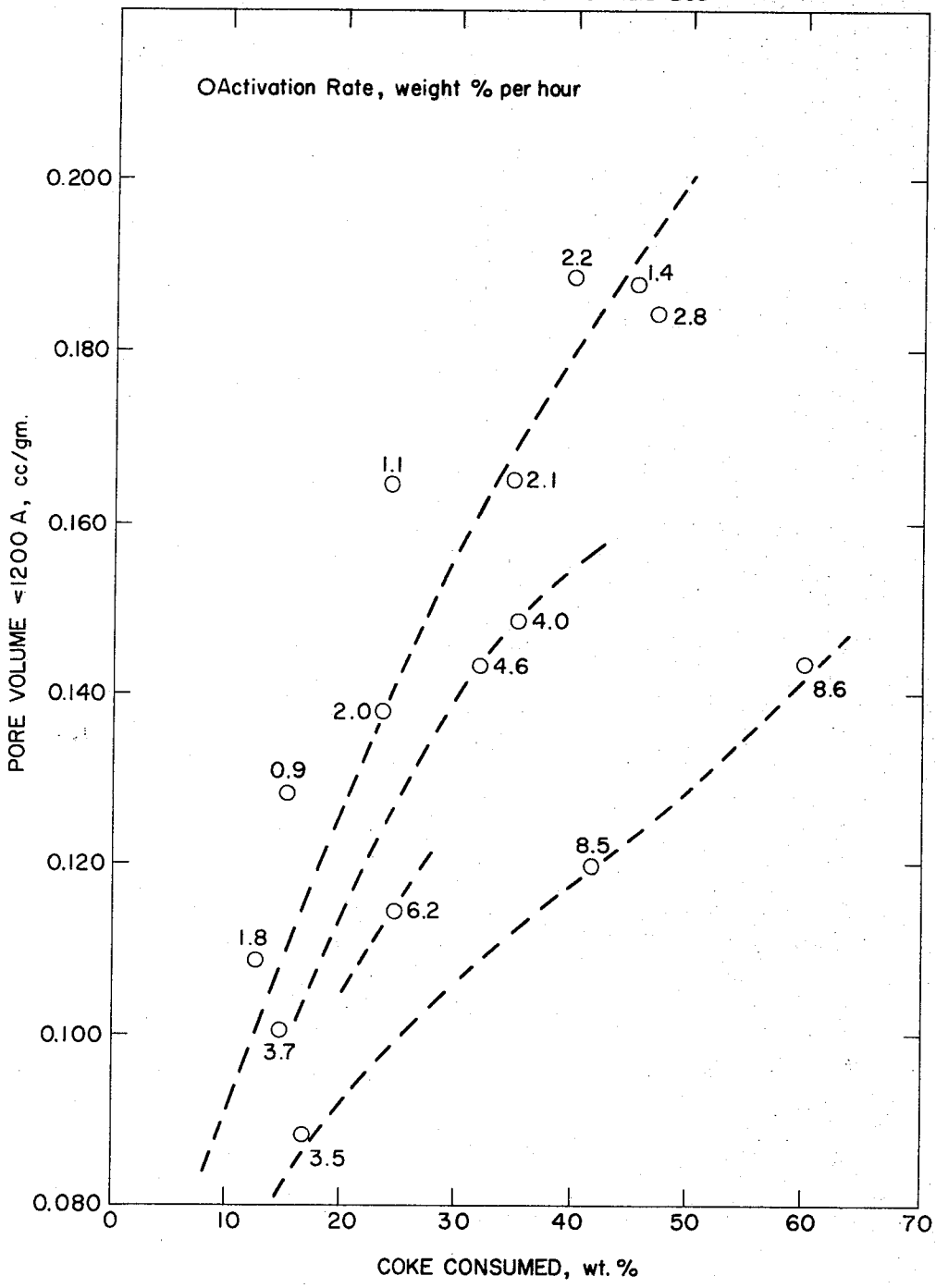
PROCESS FOR ACTIVATING CARBONACEOUS MATERIALS

