United States Patent [19]

Miller

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[54] **SHAPED LIGNOCELLULOSIC-BASED ACTIVATED CARBON**

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[51] **Int. Cl.^{6}** **B01J 20/02**

[52] **U.S. Cl.** **502/416**; 502/80; 502/423; 502/428; 502/429; 502/174; 502/180; 502/182

[58] **Field of Search** 502/416, 423, 502/428, 429, 80, 174, 180, 182

[56] **References Cited**

U.S. PATENT DOCUMENTS

4,677,086   6/1987   McCue et al. 502/80

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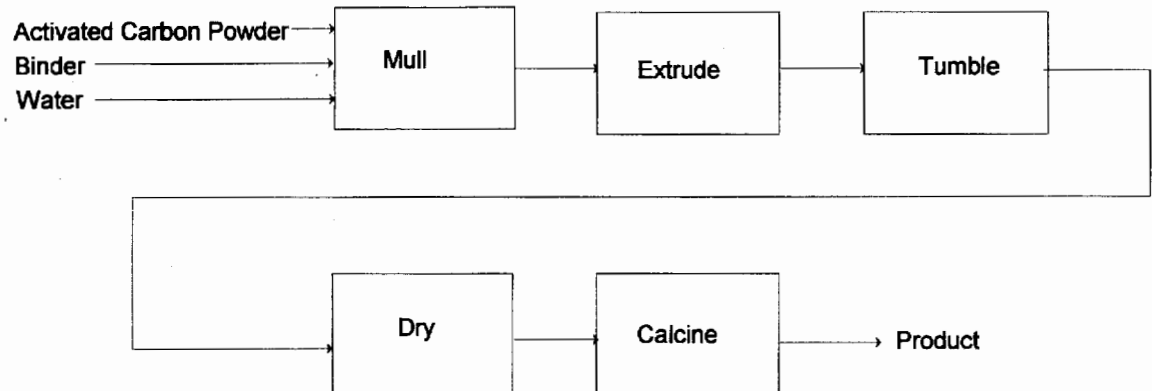
[57] **ABSTRACT**

Extruded pellets comprising a majority of activated carbon particles and a minority of a binder material are disclosed to provide improved performance when processed through tumbling equipment while the pellets are in their "green" state (i.e., pellets which are fresh off the extruder and contain activated carbon), binder material, and water and have not been subjected to any thermal processing (drying or calcining). The tumbling action both smooths and densifies (i.e., reduces void volume within) the pellet, thereby closing any cracks and greatly improving appearance. Improved performance results from an ability to increase the weight of carbon pellets which can be packed into a fixed volume and thereby increase the volumetric working capacity of the bed for adsorbing/desorbing vapors. Another benefit is to greatly reduce the levels of dust associated with the carbon, both the initial dust and the dust attrition.

