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# (54) METHOD OF CO-PRODUCING ACTIVATED CARBON IN A CIRCULATING FLUIDIZED BED GASIFICATION PROCESS

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## (57) ABSTRACT

A method of co-producing activated carbon in a circulating, fluidized bed gasification process includes gasifying carbonaceous fuel in a fluidized bed to form syngas and char, activating the char to form particles of activated carbon, discharging syngas and particulate solids entrained with the syngas from the reactor, separating entrained solids from the syngas with a particle separator and returning at least a portion of the separated solids to the reaction chamber, but allowing a solids product, including activated carbon and having an average size smaller than a predetermined size, to exit the particle separator with the syngas. The solids product is separated from the syngas in a dust separator to form cleaned syngas, and both the cleaned syngas and the solids product are discharged from the gasifier.

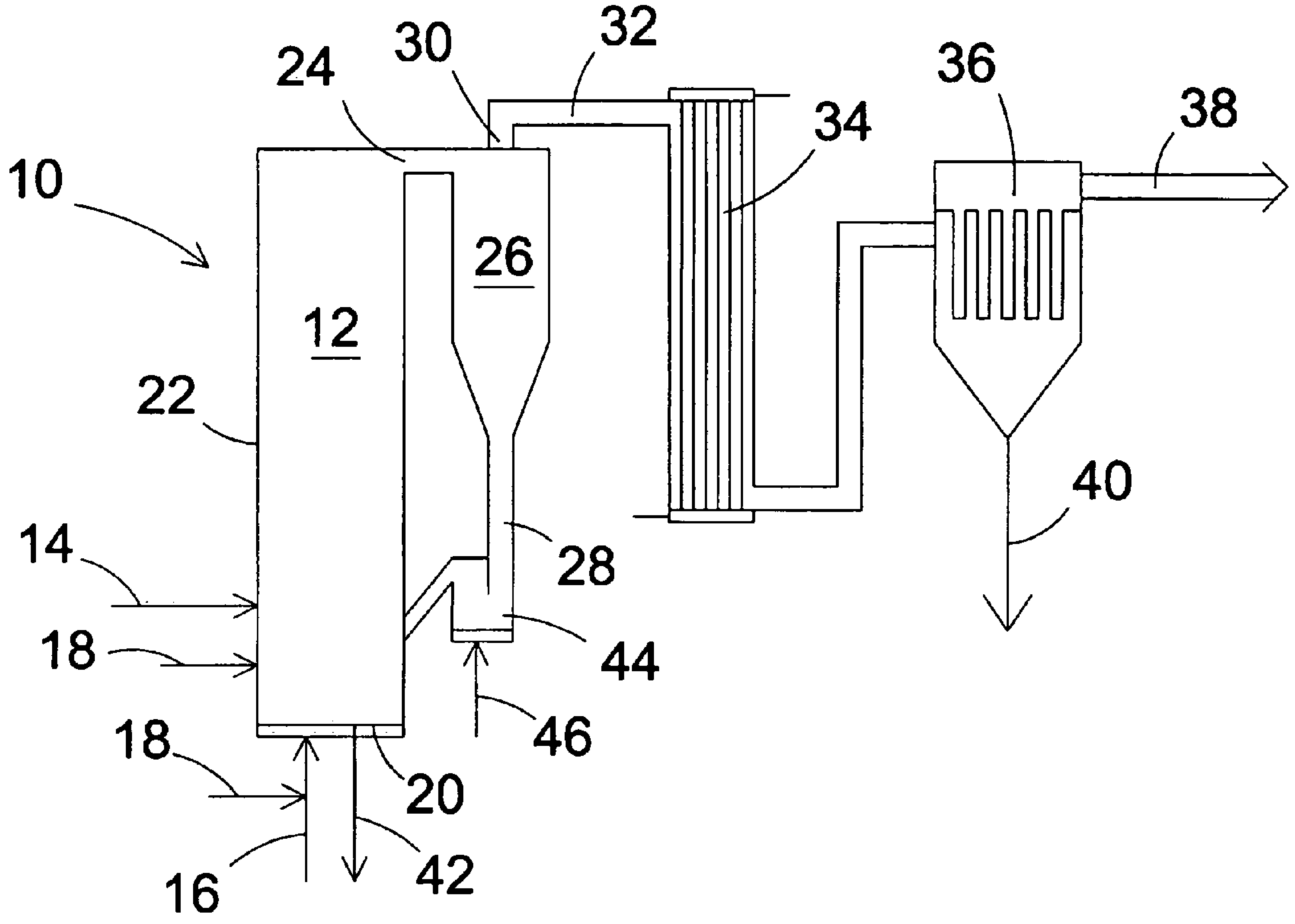

Fig. 1

# METHOD OF CO-PRODUCING ACTIVATED CARBON IN A CIRCULATING FLUIDIZED BED GASIFICATION PROCESS

## BACKGROUND OF THE INVENTION

**[0001]** 1. Field of the Invention

**[0002]** The present invention relates to a method of co-producing activated carbon in a fluidized bed gasification process, which activated carbon is especially suitable for removing mercury from the flue gases of combustion processes.

