



Energeia

Activated Carbons from Agricultural Byproducts for Adsorption of Organics and Metals

Christopher A. Toles, Wayne E. Marshall and Mitchell M. Johns
USDA-ARS-Southern Regional Research Center,
New Orleans, LA

Abstract

Granular activated carbons (GACs) were developed from hard and soft lignocellulosic byproducts. Three activation strategies were evaluated which employed phosphoric acid, carbon dioxide or steam. A portion of these carbons were also subjected to air oxidation after activation. Uptake of both non-polar and polar, small organic compounds were followed as was the adsorption of copper. Our results indicate that GACs produced from agricultural byproducts can adsorb polar organics and copper to a greater degree than representative commercial carbons in a side-by-side comparison.

Introduction

Disposal of agricultural byproducts is a major economic and ecological issue for nut shelters, grain millers, oilseed crushers and raw sugar factories in the United States. These processors create over 100 billion lbs of shells, hulls, cobs, and fiber each year from renewable resources. Almost all of this material is used for low value products such as mulches, oil drilling lubricants, soil amenders, animal bedding and animal feed. Therefore, additional outlets need to be identified to create higher value-added products in which the potential markets are large enough to consume a significant portion of these byproducts.

The conversion of agricultural byproducts to adsorbents, such as activated carbon, represents a possible outlet. This would result in the creation of a versatile value-added product. The versatility of activated carbon in applications where a good adsorbent is needed is well known. These high porosity, high surface area materials are used by industry, municipalities or



individual households for one or more of the following applications: environmental remediation, purification and chemical recovery operations and water treatment. They can be produced from a number of feedstocks or precursor

materials including coal, peat, wood and agricultural wastes. The feedstocks are normally exposed to several activation methods in an effort to achieve an activated carbon with the best qualities for a particular application.

Because of their large surface area and their mostly non-polar surfaces, many activated carbons are used for the adsorption of small, non-polar organic compounds found in contaminated air and water. However, some carbons possess regions of polarity due to the presence of surface functional groups containing oxygen. These carbons have been shown to adsorb metals and polar organic molecules, but to a limited degree. A major goal of our research at the Southern Regional Research Center is to develop granular activated carbons (GACs) with greater adsorption of metals and polar organics compared to commercial activated carbons. Thus, we wish to produce more versatile carbons for a wider variety of potential applications, especially for water and wastewater cleanup. We selected a number of agricultural byproducts as carbon

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Emission of Toxic Explosive and Fire Hazardous Gases in Coal Piles Stored Under Atmospheric Conditions (Part I of a II Part Article)

Samuel L. Grossman^{1,2} and Haim Cohen^{*1,3}

¹R. Bloch Coal Research Centre-Chemistry Department, Ben Gurion University of the Negev, P.O. Box 653, Beer Sheva, Israel.

²National Coal Supply Corporation, P.O. Box 21253, Tel Aviv 61212, Israel.

³Chemistry Department, NRCN, P.O. Box 9001, Beer Sheva, Israel.

* To whom correspondence should be addressed.

Background

Bituminous coal stockpiles stored in open air undergo weathering processes due to low temperature oxidation (40-100 °C) resulting in quality deterioration. The process is accompanied by emission of hazardous explosive gases such as molecular hydrogen and low molecular weight organic gases.

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Activated Carbons, continued

feedstocks, including several different hard, dense nutshells and softer, less dense material such as rice straw, sugarcane bagasse, and the hulls of soybeans, cottonseed, rice and peanuts. These byproducts offer the advantage of a greater percentage of non-carbon constituents in their composition compared to coal or peat and therefore afford a greater chance of retaining functional groups, especially oxygen, in the carbonized product. However, the lower carbon content of the byproducts translates to lower activated carbon yields, but the low cost of the feedstock and the anticipated improvement in metals and polar organic adsorption compared to coal or peat-based carbons should more than cancel out the effect of lower yields.

This article presents our attempts to improve the adsorption of metals and polar organics beyond adsorption normally encountered with commercial carbons. This research was carried out by employing several activation strategies combined with air oxidation of the carbon surfaces.

