogen can then be brought into a second combustion zone or unit, which may be in the form of a conventional utility boiler, and reacted therein with oxygen of the air to oxidize the combustible gases to CO<sub>2</sub> and water with the release of heat.

### BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be more clearly understood by reference to the detailed description below of certain preferred embodiments taken in connection with the accompanying drawings wherein:

FIG. 1 is a flow chart illustrating generally the process of the present invention;

FIG. 2 is a schematic illustration of a preferred form of reactor containing the molten salt;

FIG. 3 is a flow chart of an alternative molten salt combustion process according to the invention, employing a pressurized gas feed; and

FIG. 4 is a graph illustrating the effect of carbon content of the melt on CO/CO<sub>2</sub> ratio obtained during partial combustion in the molten salt reactor.

#### DESCRIPTION OF THE PREFERRED **EMBODIMENTS**

To illustrate the above noted mode of partial combustion of the carbonaceous material in the molten salt, in the case of carbon, for example, in the partial combustion reaction in the molten salt the carbon is partially oxidized to carbon monoxide with the release of its heat of combustion of about 26 kcal. The CO is then brought into a second reaction zone or combustion unit such as a utility boiler, wherein the CO is oxidized to overall heat of combustion of carbon to  $CO_2$  of 94 kcal, 26 kcal or about 28 percent is released in the molten salt and 68 kcal or about 72 percent is released in the secondary combustion zone or unit. In the case of coal, hydrogen and hydrocarbons are also present in the gaseous effluent released from the salt, in addition to the CO and CO<sub>2</sub> present.

An important advantage of the process of the present invention is that complex cooling equipment is not re-<sup>60</sup> quired for the removal of heat from the molten salt, since the amount of heat generated by the oxidation reaction in the molten salt is essentially only that amount of heat which is required to maintain the salt in its molten condition. Most of the heat is generated by combustion of the gaseous effluent from the molten salt. This combustion takes place in a secondary combustion zone or boiler separate from the molten salt. Thus, a given size molten salt furnace will permit a much higher feed rate of fuel or carbonaceous material where only partial combustion is carried out therein for production of a combustible gas containing a substantial proportion of CO and hydrogen in accordance with the present invention. Since the separate secondary combustor <sup>5</sup> or boiler for large-scale combustion is less expensive than a larger molten salt furnace which would be required for complete combustion, the overall economics of the process are substantially improved. The application of the invention concept to the gasification particularly of coal is especially important since large throughputs of coal must be processed in the most economical manner.

In carrying out the invention process, in order to particularly obtain a product gas having a volumetric ratio 15 of carbon monoxide to carbon dioxide substantially greater than 1, the air is introduced into the molten salt in a proportion to provide an amount of oxygen less than about 60 percent of that theoretically required for complete combustion of the carbonaceous material to 20 CO<sub>2</sub> and H<sub>2</sub>O. Generally, the air is employed in an amount to provide from about 30 percent to about 60 percent, preferably from about 35 to about 45 percent, of the amount of oxygen theoretically required for complete combustion of the carbonaceous material. If <sup>25</sup> more than 60 percent of the oxygen needed for complete stoichiometric combustion is provided, then the resulting gas has a carbon monoxide:carbon dioxide ratio generally less than one, which is undesirably low. If less than about 30 percent of the oxygen stoichiomet- 30rically required for complete combustion is provided, then unburned coal or char begins to accumulate in the molten salt until its viscosity becomes too high.

The invention process and the conditions of operation, particularly when using coal as the preferred car-35 bonaceous material or fuel, and air as the preferred source of oxygen, are chosen so as to obtain from the partial combustion reaction in the molten salt, a combustible gas product containing as much CO as possible and as high a BTU content as possible, with the minimum amount of heat evolution in the molten salt as possible, sufficient to maintain the salt in the molten state. Thereby the combustible product gas will provide a maximum amount of heat in the secondary combustion zone. For this purpose, it is desirable to employ a 45minimum amount of oxygen for carrying out the partial combustion reaction in the molten salt, consistent with efficient overall operation and heat requirements within the ranges noted above.

