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# **Granular Activated Carbons From Agricultural By-Products: Preparation, Properties, and Application in Cane Sugar Refining**

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# **Granular Activated Carbons From Agricultural By-Products: Preparation, Properties, and Application in Cane Sugar Refining**

Mohamed Ahmedna<sup>1</sup>, Wayne E. Marshall<sup>2</sup>, and Ramu M. Rao<sup>3</sup>

## **INTRODUCTION**

The annual harvest and processing of various agricultural crops grown in the United States yield considerable quantities of agricultural by-products. Taking three major commodities grown in Louisiana as an example, the United States produced 62 billion lbs of sugarcane, 17 billion lbs of rough rice, and 182 million lbs of pecans during the 1997 crop year (Agricultural Statistics, 1997). Production and processing of these commodities generated an estimated 21 billion lbs of sugarcane bagasse, 3.8 billion lbs of rice hulls/straw, and 91 million lbs of pecan shells as by-products. These agricultural by-products have little or no economic value, and their disposal not only is costly but may also cause environmental problems. Conversion of these agricultural by-products into carbonaceous adsorbents that can be used in food applications such as sugar refining or wastewater treatments would add value to these agricultural commodities, help reduce the cost of

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waste disposal, and provide a potentially cheap alternative to existing commercial carbonaceous adsorbents.

Four systems of decolorization are used in the sugar refining process: bone char, granular activated carbons, ion exchange resins, and cationic color precipitants or flocculants. Of these, bone char remains the most commonly used decolorant in Louisiana cane sugar refineries and in the United States in general. Bone char, made by carbonizing specially selected sun-dried cattle bones, has a bulk cost of \$0.55-0.60 per lb. Bone char is generally considered an excellent adsorbent for anionic color components, ash, and certain color precursors found in sugar liquor. However, bone char is primarily a product imported from Brazil and India, and its cost and supply can vary according to the current political situation in the supplying countries. Since ion exchange resins are known to provide good ash and color removal and can be regenerated chemically, they are being introduced in sugar decolorization by some refineries. However, the main obstacle for the widespread use ion exchange resins in sugar refineries is their relatively high cost, \$5-20/lb.

Granular activated carbons (GAC), on the other hand, are prepared from a variety of local raw materials of vegetable origin, such as wood and peat, or of mineral origin, such as coal. It is activated by various methods, including thermally and chemically, with acids and various salts. The method of activation determines the effectiveness of the carbon as a decolorizer of sugar syrup. Granular activated carbons remove color better than bone char, but they do not remove ash as well as bone char does. GAC also cost more than bone char, but the service time and the period between regeneration are both longer for a given volume of sugar syrup. Consequently, the physical size and cost of both the operating and the regeneration facilities are less than for a bone char facility of a similar capacity. Much of the GAC is made in the United States, and the cost is usually constant. However, GAC is costly (\$2/lb, including cost of regeneration) and is derived from a non-renewable resource, namely coal, and therefore competes with the energy industry for this diminishing commodity.

Abundance and low cost of agricultural by-products make them good candidates as precursors of activated carbons. By-

product-based GAC are expected to cost below \$0.5/lb. Agricultural by-products used as precursors of carbon can be classified into two groups. "Group 1" materials consist of soft compressible waste products of low density, such as sugarcane bagasse, rice straw, soybean hulls, peanut shells, and rice hulls, and "group 2" materials, such as nutshells from pecan and walnut, are hard, dense, and not easily compressed. Rice hulls, rice straw, and sugarcane bagasse, group 1 by-products from economically important Louisiana crops, have been used as a source of powdered activated carbons by several authors (Pollard et al., 1992; Youssef and Mostafa, 1992; Tecker et al., 1997; Lavarack, 1997; Bernardo et al., 1997; Mackay and Roberts, 1982a). However, the use of powdered activated carbons remains limited because granular activated carbons are generally considered more versatile due to their regenerability. Because of their versatility, GAC command a large percentage of the carbon market (Activated Carbon Markets, 1994), especially for raw sugar decolorization. To produce GAC, group 1 precursors must be mixed with suitable binder and compressed into briquettes or pellets to increase the density of the final product. Production of GAC from these soft materials also uses binders to ensure intimate contact of the lignocellulosic particles during pyrolysis. Group 2 by-products, on the other hand, are suitable as GAC precursors without binder or briquette formation. Nevertheless, limited knowledge is available on the production of granular activated carbons from soft agricultural by-products (group 1), in particular, and from group 2 by-products.

The objectives of this investigation were to convert select Louisiana agricultural by-products to GAC and to characterize these carbons in terms of those physical (surface area, pore structure) and chemical (surface charge, functional groups) properties directly related to adsorption of raw sugar colorants. Other physical properties (density, hardness) and chemical properties (pH, mineral content) of the GAC were also determined. These properties may not directly relate to sugar decolorization effectiveness, but they are important to the commercial utilization of these carbons.

The experimental work is presented in two phases. Phase I describes the conversion of agricultural by-products to GAC using

a group 1 feedstock (pecan shells) or group 2 feedstocks (rice straw, rice hulls, or sugarcane bagasse, all with binders). Pyrolysis and activation conditions are also described. In Phase II, physical and chemical properties of the carbon surface (e.g. surface area, pore structure, surface charge, surface functional groups) of the best carbons selected in Phase I were correlated with raw sugar decolorization. Multivariate Analysis of Variance was used to select the best carbons in terms of adsorption of raw sugar colorants. Furthermore, principal component and cluster analyses were used as the basis to group GAC based on similarities using all the properties combined. Conclusions and recommendations were made to suggest improvement in carbon performance and to outline a manufacturing process for the production of by-product-based GAC specifically designed for sugar decolorization.

## **REVIEW OF LITERATURE**

### **Production of granular activated carbons**

Granular activated carbon (GAC) represents one of the most important types of industrial carbons. GAC can be produced from a large number of raw materials of biological origin including coconut shells, wood, peat, olive stones, and coal (Gergova et al., 1992; Girgis et al., 1994; Rodriguez-Reinoso and Solano, 1989). GAC is produced by pyrolysis and activation of the precursor. During carbonization, most of the non-carbon elements, particularly oxygen, nitrogen, and sulfur, are removed by the pyrolytic decomposition of the precursor in the presence of an inert gas such as nitrogen. The pyrolyzed product or char consists of more or less disordered elementary graphitic crystallites, with a poorly developed porous structure. Subsequent activation is required to dramatically increase surface area and create a highly developed pore structure for the selective adsorption of molecules of different sizes and polarities. Activation can be a physical process with the use of carbon dioxide or water vapor as activating agents or a chemical process employing activating agents such as phosphoric acid ( $\text{H}_3\text{PO}_4$ ) or zinc chloride ( $\text{ZnCl}_2$ ).