Filed June 28, 1972 3 Sheets-Sheet 1

Figure 1

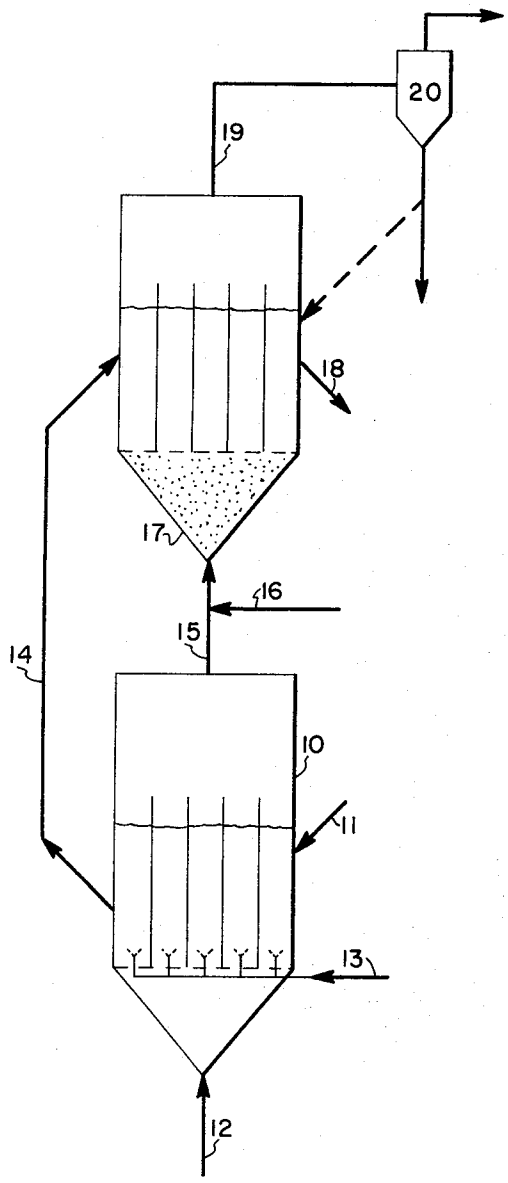
PORE VOLUME vs. COKE CONSUMPTION
Air Activation of Coke in a Fluid Bed