Air is the preferred source of reactant gaseous oxy-<sup>50</sup> gen for use in the present process. While oxygenenriched air or pure oxygen can be used, thereby resulting in a combustible product gas of higher BTU content, the use of oxygen would ordinarily be economically undesirable for the production of such com-<sup>55</sup> bustible product gas, since this would ordinarily require an oxygen plant. Accordingly, the present invention will be particularly described and illustrated using air as the source of oxygen.

The present process finds its principal and significant <sup>60</sup> utility when integrated into a conventional coal-fired steam plant. This involves the incorporation of the molten salt furnace and its associated auxiliary equipment into the coal feed system of the plant boiler. The molten salt furnace can thus be considered as an additional step in the treatment of the coal prior to its combustion in the boiler. This step takes the pulverized coal and converts it into a high temperature (about 980°C.) low

heat content (about 150 BTU/scf) fuel gas. This low BTU fuel gas is then burned in the boiler as a non-polluting fuel. The ash and sulfur are retained in the melt and removed in the auxiliary equipment associated with the molten salt furnace. Thus the low BTU gas which is generated is burned on site. However, various features of the present process may be utilized, using pure oxygen as the feed gas, together with certain significant modifications and additions to the process, to produce a high BTU pipeline gas, not intended for onsite heat generation. The process for producing such a synthetic pipeline gas does not form part of the present invention.

The air and the carbonaceous material, preferably coal, are fed into the molten salt, which is maintained at a temperature generally ranging from about 1400°F to about 2000°F (about 760°C to 1100°C), and in preferred practice the temperature of the molten salt is maintained between about 1600° and about 1800°F. (about 870°C to 980°C). When the molten salt is principally sodium carbonate containing from about 1 to about 25 wt. percent sodium sulfide, a temperature preferably from about 1600° to about 2000°F is utilized. It is desirable to maintain the temperature low enough so that essentially no oxides of nitrogen are formed during the partial combustion reaction and so that particulate emission is minimized.

The initial molten salt mixture can contain either alkali metal sulfate or sulfide. It preferably consists essentially of sodium carbonate containing from about 1 to 15 wt. percent sodium sulfate, an amount between about 3 and 10 wt. percent sodium sulfate being particularly preferred. Alternatively, a binary or ternary mixture of the carbonates of sodium, potassium and lithium can be employed, a preferred binary mixture being the Na<sub>2</sub>CO<sub>3</sub>-K<sub>2</sub>CO<sub>3</sub> eutectic. The sulfur compound may be added initially as sulfate, it being converted to sulfide under steady-state conditions. Any of the sulfates of the foregoing alkali metals may be utilized. Sodium sulfate is generally preferred because of its ready availability and low cost. The sulfur (as sulfide) content of the molten salt can also be furnished either wholly or partially from the sulfur content of the carbonaceous material, e.g., coal, employed, so that alkali metal sulfate or sulfide need not then be added initially to the alkali metal carbonate.

In the molten salt reaction medium, under the conditions of reaction in the present process, wherein a stoichiometric deficiency of oxygen is provided for initial <sup>50</sup> incomplete combustion, the sodium sulfide is considered to catalyze the combustion reaction by a complex reaction mechanism. While various exemplary intermediate reactions may be postulated, precise knowledge as to the details of the reaction mechanism is still lack-<sup>55</sup> ing. Thus it is not intended that the present invention be considered limited by the following explanation.

The net overall reaction that occurs is the partial oxidation of the carbonaceous material or coal. However, the combination of the oxygen and carbon is believed to occur indirectily in that each of such components reacts separately with a component present in the molten salt. Thus, the alkali metal sulfide, e.g., sodium sulfide, functions to increase the burning rate. The alkali metal carbonate provides a compatible salt medium at practical operating temperatures and acts as a dispersing medium for both the fuel being combusted and the primary air used for the combustion. In addition, the carbonate melt neutralizes the acidic pollutants, such as

oxides of sulfur and chlorine-containing gases, formed in the partial oxidation reaction, and retains the resulting products. The carbonate melt also acts as a heat sink, with high heat transfer rates for absorbing and distributing the heat of combustion, as a heat source for 5the distillation of the volatile matter of the fuel, and as an absorbent for the ash from the fuel.