During the activation process, the spaces between the elementary crystallites become cleared of less organized, loosely bound carbonaceous material. The resulting channels through the graphitic regions, the spaces between the elementary crystallites, together with fissures within and parallel to the graphitic planes, constitute the porous structure, with large internal surface area (Rodriguez-Reinoso and Solano, 1989). The extensive use of activated carbon is generally attributed to this large surface area which can attain values up to 2000 m<sup>2</sup>/g, making it a powerful adsorbent, capable of adsorbing most organic and many inorganic compounds. Thus activated carbons are commonly used in water and wastewater treatment, in the food processing industry such as sugar refining, and in pharmaceutical purifications (Rivera-Utrilla et al., 1991; Ying and Tucker, 1990).

## **Raw sugar decolorization**

Decolorization by adsorption is the final purification step in the manufacture of white sugar (Valter, 1970; Chou, 1985). The typical process of sugar decolorization consists of passing clarified raw sugar liquor through vertical columns packed with activated carbon. The temperature and pH of the liquor are carefully controlled to prevent color formation. In addition, factors such as sugar concentration, liquor/carbon ratio, and time of contact are monitored to ensure optimal removal of sugar colorants.

### **Colorants in cane sugar**

Colorants in cane sugar originate from two main sources: the sugarcane and the sugar refining process. Each cane sugar colorant is placed into one of four descriptive groups: 1) phenolics and flavonoids, 2) caramels, 3) melanoidins, and 4) alkaline degradation products of sucrose. In addition to these four groups, there are also color precursors that do not themselves exhibit color but will react with another non-colored compound to form a colored compound under favorable reaction conditions. Examples of these are amino acids, hydroxy acids, aldehydes, iron, and reducing sugars (Nick, 1992; Clarke et al, 1984; Carpenter, 1985).

The phenolics and flavonoids come from the cane, where they exist as glycosides attached to sugar residues (Clarke et al., 1984).

Smith and Gregory (1971) found that approximately two-thirds of the color in raw sugar comes from the phenolics and flavonoid group. Some phenolics are not colored when they first come from the plant, but oxidize, complex, or react to form colorants during processing. Cane colorants usually possess an electrostatic charge at high pH and, if unreacted, exhibit an average molecular weight of about 5 kDa (Clarke et al., 1984). Molecules in the other chemical groups develop color during the refining process. These include caramels, melanoidins, and alkaline degradation products of the fructose moiety of sucrose. Caramels are known to originate from thermal degradation of glucose, while melanoidins are formed through the Maillard reaction involving amine compounds and the alcoholic hydroxyl groups on the sugars.

### **Removal of sugar colorants**

Decolorization has traditionally been accomplished with carbon adsorbents (bone char), although additional materials (i.e. anion exchange resins) have also been used. Adsorption is a process in which a molecule is transferred from solution to the surface of a solid whereon the molecule is held by physical/chemical forces. Various forces exist between molecules in proximity to a solid surface and the surface molecules, all having their origin in the electromagnetic interactions of nuclei and electrons.

Two types of binding forces are commonly distinguished: physicosorption and chemisorption (Weber and Vliet, 1980). The mechanism by which sugar colorants are adsorbed onto a carbon surface may be divided into four consecutive steps: 1) dispersion, 2) interparticle film diffusion, 3) intraparticle diffusion, and 4) adsorption onto surface sites. The diffusion of the color components is a function of the temperature and viscosity of the sugar solution and the molecular size of the colorants (Chou, 1982).

### **Properties of activated carbon for use in sugar decolorization**

Physical, chemical, and surface characteristics of activated carbon determine its efficiency in removing the targeted sugar colorants.

#### **Physical properties**

## ***Particle size***

The smaller the particle size of a porous carbon, the greater the rate of diffusion and adsorption. Intraparticle diffusion is reduced as the particle size decreases, because of the shorter mass transfer zone, causing a faster rate of color adsorption (Cookson, 1978). Powdered activated carbon mixes intimately with liquid, providing a higher contact area than granular activated carbon and, therefore, has better decolorizing power. However, very fine powdered carbon, that is, the fraction that can pass through a No. 70 sieve, is undesirable and is discarded as dust because these particles adversely affect filtration flow rate and promote channeling (Carpenter, 1985). This causes shorter filter cycles and increases carbon treatment cost. Therefore, it is essential that carbon particles be of the correct size and structure to act as good filter aids and to reduce pressure drop during filtration. A carbon with proper particle size should form a good filter cake and should not require additional materials such as Fuller's earth to aid in filtration.

## ***Bulk density***

Density is particularly important in sugar decolorization where a high viscosity syrup is displaced through a column of activated carbon. Bulk density is important when carbon is removed by filtration because it determines how many pounds of carbons can be contained in a filter of a given solids capacity and how much treated liquid is retained by the filter cake (Hutchin, 1988). In addition, when two carbons differing in bulk density are used at the same weight per liter, the carbon having higher bulk density will be able to filter more liquor volume before the available cake space is filled. Carbons with an adequate density also help to improve the filtration rate by forming an even cake on the filter surface. Generally, a carbon with a bulk density of about 0.5 g/mL is adequate for sugar decolorization. Bone chars, currently used for sugar decolorization, have a bulk density of about 0.6 g/mL (Carpenter, 1985).

## ***Hardness***

A carbon should possess sufficient mechanical strength to withstand the abrasion resulting from continued use. In the course of carbon usage, particle breakdown and dust formation occur due to the continuous mechanical friction between carbon particle and sugar liquor. Dust formed by attrition is undesirable because it slows down the filtration rate and decreases the amount of regenerated carbon. Therefore, carbons designed for sugar decolorization should have enough abrasion resistance to minimize attrition.

## **Chemical properties**

### ***pH***

Activated carbon pH may influence color by changing the pH of the sugar solution. Such a change affects the pH-sensitive fraction of solution colorants, causing unreliable color measurements (Ahmedna et al., 1997a). Moreover, acid carbons, for example, may be a better decolorizer (Paton and Smith, 1983); but a sugar refiner would seldom employ a highly acidic carbon because the acid would cause inversion of sucrose to noncrystallizable sugars, with subsequent lower yield (Mantell, 1946). Bernardin (1985) reported that, in sugar decolorization, a distinctly acidic activated carbon may cause inversion of sucrose, and a distinctly alkaline carbon may cause color development through alkaline degradation of organic impurities. Hence, a carbon pH of 6-8 is acceptable for most applications.

### ***Ash (minerals)***

Ash content of carbon is the residue that remains when the carbonaceous portion is burned off. The ash consists mainly of minerals such as silica, aluminum, iron, magnesium, and calcium. Ash in activated carbon is not desirable and is considered an impurity. Ash leached into sugar liquor during the process of decolorization is known to cause uneven distribution of heat in the boiler during sugar crystallization. Ash may also interfere with carbon adsorption through competitive adsorption and catalysis of adverse reactions. For instance, the ash content may affect the pH of the carbon since the pH of most commercial carbons is produced by their inorganic components. Usually, materials with the lowest ash content produce the most active products.

