Development of Carbon Adsorption Blocks
for Evaporative Loss Control

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Abstract

Active carbon blocks from powder and granules have been fabricated and their performance characterized for evaporative loss control of hydrocarbons. The active carbons primarily studied were a Westvaco carbon, WVA 1100, used extensively for evaporative loss control devices (ELCD) and Amoco PX-21, a very high surface area carbon (2800 m^2/g BET area) developed in the late 1970s. A bonding technology has been developed to consolidate and densify carbon granules and powders to a solid block. Most binding agents fill the small pores in the carbon and significantly reduce the surface area and adsorption capacity. Particulate carbon has been successfully bonded into a variety of shapes with acceptable strength while maintaining most of the original adsorption capacity. The technology is based on a family of polymer binders, some suited for moderate temperatures around 200 ^{O}C while the others will withstand 350 ^{O}C without degrading.

One important application for carbon blocks is the capture of gasoline vapors from automobiles; a canister is located in the hood for the control of diurnal and hot soak conditions as well as now in the more demanding fuel filling cycle. The performance of carbon blocks for this application has been evaluated in static and dynamic tests. Butane adsorption and pressure drop were measured in a laboratory scale simulation test. The butane working capacity (BWC) of the bonded carbon is significantly higher, increasing from 11 to 13 g/100 ml for powders and as high as 17 g/100 ml for bonded granules. Most of this increase can be explained by the densification of the carbon from the bonding process. Dynamic performance of the carbon blocks for butane breakthrough depends strongly on how the block is formed, flow channels, and type/size of starting material. Most importantly, there are certain cases where the bonded carbon is noticeably better than a granular bed. Pressure drop of the carbon block depends on the form of the starting carbon and the incorporation of flow channels. Bonded carbon granules with moderate flow channel density gives very acceptable performance for the ELCD applications. Hydrocarbon break-through time is sufficiently long and pressure drop through the adsorption block low enough to adequately handle the higher flows during the fuel filling cycle.

Keywords: carbon, canister, gasoline, vapor, bonding, blocks

Introduction

Activated carbon used in automotive canisters in the early 1970s was typically coal-based granular carbon with a butane working capacity (BWC) [1] in the range of 5 g/100ml. In the mid 1970s, wood-based granular carbon was introduced in the United States for the automotive application and it rapidly gained a large market share due to its performance advantages. To date, wood-based carbon has been used in over 150 million vehicles for control of evaporative emissions. Also the BWC has more than doubled to 11g/100ml [2],but we now see a need to further increase that value due to even more stringent regulations by the EPA. More specifically, the control of diurnal and hot soak emissions have been augmented by now having to capture the gasoline vapors during the fill cycle. In the filling cycle, a stream containing ~50% hydrocarbon flows through the carbon canister at rates as high as 2 CFM (56.6 l/min) and the targeted maximum pressure drop is 4 inches water. Carbon canister development has been an area of intensive research at major automotive companies[3]

So far, the strategy for making improvements has been to alter the pore size distribution for adsorption capacity and to use uniformly shaped pellets to lower the pressure drop. Westvaco WVA 1100 granular carbon is uniquely tailored for ELCD with the majority of the pores in the range of 20-100 A^{O}. This facilitates reversible adsorption-desorption of hydrocarbons with the amount irreversibly adsorbed kept low. Without reversible adsorption, the gasoline vapors cannot be withdrawn from the carbon by air supplied to the fuel injector and thus the carbon remains loaded; it must perform in thousands of filling cycles and can only do that if hydrocarbon is desorbed by cobustion air and burned in the engine. The Westvaco product, BAX-950, is a good example of a special 2 mm pelletized carbon for use in the automotive industry with lower pressure drop than its granular counterpart. Carbon adsorption blocks show promise in extending performance beyond particulate carbon. We can summarize some of the relative differences between these two forms of carbon in Table 1.

We have developed an improved bonding technology for making carbon blocks. It basically consists of making a carbon slip with a polymer binder. The slip can be extruded, slip-cast, or compression molded to a variety of shapes (blocks, cubes, etc). There are two families of binders, one for moderate (200 ^{O}C) and the other for higher temperatures(350 ^{O}C) and they both cure at temperatures between 100-200 ^{O}C eliminating the need for high temperature calcination. Most importantly the adsorption capacity is preserved by minimizing the filling the carbon pores with the binding agent.