Precursor Preparation

The softer, less dense lignocellulosic materials, such as soybean hulls, sugarcane bagasse and rice straw, require a binder to increase the density of the final GAC. We used sugarcane molasses, a byproduct of cane sugar refining, as our binder. Prior to char formation, the precursors were mixed with binder, usually at a 1:2 (binder:precursor) ratio and pressed into cylindrical briquettes, resembling a hockey puck, to a density of about 1.2 g/cm³. The harder, more dense nutshells required no preparation other than grinding the precursors to a 10-20 mesh size where they were charred and activated as such. Pyrolysis or char formation was carried out in an inert atmosphere of nitrogen. The briquetted chars were milled and sieved to a 10-20 mesh particle size prior to activation. Pyrolysis creates a cross-linked carbon skeleton whose porosity is largely filled with lighter thermal breakdown products.

Activation Strategies

Chars were activated by physical activation with carbon dioxide or steam. Carbon dioxide activation was carried out using several mixtures of carbon dioxide and nitrogen gas at several activation temperatures. Limited steam activation was performed on both hard and soft lignocellulosic precursors. Both carbon dioxide and steam serve to gasify the light hydrocarbons that block

existing pores and also create additional pores in the carbon structure. After activation, part of the sample was treated with air at elevated temperatures to increase the adsorbed oxygen on the carbon surface. The activated or activated/oxidized GACs were evaluated for physical and adsorptive properties.

Chemical activation or phosphoric acid treatment of nutshells differed from the physical activation strategies. Phosphoric acid activation was accomplished by soaking the nutshells with acid, then subjecting them to a two stage activation. First, the acid soaked nutshells were given a relatively low temperature treatment for a short period. Second, the temperature was quickly increased and the precursors exposed to the higher temperature for a longer period. Phosphoric acid is a non-oxidizing acid which appears to act as an acid catalyst for the production of a porous, cross-linked carbon framework. The acid also appears to fix more of the carbon into the structure than is seen in physical activation. Thus production yields are significantly higher. There may be an important role for oxygen in the cross-links within the structure itself. After activation the samples were air oxidized at elevated temperature.

After activation, the carbon was washed in a soxhlet extractor until the pH of the wash water was neutral and there was no evidence of free or loosely bound phosphates. The phosphoric acid was reclaimed in a rotary evaporator. It can be mixed with fresh acid and reused in future activations. The reclaimed acid cannot be used as is because the activation and reclamation steps use ceramic crucibles and silica-rich glassware. At the temperature used for activation and reclamation, silica leaches from the crucibles and glassware and appears to increase the silica content of the phosphoric acid,

thus rendering it less effective as an activant in subsequent runs and requiring more fresh acid. Additional inert containment vessels must be found to reduce silica contamination and allow for reuse of the original acid, thereby keeping acid usage and cost low. ³¹P NMR analysis, however, indicated very little evidence of polyphosphate formation in recycled acid.

Carbon Characterization

We characterized our granular activated carbons (GACs) by determining final yield from precursor to product, evaluating surface area by nitrogen adsorption and the BET equation, measuring adsorption of low molecular weight, non-polar and polar organic compounds and determining uptake of copper from solution. Adsorption of organics was quantified by placing the carbon in contact with a test solution containing a suite of organic compounds with a broad range of polarities. The suite included in order of increasing polarity: toluene, benzene, 1,4-dioxane, acetone, acetonitrile, and methanol. After the test solution had been in contact with the carbon for 24 hours, the headspace gas was drawn off and absorbed to a solid surface using solid phase microextraction. Analyte concentration in the headspace was determined by gas chromatography to quantify the amount of analytes left unadsorbed by the carbon. We determined the carbon's ability to sequester copper (cupric ion) from solution at pH 5.0 by mixing GACs with buffered copper chloride solutions of different concentration. After 24 hours of contact, the amount of copper left in solution was measured by Inductively Coupled Plasma spectrometry.