PROCESS FOR ACTIVATING CARBONACEOUS MATERIALS

Filed June 28, 1972 3 Sheets-Sheet 2

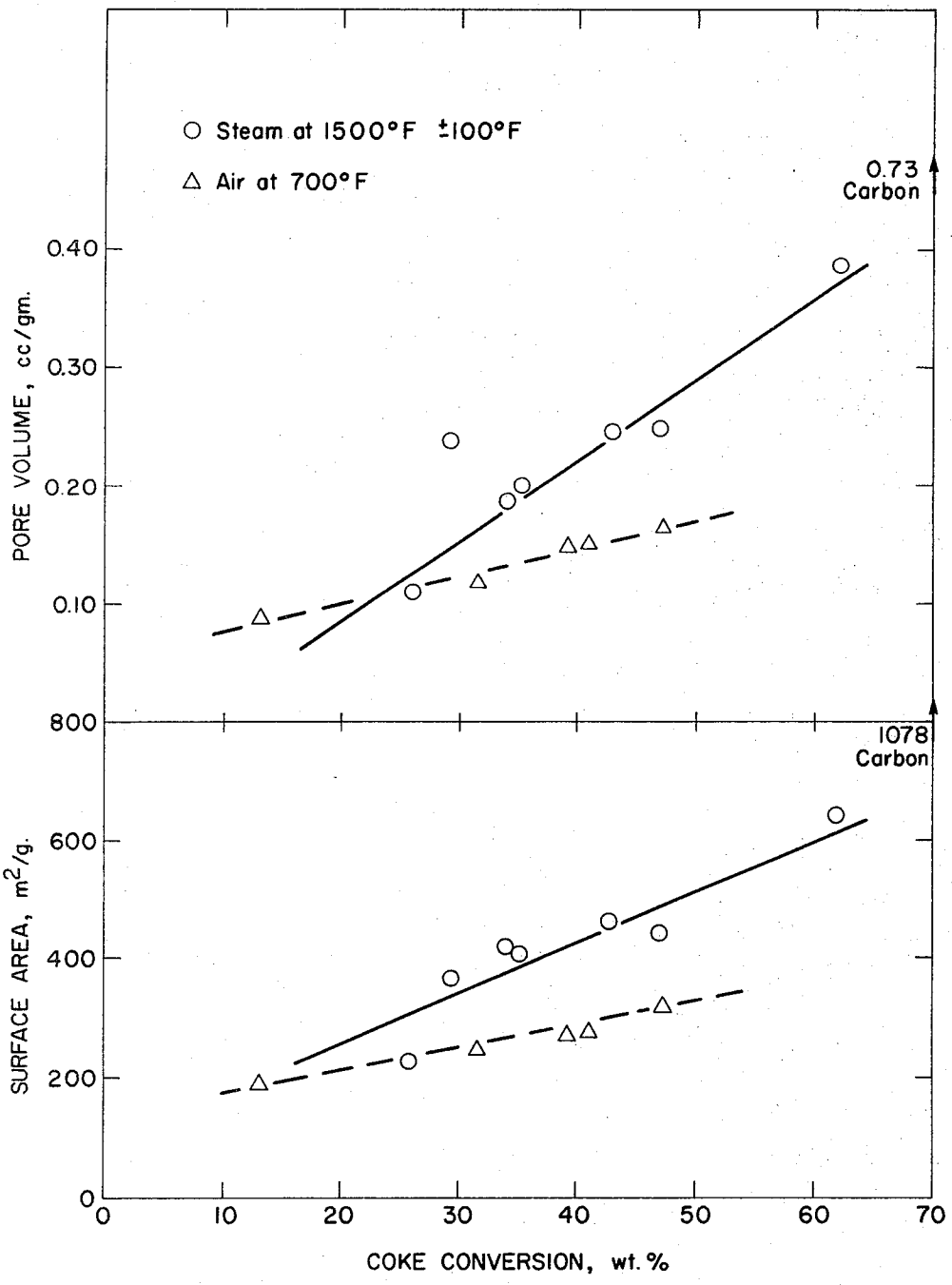
Figure 2
COKE ACTIVATION PROCESS



PROCESS FOR ACTIVATING CARBONACEOUS MATERIALS

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Figure 3
ACTIVATION OF FLUID COKE



United States Patent Office

3,840,476

Patented Oct. 8, 1974

3,840,476

PROCESS FOR ACTIVATING CARBONACEOUS MATERIALS

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Filed June 28, 1972, Ser. No. 267,259
Int. Cl. C01b 31/08
U.S. Cl. 252—445 4 Claims

ABSTRACT OF THE DISCLOSURE

Carbonaceous materials, and in particular fluid coke, are activated by contacting the fluid coke with a gaseous stream containing oxygen, i.e., air, at elevated temperatures for a period of time such that the conversion of the carbonaceous materials, i.e., fluid coke, to gaseous products is maintained at a rate of less than 4 weight percent an hour, and preferably in the range of between about 1 and 3 weight percent an hour, in order to maximize the pore volume of the activated carbonaceous material. In a preferred embodiment, the carbonaceous material is initially activated with air in a fluid bed at a carbonaceous conversion rate of less than 4 weight percent an hour in order to convert from about 15 to about 35 weight percent of the carbonaceous materials to gaseous products and thereafter further activating the partially activated carbonaceous material with a gaseous stream containing steam for a period of time sufficient to achieve a total conversion of 45 to 70% of the starting carbonaceous material to gaseous products. The activated carbonaceous materials prepared by the instant invention find use as an excellent absorbent, particularly in removing organic impurities from refinery waste water streams.