## **Surface properties**

### ***Surface area***

Activated carbon has the highest adsorptive porosity of any material known. Because of its large surface area (1 quart of granules = 6 football fields of area), activated carbon has a great ability to adsorb organic and inorganic molecules from liquids or vapors (Roy, 1995). Surface area is the single most important characteristic of activated carbon designed for adsorption of compounds from liquid media such as sugar liquor (Weber and Vliet, 1980). Large surface area is generally a requirement for a good adsorbent. However, the total surface area has to possess adequate pore size distribution and surface chemistry to adsorb the targeted species.

### ***Pore size distribution***

The large internal surface area of activated carbon is due to its porosity. The total porous structure of an activated carbon is formed by a wide range of pore sizes. For practical reasons, pore sizes are classified into three main types according to their width: macropores ( $> 50$  nm), mesopores (2-50 nm), and micropores ( $< 2$  nm). The macropores act as “tunnels” that enable molecules to reach the smaller pores in the interior of the carbon where they are adsorbed or bonded to the carbon surface. Macropores do not significantly contribute to the overall adsorptive process since they have a relatively low surface area, but they affect the rate of admission of the molecules to the meso- and micropores. Mesopores, which branch from the macropores, serve as passages by which molecules reach the smaller micropores. The micropores constitute the largest part of the internal surface area of an activated carbon and, consequently, most of the adsorption takes place there. The suitability of an activated carbon for a particular application (e.g., sugar decolorization) depends on the macropore:mesopore:micropore ratio. A carbon with substantial mesoporosity is generally recommended for adsorption of sugar colorants, which are made up of mixtures of compounds with varying molecular size.

### ***Surface chemistry***

The adsorption capacity of activated carbons is determined by their porous structure and surface area but is also strongly influenced by the presence of functional groups at the carbon surface. Activated carbons are known to contain a variety of heteroatoms such as oxygen, hydrogen, chlorine, and sulfur. Heteroatoms are either derived from the starting material, and become a part of the chemical structure as a result of imperfect carbonization, or chemically bonded to the carbon during activation or during subsequent additional treatments, such as oxidation. These heteroatoms are bound to the edges of the carbon layers and form surface groups that greatly affect the adsorption behavior of the activated carbon, with carbon-oxygen surface structures being by far the most important in influencing surface characteristics (Bansal et al., 1988; Boehm, 1994). The most common are carboxyl, carbonyl, carbonyl (quinone type), phenolic hydroxyl, anhydride, ether-type, lactone, and lactal. The presence of surface oxygen complexes imparts a polar character to the activated carbon surface, which should affect preferential adsorption of polar organic solutes. The type and net charge of functional groups bonded to the carbon surface is important in understanding the mechanism of adsorption between ionic adsorbates and the activated carbon. Although raw sugar colorants are made up of a complex mixture of polydispersed compounds of differing molecular size and net charges, sugar colorants are predominantly anionic. Therefore, the diversity of functional groups on the carbon surface affects the surface behavior of carbon and thus enhances or reduces the affinity of carbon to the adsorbed raw sugar colorants via electrochemical mechanisms.

## **MATERIALS AND METHODS**

### **Materials**

Agricultural by-products were obtained from the following sources: sugarcane bagasse (SB) from Audubon Sugar Institute, Louisiana State University Agricultural Center, Baton Rouge, LA; rice hulls (RH) and rice straw (RS) from Supreme Rice Mill, Crowley, LA, and pecan shells (PS) from Sun Diamond of New Mexico, Las Cruces, NM.

Binders were procured from the following sources: sugarcane molasses (CM) from Alma Sugar Company, Baton Rouge, LA; sugar beet molasses (BM) from American Crystal Sugar Company, Moorhead, MN; corn syrup (CS) from A. E. Staley Manufacturing Company, Decatur, IL; and coal tar pitch (CT) from Koppers Industries, Follarsbee, WV.

The reference carbons were Calgon CPG-LF and Cane Cal from Calgon Carbon, Pittsburgh, PA. The commercial GAC were made from bituminous coal with coal tar as a binder and were selected on the basis of manufacturer recommendations as excellent decolorizers of organic liquids such as raw sugar liquors (Calgon, 1987).

## **Methods**

The by-product/binder combinations and pyrolysis/activation conditions used were based on the results and recommendations from preliminary studies conducted in our laboratory (Ahmedna et al., 1997b; Pendyal et al., 1999a).

### **Preparation of granular activated carbons**

#### ***Phase I***

Group 1 by-products (sugarcane bagasse, rice hulls, and rice straw) were milled in a cross-beater mill (Glen Mills Inc., Clifton, NJ) to 5- to 10-mesh size (US standard sieve).

Sugarcane bagasse was mixed with each one of four binders (sugarcane molasses, sugar beet molasses, corn syrup, and coal tar), while rice hulls were blended with sugarcane molasses or coal tar and rice straw was mixed with corn syrup or coal tar in a by-product/binder ratio of 1:0.5 (w/w). Sugarcane molasses, sugar beet molasses, and corn syrup were heated to 80 C, then combined with the by-products in a laboratory mixer until homogeneous. The blends were cooled to room temperature and placed in a stainless steel cylinder 5.7 cm in diameter and 7.0 cm in height. A pressure of 5000 psi was applied to the cylinder contents by means of a laboratory press (F.S. Carver Inc., Wabash, IN) for 5 min. to form briquettes. The coal tar pitch was heated to 140 C during mixing. The hot blend was quickly added to the cylinder

and pressed into briquettes before the coal tar could solidify. All briquettes were stored at room temperature for 2-3 days. Briquettes were pyrolyzed in an atmosphere of nitrogen gas at 750 C for 1 hr using an inert atmosphere furnace (Model BAF-8128, Grieve Corp., Round Lake, IL) with retort. The pyrolyzed samples were cooled overnight in the furnace in a nitrogen atmosphere. The pyrolyzed briquettes were crushed and sieved to produce samples of 12- to 40-mesh particle size. The granules were activated in the same furnace at 900 C using gas mixtures of 13% CO<sub>2</sub> and 87% N<sub>2</sub> until approximately 30% burn-off was achieved, which occurred between 4 and 20 hrs, depending on the binder used. The GAC were cooled overnight in the furnace under nitrogen gas, then washed with 0.1 N HCl to remove surface ash particles. The GAC were water washed until the slurries reached pH 6-8. GAC were subsequently dried overnight at 50 C. Carbon yields recorded for these samples were 47% to 52%, 25% to 30%, 24% to 26%, and 25% to 31% for the GAC made from group 1 by-products using coal tar, cane molasses, corn syrup, and beet molasses, respectively.

Pecan shells were milled in a cross-beater mill (Glen Mills Inc., Clifton, NJ) to 10- to 20-mesh size (US standard sieve). Milled pecan shells were subsequently pyrolyzed and activated by either physical activation or chemical activation as described below, using an inert atmosphere furnace with retort.