**[0003]** 2. Description of Related Art

**[0004]** Activated carbon (AC) is an effective adsorbent primarily due to its extensive porosity and very large available surface area. It is capable of removing low levels of organic and inorganic contaminants or impurities via transfer from the gas or liquid phase of a fluid that is being treated to the solid carbon surface of the AC. Activated carbon has been widely used to treat fluids in a large number of civil and industrial applications, such as water purification, wastewater treatment, sugar refining, beverage filtration, and air pollution control.

**[0005]** One of the applications for AC is mercury capture from the exhaust gases of industrial and combustion processes, especially from the flue gases of coal-fired power plants. Even if the levels of mercury in coals are low, mercury emissions from coal-fired power plants have recently been determined to pose a significant risk to public health. Thus, the reduction of mercury in the flue gases of combustion processes is of great importance.

**[0006]** AC injection is today the prevailing mercury control technology of combustion processes. Fine-grained AC is usually injected in the exhaust gases upstream of a dust collector, usually a baghouse or an electrostatic precipitator, and the spent AC is collected and disposed together with other combustion products, such as ashes. This technology has been commercialized for applications such as municipal waste and hazardous waste incinerators, and it is currently being demonstrated for application in coal-fired utility power plants. Thus, it is expected that the demand for AC will significantly increase over time.

**[0007]** AC is generally produced from a wide variety of carbon-rich raw materials, including wood, coal, peat, coconut shells, nut shells, bones and fruit stones. The raw material, from which a given activated carbon is produced, often has a substantial effect on its porosity distribution and surface area. As a result, activated carbons produced from different raw materials may have clearly different adsorbent qualities. Particle size distribution of the carbon particles is also important in AC systems because the particle size distribution influences the handling of the AC material, as well as the adsorption rates of pollutants.

**[0008]** One of the methods of producing AC is a two-step process including thermal activation. The first step is carbonization, during which most of the volatile matter in the raw material is removed, and porous char particles are formed. The second step is activation by steam, during which slow and controlled oxidation further develops the porous structure of the char particles, especially so-called micropores and mesopores, and increases the total surface area.

**[0009]** The use of AC for air pollution control applications, such as mercury capture, has requirements which differ from those in the traditional use of AC for purification and filtration. First, the removal of pollutants is limited by diffusion of the pollutants to the carbon surface during a short contact time (about 1 second) rather than the capacity or activity of the adsorbent. Secondly, because the spent AC is disposed of with the ash, leach out of impurities in the carbon is of much less concern than in water, food or pharmaceutical applications. Thirdly, unlike in filtration and purification applications that prefer granular or pelletized AC, in pollution control applications, such as mercury capture, AC is preferably injected in powder form to enhance its distribution and transfer with the flue gas.

**[0010]** U.S. Pat. No. 4,848,249 shows an atmospheric bubbling fluidized bed process for gasifying biomass, in which particulates containing activated carbon, with relatively low porosity, are separated from the produced combustible gas by using cyclonic separators. U.S. Pat. No. 4,883,499 discloses a gasification process in a layered, fixed bed adapted to produce activated carbon from organic input material. U.S. Pat. No. 5,089,030 shows a three-stage gasification apparatus and method for producing generator gas and activated carbon.

**[0011]** Due to the increasing use of activated carbon in pollution control applications, there is a need for low cost production of activated carbon with relatively low purity, moderate activity and fine particle size.

## SUMMARY OF THE INVENTION

**[0012]** An object of the present invention is to provide an efficient method of co-producing activated carbon from a fluidized bed gasification process.

**[0013]** Another object of the present invention is to enhance the competitiveness of coal gasification by co-producing activated carbon as a valued byproduct.