BACKGROUND OF THE INVENTION

This invention relates to a method of activating carbonaceous materials with air in order to maximize the pore volume of the activated carbonaceous material. More particularly, this invention relates to contacting carbonaceous materials, preferably fluid coke, with excess oxygen, i.e., air, in a fluidized bed at elevated temperatures for a period of time such that the conversion of carbonaceous materials to gaseous products is maintained at a rate of less than about 4 weight percent per hour. Preferably, fluid coke is employed as the carbonaceous material and is treated with air in a fluid bed at a temperature in the range of from about 500° to about 800° F. for a period of time to maintain the conversion rate of the fluid coke to gaseous products to less than 4 weight percent an hour, and preferably between about 1 to 3 weight percent an hour. In a preferred embodiment of the instanst invention, fluid coke is contacted with air in a fluid bed at elevated temperatures for a period of time to maintain the fluid coke conversion rate at less than about 4 weight percent per hour in order to convert from about 15 to about 35 weight percent of the fluid coke to gaseous products. Thereafter, the partially activated fluid coke is further activated by contact with a gaseous stream containing steam at a temperature in the range of from about 1400° to about 1650° F. for a period of time sufficient to achieve a total conversion of 45 to 70 weight percent of the starting fluid coke to gaseous products. The activated carbonaceous material formed by the process of the instant invention finds use as an excellent adsorbent, particularly in removing organic impurities for refinery waste water streams.

DESCRIPTION OF THE PRIOR ART

In U.S. Pat. No. 2,721,168, there is described a process for the benefaction of petroleum coke by subjecting a portion of coke withdrawn from a fluid coker to controlled oxidation in order to increase its friability and thereby cause attrition of the coke particles. Specifically, fluid coke withdrawn from the coking zone is subjected to oxidation at temperatures in the range of 600° to 1000° F. in order to consume 5 to 200 weight percent of the material in the oxidation zone, preferably 7 weight percent, in order to produce a seed coke having a particle size in the range of from about 50 to 200 microns. In addition, there is described in U.S. Pat. No. 3,322,550, which patent relates to preparing a mixture of petroleum coke particles and an agglutonating carbonaceous binder, a method for activating fluid coke by treating the fluid coke in an atmosphere of air at temperatures in excess of 450° C. (840° F.) for periods exceeding 5 minutes. While the patent literature has broadly disclosed that carbonaceous materials, including petroleum coke, may be treated with steam and/or air in an attempt to activate such a material, the fact that an activated fluid coke material in the nature of an activated carbon has not been introduced in the market place is further evidence that the art is in need of a process for preparing such an activated fluid coke material which possesses sufficient physical properties in order to act as a suitable adsorbent.

SUMMARY OF THE INVENTION

It has now been discovered that carbonaceous materials, and in particular fluid coke, may be activated by contacting a carbonaceous material such as fluid coke in a fluid bed with air at elevated temperatures, preferably in the range of from about 500° to about 800° F. for a period of time so as to maintain the conversion of the carbonaceous materials to gaseous products at a rate of less than 4 weight percent an hour. It has been found that by maintaining the consumption rate, that is, the amount of carbonaceous materials converted to gaseous products per hour, to less than 4 weight percent, preferably in the range of from about 1 to about 3 weight percent an hour, maximizes the pore volume of the activated carbonaceous material. It is highly desirable in forming activated carbonaceous materials to maximize the pore volume in view of the fact that there appears to be a direct relationship between the pore volume of a given activated carbonaceous material and the ability of that activated carbonaceous material to act as an effective adsorbent material. In preferred embodiment of the instant invention, fluid coke is first activated with air in a fluid bed at a temperature in the range of from about 500° to about 800° F. for a period of time in order to maintain the conversion of the fluid coke to gaseous products to less than about 4 weight percent an hour, and preferably in the range of from about 1 to about 3 weight percent an hour, in order to achieve an initial conversion of about 15 to about 35 weight percent of the fluid coke to gaseous products. Thereafter, the partially activated fluid coke is contacted in a fluid bed with a gaseous stream containing steam at a temperature in the range from about 1400° to about 1650° F. and preferably at a temperature of 1500° to 1650° F.

for a time sufficient to achieve a total conversion of 45 to 70 weight percent of the fluid coke to gaseous products.