Many forms of carbonaceous materials, i.e., those providing an effective source of reactive carbon, can be 10 used as the fuel or reductant in the invention process. Thus, all of the common forms of carbonaceous fuels can be used including coal, coke, fuel oil, petroleum residue, lignite, peat, wood, photographic film, plastics, pesticides and their containers, and municipal wastes 15 such as household trash and garbage, and sewage sludge; industrial wastes such as polyvinyl chloride and scrap rubber, and agricultural wastes including plant and animal waste material. For purposes of the present invention, generally coal is the preferred carbonaceous 20 material. The present process is further advantageous in its ability to handle a wide variety of coals, including lignite, subbituminous bituminous, and anthracite coals, without any need for pre-treatment of caking coals. Tar formation is also absent in the present pro-25cess.

In addition to a feed of a carbonaceous material and a reactive source of oxygen, it is sometimes desirable to include an additional catalyst in the molten salt other than the alkali metal sulfide for the above reduction re-30 action. Iron compounds have been found to be good catalysts for this reaction, employing an amount of iron ranging from about 0.5 to about 3 weight percent of the melt. The iron can be added in the elemental form or preferably in the form of compounds containing iron, 35 such as iron sulfide or iron sulfate.

During operation of the partial combustion reaction in the molten salt mixture, impurities present in the carbonaceous material are retained in the melt. The amount and type of impurities present in the melt will 40vary depending upon the source of carbonaceous material or feed. The most common impurities are ash and sulfur, the sulfur generally being present as a sulfur compound such as sodium sulfide in the melt. To remove such impurities, a portion of the alkali carbonate 45 melt is withdrawn continuously and processed in a regeneration system which removes the ash and sulfur compounds retained in the melt and returns the regenerated sodium carbonate back to the molten salt furnace. A typical impurity removal process for this pur- 50 pose is described in above U.S. Pat. Nos. 3,710,737 and 3,708,270.

The effluent gas mixture from the partial combustion reaction in the molten salt contains carbon monoxide and carbon dioxide having a volumetric ratio of CO to 55 CO<sub>2</sub> substantially greater than 1, and generally ranging from about 5:1 to about 20:1. A combustible gaseous effluent according to the invention can contain from about 90 to about 95 percent CO and about 5 to about 10 percent CO<sub>2</sub>, by volume, based on these two compo-60 nents. Where coal is employed, the effluent gas will also contain hydrogen and hydrocarbons, together with nitrogen and water. It has been found that CO concentrations in the gaseous effluent will increase with (1) reduction in the percentage of oxygen stoichiometri- 65 trated a type of molten salt gasification furnace which cally required for complete combustion, (2) increasing carbon content in the melt, (3) higher temperatures of reaction and (4) increasing sulfide content of the melt.

The carbon content of the melt can range, for example, from about 1 to about 10 percent.

Where coal is employed as the carbonaceous material, and air is used as a source of oxygen, the combustible effluent gas containing the above noted high ratios of carbon monoxide to carbon dioxide, has a relatively low BTU heating value, which can range from about 100 to about 200 BTU per cubic foot. When such a low BTU gas is combusted in a secondary burner or combustion zone, such as a boiler, the major portion of the heat of reaction from the overall heat of combustion by complete combustion of the carbonaceous material to CO<sub>2</sub>, is released in the secondary combustion zone.

The molten salt combustion system is operated at a pressure between 1 and 20 atmospheres, preferably between 5 and 10 atmospheres. By operating at pressures above atmospheric, a higher throughput of coal and air is obtained than at atmospheric pressure. Thereby the combustion reaction can be accomplished in a smaller vessel for a given rate of coal feed to the vessel.