Experimental

Butane Working Capacity (BWC) Test- In the BWC test, activated carbon is loaded with pure gaseous butane until equilibirium is reached followed by flowing air in a desorbtion cycle to again reach equilibrium. The increase in weight by adsorption until equilibrium in g/100 ml of activated carbon is called activity. The difference between equilibrium loading and loading after desorption of the activated carbon is called working capacity. In this study, we used butane to load the test specimen for 10 minutes at 25^{O}C. After noting the weight of butane adsorbed, (Butane Adsorption Capacity), the carbon bed is purged with dry nitrogen rather than air, and should yield equivalent results. The total purge is approximately 600 bed volumes. The amount of butane desorbed is noted and reported as the butane working capacity in grams butane / 100 ml carbon. Cylindrical carbon blocks, about 15 mm diameter and 15 mm long were the typical test specimens while granular carbon was simply loaded into a small 20 mm tube packed with glass wool. All samples were dried at 100 ^{O}C for one hour prior to testing to remove any adsorbed water. Samples were weighed and the dimensions recorded so that the bulk density could be used to express the butane working capacity on both a unit weight and volume basis.

Dynamic Test Apparatus -The dynamic performance of carbon blocks and granules in trapping automotive gasoline emissions was simulated with small bench scale apparatus shown in Figure 1. More specifically, the adsorption capacity for butane and the pressure drop were measured and scaled according to the actual situation during the filling cycle of an automobile. The basis for the test conditions used in the simulation test are summarized below in Table 2.

The carbon sample was placed in a plastic tube, about 5 cm in diameter fitted with end caps for dynamic testing. For granules, the carbon was supported on a screen at the bottom while the blocks were sealed to the inner wall of the tube with silicone cement. Pressure taps were located up and downstream of the sample and a differential pressure gauge(0-10" water) was used to measure the pressure drop. A thermal conductivity (TC) cell was located down stream of the carbon and a split stream from the effluent continuously passed through one side of the cell with nitrogen reference gas on the other. The output signal from the thermal conductivity cell was recorded on a strip chart recorder.

Adsorption Test Procedure-

Dynamic adsorption capacity was measured by initially flowing 1 l/min of nitrogen through the carbon test specimen. At time zero, 1 liter/min of butane was mixed with the nitrogen stream and then the break through profile was measured. For the base case of Westvaco WVA 1100 carbon granules, the first indication of butane break through was typically 2 minutes after starting butane to the test specimen. Holdup time without carbon in the test container in the system was 12 seconds.

After the adsorption cycle, the butane was stopped and then the unit was purged with nitrogen to desorb the butane from the carbon. Since some of the butane in the small pores will not desorb (heel effect), it was necessary to perform a repeat run on all samples with the second repeat adsorption test used to characterize the dynamic adsorption capacity of the carbon specimen. The highest signal from the thermal conductivity cell that was observed during the break through test was used to normalize the readings; Output at time t/Max Output (C/Co) was plotted versus time for each test to make comparisons between various samples.

Pressure Drop Test

After the dynamic adsorption test was finished, the pressure drop across the sample at flow rates between 0-25 liter/min was measured. Nitrogen was passed through the bed and the pressure drop measured with a differential pressure meter. Pressure drop per unit length is plotted versus volumetric flow rate for each sample and used to compare the effect of flow channels, and other bonding variables. All tests were performed at room temperature.

Active Carbon Samples

Westvaco NUCHAR WV-A 1100: The Westvaco carbon is a premium activity granular carbon (10x25 mesh) for use in automotive canisters designed for the control of hydrocarbon emissions. The tamped bulk density of the granular material is 0.29 g/ml and the butane working capacity is nominally 11 g butane/100 ml carbon. It is wood based and requires both thermal and chemical activation.

Calgon BL: This is a coal based activated carbon and is most commonly used for treating drinking water. The BET surface area is 1000 m^2/g and the bulk density, 0.51g/ml. The Iodine Number is 1550 mg/g.

Amoco PX-21 Super Activated Carbon: This carbon was patented in 1978 by O Grady and Wennerberg[4] and subsequently commercialized by Kansai Coke and Chemical. It has a nominal surface area(BET) of 2600 m^2/g and pore volume of 1.8 cc/g. The Iodine number is 3000 mg/g and methylene blue number of 600 mg/g. The commercial name give by Kansai is MAXSORB. It is produced from petroleum coke, coconut shell char and other raw materials with the activation process consisting of 3 parts KOH/1 part carbon followed by two stage activation at 500 ^{O}C and 900 ^{O}C respectively.[5, 6]The bulk density is typically 0.24 g/ml (tapped) or 0.31 g/ml when packed tightly.