The carbonaceous material that may be employed in the practice of this invention can be any material suitable for the preparation of activated carbon such as non-caking coal; semi-carbonized lignite; carbonized vegetable materials, such as coconut shells, pecan hulls, wood, fruit pits; petroleum coke, including delayed coke and fluid coke; and bone char. The preferred carbonaceous material is petroleum coke, and in particular fluid coke.

Fluid coke is produced in a fluid coking unit consisting basically of a reaction vessel or coker and a heater or burner vessel. In a typical operation, the heavy oil to be processed in injected into the reaction vessel containing a dense, turbulent fluidized bed of hot inert solid particles, preferably coke particles. Uniform temperature exists in the coking bed. Uniform mixing of the bed results in virtually isothermal conditions and effects instantaneous distribution of the feedstock. The reaction zone feedstock is partially vaporized and partially cracked. Product vapors are removed from the coking vessel and sent to a fractionator for the recovery of gas and light distillates therefrom. Any heavy bottoms is usually returned to the coking vessel. The coke produced in the process remains in the bed coated on solid particles. Stripping steam is injected into the stripper to remove oil from the coke particles prior to the passage of the coke to the burner. The heat for carrying out the endothermic coking reaction is generated in a burner vessel. The stream of coke is transferred from the reactor to the burner vessel employing a standpipe and riser system; air and/or steam being supplied to the riser for conveying the solids to the burner. Sufficient coke or carbonaceous matter is burned in the burning vessel to bring the solids therein up to a temperature sufficient to maintain the system in heat balance.

The fluid coke product is laminar in structure and may comprise from 30 to 100 superimposed layers of coke. Product distribution is such that a predominant portion, i.e., about 90 weight percent, of the coke particles has a diameter smaller than 400 microns, while the remaining coke particles range in size from about 75 to about 850 microns. The above-mentioned carbonaceous materials are contacted with an oxygen-containing gas in a fluid bed at a temperature in the range of from about 500° to about 800° F. Suitable oxygen-containing gases that may be employed in the practice of the instant invention include air; air and steam; oxygen and steam; air, oxygen and steam; or air, steam and carbon oxides. The steam may be generated in situ by spraying water into the fluid bed to control bed temperature. Preferably, air is employed as the oxygen-containing gas and is employed in an amount in the range of from about 0.3 to about 10 cubic feet of oxygen per hour at standard conditions.

It is a critical feature of the instant invention that the carbonaceous material, i.e., fluid coke, be contacted with an oxygen-containing gas at elevated temperatures for a period of time such that the conversion rate of the carbonaceous materials to gaseous products is less than about 4 weight percent per hour. Preferably, the carbonaceous material is contacted with the oxygen-containing gas in a fluid bed at a temperature in the range of from about 500° to about 800° F., and still more preferably at a temperature in the range of from about 600° to about 750° F. for a period of time such that the conversion of the carbonaceous materials to gaseous products is less than about 4 weight percent an hour, preferably in the range of from about 1 to about 3 weight percent an hour. When the single stage activation system of the instant invention is employed, it is preferred that the amount of carbonaceous material that is gasified, that is the amount of carbonaceous material that is converted to gaseous products, be in the range of from about 30 to about 50 weight percent, more preferably in the range of from about 35 to about 45 weight percent.

This invention will be more clearly understood by reference to the accompanying figures.

FIG. 1 is a plot of the conversion of the carbonaceous material in weight percent versus the pore volume of the activated material. Fluid coke was employed as the carbonaceous material and was activated by air in accordance with the conditions specified in Table I below.

TABLE I.—AIR ACTIVATION OF COKE FOR WASTE WATER TREATMENT

[Activation in a fluidized bed at 0.4–0.6 (superficial vel.) ft./sec.]