**[0014]** According to a preferred embodiment of the present invention, a method of co-producing activated carbon in a circulating fluidized bed gasification process is provided. The method comprises the steps of feeding carbonaceous fuel to a reaction chamber of a gasifier so as to form a particle bed in the reaction chamber, fluidizing the particle bed with oxygenous gas so as to partially oxidize the fuel to form syngas and char, and feeding an activation agent comprising at least one of steam and carbon dioxide to the reaction chamber so as to activate the char to form a particulate of activated carbon. Syngas and particulate solids entrained with the syngas from the reactor are discharged and entrained solids from the syngas are separated with a particle separator and at least a portion of the separated solids are returned through a return duct to the reaction chamber, but a solids product, comprising entrained solids of activated carbon and having an average size smaller than a predetermined size, is allowed to exit the particle separator with the syngas. The solids product is separated from the syngas in a dust separator, so as to form cleaned syngas. The cleaned syngas is discharged from the dust separator, and is supplied to a location for use in at least one of a combustion process and a chemical process. The solids product is discharged from the dust separator, and is supplied to a location for use in removing contaminants from a fluid. Preferably, the method further comprises the step of utilizing the separated solids product to remove contaminants from a fluid in at least one of a water purification process, a wastewater treatment process, a sugar refining process, a beverage filtration process, and an air pollution control process. More preferably, the separated solids product is used in capturing mercury from the flue gases of a combustion process.

**[0015]** The gasification of the fuel includes carbonization, during which most of the volatile matter of the fuel is removed and char particles are produced, and slow and controlled oxidation of the char particles. Activation of the char is realized within the gasifier system by injection of steam and/or $CO_2$. The steam and $CO_2$ remove carbon from the char by further oxidation through following reactions:

$$C+H_2O \rightarrow CO+H_2$$

$$C+CO_2 \rightarrow 2CO$$

**[0016]** The rates of the reactions are strictly controlled to maximize the internal surface area of the char. Both reactions are endothermic and supported with energy from the thermal energy of the circulating bed material originating from controlled oxidation of char and volatile matter. Steam and/or $CO_2$ may be injected into the bottom of the reaction chamber of the gasifier premixed with oxygenous fluidizing gas (preferably air). Additionally or alternatively, steam and/or $CO_2$ may be introduced into higher elevations in the reaction chamber through a sidewall of the chamber, or to a fluidized bed formed in the return duct.

**[0017]** According to a preferred embodiment of the present invention, the gasifier is operated at an elevated pressure. By using an operating pressure of the gasifier from about 2 bar to about 70 bar, the quality of the solids product can be optimized according to the requirements of the application. According to another preferred embodiment of the present invention, the gasifier is operated at a pressure suitable for combusting the produced syngas in a gas turbine combustor, preferably at a pressure from about 10 bar to about 20 bar. In some applications, the syngas is combusted in an atmospheric combustor (e.g., in a utility boiler), and the gasifier can be operated at, or close to, atmospheric pressure. It is also possible to utilize the syngas in a chemical process (e.g., in producing hydrogen, ammonia, liquid fuels or fine chemicals).

**[0018]** In a circulating fluidized bed gasifier, the fuel is circulating for an extended time from the reactor to the particle separator and via the return duct back to the reactor. Thus, the total residence time of the fuel in the fluidized bed and, consequently, the time being affected by the activating agent, is long enough to impart a highly porous structure to the char particles, so as to produce activated carbon in the solids product. A circulating fluidized bed gasifier provides a relatively uniform and controllable temperature, so that the activation process of the char can be optimized to provide a desired pore structure to the produced activated carbon. Also, the activation agent is effectively mixed with the char in the strongly turbulent bed of particles, and causes efficient activation of the char.

**[0019]** The present method is especially advantageous when using bituminous or subbituminous coal or lignite as fuel. It has been observed that, when using subbituminous coal, activation in the fluidized bed in the reaction chamber is usually sufficient to produce activated carbon applicable to air pollution control applications, especially for reducing mercury from the flue gas of a combustion process. However, especially when the fuel is bituminous coal, it has been found to be beneficial to add a further step of activating the char with at least one of steam and carbon dioxide in a fluidized activation chamber arranged in a hot loop of the circulating fluidized bed gasifier. In some cases, such an activation chamber may be needed for subbituminous coals and lignite, as well. Preferably, the average activation time for the char is at least twenty (20) minutes; even more preferably, at least forty (40) minutes. When using a separate activation chamber in the hot loop, the average activation time is preferably at least about sixty (60) minutes.

**[0020]** The activated carbon, produced in a process in accordance with the present invention, has sufficient activity for applications such as air pollution control and wastewater treatment when the adsorbent is used once and then disposed of. Depending on the application, the activated carbon product from this process may be further enhanced or modified by one or more conventional chemical processes, such as sulfur impregnation.