8 Claims, 2 Drawing Sheets

FIGURE 1

Activated Carbon Powder

Binder

Water
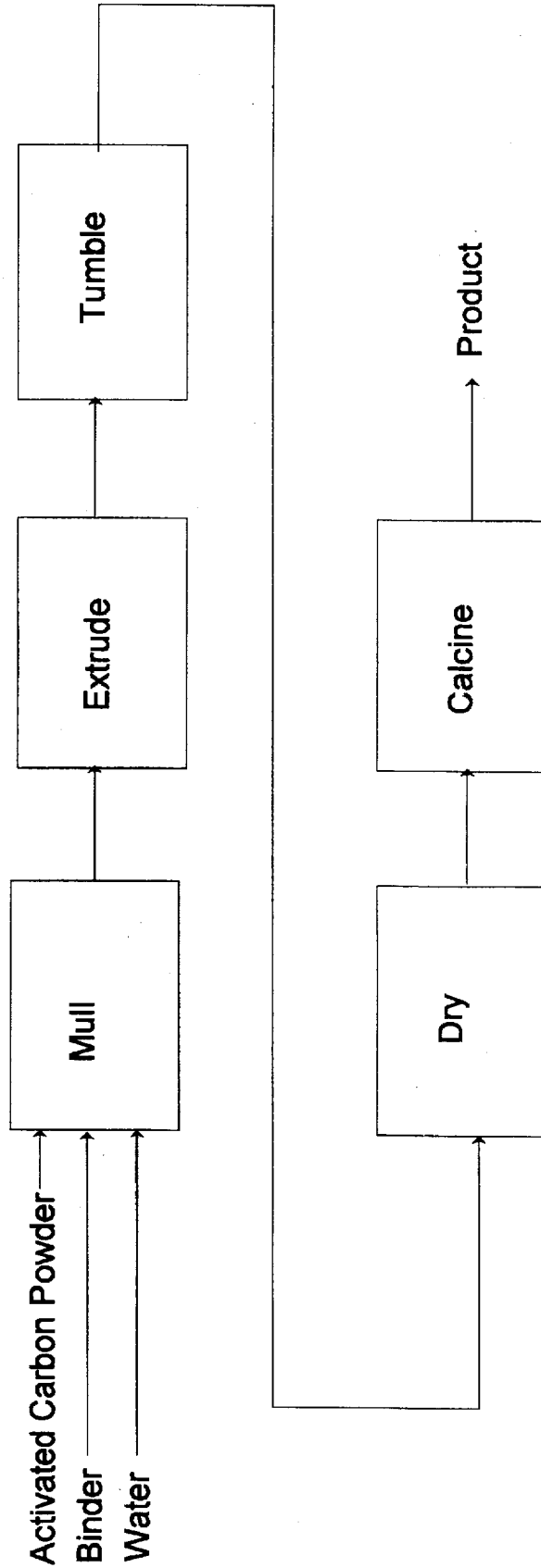
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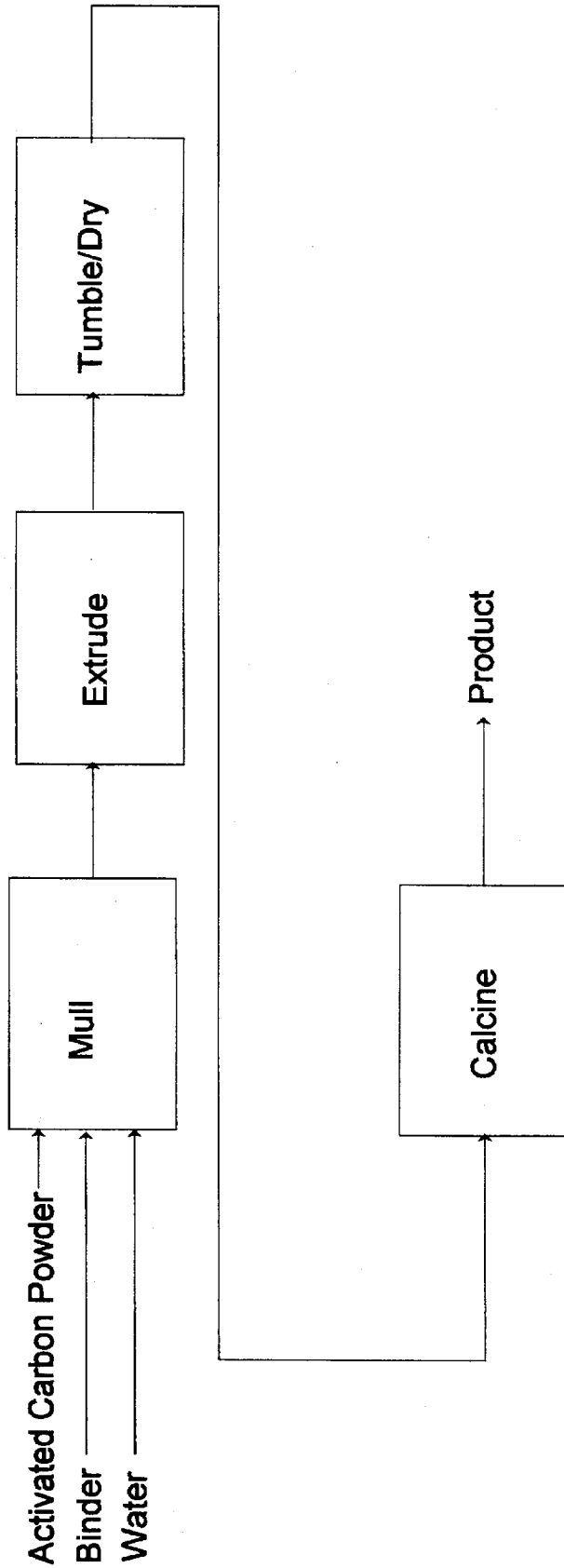
Extrude