Fluid coke [1]	Time, hrs.	Temp., ° F.	Coke consumed, wt. percent	Pore Volume [2] <1,200 A, cc./gm.	Coke consumption, rate, percent/hr.
A	17	650	15.4	0.128	0.9
A	2	850	17.0	0.088	8.5
A	32	650	45.7	0.187	1.4
A	7	800	60.2	0.143	8.6
A	17	700	47.4	0.185	2.8
A	7	750	32.1	0.143	4.6
A	4	750	14.7	0.101	3.7
A	23	650	24.6	0.165	1.1
A	4	800	24.8	0.114	6.2
A	7	700	12.8	0.109	1.8
A	17	[3] 686	[3] 35.6	0.165	2.1
B	17	625	39.2	0.171	2.3
C	17	695	33.9	0.171	2.0
D	17	650	46.4	0.184	2.7
E	18	640	39.6	0.188	2.2

[1] Analysis of fluid coke:

Coke	Weight percent				Surface area, m.²/g.
	Carbon	Hydrogen	Sulfur	Ash	
A	86.75	2.29	5.8	0.16	12
B	86.64	2.10	4.5	0.32	
C	Detailed analysis not obtained				
D	86.26	2.05	6.8	0.68	11
E	87.24	2.11	4.6	0.58	1

[2] Determined by equilibrium H^2O absorption from vapor pressure of a 0.50 molar solution LiCl at 25° C.

[3] Average of two runs which were composited.

As can be seen from the results as shown in Table I, an unexpected increase occurs in the pore volume per unit consumption of those activated carbonaceous materials which were activated, such that the amount of carbonaceous materials converted to gaseous products per hour was maintained at an activation rate of less than 4 weight percent per hour. At an activation rate of 4.6 weight percent per hour a carbon having a 0.143 cc./gm. of pores smaller than 1200 A. was obtained with a coke conversion of 32.1 weight percent, whereas it required 60.2 weight percent conversion of coke to attain the same pore volume at an activation rate of 8.6 weight percent per hour. Thus the yield* of high quality coke was increased from 39.2 weight percent to 67.9 weight percent by reducing the activation rate in accordance with the process of the instant invention.

In a preferred embodiment of this invention, the carbonaceous materials are activated in a two-step process. Initially, the carbonaceous material is contacted with an oxygen-containing gas stream, as described above, at elevated temperatures, preferably in the range of from about 500° to about 800° F., for a period of time to maintain the conversion of the carbonaceous materials to gaseous products below 4 weight percent an hour, preferably in the range of from about 1 to about 3 weight percent per hour, in order to achieve an initial conversion of from about 15 to about 35 weight percent carbonaceous products. This partially activated carbonaceous material is then reacted in a second stage with a gaseous stream containing at least 50 weight percent steam at a temperature in the range from about 1400° to 1650° F. for a period of time in order to achieve an overall conversion of from about 45 to about 70 weight percent of the carbonaceous materials.

Referring now to FIG. 2, carbonaceous materials, preferably fluid coke, are introduced into the first reaction

*Yield of Coke=100%—Percent Converted.