Product Yields and Surface Areas

Table I lists product yields and surface areas of agricultural byproduct-based
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Table 1. Select physical properties of by-product based GAC's produced by different activation strategies.

Precursor	Treatment	Product Yield (%)	Surface Area (S _{BET} , m ² /g)
Pecan Shells	Carbon dioxide/unoxidized	23	485
	Carbon dioxide/oxidized	22	507
	Steam/unoxidized	18	721
	Steam/oxidized	17	725
Pecan Shells	Phosphoric acid/unoxidized	41	1186
	Phosphoric acid/oxidized	40	1124
Soybean hulls ^a	Carbon dioxide/unoxidized	18	180
	Carbon dioxide/oxidized	17	338
	steam/unoxidized	11	380
	steam/oxidized	10	700

^aSoybean hulls were combined with sugarcane molasses in a 1:2 ratio (molasses:hulls) before pyrolysis

Activated Carbons, continued

GACs which represent the two classes of precursors we have evaluated. Pecan shells represent the hard, high-density lignocellulosics and soybean hulls represent the soft, low density byproducts which require a binder for GAC production. For pecan shells as well as other nutshells we have examined, phosphoric acid activation gives higher product yields and surface areas than physically activated GACS. When physical activation is considered, carbon dioxide treatment appears to give slightly higher yields but significantly lower surface areas than steam activated pecan shells or soybean hulls. However, our experience with steam treatment of byproducts is limited and further data is necessary to make unequivocal statements about differences in carbon dioxide and steam activation. Indeed, if product yields from steam activation can be increased to the 20-25% range without sacrifice of surface area, and time and temperature parameters are equivalent to carbon dioxide activation, steam treatment would be economically advantageous due to activant costs. Steam is significantly less costly to use than carbon dioxide. We intend to pursue further research on steam activation of both hard and soft precursors.

From an economic viewpoint, phosphoric acid activation would appear to be the activation strategy of choice, producing

byproduct-based GACs with high yield and high surface area. However, the process is potentially expensive due to acid costs unless most of the acid can be recovered and reused. We are currently working on such a strategy.

Organics and Metals Adsorption

Table 2 shows the ability of representative GACs made from hard and soft lignocellulosics to adsorb both polar (methanol, acetonitrile, acetone, 1,4-dioxane) and non-polar (benzene, toluene) organic compounds and copper as Cu^{2+} from solution. These adsorption characteristics were compared to two commercial carbons, Calgon Carbon's Filtrasorb 400 and Norit's RO 3515. They were chosen for comparison because they are widely used GACs and have recognized applications for organics remediation in liquid and gaseous media (F-400) and precious metals recovery from wastewater (RO 3515).

Organics adsorption is divided into uptake of two classes of compounds, polar and non-polar. Commercial carbons are recognized for their ability to sequester non-polar organics, such as those in the BETX group. Their ability to adsorb polar organics has been limited due to the non-polar nature of their internal surfaces. GACs which have a greater ability to adsorb polar organics than commercial carbons, while retaining

their ability to sequester nonpolar organics, would be welcome for their versatility and use in a wider variety of commercial applications.

Table 2 data show nutshell carbons, represented by pecan shells, developed by either carbon dioxide or steam activation, are excellent adsorbers of polar organics. However, oxidation of these GACs caused very little change in this type of adsorption. Carbon dioxide activation of soft, lowdensity byproducts with binder, represented by soybean hulls, produced a reduced ability to adsorb polar organics, compared to nutshell GACS. Oxidation of this material caused a substantial increase in adsorption of polar organics. Oxidation of steam activated samples, however, resulted in a sharp decline in adsorption. Phosphoric acid activation of nutshells produces GACs with considerably less affinity for polar organics than those produced from physical activation. Oxidation of acid-treated samples dramatically improved polar organics uptake. In terms of polar organics adsorption, all of the pecan shell- and some of the soybean hull-based GACs performed substantially better than the commercial carbons. All activated carbons in Table 2, experimental and commercial alike, appear to adsorb non-polar organics about equally well.