Referring to FIG. 1 of the drawing, a carbonaceous feed material 10, such as coal or a waste material, and air 12, as a source of reactive oxygen, are supplied to the molten salt furnace or reactor 14 containing a Na2. CO<sub>3</sub>-Na<sub>2</sub>S melt. Furnace 14 is maintained at a pressure between 5 and 10 atmospheres. The air may be introduced in the bottom portion of the reactor zone so as to pass upwardly through the melt and thereby provide for an intimate mixing of the air, coal, and molten salt. The heat generated by such oxidation reaction is sufficient to maintain the melt in the molten condition within the desired temperature ranges noted above for effective partial oxidation and substantially complete gasification of the carbonaceous fuel according to the invention.

A combustible gaseous effluent 16 from the molten salt furnace 14 contains CO and CO<sub>2</sub>, in the above noted volumetric ratio of CO to CO2 substantially greater than 1, and preferably at least 5 to 1, and also contains H<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub> and small amounts of hydrocarbons. Such low BTU gaseous effluent, preferably having a heating value in excess of 100, and most desirably of the order of about 150 to about 200 BTU per standard cubic foot, is introduced or injected into a secondary burner or boiler 18, together with air 20. Heat from the reaction of carbon monoxide in such combustible gas with oxygen from the injected air, forming carbon dioxide, plus a major portion of the sensible heat content of the products of combustion passing through the boiler, are transfered to water within the boiler 18, converting it into steam, which can then be fed to a steam turbine. The resulting gaseous combustion products pass out of the boiler 18 by way of a conduit 22. Such gaseous combustion products consist essentially of CO2, H2O, and N2. Such completely oxidized combustion products can be vented or passed into a heat exchanger (not shown) for extraction of additional sensible heat, e.g., for preheating boiler feed water. Operation of the molten salt furnace takes place preferably at a pressure between 5 and 10 atmospheres, although a pressure just high enough above ambient to allow the fuel gas generated to be injected into the fuel nozzles of the boiler is also suitable.

Referring now to FIG. 2 of the drawing, there is illuscan be employed in the invention process. In FIG. 2, a reactor vessel 100 contains a body of molten salt 102, e.g. comprising sodium carbonate and 1 to 15 wt. per-

cent sodium sulfide. The reactor is provided with an insulated air or water cooling jacket 104, and there is provided a primary air inlet 106 and an air manifold distributor system 108, and coal inlets 110, the air manifold and coal inlets being interconnected. The coal in-5 lets can also serve for introduction of alkali metal carbonate into the reactor. The reactor is also provided with a melt outlet 112 and a gaseous outlet 114. The outlet 114 is provided with a conventional demister 116 for removing liquid and solid particulates from the 10effluent gas. The reactor is also provided in the interior thereof with an overflow weir 118, to maintain a constant level of molten salt, and a drain 120. Air is supplied to the reaction or partial oxidation zone 122 comsystem 108.

In the molten salt furnace, the carbonaceous material is partially combusted to CO, CO<sub>2</sub> and H<sub>2</sub>O, with release of hydrogen and hydrocarbons into the resulting gases. The partial combustion and the gasification take 20 place rapidly at relatively low temperatures, e.g. of the order of 1,700°-1,800°F, because of the high contact areas and high heat transfer rates, and more importantly, because of the catalytic effect of the sodium sulfide dissolved in the melt.

Under the conditions of reaction according to the present invention, employing a proportion of air to provide less than about 60 percent of the amount of oxygen stoichiometrically required for complete oxidation of the carbonaceous material, preferably about 35 to  $^{30}$ about 45 percent of such stoichiometric amount, partial oxidation of the coal occurs in the molten salt reaction zone 102. The gaseous effluent exiting the reactor at 114 contains at least 5 to 1 volumetric ratio of cargen, hydrocarbons and water, and also nitrogen from the air supply.