Physical activation was achieved by pyrolyzing pecan shells in an atmosphere of nitrogen gas at 700 C for 1 hr. Upon pyrolysis, the resulting char was immediately activated at 900 C using gas mixtures of 13% CO<sub>2</sub>/87% N<sub>2</sub> (PS9), 30% CO<sub>2</sub>/70% N<sub>2</sub> (PS18), or 75% CO<sub>2</sub>/25 % N<sub>2</sub> (PS22, PS23) for a duration of 2 to 8 hrs. The GAC were cooled overnight in the furnace under nitrogen gas, then washed and dried overnight at 50 C. Yields for carbons produced by physical activation were 14% to 26%.

Chemical activation was carried out by soaking milled pecan shells in either 25% or 50% H<sub>3</sub>PO<sub>4</sub> (w/w) for 2 hrs at room temperature. Phosphoric acid-shell mixture was pyrolyzed at 170 C for ½ or 1 hr, then activated at 450 C for 1 hr. Activation of the char was carried out under nitrogen gas (PS10, PS11) or air (PS24, PS26). Activated carbon was subsequently cooled overnight under nitrogen gas and washed in a soxhlet extractor until no residual



phosphoric acid was present as shown by the absence of a precipitate when 10 drops of 0.01 M lead acetate were added to 100 mL of the final wash water. The GAC were then dried overnight at 50 C before use. Final yields for chemically activated pecan shells were 37% to 41%.

## ***Phase II***

Granular activated carbons were produced from the combination of group 1 by-product/binder and group 2 by-product/activation that yielded the best GAC overall in Phase I. The production of GAC from sugarcane bagasse and pecan shells followed the same procedures described in Phase I. However, in Phase II, two binder (corn syrup, coal tar)/by-product ratios (1:1 and 1:2) were used with sugarcane bagasse, and steam activation of pecan shells was introduced. Carbon yields for the bagasse- and pecan shell-based GAC were similar to the carbons described in Phase I.

Steam activation was carried out by pyrolysis of pecan shells at 700 C for 1 hr under a nitrogen atmosphere. After pyrolysis, the resulting char was steam activated at 850 C by metering water into the retort chamber at a rate of 120 mL/hr for 6 hr using nitrogen gas as a carrier for the water. After activation, the GAC sample (PS63) was cooled overnight in the furnace under nitrogen gas, then water washed and dried overnight at 50 C. Carbon yield was 24%.

## **Physical properties: Apparent (bulk) density and hardness**

Bulk density and hardness were determined following the procedure of Ahmedna et al. (1997b). The same procedures were used in both phases I and II.

## **Measurement of chemical properties: ash, pH, and conductivity**

Ash, pH, and conductivity of GAC were measured based on the procedures described by Ahmedna et al. (1997b). The procedures used to determine chemical properties were the same for phases I and II.

## **Determination of surface properties**

Total surface area, pores size distribution, and surface chemistry were evaluated using the methods described by Ahmedna et al. (1999). In Phase I, the only surface property evaluated was the total surface area, while in Phase II, all the surface properties were determined.

### **Measurement of adsorption properties: molasses test and raw sugar decolorization**

The molasses and sugar decolorization tests were conducted using the methods described by Ahmedna et al. (1997b). Determination of adsorption properties in both phases I and II followed the same procedures. However, in Phase II, a carbon dosage of 4% (w/v) instead 1% (w/v) was used in both molasses and sugar decolorization tests.

### **Statistical Analysis**

All experimental data were analyzed using the generalized linear model procedure of the Statistical Analysis System (SAS, 1988). Multivariate Analysis of Variance (MANOVA) was used to compare the mean values of physicochemical and adsorption properties among various GAC. Tukey's post ANOVA test was used in multiple comparisons of the carbons. Multiple regression was used to generate graphs relating carbon surface properties to the decolorization efficiency of GAC. Finally, principal component and cluster analyses served as tools by which the experimental and commercial carbons were grouped based on their similarities in terms of all the properties investigated combined. The first and second principal components were used as the criteria for carbon ratings. In addition, cluster analysis (SAS, 1989) was used. Experimental carbons were divided into three clusters based on similarities with the reference carbons in terms of their individual properties (physical, chemical, or adsorption) or combined properties.

## RESULTS AND DISCUSSION

### Phase I

#### Physical and chemical properties

The highest bulk density among the experimental carbons was observed in carbons using coal tar (CT) as a binder (Table 1). Regardless of the by-product, carbons using sugarcane or sugar beet molasses (CM or BM) or corn syrup (CS) as binders exhibited relatively low bulk densities. Carbons derived from pecan shell had bulk densities slightly lower than those of the reference carbons, with the chemically activated carbon generally showing the lowest bulk densities among the pecan shell-based carbons. The high bulk density of carbons containing coal tar can be attributed to coal tar's high carbon content. Coal tar has a higher carbon content than molasses or corn syrup and, therefore, would be volatilized to a much lesser extent and undergo less weight loss than these binders (Pendyal et al., 1999a) yielding more compact material.

Physically activated pecan shell-based carbons and carbon samples containing coal tar as the binder showed the highest hardness numbers (Table 1). Hardness of these carbons was similar to the commercial GAC. As with bulk density, the high carbon content of coal tar could have resulted in low volatilization of the briquettes containing coal tar, yielding a more compact carbon material with high hardness and limited porosity. The softest carbon was made with sugar beet molasses as binder. Similar observations were reported by Pendyal et al. (1999a), who found that carbons made with sugar beet molasses were soft and friable. These authors concluded that such soft carbons would not be suitable for decolorization because of their high attrition that could reduce the yield of carbon after regeneration and reduce the rate of filtration. The hardness of pecan shell-derived carbons varied, depending on the conditions of activation. Physical activation appeared to consistently produce the hardest GAC, while chemical activation yielded relatively softer carbons.