Tumble/Dry

Calcine

Product

FIGURE 2

SHAPED LIGNOCELLULOSIC-BASED ACTIVATED CARBON

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an active carbon pellet prepared by extruding activated lignocellulosic-based carbon with a binder material. More particularly, the invention relates to an improved active carbon pellet characterized by low pellet void volume and low dust attrition.

2. Description of the Prior Art

Granular carbons and carbon pellets are typically used in columns or beds for gas and vapor systems as well for processing a number of liquids. Such carbons have been used in canisters in automobiles through which gasoline tank and carburetor vapors are directed prior to release to the environment. To qualify for this application, a carbon must possess sufficient mechanical strength to withstand the abrasion incident to continued use.

There generally is a direct correlation between the mechanical strength of the granular activated carbon product and the mechanical strength of its precursor raw material. Thus, coal-based active carbon generally exhibits a high mechanical strength and density; whereas, lignocellulosic-based active carbons, derived from a much "softer" precursor relative to coal, generally exhibit low mechanical strengths and densities.

Also, gas-adsorbing carbons should be as dense as is consistent with high adsorption capacity so as not to require a large space for the adsorber. The development of high adsorption capacity during thermal activation, however, is accompanied by a loss of mechanical strength and density; therefore, some compromise is required in selecting the degree to which the activation is conducted. So, with ligno-cellulosic precursors (or, for lignocellulosic-based active carbons), the problem is compounded.

Several approaches have been taken to address the problem of low mechanical strength and density of lignocellulosic-based active carbons. In U.S. Pat. No. 3,864,277, Kovach emphasizes the binder additive in teaching the phosphoric acid activation of wood, straw, or low-rank brown coals in the presence of a carbonaceous binder material such as lignosulfonates and polyvinyl alcohol, followed by forming solid granular shaped particles from the mixture, and heat-treating at less than 650° C. to give a granular product having a ball-pan hardness of greater than 85%. Given the teaching of Kovach and employing the knowledge of the relationship of precursor mechanical strength and density with those characteristics of the active carbon product, MacDowall (in U.S. Pat. No. 5,162,286) teaches increasing lignocellulosic-based active carbon density by the use of young carbonaceous vegetable products high (>30%) in natural binding agent, such as nut shell, fruit stone, almond shell, and coconut shell, as precursors for treatment with phosphoric acid followed by carbonization.

A third approach, which relates to the present invention, is taught by McCue et al. in U.S. Pat. No. 4,677,086. To achieve, in a wood-based active carbon, the mechanical strength and product density approaching that achieved with coal-based products, McCue et al. teach extruding an active wood-based carbon with bentonite clay, followed by calcining the extruded active carbon/clay pellets. This technology has been the basis for the commercial products NUCHAR® BAX-950 and NUCHAR® BAX-1100 marketed by West-vaco Corporation.

Carbons of suitable mechanical strength and density for use in an evaporative emission control device (automotive canister) for adsorbing gasoline vapors preferably also exhibit a butane working capacity of about 10 to about 17 g/100 cc and an apparent density from about 0.25 to about 0.40 g/cc.