Results and Discussion

Mega-Cast Bonding Technology

A bonding process called Mega-Cast has been developed to bond carbon powders and granules into adsorbent blocks. Two patents have been granted on this technology. What makes Mega-Cast bonding unique is that very little of the adsorption capacity is lost due to pore plugging. The illustration of the bonded carbon in Figure 2 is one way to view the process with the carbon particles bonded at various points by a polymer binder. Carbon particles are shown darker and are bonded by the polymer droplets shown in the lighter shade. Every carbon is different and adjustments are always necessary in the formulation. Blocks can be cast routinely but extrusion is a special challenge and requires additives to impart desired rheological properties and stabilization of the slip.

To prepare a carbon adsorbent block, a carbon slip is first prepared with a polymer binder. There are two types of binders, one suitable for temperatures in the range of 200 ^{O}C and the other a higher temperature version which retains its strength at temperatures as high as 350 ^{O}C. The carbon slip can be prepared from either powder or granules and is then extruded, slip-cast, or compression molded to a variety of shapes(blocks, cubes, etc.). The binder cures at modest temperatures, eliminating the need for high temperature calcination and most of the adsorption capacity is preserved. The use of compression during the forming process translates into higher bulk densities and will frequently lead to adsorption capacity per unit volume (ie Butane Working Capacity) also increasing.

Effect of Binder Level on Strength and Adsorption Capacity

Amoco PX-21 Carbon: This carbon was bonded into small cylinders, 15mm diam x 15 mm high, at various levels of binder (4,8, and 17%) and then evaluated for surface area loss and crush strength. The surface area was measured indirectly using an Iodine number test and then relating it to the BET surface area. This correlation is shown in Figure 3 for the PX-21 carbon for both the Amoco and Kansai-produced high surface area carbon. The crush strength was measured by pushing on the two flat faces of the cylinder and recording the pressure required to fracture the carbon cylindrical block.

These data are shown below in Figure 4 with the BET surface area on the left axis and the crush strength on the right axis plotted versus binder level.
The surface area of the unbonded powder is 2600 m^2/g and then gradually decreases to 2200 m^2/g on the far right at the 17% binder level. If we base the surface area on carbon alone, then the decrease is relatively small. Crush strength is 600 psi at 4% binder and increases to 1600 psi at the 17% binder level. Therefore increasing the binder has pronounced effect on strength and implies a balance of strength versus surface/adsorption properties should be considered for each application.

Westvaco WV-A 1100 Carbon:

The Westvaco carbon used in ELCD canisters was primarily focused on in this investigation. Specifically, the goal was to increase adsorption capacity and decrease pressure drop by employing active carbon in a block form. The static adsorption capacity is characterized with the butane working capacity (BWC) test. The BWC of the Westvaco WV-A 1100 granular carbon is typically 11 g butane/100 ml carbon (weight basis corresponds to 42.5 g/100 g). The granules were ground to a powder and then bonded into blocks at three levels of binder. BWC increases from 11 for the granules to values of 14.7, 13.5 and 13.2 for corresponding binder levels of 2.5%, 5%

and 10% as shown in the Figure 5. Coprrespondingly the BWC per unit weight decreases from 42.5 to 30 g/100g.

The primary reason for the increase in BWC is due to the increase in bulk density. Bulk density for the granular and bonded versions of two carbons, Westvaco WV-A 1100 and Amoco PX-21, are shown in Figure 6. Compression casting the carbon into a solid block results in a 40-50% increase in bulk density. Although the BWC per unit weight decreases by 25%, the density increase easily compensates for this loss translating into higher volumetric adsorption capacity.

The crush strength for the Westvaco WV-A 1100 bonded carbon exhibits a similar trend to the Amoco PX-21 discussed earlier. The crush strength test was performed differently, with the cylindrical block placed on its side, as is commonly done for testing extrudates and measures the hoop strength. The crush strength was 0.22, 1.30, and 4.12 kg force/cm length for the three binder levels of 2.5%, 5% and 10% respectively.

Dynamic Adsorption Tests

New EPA mandated constraints for the fuel fill cycle require capture of gasoline vapors on board the vehicle rather than vapor recovery nozzles at the pump. A target for pressure drop is to be around 4 inches water for flow rates of 2 ft^3/min(56 liter/min).

Vapor displaced from the fuel tank passes through a canister packed with granular activated carbon (ie fixed bed) with the gasoline desorbed from the bed when the engine is running. The dynamic performance of the carbon granules and blocks was measured with a bench scale test. Adsorption performance was measured by flowing a 50/50 mixture of butane/nitrogen at the representitive volumetric space velocity as used in the fill cycle of an automobile(ie 16 min^{-1}). For the smaller 128 ml block, this corresponds to a total flow rate of 2 liter/minute. The pressure drop test used a different basis with the air velocity held constant by adjusting the flow for different cross-sectional areas. Flow rate was varied between 0-21 liters/min for the smaller specimen which corresponds to 0-31 liters/min canister flows. The measured pressure drop was then adjusted for its flow length and reported in inches water per foot of block so that clear comparisons could be made.