As the reaction proceeds in the molten salt body 102, acidic contaminants such as sulfur or sulfur-bearing materials in the carbonaceous material or coal pass into the molten salt, the sulfur-bearing materials forming alkali metal sulfides such as sodium sulfide. The capacity of the salt melt for retaining the sulfur and ash of the coal is limited by the maximum allowable concentration of these materials in the melt. When this concen- 45 tration is reached, any undesirable buildup of sulfur and ash in the melt is prevented, and a steady-state condition is established by continuous withdrawal of the side stream 112 of sulfur-and ash-containing melt and addition of regenerated sodium carbonate and carbon-50 ate makeup back into the molten salt furnace. This side stream is quenched in water, which dissolves the sodium carbonate and sulfur compounds. The insoluble ash and any uncombusted carbon are removed from the solution by clarification and/or filtration, prefera- 55 bly in the presence of CO<sub>2</sub> to decrease silicate formation. Carbonation of the filtrate with flue gas and steam stripping are employed to regenerate the sodium carbonate and release hydrogen sulfide. The hydrogen sulof elemental sulfur or sulfuric acid. The sodium carbonate is crystallized out of its water solution, and after addition of makeup, is returned to the molten salt furnace

Although the combustion of the combustible gaseous 65 product from reactor 102 has been described above and illustrated in FIG. 1 of the drawing as being further combusted in a separate combustor or burner 18, it will

be understood that such combustible gaseous product may be combusted, e.g., in the reactor vessel, in a zone above the body of the melt 102.

As a further feature, integration of the molten salt combustion and gasification process of the present invention into a conventional coal-fired steam plant can be achieved by incorporating the molten salt furnace and its associated auxiliary equipment into the coal feed system of the boiler. The molten salt furnace can thus be considered as an additional initial step in the treatment of the coal prior to combustion of the product gas in the boiler. The integration of the molten salt furnace system into a conventional power plant can be done in various ways, the simplest involving the instalprised of the salt melt 102 through the air distributor <sup>15</sup> lation of the molten salt furnace as a supplementary unit upstream of the boiler.

Operation of the molten salt furnace at a pressure just high enough above ambient to allow injection of the gas generated into the boiler, as in conventional operation, has the disadvantage that it requires a large cross section molten salt furnace, since the controlling parameter involved is the superficial velocity of the fuel gas generated. To decrease the cross section of the molten salt furnace, operation of this furnace can be 25 carried out under pressure. Typically a pressure of 5 atmospheres will decrease the diameter of the furnace by a factor of 2.2. The amount of energy required to compress the primary air feed is however appreciable and, for economic reasons, it is important that this energy be recovered by expanding either the fuel gas produced or the off-gas from the system through a gas turbine. A process and system employing such concept is illustrated in FIG. 3 of the drawing.

In FIG. 3, air is compressed in a compressor 200, and bon monoxide to carbon dioxide, together with hydro-<sup>35</sup> fed together with coal at 202 into a molten salt furnace 204. The combustible flue gas from the molten salt furnace and containing a volumetric ratio of CO to CO2 substantially greater than 1 according to the invention, is fed to a secondary combustion chamber 206 where 40 the gas is completely combusted. The combustion gases at 208 are introduced into a gas turbine 210, generating power for operation of compressor 200, and the expanded gases from the gas turbine are introduced at 212 into a waste heat boiler 214 which generates the steam for a steam turbine 216 for the steam cycle portion of the plant. The process also includes a melt regeneration system 218, described above. Thus, in this process a combination molten salt furnace and secondary combustion chamber can be used as a substitute for the combustion chamber of a conventional gas turbine.

In an alternative method to the method illustrated in FIG. 3, the fuel gas from the molten salt furnace can be fed directly to a gas turbine to generate power, and the turbine discharge gas which is still uncombusted and containing a major portion of CO with respect to CO<sub>2</sub> according to the invention, is fed to a power plant boiler functioning as the secondary combustion zone to effect complete combustion of the fuel gas from the molten salt furnace. A major advantage of this embodifide is processed in a conventional manner for recovery <sup>60</sup> ment is that the gas turbine expansion lowers the temperature of the fuel gas by several hundred degrees, with a consequent decrease in the combustion temperature in the secondary combustor and therefore a reduction in the oxides of nitrogen present in the stack gases.

Thus, the advantages of the above-noted alternative embodiments employing a compressed air feed and a gas turbine include a significant reduction in molten

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salt furnace cross-section as compared with the unpressurized operation, and generation of electric power in excess of that required for compression of the primary air feed, thereby permitting a significant improvement in the overall net heat rate of the plant.

The following examples illustrate the practice of the invention, it being understood that such examples are not intended as limitations of the invention.