In addition to gas column (or, packed bed) requirements for high mechanical strength and high density, it is also desirable to reduce the bed void volume in order to maximize the carbon content of the bed, and subsequently maximize the adsorptive capacity. This is primarily determined by the shape of the granular or pelleted carbon. In fact, because of the irregular shape of granular carbon, more regularly shaped carbon pellets are preferred for their better "packing." However, as a result of uneven cutting of the extrudate to form the pellets, the pellets are, in fact, irregularly shaped, and fissures and cavities often appear along the pellet surface. This creates two problems. The resulting irregularities in shape prevent optimization of bed (or column) packing and detract from maximizing the carbon content for a given pellet volume. In addition, the surface irregularities are often removed from the pellet due to abrasion. These material losses, in addition to debris caused by cutting the pellets to size, present another problem: dust. Typically, dusting due to abrasion, or dust attrition, may be retarded or precluded by spraying a coating on the surface of the pellet. Invariably, this remedy is at the expense of butane working capacity; thereby providing another trade-off for the working life of the active carbon material.

Besides having a product which may appear to disintegrate, attrited dust in a packed bed, such as a column or an automotive canister, can fill the bed voids to create high pressure drops and impede the flow-through of vapors to be treated. A particular problem in the automotive application is concern that the dust will act to interfere with various sensing devices connected to the canister to monitor performance, resulting either in false readings or in failure of the sensing devices altogether.

Therefore, an object of this invention is to provide an improved lignocellulosic-based activated carbon pellet of a smoother surface and more uniform shape which provides optimal bed packing, exhibits increased density, and is less susceptible to dust attrition. An additional object of this invention is to provide an improved method of manufacture of such activated carbon pellet.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows a block flow diagram of the invention process wherein tumbling is carried out on the green extrudate, followed by drying and calcination.

FIG. 2 shows a block flow diagram of the invention process whereby tumbling is carried out on the green extrudate as it is being dried, followed by calcination.

SUMMARY OF THE INVENTION

The object of the invention is achieved in the discovery that extruded pellets comprising a major portion of activated carbon particles and a minor portion of inorganic or organic binder provides improved performance when processed through tumbling equipment while the pellets are in their "green" state. Green pellets are those which are fresh off the extruder and contain activated carbon, binder, and moisture (from 50–70% water, by weight) and have not been subjected to any thermal processing (i.e., drying or calcining). The tumbling action both smooths and densifies (i.e., reduces interparticle voids within) the pellet, thereby

sealing, or otherwise closing, any cracks and greatly improving appearance. (Interestingly, debris caused by cutting the pellets to size is assimilated by the tumbling pellets.) Improved performance results from an ability to increase the weight of carbon pellets which can be packed into a fixed volume and thereby increase the volumetric working capacity of the bed for adsorbing/desorbing vapors. Another benefit is to greatly reduce the levels of dust associated with the carbon, both the initial dust and the dust attrition.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

The process steps for the alternative embodiments of the invention process are set forth in the drawings. FIG. 1 shows that activated carbon powder (produced from grinding granular lignocellulosic-based activated carbon), binder material, and water are sequentially mulled, extruded, tumbled, dried, and calcined to produce the invention active carbon pellet. FIG. 2 shows the activated carbon powder, binder material, and water to be sequentially mulled, extruded, dried while tumbling, and calcined to produce the invention active carbon pellet. The process steps are described in greater detail in the Examples which follow. Also, with the exception of the invention improvement, the process generally follows the teaching of U.S. Pat. No. 4,677,086, which disclosure is incorporated herein by reference.

Basically, the blend of activated lignocellulosic-based carbon, binder material, and water are mixed and then fed through an extrusion device. The generally continuous extrudate is cut at consistent intervals to produce a cylindrical pellet, relatively uniform in length and diameter. The invention process improvement involves taking these "green" pellets soon after they are generated and subjecting them to a tumbling process for a period of time sufficient to produce a pellet that, upon subsequent drying and/or calcination, exhibits a pellet void fraction of less than 0.19 (determined as the actual pellet density divided by the base pellet density and subtracted from 1) and a dust attrition rate of less than 1.2 mg/100 cc/minute. In a preferred embodiment of the invention composition, the pellet void fraction is less than 0.17 and the dust attrition rate is 1.0 mg/100 cc/minute. In the most preferred embodiment, the pellet void fraction is less than 0.15 and the dust attrition rate is less than 0.8 mg/100 cc/minute. In particular, it has been found that the rambling step is effective to provide the improved composition of the invention if it is performed in lieu of immediately drying the green pellets in additional equipment.