We believe the type of precursor and activation method are important in developing GACs with high adsorption of polar organics. Agricultural byproducts have a lower carbon content than bituminous coal or peat and therefore possess a higher content of potential functional groups on the carbon surface, such as nitrogen or particularly oxygen. For some byproducts, such as the nutshells, some of these functional groups are probably retained after pyrolysis and activation. Therefore, their adsorbing surfaces contain regions of polarity which assist in attracting polar compounds. Air oxidation of activated carbon surfaces would be expected to create additional oxygen functional groups and therefore improve adsorption of polar organics. However, oxidation of steam activated hard and soft precursors showed no increase in adsorption of polar compounds. We are not certain why this group of GACs exhibited different behavior.

Table 2 also shows copper uptake data for experimental and commercial carbons. Using adsorption data for the commercial GACs as a baseline, oxidized samples, regardless of the initial activation, sequestered two to four times as much copper

Table 2. *Organics and metals adsorption of by-products-based GAC's produced by different activation strategies*

Precursor	Treatment	Organics Adsorption (mmoles/g)		Copper (Cu^{2+}) Adsorption (mmoles/g)
		Polar ^a	Non-polar ^b	
Pecan Shells	CO_2 /unoxidized	0.407	0.189	0.11 ^c
	CO_2 /oxidized	0.429	0.188	0.18 ^c
	Steam/unoxidized	0.457	0.206	0.36 ^d
	Steam/oxidized	0.420	0.194	0.34 ^d
Pecan Shells	Phosphoric acid/unoxidized	0.206	0.177	0.04 ^c
	Phosphoric acid/oxidized	0.328	0.176	0.27 ^c
Soybean hulls	CO_2 /unoxidized	0.270	0.169	0.02 ^d
	CO_2 /oxidized	0.383	0.196	0.67 ^d
	steam/unoxidized	0.403	0.208	0.38 ^d
	steam/oxidized	0.295	0.186	0.74 ^d
Filtrasorb 400 RO 3515	steam/unoxidized	0.329	0.188	0.09 ^c ; 0.17 ^d
	steam/unoxidized	--	--	0.09 ^c ; 0.22 ^d

^aPolar organics adsorbed were methanol, acetonitrile, acetone, and 1,4-dioxane

^bNon-polar organics adsorbed were benzene and toluene

^cThese GAC's were exposed to a 3.0 mM copper solution

^dThese GAC's were exposed to a 10.0 mM copper solution

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Multiple Honors Bestowed on CAER Student

CAER undergraduate co-op student, Tapiwa Gurupira recently won two prestigious University of Kentucky awards. He is the recipient of the Lyman T. Johnson Odyssey Award; and the International Student Merit Scholarship. The Lyman award is named in honor of the first African-American student to enroll at the university. The second honor is an endowed scholarship to recognize an

undergraduate foreign student of exceptional merit for strong academic performance and integrity. Both awards carry with them substantial scholarships.

Tapiwa is from Zimbabwe, and has worked part-time at the CAER for three years. He is a mechanical engineering major, who just completed his junior year. His plans include graduate school in the U.S.

Emissions, continued

Introduction

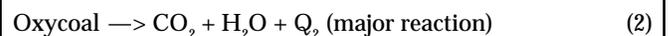
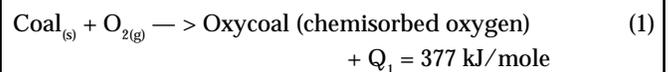
The worldwide trade in bituminous coals has grown at a consistent rate over the past 20 years. At present it is estimated that approximately 430 million tons are traded annually, mainly using large ships as a method for transportation (over 60,000 tons). Large amounts of coal must be stored for relatively long periods (weeks or a few months) in large stockpiles under open air (at the harbors, or in storage facilities near the power stations) or in ship holds in confined spaces. Israel, for example, presently consumes over 8.5 million metric tons of bituminous steam coal per year that is imported from South Africa, the USA, Colombia, Australia and Indonesia. The typical transportation period is 2.5 weeks. Due to the fact that Israel has no indigenous coal, large amounts must be stored uncovered for extended durations under the hot and dry climate prevalent in the country. Coal is stored in three storage facilities in large piles (60-150,000 tons/pile) and held for about 6 weeks in the pile prior to combustion. The coal is uncompacted or partially compacted (bulk density 850-920 kg/m³). Consumption will increase to more 11.5 million tons in the next 3 years.