#### **EXAMPLE 1**

Gasification of Kentucky No. 9 Seam Coal at 1,800°F.

A series of tests were run employing Kentucky No. 9 Seam Coal having the following analysis:

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The moisture content of the gas exiting the reaction zone was calculated assuming saturation at the temperature measured. Furnace heat was used to maintain the desired temperature of the melt.

All gas analysis except those for hydrogen were made using a Beckman GC-2A gas chromatograph and helium as carrier gas. The carbon dioxide and hydrocarbons were determined using a Poropak Q column at 130°C. The oxygen, nitrogen and carbon monoxide <sup>10</sup> were determined using a Molecular Sieve 13X column

at room temperature. Hydrogen was determined using a Perkin Elmer 820 gas chromatograph, a Molecular Sieve 5A column at 190°C and argon as a carrier gas. The results and data of these tests are set forth in 15 Table 1 below:

TABLE 1

Gasification 7		Average of Thirty Minutes;							
Steady State ( Average Actual Theoretical Air, %	Melt Temp.,	% CO	Gas Analyses %CO2 %CH4 <sup>*</sup> %C2H8			%н,	Higher Heating Value BTU/scf.	Particu- lates, Grains/ scf.	Exit Gas Moisture Grams/ scf.
33.2	983	30.8	3.5	1.2	0.11	13.7	151	1.97	1.39
40.1	988	27.0	6.4	1.1	0.08	12.2	138	1.29	1.28
46.7	985	23.0	8.4	0.7	0.05	10.8	118	1.52	1.39
74.7	987	6.3	15.3	0.6	<0.05	2.9	36	0.81	1.31

scf. denotes standard conditions at 70°F. and 14.7 psia.

6.18% For each of the four stoichiometries set forth in Table 62.19 30 1 above, data were obtained at certain time intervals 4.29 1.31 during the one-hour period of the test, the data for the 0.04 stoichiometry of 33.2 percent average actual theoreti-4.22 15.34 cal air being given in Table 2 below as illustrative. Oxygen (by difference) 6.43 TARLE 2

						IADEL	4	de la serie	e a transforma	
		Gasificatio	n of Ke	ntucky No	. 9 Sear	n Coal at	Average	% Theor	etical Air o	of 33.2%
					Air R	ate — 1.6	3 scfm.		1.1	
				Coal Rate — 19.30 g/min.						
		Melt								Higher Heating
	Time, Min.	Temp., °C.	%CO	%CO2	%O2	%CH₄	%C <sub>2</sub> H <sub>6</sub>	%H <sub>2</sub>	%N2	Value BTU/scf.
	 0	982	;		<u> </u>	···	· _	·	· · · · · · · · · · · · · · · · · · ·	·
	5	979	26.2	6.0	1.1	- 1.1	0.14	13.0	49.0	140
	15	080	30.0	4 9	1.1	1 2	0.14	136	177	156

1.5

1.0

0.14

0.11

0.11

0.1

13.1

51.2

53.3

53.3

158

144

144

Particulates - 19.7 grains/scf.

982

982

983

985

30

40

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Exit Gas Moisture Content - 1.16 grams/scf.

30.0

30.6

31.2

31.2

No H<sub>2</sub>S, COS or SO<sub>2</sub> detected, limits of detection about 80 ppm.

2.8

44

2.6

0.4

Heating Value: BTU/lb

Moisture

Carbon

Hydrogen

Nitrogen

Chlorine

Sulfur

Ash

11,266

50 It is seen from Table 1 above that when employing from about 33 to about 47 percent average theoretical air, the ratio of  $CO/CO_2$  is substantially greater than 1 and ranges from about 3 to 1 for 46 percent theoretical air to about 9 to 1 for 33 percent theoretical air. On the other hand, when employing about 75 percent average theoretical air the ratio of CO/CO<sub>2</sub> is substantially less than 1.

It is also noted that the exit gas heating value varied from 36 BTU/scf. for 75 percent average theoretical air, to 118 BTU/scf. for about 47 percent theoretical air, and for the runs employing 33 percent theoretical air according to the invention, it is noted that the heating value of the effluent gas was 151 BTU/scf.