## BRIEF DESCRIPTION OF THE DRAWING

**[0021]** The above brief description, as well as further objects, features, and advantages of the present invention will be more fully appreciated by reference to the following detailed description of the presently preferred, but nonetheless illustrative, embodiments in accordance with the present invention, when taken in conjunction with the accompanying drawing.

**[0022]** **FIG. 1** is a schematic view of a circulating fluidized bed gasifier in accordance with the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0023]** **FIG. 1** schematically illustrates a circulating fluidized bed (CFB) gasifier **10** which can be used in a preferred embodiment of a gasification process in accordance with the present invention. The CFB gasifier **10** comprises a reaction chamber **12** with a fuel supply **14** for feeding carbonaceous fuel to a particle bed formed in the reaction chamber **12**. The chamber **12** also comprises an oxidizing gas supply **16** for feeding oxidizing gas (usually air), and an activating agent supply **18** for feeding activation agent, steam, and/or carbon dioxide, at controlled rates into the reaction chamber **12**. The activation agent supply **18** may be fed to the reaction chamber **12** through the bottom grid **20**, possibly premixed with the oxidizing gas (the lower instance of activation agent supply **18** in **FIG. 1**), and/or at higher elevations through a side wall **22** of the reaction chamber **12** (the upper instance of activation agent supply **18** in **FIG. 1**).

**[0024]** The fuel and other particulate solids in the bed are fluidized in a conventional way with less than stoichiometric oxygen present, causing gasification of the fuel to syngas and char. When the char is further activated with the activation agent, the porosity of the char is highly enhanced and activated carbon is formed. A turbulent fluidized state of the bed creates a nearly isothermal temperature zone with high thermal inertia, and enables accurate control of the reaction temperature.

[0025] The reaction chamber **12** is advantageously operated at a predetermined temperature, preferably at a temperature between about 500° C. and about 1100° C. The temperature can, at least to a certain extent, be optimized for rapid activation so as to produce activated carbon with a desired porous structure. According to a preferred embodiment of the present invention, the operating temperature range of the reaction chamber **12** is from about 800° C. to about 1000° C. The superficial fluidizing velocity in the reaction chamber **12** is preferably from about 1.5 m/s to about 9 m/s, even more preferably from about 3 m/s to about 6 m/s.

[0026] The produced syngas carries solid particles vertically up through the reaction chamber **12**. The syngas and solids entrained with the syngas are discharged through an outlet **24** in the upper portion of the reaction chamber **12** to a particle separator **26**. Most of the solids entrained in the syngas are separated from the syngas in the particle separator **26** (preferably, a cyclone separator) to be returned via a return duct **28** to the lower portion of the reaction chamber **12**. The finest portion of the entrained solids, comprising mainly activated carbon, is discharged from the particle separator **26**, together with the syngas, through a gas outlet **30** to a syngas line **32**. The syngas is cooled by a syngas cooler **34** arranged in the syngas line **32**.

[0027] The remaining fine particles are separated from the syngas in a dust separator **36** (preferably, a barrier filter). The cleaned syngas is discharged from the dust separator **36** through a gas discharge line **38** to a combustion process (e.g., to drive a gas turbine generator), or to a chemical process (e.g., to produce high value products such as hydrogen, ammonia, liquid fuels or fine chemicals). The solids product, which comprises mainly fine activated carbon particles separated from the syngas in the dust separator **36**, is discharged from the dust separator **36** through a solids discharge line **40**, to be used in a suitable application, such as in capturing emissions (especially mercury) from a combustion process, or in wastewater treatment.

[0028] Coarse char accumulating at the bottom of the reaction chamber **12** is drained therefrom through a bottom outlet **42**. It may be useful in some applications to grind the drained coarse char to a desirable particle size, and mix it with the solids product discharged from the dust separator **36** through the solids discharge line **40**.

[0029] In the process, the particle size of the solids product can to some extent be controlled by adjusting the particle size of the raw material fed to the reactor chamber. However, significant size reduction occurs in the CFB gasifier due to fragmentation and attrition. The particle separator **26** works as a classifier that mainly allows only particles smaller than a certain size to exit the separator with the syngas. Thus, the particle size of the solids product can be controlled by controlling the separation efficiency of the separator **26**. Preferably, the separation efficiency of the particle separator **26** is such that the average particle size of the particles discharged from the separator with the syngas is less than about 60 μm, even more preferentially less than about 45 μm.

[0030] Conventional activated carbon production methods comprise separate steps for pyrolizing the raw material and for activating the pyrolized material. In a fluidized bed gasifier, both of the steps of pyrolizing and activating take place in a single system. In a circulating fluidized bed gasifier, the total residence time of the fuel in the reactor is fairly long. Typically, fuel and char particles circulate several hundreds of times from the reactor **12** to the separator **26** and back to the reactor through return duct **28**, until they are reduced in size enough to escape from the loop via the gas outlet **30**. Before that, the char has been affected by the activating agent, steam or carbon dioxide, long enough that a highly porous structure of activated carbon is formed.