Regardless of the binder used, group 1 by-products yielded carbons with limited surface area (Table 1). In contrast, carbons

**Table 1. Physical and chemical properties of experimental granular activated carbons and reference carbons for Phase I**

Carbons	Bulk Density (cm <sup>3</sup> /g)	pH	Hardness (% survival)	Conductivity (μS)	Ash (%)	Molasses (%)	Sugar Decolorization (%)	Surface Area (m <sup>2</sup> /g)
<b>Group 1 By-products</b>								
SB-BM	0.31	10.63	4.70	377.50	57.74	10.36	9.04	66.50
SB-CM	0.28	9.92	48.42	365.00	42.74	6.49	7.17	182.50
SB-CS	0.30	7.14	53.33	76.00	9.01	32.45	16.94	298.00
SB-CT	0.62	7.48	88.79	25.50	24.64	9.69	10.40	42.50
RH-CM	0.36	9.95	57.67	372.50	41.71	7.08	9.74	264.00
RH-CT	0.49	8.22	63.67	110.00	22.82	15.27	12.25	103.50
RS-CS	0.33	8.88	74.06	180.00	27.77	9.22	8.01	140.50
RS-CT	0.53	8.10	93.01	77.50	18.36	11.54	8.37	79.50
<b>Commercial Reference Carbons</b>								
CCAL	0.50	8.70	70.90	7.25	9.32	32.43	18.01	920.00
CPGLF	0.54	7.37	93.33	6.00	4.73	28.69	15.43	903.00
<b>Group 2 By-products</b>								
PS18	0.44	5.93	96.48	135.00	2.70	11.36	15.09	417.00
PS23	0.40	6.33	96.25	90.00	1.58	24.32	13.32	655.00
PS9	0.42	6.24	95.33	82.50	2.19	23.24	15.33	464.00
PS22	0.42	7.48	97.06	177.50	3.25	16.79	16.07	594.00
PS26	0.45	7.60	53.51	402.50	6.01	9.41	7.06	911.00
PS24	0.37	6.65	54.22	160.00	5.48	22.54	7.92	1138.00
PS11	0.34	8.21	83.66	165.00	2.20	28.97	7.70	1267.00
PS10	0.34	5.88	94.17	58.50	2.95	27.54	12.37	1258.00

SB-BM, SB-CM, SB-CS, SB-CT = Sugarcane Bagasse with Beet Molasses, Cane Molasses, Corn Syrup, and Coal Tar, respectively; RH-CM and RH-CT = Rice Hulls with Cane Molasses and Coal Tar, respectively; RS-CS and RS-CT = Rice Straw with Corn Syrup and Coal Tar, respectively; CCAL and CPGLF are commercial reference carbons, and PS = Pecan Shells (see Table 1 for description of PS-based carbons). Carbons labeled PS18, 23, 9 and 22 were physically activated with CO<sub>2</sub> and carbons PS26, 24, 11, and 10 were chemically activated with phosphoric acid. Values represent the means of duplicate measurements with standard deviation less 5%.

prepared from the group 2 by-products by chemical activation exhibited surface areas larger than for the reference carbons. Physical activation of pecan shells produced GAC with relatively lower surface area. The observed difference in surface area among the carbons investigated might be attributed to the nature of the precursor, the pyrolysis temperature, and the type of activation (Mattson and Mark, 1971; Girgis et al., 1994). Mackay and Roberts (1982a) reported that different classes of lignocellulosic precursors are known to develop microporosity to different extents during pyrolysis. The same authors found that the components (lignin, cellulose) of lignocellulosic materials yield chars of similar microporosity, while inorganics (ash) may fill or block some portion of the existing micropore volume. This may partially explain the low surface area observed in carbons with high ash content. Furthermore, it is well known that the lignocellulosic composition of the precursors determines char yield and porosity due to the difference in thermal stability of the major components (lignin, cellulose, hemicellulose) (Mackay and Roberts, 1982a; Mackay and Roberts, 1982b; Mattson and Mark, 1971).

In our case, the composition of by-products and binders would have affected the final surface characteristics of the experimental GAC. The method of activation is also another potential cause for the observed differences in surface area among the by-product-based carbons. When using the same precursor, carbons obtained by physical activation had lower surface areas than carbons obtained by chemical activation. This is probably due to the mechanism by which pore formation is achieved by each activation method. Physical activation relies on diffusion of gases (CO<sub>2</sub>) through the carbon matrix to drill, deepen, clear, and/or volatilize impurities. In chemical activation, the chemical is introduced into the precursor, where it produces physical and chemical changes modifying the thermal degradation process (Rodriguez-Reinoso and Molina-Sabio, 1992). The chemical used in our case was phosphoric acid, which is impregnated into the raw material to influence the pyrolysis such that the tar formation and volatilization are kept to a minimum (Pollard et al., 1992). Chemical activation is carried out at lower temperatures than physical activation. Carbon produced at lower temperatures is likely to possess an extensive surface area and a well-developed microporosity (Girgis et al., 1994).

The ash content of by-product-based carbons is dependent on the ash content of the materials that compose the carbon. The ash contents of all by-product-based carbons made from group 1 materials were considerably higher than for any of the other carbons (Table 1). Specifically, GAC with cane and beet molasses as binders produced the highest ash contents among all the carbons. This is due to the high ash content of these binders. The high ash content of GAC made from rice straw and rice hulls can be explained by their high specific mineral content, especially their richness in silica (Mantell, 1946) and the addition of high ash binders such as sugarcane and sugar beet molasses. Carbons from pecan shells, on the other hand, exhibited ash contents lower than the reference carbons. The low ash content of shell-based carbons is due to the inherently low mineral content of the shells (Mattson and Mark, 1971) and to the absence of binder in their preparation.

Activated carbons prepared from pecan shells had pH values similar to or slightly lower than the commercial carbons (Table 1). The carbons in which cane molasses or beet molasses were used as binders were alkaline, with pH values above 9. The pH variation among experimental carbons may be explained by variation in their ash content. Ash and pH values were positively correlated ( $R = +0.83$ ,  $p < 0.05$ , data not shown). Carbons with pH of 6-8 (group 2 precursors) had relatively low ash contents, while those with a pH of 7-11 (group 1 precursors) had high ash contents. Hassler (1963) reported that the pH of most commercial carbons is due to inorganic constituents originating from the precursor or added during manufacture. Therefore, the high ash binders (cane and beet molasses) used with group 1 by-products may explain their richness in minerals, which in turn may have contributed to their relatively high pH. A neutral pH range of 6-8 is recommended for sugar decolorization (Hassler, 1963). According to Hassler (1963), an acidic carbon would be a better sugar decolorizer, but its efficiency may be offset by the losses due to the conversion of sucrose into non-crystallizable sugars.

With the exception of the carbon derived from sugarcane bagasse with coal tar as the binder, all the experimental carbons exhibited conductivity values significantly higher than those of the reference carbons (Table 1). The highest conductivity was observed in carbons prepared with cane or beet molasses. This was expected, given the high ash content of these binders. In

comparison to the commercial carbons, most of the experimental carbons exhibited high conductivity values indicating that an acid or water wash was not enough to reduce leachable ash to the level observed in commercial carbons. The results of electrical conductivity indicated that even though the tested samples were acid or water washed, substantial amounts of water-soluble minerals remain in the carbons. Such high leachable mineral contents are unacceptable when the carbons are to be used for commercial sugar decolorization. This is because ash, especially leachable ash, in activated carbon is not desirable and is considered an impurity. Ash leached into sugar liquor during the process of decolorization is known to cause uneven distribution of heat in the boiler during sugar crystallization. Ash may also interfere with carbon adsorption through competitive adsorption, catalysis of adverse reactions, and blockage of carbon pores. Consequently, more extensive washing with acid would be necessary to reduce the amount of water-soluble minerals to a level similar to that of the reference carbons. Reducing the soluble mineral contents of the carbons would also reduce any deleterious effects on pH.