It is particularly noted that a 150 BTU gas is produced when the amount of air employed is about 33 percent of theoretical. Whe producing such a 150 BTU gas, the particulate loading is about 2 grams/scf, with close to 50 percent of the particulates being carbon.

The salt bed utilized in these tests had a composition at the start of these tests of 803 percent sodium carbonate, 134 percent sodium sulfate and 63 percent ash.

The coal was ground and dried before being fed by 55 means of a screw feeder to a bench-scale reactor containing the molten salt mixture. Air was fed at a rate of about 1.6 to about 2.1 scfm (ft.3/min. at standard conditions of 70°F and 14.7 psia) to the reactor, and the coal feed at a rate of about 11 to about 19 g/min. Air <sup>60</sup> rates and coal rates were chosen to give 1 ft/sec superficial velocity for the product gas exiting the salt bed. Each run was made employing the same time pattern, the runs being 1 hour in length, with 1/2 hour being allowed to reach steady state. This series of tests was car- 65 ried out at a melt temperature of approximately 1800°F (about 980°C) using four different air stoichiometries, as noted in Table 1 below.

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The bench scale equipment employed in these tests was not designed for demisting of the melt nor the deentrainment of air-borne solids so that the particulate emission is not an absolute value to be expected in actual plant operations.

It is also noted that no H<sub>2</sub>S, COS or SO<sub>2</sub> was detected in the exit gas, the limits of detection in these tests being about 80 ppm.

#### **EXAMPLE 2**

Gasification of Kentucky No. 9 Seam Coal at 1700°F. (927°C.)

The procedure of Example 1 was substantially followed in running another series of tests at four different 15 air stoichiometries, similar to Example 1 in which steady-state conditions were attained, but in this case the molten salt bed temperature was maintained at about 1700°F. The data and results of these tests are set forth in Table 3 below:

TABLE 3

and in the CO/CO<sub>2</sub> ratio with time apparently as a result of decrease in the carbon content of the melt with time.

The plot shows that the  $CO/CO_2$  ratio in the effluent gas resulting from partial combustion of the char increases as the amount of carbon in the melt increases. Thus, referring to curve A, when employing an air velocity of 1 ft. per second, with percent carbon in the melt increasing from about 3 to 7.5 percent, the CO/-10 CO<sub>2</sub> volumetric ratio in the effluent gas increased from 5 to 25. As seen from curves A and B, the CO/CO<sub>2</sub> volume ratios at superficial air velocity of 1 ft/sec were

substantially higher than at 3 ft/sec, for corresponding percentages of carbon in the melt.

From the foregoing, it is seen that the invention provides an efficient improved procedure for the production of low BTU gas by a molten salt combustion process for carbonaceous materials, particularly coal. This is accomplished by employment of an amount of air

Gasification T		ntucky N		Average of Thirty Minutes;					
Steady State ( Average Actual Theoretical	Melt Temp.,			Gas Analy	Higher Heating Value	Particu- lates, Grains/	Exit Gas Moisture Grams/		
Air, %	°C.	%CO	%CO2	%CH₄	$%C_2H_6$	%H <sub>2</sub>	BTU/scf.	scf.	scf.
33.7	908	25.9	5.8	1.1	0.18	11.7	138	2.01	1.19
42.8	915	23.3	7.4	0.8	0.14	9.3	117	1.54	1.18
49.8	934	12.4	7.4	0.8	0.08	8.3	75	0.87	1.26
79.9	945	6.8	14.1	0.6	< 0.05	3.3	39	1.02	1.58

From Table 3 above, it is noted that for about 80 percent theoretical air the CO/CO2 content of the effluent gas was substantially less than 1 to 1. On the other 35 hand, when employing air stoichiometries ranging from about 33 to 50 percent according to the invention, the ratio of  $\text{CO}/\text{CO}_2$  in the effluent gas ranged from about 2 for 50 percent theoretical air to almost 5 for about 34 percent theoretical air.