zone **10** by way of line **11**. The reaction zone **10** is preferably provided with one or more partitions "P" to effect solids staging. The oxygen-containing gas, preferably air, in an amount in the range of from about 0.3 to about 10 cubic feet of oxygen at standard conditions of temperature and pressure per pound of carbon is introduced into reaction zone **10** by way of line **12** at a temperature in the range of from about 100° to about 600° F. The reaction of oxygen with carbon to activate the coke is an exothermic reaction. Process heat must be removed to control the reaction. Steam and/or water may be introduced by way of line **13** into reaction zone **10** in order to assist in fluidization of the bed and to control the temperature in the reaction zone such that the conversion of the fluid coke to gaseous products is maintained in the range of from about 1 to about 4 weight percent an hour. The carbonaceous materials which have been initially activated in reaction zone **10** for a period of time in order to convert about 15 to about 35 weight percent of the fluid coke to gaseous products are removed from reaction zone **10** by way of line **14** and introduced into reaction zone **17** by way of line **14**. The gaseous products emanating from the fluid bed of reaction zone **10** are collected and passed by way of line **15** along with the further addition of a gaseous stream consisting of either steam, air, fuel gas or combustion products of a combination of these gases by way of line **16** into the bottom of reaction zone **17** in order to supply the process heat requirements for the endothermic reaction of steam and the partially activated carbonaceous material, as well as part of the fluidization medium for reaction zone **17**. The temperature of the gaseous stream which is introduced by way of line **15** into reaction zone **17** is maintained in the range of from about 1000° to about 2800° F., and more preferably from about 1200° to about 2600° F., in order to maintain the temperature in the fluid bed in the range of from about 1400° to about 1600° F. Temperatures are in the lower range when excess oxygen is available to supply part of the heat. The pressure maintained in reaction zone **10** as well as in reaction zone **17** may vary from about 10 to about 75 p.s.i.a., and more preferably from about 20 to about 30 p.s.i.a. The preactivated carbonaceous materials are maintained in reaction zone **17** for a time in the range of from about 1 to about 10 hours in order to achieve the overall conversion of the initial fluid coke material to gaseous products of from about 45 to about 70 weight percent. Partitions "P" are preferably provided in reaction zone **17** to effect solids staging. The activated coke material is then withdrawn by way of line **18**, while the gaseous products emanating from the top of the fluid bed in reaction zone **17** are collected and passed along by way of line **19** into a cyclone **20**, wherein the fines are separated out and the gaseous products are recycled for heat recovery.

The above-described two-step process achieves the activation of carbonaceous materials by combining the advantages inherent in both steam and air activation of carbonaceous materials.

Refering now to FIG. 3, it can be seen that the air activation of carbonaceous materials up to approximately 25 weight percent conversion of the carbonaceous material results in an activated carbonaceous material exhibiting essentially the same characteristics, i.e., pore volume and surface area, as an activated carbonaceous material that was activated totally in steam alone. Above about 35 weight percent conversion of the carbonaceous materials, activation by steam produces a significantly improved activated carbon over that activated by air alone. The two-stage activation process of the instant invention utilizes the relatively inexpensive low temperature exothermic air activation to accomplish the initial activation of 15 to 35 weight percent conversion, preferably 20 to 30 weight percent conversion, and then completes the activation with steam as the activating agent to a total conversion of 45 to 70 weight percent.

This invention will be further understood by reference to the following example.

EXAMPLE

In the following example, commercially available fluid coke was employed as the carbonaceous material to be activated. Fluid coke having a particle diameter ranging from 150 to 550 microns was contacted with 3.5 cubic feet per hour of oxygen per pound of coke at standard conditions of temperature and pressure with the air flowing at a superficial gas velocity of between about 0.4 to 0.6 ft./sec. in a fluidized solids bed contained in an electrically-heated Vycor tube, 1 inch in diameter and 18 inches high, at a temperature of about 680° F. for a period of 11 hours. The coke conversion during this period was 23.2 weight percent or 2.1 weight percent per hour. This partially activated coke was subsequently recharged to a heated tube where it was further contacted with nitrogen and steam in a fluidized bed at a superficial velocity of 0.4 to 0.6 ft./sec. The steam rate was 9.0 ft.^{3}/hour of steam per pound of carbonaceous material and the coke was activated for an additional 6 hours at 1580° F. Total conversion (air activation plus steam activation) was 70 weight percent. An identical fluid coke was activated in a similar manner in steam for 13 hours at 1600° F. These two activated fluid coke materials, along with a high quality commercially available granular activated carbon were tested by determining isotherms to establish their relative ability to reduce the Chemical Oxygen Demand (COD) of a refinery waste stream. The refinery waste stream orginally had a COD of 405 p.p.m., as determined by *Standard Methods for the Examination of Water and Waste Water,* 13th edition, 1971, p. 495. The isotherms were determined by a technique described in *Advanced Waste Water Treatment,* Culp and Culp, Van Nostrand-Reinhold, pp. 252–255. Results are described in Table II.