It is envisioned that the moisture level of the green pellets is important in the effectiveness of the tumbling step, and that a critical moisture level may exist below which densification and reduction of dust levels may not occur. As a result, in an additional embodiment of the invention, the tumbling equipment can also be used to dry the green pellets, if the drying rate is kept to a level low enough to give a sufficient residence time before the critical moisture level is reached. The critical moisture level is in the range of 50–70% water, by weight. A preferred moisture level is 55–65% water, by weight. The most preferred moisture level for the tumbling operation of the green pellets is 58–62% water, by weight.

Any commercial tumbling equipment, based on the nature and volume of material to be treated and whether the process is to be batch or continuous, is considered suitable for use in the invention process. Equipment which would be expected

to produce the beneficial product properties in the invention composition are considered to be equivalent to the equipment employed in the examples below. The tumbling operation may be employed for up to 30 minutes. The process is considered to offer little or no benefit once the moisture level in the pellets is significantly reduced (<50%).

The lignocellulosic material precursor to the lignocellulosic-based active carbon used in the invention process to form the invention composition is selected from the group consisting of wood chips, wood flour, sawdust, coconut shell, nut shells, fruit pits, kernal, olive stone, and almond shell.

The binder materials include bentonite clays or chemically modified bentonite clays. Preferred binders are sodium bentonite and calcium bentonite.

In the Examples to follow, the various analyses were performed in measurements determining the benefits of the invention product and process:

Apparent Density (AD)-ISO No. 960-050: weight of dry carbon per unit volume of the carbon bed;

Butane Working Capacity (BWC)-ISO No. 960-080: weight of butane purged from a sample of dried carbon after it had been saturated with butane per unit volume of the carbon bed;

Dusting Attrition (DA)-ISO No. 960-380: weight of dust attrited from a 100 ml sample of carbon per unit time;

Initial Dust (ID)- same as dusting attrition: weight of dust initially present on a 100 ml sample of carbon prior to attrition test;

Actual Pellet Density (APD); weight of dry carbon per unit volume of entire carbon pellet, determined using mercury porosimetry;

Base Pellet Density (BPD); weight of dry carbon per unit volume of carbon pellet including only pore space less than 0.5 microns equivalent diameter, determined using mercury porosimetry;

Bed Void Fraction (BVF): volume of space between carbon pellets per unit volume of carbon bed, determined by the equation 1-(AD/APD); and

Pellet Void Fraction (PVF) (pellet interparticle void fraction): volume of space within a carbon pellet including only pore space greater than 0.5 microns equivalent diameter per unit volume of entire carbon pellet, determined by the equation 1-(APD/BPD).

The invention process and composition are further described in the following specific examples:

EXAMPLE 1

Ground wood-based activated carbon was mixed with bentonite clay and water in a muller mixer. The dry basis clay concentration was 14 wt %. The mixture was mulled until it reached a consistency which could be extruded. It was extruded in a twin screw auger extruder through a die plate containing 2 mm holes and cut as it exited the die plate into "green" pellets ranging in length from 2–6 mm. The green pellets had a moisture content of approximately 55–60 wt % (wet basis). Following extrusion, a portion of the green pellets was loaded into a rotating disc pan pelletizer in order to tumble the pellets. The pan was angled above the horizontal to retain the pellets and rotated at 15 rpm for 5 minutes. After 5 minutes, pellets were collected from the pan and dried in a batch, convection oven. The portion of green pellets which was not tumbled was also dried in the same oven for the same amount of time. The two batches of dried pellets were calcined separately to 1200° F. in a batch

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