Also, when employing 80 percent theoretical air, the heating value of the effluent gas is only 39 BTU/scf. On the other hand, when employing from about 34 to 50 percent theoretical air according to the invention, the heating value of the effluent gas ranged from 75 BTU/scf, for 50 percent theoretical air to 138 BTU/scf. for about 34 percent theoretical air.

#### EXAMPLE 3

## Conditions for Obtaining High CO/CO<sub>2</sub> Ratios

Tests were carried out employing coal char (coal from which the volatiles have been removed) on a laboratory batch scale for producing a combustible gas containing carbon monoxide according to the invention, in a bed of molten sodium carbonate containing 12 per- 55 cent sodium sulfide. Air was introduced into the molten salt maintained at a temperature of about 1700°F. One set of tests was carried out at a superficial air velocity of 1 ft. per second, and another set of tests was carried out at a superficial air velocity of 3 ft. per second.

In each of these two sets of tests the CO/CO2 volumetric ratio in the effluent gas was measured based on varying percentages of carbon in the melt.

FIG. 4 shows the plot of such CO/CO<sub>2</sub> ratio against percent carbon in the melt, for superficial air velocities 65 of 1 and 3 ft. per second, as represented by curves A and B, respectively. It was noted that during these runs there was a gradual decrease in the CO concentration

providing less than about 60 percent of the oxygen that is stoichiometrically required for complete oxidation of the carbonaceous material. There is provided partial combustion and complete gasification of the carbona-

- ceous material or coal in the salt melt, thus permitting recovery of a combustible gaseous effluent free of acidic pollutants, and containing a high ratio of carbon monoxide to carbon dioxide, substantially greater than 1. The resulting low BTU gas can be readily combusted
- to complete oxidation for extraction of the heating value of the gas. The process permits economical processing of large coal throughputs while providing a pollution-free exhaust gas.

It will be of course realized that various modifications  $^{45}$  can be made in the design and operation of the present invention without departing from the spirit thereof. Thus, while the principle, preferred construction, and mode of operation of the invention have been explained and what is now considered in represent its best 50 embodiment has been illustrated and described, it should be understood that within the scope of the appended claims the invention may be practiced otherwise than as specifically illustrated and described. We claim:

1. A continuous process for gasifying coal which comprises:

- a. providing in a reaction zone a molten salt consisting essentially of a major portion of sodium carbonate and a minor portion of from about 1 to about 25 wt. percent sodium sulfide;
- b. maintaining said molten salt at a temperature of from about 1600°F to about 2000°F;
- c. maintaining from about 1 percent to 10 percent carbon in said molten salt;
- d. maintaining said reaction zone under a pressure of from about 1 to 20 atmospheres;
- e. concurrently introducing into said carbon-containing molten salt a sulfur and ash-containing coal and

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air, the air being introduced into the lower portion of the reaction zone at a superficial velocity of less than about 3 ft/sec and in an amount to provide from about 35 percent to about 45 percent of the amount of oxygen stoichiometrically required for complete oxidation of the introduced coal, and

f. controlling the conditions set forth in paragraphs (a)-(e) to promote carbon monoxide production and thermally decompose the coal to produce a 10 substantially sulfur and ash-free combustible, low BTU gaseous effluent containing a volume ratio of carbon monoxide to carbon dioxide of at least 5:1 and having a heating value within a range of from about 100-200 BTU/scf, the sulfur and ash content of the coal being retained in the molten salt.

2. The process as defined in claim 1, which includes passing said combustible gaseous effluent into a secondary combustor in the presence of air and completing combustion of said combustible gaseous effluent to convert carbon monoxide and hydrogen present substantially to carbon dioxide and water vapor, and recovering the heat of combustion in said secondary combustor.

3. The process as defined in claim 1, which includes initially compressing said air prior to introduction thereof into said molten salt, passing said combustible gaseous effluent from said molten salt into a secondary combustor in the presence of air and completing combustion of said combustible gaseous effluent, and employing said gaseous effluent from said molten salt or the combustion gases from said secondary combustor  $_{15}$  in a gas turbine to generate power.

4. The process as defined in claim 1 wherein in paragraph (c) there is maintained from about 3 percent to 7.5 percent carbon in said molten salt. \*

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