TABLE II

Activation Conditions	Coke source: Fluid coke: Air followed by steam	Coke source: Fluid coke: Steam alone	Coke source: Commercial granular activiated carbon
Coke properties*:			
Surface area, m²/gm	524	543	1,078
Pore volume, cc./gm	0.33	0.35	0.73
Evaluation for waste water treatment:			
Activated carbon dose of 20 lb./1,000 gal:			
Equilibrium COD	155	180	160
Equilibrium capacity mg. COD/gm. carbon	102	93	103
Activated carbon dose of 200 lb./1,000 gal:			
Equilibrium COD	38	56	42
Equilibrium capacity mg. COD/gm. carbon	15.6	14.9	15.4

*By nitrogen adsorption.

In the isotherm tests the key indices of performance are the capacity to pick up COD at low ratio of carbon to water and the equilibrium COD at high ratio of carbon to water. As can be seen from the results shown in Table II, the fluid coke activated in the manner prescribed in this invention is essentially equivalent to a commercially available high quality granular activated carbon which has been used for waste water treatment and is in fact slightly superior to the steam activated fluid coke. This excellent performance is attained even though the fluid coke of this invention has a lower surface area and pore volume than the other two activated cokes. This indicates that these may be some unusual advantages for activation in the manner prescribed.

Carbonaceous materials activated in the manner prescribed in this invention could also be used for clarification of other liquids or for gas adsorption. In addition, the process of the instant invention may also be employed to regenerate activated carbonaceous materials which

have become deactivated by the adsorption of contaminants during waste water treatment.

What is claimed is:

1. A two-step process for activating fluid coke for use in removing organic contaminants from waste water which comprises contacting said fluid coke to exothermically partially activate said coke with a gaseous stream containing oxygen in a fluid bed reaction zone at a temperature in the range of from about 500° to about 800° F. for a period of time to convert about 15 to about 35 weight percent of the fluid coke to gaseous products at a conversion rate in the range of from about 1 to about 4 weight percent an hour and thereafter passing said partially activated fluid coke into a second fluid bed reaction zone wherein said partially activated fluid coke is contacted with a gaseous stream containing stream to endothermically react with and further activate said partially activated coke at a temperature in the range of from about 1400° to about 1650° F. in order to convert from about 45 to about 70 weight percent of the total fluid coke to gaseous products, and recovering said activated fluid coke

2. The process of claim 1 wherein said fluid coke is contacted with said gaseous stream containing oxygen for a period of time to convert about 20 to about 30 weight percent of the fluid coke to gaseous products.

3. The process of claim 1 wherein the contacting of said fluid coke with a gaseous stream containing oxygen takes place at a temperature in the range of from about 600° to about 750° F., and wherein the contacting of said partially activated fluid coke with a gaseous stream containing steam takes place at a temperature in the range of from about 1500° to about 1650° F.

4. A two-step process for activating fluid coke for use in removing organic contaminants from waste water which comprises:

(a) contacting said fluid coke to exothermically partially activate said coke with a gaseous stream containing oxygen in a primary fluid bed reaction zone at a temperature in the range of from about 500° to about 800° F. for a period of time to convert about 15 to about 35 weight percent of the fluid coke to gaseous products at a conversion rate in the range of from about 1 to about 4 weight percent an hour;

(b) passing said gaseous products and said partially activated fluid coke to a secondary fluid bed reaction zone wherein said partially activated fluid coke is contacted with a gaseous stream containing steam to endothermically react with and further activate said partially activated coke at a temperature in the range of from about 1400° to about 1650° F. in order to convert from about 45 to about 70 weight percent of the total fluid coke to gaseous products; and

(c) recovering activated coke from step (b).

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U.S. Cl. X.R.

201—25, 31, 38; 210—139; 252—421