From the moment that coal is exposed to air, it is prone to low temperature oxidation by oxygen which results in induced autogenous heating because of the exo-

thermic nature of the reaction. This process can be sustained only if the heat produced by the exothermic oxidation (mainly chemisorption of oxygen at the coal surface and emission of carbon dioxide) cannot be sufficiently dissipated by heat transfer within the stockpiles.

If the stockpile's temperature rises above 80 °C, the result will be vaporization of the coal's moisture content. The oxidation process is accompanied by emission of low molecular weight organic gases (C1-5 like methane and ethane) and carbon monoxide which are toxic and fire hazardous. Recently it has been observed that molecular hydrogen is also released at relatively low temperatures (40 °C). The presence of these products appreciably lowers the self ignition temperature of the coal in question. In extreme cases spontaneous combustion can occur. Storage of coal in confined spaces like ship holds, silos, bunkers, train wagons etc. is of course much more susceptible to self ignition, if the storage period is more than a month. The presence of molecular hydrogen, in addition to methane, increases the risk of explosion in the vicinity of the stored coal. The autogenous heating of stockpiled coal is generally restricted to small distinct areas commonly referred to as "hot

spots" that are characterized by good oxygen diffusion and insufficient heat transfer. Thus coal stockpiles can be envisaged as large outdoor reactors in which the reactions that take place can be generalized as follows:



Hence, the oxidation induced autogenous heating ($Q_1 + Q_2 = 33,400 - 35,100 \text{ kJ/kg Coal}$) of coal not only poses a safety and handling problem, but causes a loss of the energy that was prevalent in the unoxidized coal. Furthermore the reacted coal is liable to have lost volatility and to have undergone physical changes as well (decrepidation). The resultant coal is now less desirable for usage in power stations.

In order to assess the oxidation resistance of the various coals stored in Israel, extensive simulation experiments in small glass batch reactors were performed as well as monitoring of temperatures and gases evolved in large coal piles stored in open air. The monitoring and sampling of the gases has been performed using a portable unit developed at our laboratory which can penetrate up to 7 meters inside a coal pile.

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Don't Fear Technology

Richard Lawson
President, National Mining Association

The positive side of technology is not hard to understand. Throughout history, technological improvements have been closely tied to what humanity has come to perceive as the advancement of civilization -- be it Gutenberg's printing press, Watt's steam engine, or Gould's basic idea for the laser.

The reasons behind a negative view of technology are perhaps a bit more obscure and idealistic. In the most basic sense, this view has its roots in mistrust of the new and different, as well as the motivation behind technological progress. When George Orwell wrote in 1984, he suggested that tyrants of the future would use technological advances not to help civilization, but to hold people in subjugation.

For the mining industry, this is a particularly important debate. Many of our critics, particularly those who are no-growth advocates, see technology as being part of the problem - among other things, making possible what they see as the evil of unprecedented mineral and coal production in the 20th century. Rather than recognize the vital role played by these resources in creating a sound economy and prosperous society, they see a darker side: the evolution of a greedy, materialistic, over-consuming and polluting nation.

The fact that there are extremists who think this way is not surprising. The greater danger lies in the efforts of these groups to convince the general public that all technologies and industries who employ them are bad; and that the products, conveniences and services made possible by technology are trappings of an inherently greedy and evil civilization.

They point to problems and conflicts associated with energy, and economic

and environmental issues, and suggest that technology has caused more harm than good. They declare that, if we did not have factories, automobiles and electric generating plants, the air would be cleaner. Of course, these observations are at best, oversimplifications designed to confuse, mislead and distort public opinion.

What usually happens - and what the critics of technology would have us forget - is that the benefits of technology usually far outweigh whatever risks or negatives that accompany their application.