### **Adsorption Properties**

The amount of colorants that can be removed from a solution by activated carbon depends on factors such as contact time, carbon dosage, temperature, concentration or viscosity of the solution and the intrinsic features of the carbon itself. These factors were controlled in a standardized batch test that was designed to allow direct comparison of the decolorization efficiency among the experimental carbons and reference carbons. Of all the above factors, carbon dosage is particularly important because it determines the extent of decolorization and may also be used to predict the cost of carbon per unit of sugar solution to be treated. In our case, carbon dosage could not exceed 1% (w/v), since only limited quantities of experimental carbons were available. However, adsorption of color bodies from aqueous solutions (e.g. sugar solution) as a function of carbon dosage follows a logarithmic model that can be used to predict the amount of color that would be removed at higher carbon dosages. In Figure 1, one of the commercial carbons (Calgon CPG-LF) was used as typical example to show the relationship between the percent molasses color removed and carbon dosage.

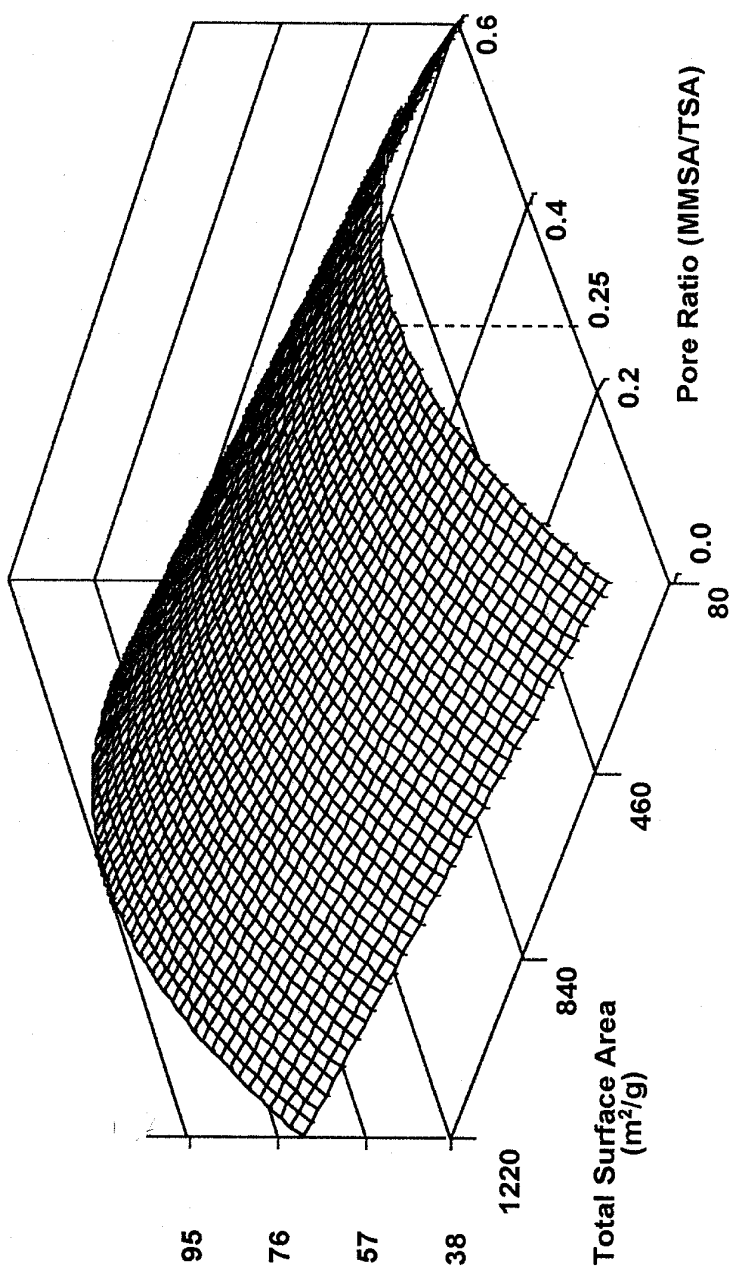


Figure 1. Removal of sugar colorants as a function of carbon dosage (Calgon CPG-LF used as typical example).



The molasses test is generally an indicator of an activated carbon's ability to adsorb color bodies, especially sugar colorants. Carbons with high molasses color removal are potentially good decolorizers. The carbon prepared from sugarcane bagasse using corn syrup as binder was the most efficient in removing molasses color (Figure 2). Percent color removed was similar to or better than the reference carbons. The remaining group 1-based carbons exhibited relatively low percent molasses color removal. Carbons derived from pecan shells had decolorization efficiencies that varied with activation conditions. Among the pecan shell-based carbons, two physically activated (PS23 and PS9) and two chemically activated (PS10 and PS11) carbons exhibited the best molasses color uptakes, achieving decolorization efficiencies close to the reference carbons.

As observed in the molasses test, carbons prepared from sugarcane bagasse and corn syrup along with the two commercial carbons were the best sugar decolorizers (Figure 3). The remaining carbons from group 1 materials had lower decolorization capacity than the commercial GAC. Decolorization efficiency of carbons prepared from pecan shells by physical activation was closest to that of the reference carbons. Chemical activation reduced the decolorization capacity. In general, similarities between the results of the molasses test and those of the sugar decolorization assays were observed. This was expected since the molasses test is normally considered as an indicator of an activated carbon's ability to remove colorants from aqueous solutions (Hassler, 1963).

Since molasses and raw sugar decolorization of GAC did not appear to vary directly with their total surface areas, their pore size distribution as well as their surface charges may have played a role in the observed differences. For instance, the carbon produced from sugarcane bagasse and corn syrup (SB-CS) exhibited a relatively low surface area but high decolorization efficiency. In contrast, PS26 (a chemically activated pecan-based carbon) had a relatively large surface area but poor ability to remove sugar colorants in both molasses and raw sugar tests. Because surface properties may have played a key role in the observed differences in the decolorization capacity of by-product-based carbons, their effects were investigated in Phase II.