Base Line Test

A baseline test for butane break-through was peformed with Calgon BL carbon. Granules (10x25 mesh) and bonded blocks of the same carbon with 35 and 70 flow channels were tested. The data are shown in Figure 7. Hydrocarbon break-through time for the granules is about 2.5 minutes whereas the 35 and 70 hole blocks exhibit break-through times of 1-1.5 minutes.. The earlier break-through time for the blocks was unexpected. When flow channels pass entirely through the block, some butane will bypass without being adsorbed and will be discussed later.

Westvaco Carbon

Dynamic adsorption capacity of Westvaco WV-A 1100 granules and blocks was then tested. Referring to Figure 8, the time for butane break-through was about 2.5 minutes for the granules. The blocks were formed from powder obtained by grinding granules and then bonding into a cylindrical block with axial flow channels provided. Similar to the baseline test, the butane breakthrough time decreased from 2.5 minutes to 1 minute for the block with axial flow channels. It is possible that early breakthrough was due to ineffective radial transport in the block; 48 cross flow channels in the radial direction were provided and the block retested. The addition of cross channels caused the butane break-through time to decrease even further, to a value of 0.5 minutes. The conclusion is that even though the bonded Westvaco carbon has a higher static butane working capacity than the granules(13 g/100 ml vs 11 g/100 ml), the dynamic adsorption performance was inferior.

Pressure Drop Characteristics

Pressure drop in the carbon adsorption block is a key concern. The pressure drop in a fixed bed can be described by the Ergun equation as follows:

Reynolds number, Re (ud_p/), for the granular fixed bed is around 2500 at 56 l/min and falls into the turbulent flow regime. When the carbon adsorbent is a block with axial flow channels, pressure drop can be described by flow in a tube. Reynolds number for a block with 60 flow channels (1 mm diameter) is around 600 at the same flow rate which is laminar flow. The friction factor for laminar flow is 16/Re so the pressure drop equation is the following:

(2)

Pressure drop across the adsorbent bed was measured over a flow range of 0-25 liters/minute and then plotted as P/L (in H_2O/ft bed) versus Qin Figure 11. As mentioned earlier, the targeted P/L is around 5. Referring to Figure 11, the pressure drop has been plotted for a granular carbon bed (10x25 mesh) and three carbon blocks (powder-based) with 18, 35, and 70 flow channels.

The 18-hole block exhibits the highest pressure drop, around 20 in H_2O/ft, at 20 liters/minute of flow. As the flow channels are increased for 18 to 35 and finally 70, the pressure drop correspondingly decreased to 14 and12 in H_2O/ft at 20 liters/min.

The application of carbon adsorption blocks for ELCD has been investigated and situations identified where they are superior to granular material. In particular, the use of bonded granules with higher bulk density, due to compressive molding, has much higher static adsorption capacity. For example, the butane working capacity will increase from 11 g/100ml carbon to values around 18. The dynamic performance of carbon adsorbent blocks must balance adsorption capacity with pressure drop through the device.

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Performance Differences between Carbon Blocks and Granules

Carbon Block	Carbon Granules
Resists abrasion due to no grinding motion of granules.	Cheaper since it is used as supplied but susceptible to abrasion
Higher bulk density since compression can be used to form the block and then cured in its compressed state.	Moderate bulk density due to higher void fraction but this helps external mass transport due to tortuous path that adsorbent stream takes while passing through the bed
Forms to many unique shapes and will not settle if positioned in another orientation	Must be enclosed in a container and bed will shift creating bypassing if tilted sideways.
Pressure drop controlled with axial flow channels, varying size and hole density and conforms to tubular flow in the laminar regime	Pressure drop affected by the shape and size of the granules. Ergun equation used to describe pressure drop relationship which is directly proportional to bed length and fluid velocity and inversely proportional to bed void fraction and particle diameter

Scaling for the Dynamic Test

	Butane Adsorption	**Pressure Drop Behavior**
On-Board Recovery System in Auto	1 liter canister with 16 l/min(~50% hydrocarbon) Volume hourly space velocity(volumetric flow rate/volume canister) = 16 min^{-1}	Canister cross-sectional area of 25 cm^2
Laboratory Test Equivalent	Test block = 128 ml corresponds to 2 liter/min total flow	Test block cross sectional area = 16 cm^2 Adjusted flow rate = 16/25 x canister flow rate for same pressure drop per unit length of adsorbent.