In the mining industry, innovations have dramatically enhanced productivity and safety while allowing us to operate in a more environmentally efficient manner. Scrubbers, electrostatic precipitators, improved clean coal and smelter technologies and other devices and approaches have combined to provide the world's cheapest, most abundant, secure source of electricity and raw materials and at the same time have greatly improved air quality in this nation over the last two decades.

The bottom line is that technology has provided the U.S. and other industrialized nations a standard of living unimaginable even a century ago. And while not perfect, technology has helped solve many more problems than it has created.

In short, if the people on Earth are to become healthier, live longer and improve their economic standard of living, it will be by continuing to embrace technology - rather than rejecting it.

A version of this editorial appeared in the January issue of Mining Voice.

Emissions, continued

Molecular hydrogen emissions were found in all types of coals studied. The concentrations of molecular hydrogen were small but in appreciable amounts. Thus in the batch reactors (5 grams coal in 120 ml volume) at 95 °C (heated for 40 hours) 220-800 ppmv of H₂ (depending on the coal type) was measured. Inside the piles, concentrations of 900-3000 ppmv have been measured. It is observed that the amount of hydrogen formed in the batch reactors is dependent linearly on the amount of oxygen consumed by the coal oxidation process and also on the temperature. Thus in pure oxygen with American coal (Pittsburgh seam), 2400 ppmv H₂ were released whereas in air, only 600 ppmv are formed and under nitrogen atmosphere <10 ppmv were measured (at 95 °C). The amount of the hydrogen produced is only slightly dependent on the coal mass (increase of 25 % in concentration for a ten fold increase in coal mass). No effect of particle size has been observed indicating that it is a process which occurs not only on the outside surface of the coal particle but also on the surface of the macropores (if not the micropores) of the coal particle (which is the major constituent of a coal's surface area). An exhaustive literature search provided the authors with only two cases in which the low temperature emission of hydrogen from coal oxidation were mentioned. But these papers dealt with oxidation at considerably higher temperatures, approximately 240 °C and so the low temperature (40 - 95 °C) oxidation correlated emission of hydrogen can be regarded as a novel result. It is rather surprising that molecular hydrogen, H₂, a reduction product, accompanies an oxidation process (oxygen chemisorption and carbon dioxide emission) of the coals and that it occurs at ambient temperatures as low as 40 °C! The results definitely show that the release of H₂ is an oxidation correlated process, namely, the larger the amount of oxygen consumed, the higher is the observed concentration of dihydrogen evolved. Calculation of the amounts of molecular hydrogen produced in the gas phase, relative to the percent of oxygen consumed by the same mass of a certain coal shows that this value is constant, approximately 11.4 ± 2 [ppmv / % O₂ consumed] at 95 °C.

The second part of this article will appear in Energeia Volume 9, Issue 4.

Haim Cohen is Professor of Chemistry at Ben Gurion University of the Negev, Beer-Sheva, Israel. Dr. Samuel L. Grossman is the Vice President responsible for coal purchasing at the National Coal Supply Co. in Israel.

Activated Carbons, continued

from solution. Generally, air oxidation greatly improved metals uptake. We believe the addition of oxygen functional groups through air oxidation plays a pivotal role in preparing the carbon surface to accept positively charged metal ions.

Conclusion

Our laboratory has produced GACs by several activation strategies from agricultural waste and determined that they are quite effective at adsorption of

organics, especially polar organics, and ubiquitous metal pollutants, such as copper. Adsorption compares quite favorably with representative commercial carbons studied in our laboratory, and in many cases they out-perform these carbons. In some cases, an oxidation step appears to be necessary to develop metals uptake greater than those determined for commercial carbons, but steam activation without additional oxidation, in particular, appeared to yield GACs with good organics or metals uptake.

Our studies thus far show that agricultural waste can be transformed into adsorbent material which can be beneficial in water and wastewater remediation systems toward the removal of organic and metal contaminants.

Chris Toles is a Research Chemist at the USDA-ARS-Southern Regional Research Center in New Orleans, Louisiana. He is a graduate of the University of Kentucky and former research assistant at the CAER.

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