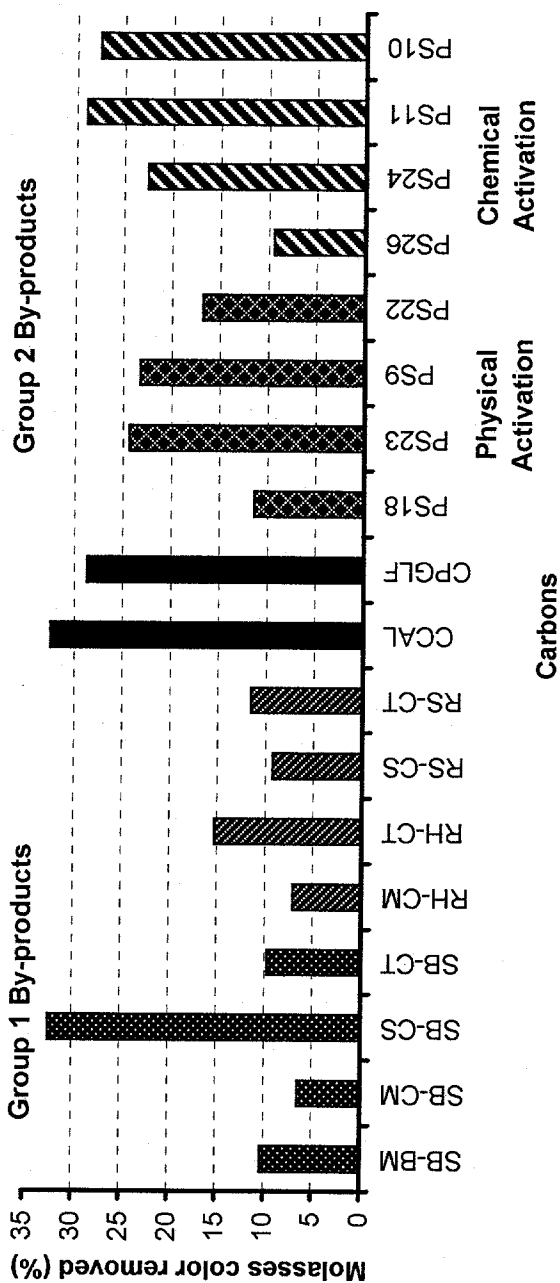


Figure 2. Percent molasses color removed for experimental and commercial carbons. SB-BM, SB-CM, SB-CS, SB-CT = Sugarcane Bagasse with Beet Molasses, Cane Molasses, Corn Syrup, and Coal Tar, respectively; RH-CM and RH-CT = Rice Hulls with Cane Molasses and Coal Tar, respectively; RS-CS and RS-CT=Rice Straw with Corn Syrup and Coal Tar, respectively; CCAL and CPGLF are commercial reference carbons, and PS=Pecan Shells. The bars represent the means of duplicate determinations where the standard error for each measurement was less than 5%.

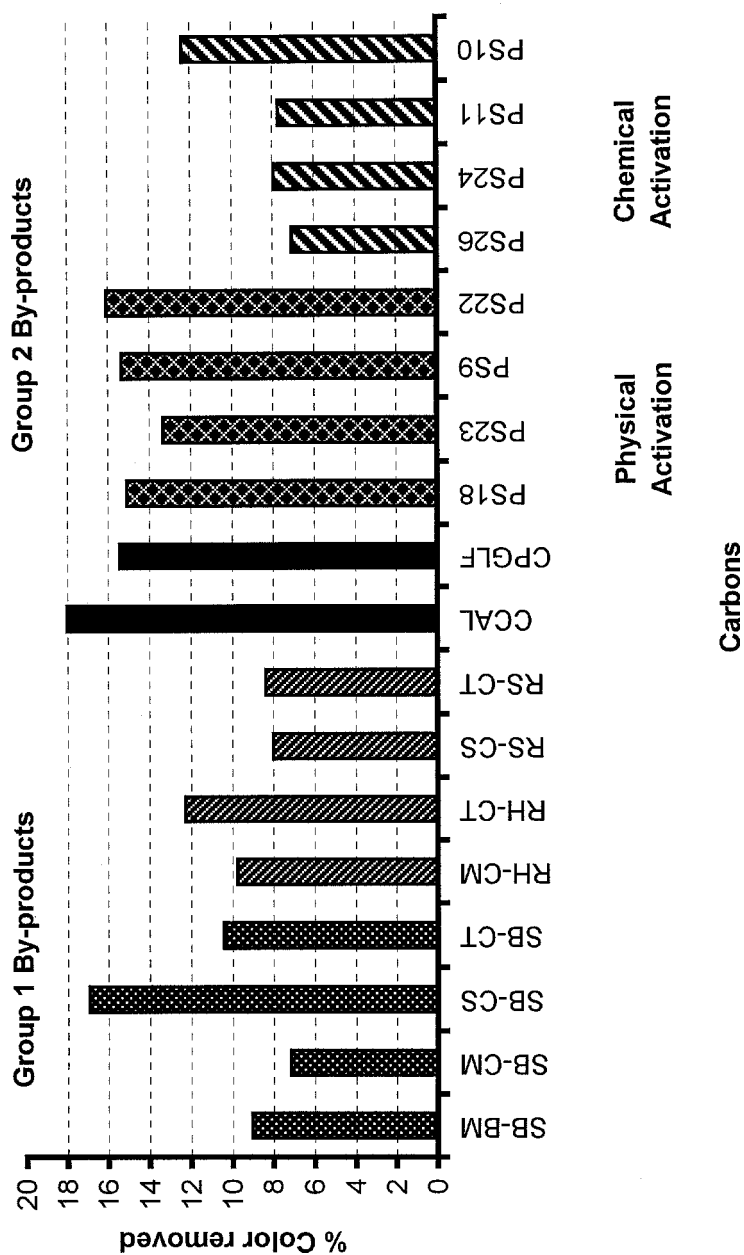


Figure 3. Raw sugar decolorization efficiency of experimental and commercial carbons. The bars represent the means of duplicate determinations where the standard error for each measurement was less than 5%. See Figure 2 for carbon identification.

## **Grouping of Experimental GAC Based on Similarities to the Reference Carbons**

Principal component analysis was used to produce a scatter plot of the relationship between the commercial reference carbons and experimental carbons in terms of their physical, chemical, and adsorption properties (Figure 4). Four quadrants were separated by the intersection of the zero values along the x- and y-axes. The experimental carbons most similar to the reference carbons are expected to cluster in the quadrant containing the latter. With the exception of PS26, all pecan shell-based carbons clustered around the two reference GAC (upper and lower right quadrants), while GAC produced from group 1 materials (except SB-CS) did not cluster in these two quadrants. Carbons containing cane or beet molasses as binders were the least similar to the commercial references, probably because of their low surface area, high ash, high conductivity, low bulk density, and brittleness. A combination of sugarcane bagasse and corn syrup produced the best overall GAC among group 1-based carbons. This carbon showed good decolorization capacity and its chemical properties were similar to those of the commercial carbons.