[0031] According to a preferred embodiment of the present invention, the gasifier **10** is operated at an elevated pressure. Preferably, the pressure in the reaction chamber **12** is from about 2 bar to about 70 bar, even more preferably from about 10 bar to about 20 bar. When the gasifier **10** is pressurized, the reaction chamber is usually enclosed in a pressure vessel and the fuel feed means and solids removal means are equipped with means for pressure adjustment. These are, however, not shown in **FIG. 1**.

[0032] The process described above can be used to produce activated carbon from many raw materials, including various ranks of coals and various types of biomass. It has been observed that activating char in the reactor of a circulating fluidized bed gasifier is usually sufficient for subbituminous coal, but not for bituminous coal. Therefore, especially when gasifying bituminous coal, a fluidized activation chamber **44** is advantageously arranged to the return duct **28** of the gasifier **10**, so as to extend the total activation time of the carbon in the ashes.

[0033] The bed formed in the activation chamber **44** is preferably fluidized, by using a fluidizing agent supply **46** with the activation agent, steam, and/or carbon dioxide. In addition, the fluidizing agent from the fluidizing agent supply **46** may be mixed with some oxygenous gas (preferably air), so as to effect some oxidation of the char, for maintaining the activation chamber **44** at a desired temperature, preferably above about 800° C. By using the activation chamber **44**, the total effective activation time of the carbon is preferably extended to about one (1) hour, or even higher.

[0034] While the invention has been described herein by way of examples in connection with what are at present considered to be the most preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments, but is intended to cover various combinations or modifications of its features included within the scope of the invention as defined in the appended claims.

We claim:

**1**. A method of co-producing activated carbon in a circulating fluidized bed gasification process, the method comprising the steps of:

(a) feeding carbonaceous fuel to a reaction chamber of a gasifier to form a particle bed in the reaction chamber;

(b) fluidizing the particle bed with oxygenous gas to partially oxidize the fuel to form syngas and char;

(c) feeding an activation agent comprising at least one of steam and carbon dioxide to the reaction chamber to activate the char to form particulate of activated carbon;

(d) discharging syngas and particulate solids entrained with the syngas from the reaction chamber;

(e) separating entrained solids from the syngas with a particle separator and returning at least a portion of the separated solids through a return duct to the reaction chamber, but allowing a solids product, comprising entrained solids of activated carbon and having an average size smaller than a predetermined size, to exit the particle separator with the syngas;

(f) separating the solids product from the syngas in a dust separator to form cleaned syngas;

(g) discharging the cleaned syngas from the dust separator;

(h) discharging the solids product from the dust separator;

(i) supplying the cleaned syngas to a location for use in at least one of a combustion process and a chemical process; and

(j) supplying the separated solids product to a location for use in removing contaminants from a fluid.

**2**. The method of claim 1, further comprising the step of utilizing the separated solids product to remove contaminants from a fluid.

**3**. The method of claim 2, wherein the separated solids product is used to remove contaminants in at least one of a water purification process, a wastewater treatment process, a sugar refining process, a beverage filtration process, and an air pollution control process.

**4**. The method of claim 2, wherein the separated solids product is used in capturing mercury from the flue gases of a combustion process.

**5**. The method of claim 1, wherein the gasifier is operated at a pressure of between about 2 bar and about 70 bar.

**6**. The method of claim 5, wherein the gasifier is operated at a pressure of between about 10 bar and about 20 bar.

**7**. The method of claim 1, wherein the predetermined size is less than about 60 μm.

**8**. The method of claim 7, wherein the predetermined size is less than about 45 μm.

**9**. The method of claim 1, further comprising the step of activating the char with at least one of steam and carbon dioxide in a fluidized bed in a hot loop of the gasifier.

**10**. The method of claim 9, wherein the fuel comprises bituminous coal.

**11**. The method of claim 1, wherein the average activation time for the solids product is at least about twenty (20) minutes.

**12**. The method of claim 11, wherein the average activation time for the solids product is at least about forty (40) minutes.

**13**. The method of claim 9, wherein the average activation time for the solids product is at least about one (1) hour.

**14**. The method of claim 9, wherein the fluidized bed in the hot loop is maintained at a temperature of at least about 800° C.

**15**. The method of claim 14, wherein the fluidized bed in the hot loop is fluidized with oxygenous gas.

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