Cluster analysis is another multivariate technique that allows grouping of GAC based on similarities using several variables simultaneously. Cluster analysis was used to classify the activated carbons into three groups based on their individual or combined physical, chemical, or adsorption properties (Table 2). Three clusters were chosen under the assumption that if there were no similarities between the commercial carbons and the GAC from group 1 and group 2 by-products, separate clusters would naturally form. Otherwise, those experimental carbons that cluster with the commercial references would be considered similar to the latter. Based on adsorption properties, three group 2-based carbons (PS9, PS10, and PS23) but no group 1-based carbons clustered with the reference GAC (Table 4). Cluster analysis appeared more selective than principal component analysis when all properties were considered, selecting only three of sixteen experimental carbons while principal component analysis selected eight of sixteen as similar. The one group 1-based GAC (SB-CS) found similar to the reference carbons by principal component analysis was not viewed as similar with cluster analysis because of its poor

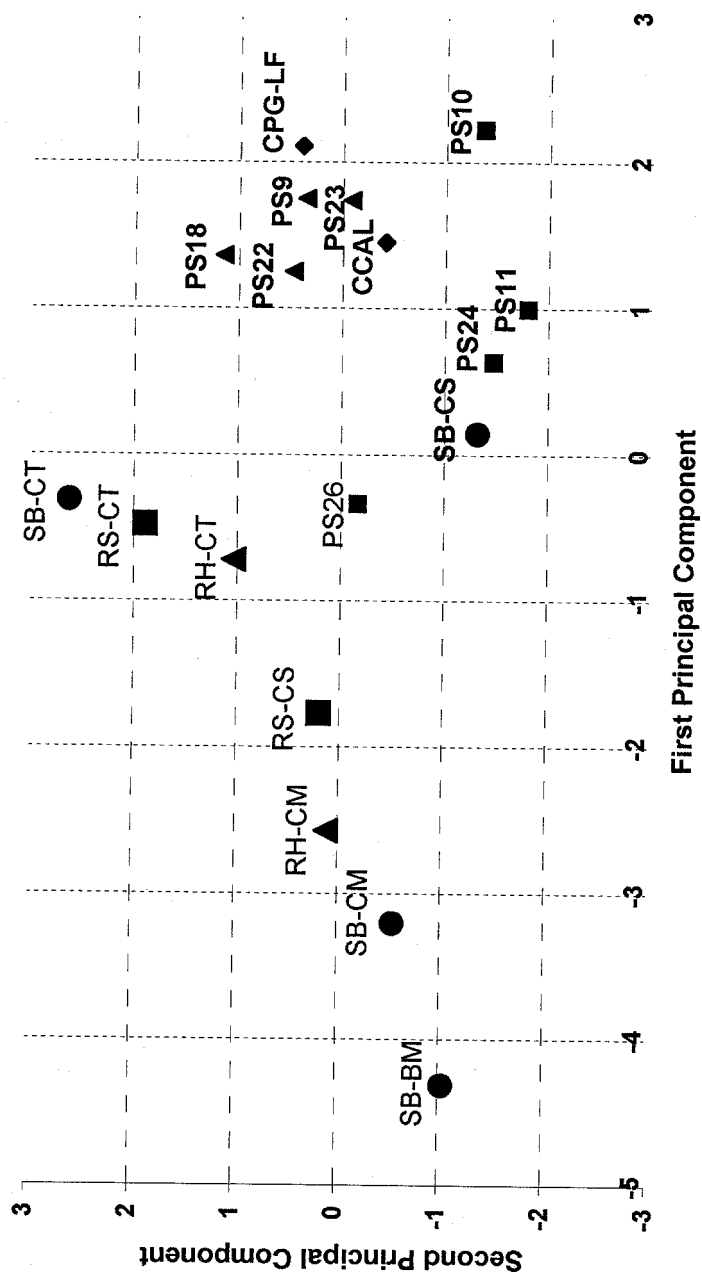


Figure 4. Grouping of GACs based on the first two principal components. See Figure 2 for carbon identification.

**Table 2: Clustering of GACs based on their individual or combined physical, chemical, or adsorption properties\***

Basis of clustering	Cluster 1	Cluster 2	Cluster 3
<b>Physical Properties</b>	PS10 PS11 <b>PS24</b>	<b>CCAL</b> <b>PS26</b> CPG-LF <b>PS22</b> <b>PS23</b>	RH-CM SB-CS <b>RS-CT</b> SB-CT RH-CT RS-CS PS18 PS9 SB-CM SB-BM
<b>Chemical Properties</b>	<b>CCAL</b> CPG-LF <b>PS23</b> <b>PS9</b> <b>RS-CT</b> <b>SB-CS</b> SB-CT PS10	PS11 PS24 PS22 RS-CS PS18 RH-CT	RH-CM SB-CM SB-BM PS26
<b>Adsorption Properties</b>	PS26 RS-CS RS-CT SB-BM RH-CM SB-CM SB-CT PS22 RH-CT PS18	<b>CCAL</b> <b>SB-CS</b> <b>PS23</b> <b>PS9</b> <b>CPG-LF</b> <b>PS10</b>	PS11 PS24
<b>All Properties</b>	<b>CCAL</b> CPG-LF <b>PS10</b> <b>PS11</b> <b>PS24</b> <b>PS26</b>	RH-CT RS-CT RH-CM SB-CM SB-CT RS-CS SB-BM	PS18 PS9 PS22 PS23 SB-CS

\* Clusters containing the reference carbons are shown in bold print.

physical properties. The greater selectivity of cluster analysis over principal component analysis is attributable to the difference in algorithm used by each method. Principal component uses the first two principal components (linear combinations), which account for most (and thus less than 100%) of the variability of the data, while cluster analysis groups carbons based on similarity using the original data without loss of information.

In contrast, regardless of the basis of analysis, carbons made from by-products using cane or beet molasses as binders did not cluster with the reference carbons and would be, therefore, inferior to the commercial carbons. Clustering of GAC on the basis of physical properties revealed that none of the group 1-derived carbons could match the characteristics of the reference carbons, mainly because of their low surface area and low hardness. Generally, results of cluster analysis were in agreement with those of principal component analysis, with the exception of PS26 and SB-CS. Both techniques revealed that three physically activated pecan shell-based carbons (PS9, PS10, and PS23) were similar to the two commercial reference carbons in all properties and thus would make good alternate choices to commercial carbons for use in raw sugar decolorization.

In summary, sugarcane bagasse showed a better potential than rice straw or rice hulls as precursor of GAC with the desirable properties of a good sugar decolorizer, especially when combined with corn syrup. Pecan shell-based GAC, which were the closest to the reference carbons, would also make good candidates for use as sugar decolorizers. The commercial production of these GAC would, however, require optimization of their activation conditions and characterization of their surface properties. This could involve selection of activation conditions (e.g., use of steam) that induce a large surface area and optimize pore size distribution and surface chemistry of GAC to adsorb sugar colorants. Phase II further investigates the relationship of the surface properties of these by-product-based GAC to their ability to remove sugar colorants. The discussion of Phase II results follows the same format as that of Phase I.

## Phase II

Based on the results from Phase I study, we selected specific GAC precursors for further analysis in Phase II. Carbons made from sugarcane bagasse with either a corn syrup or coal tar binder had desirable chemical and/or adsorption properties compared to the reference carbons and thus were included. The pecan shell-based carbons designated PS9, PS10, and PS23 were selected for further evaluation based on a combination of excellent physical, chemical, or adsorption properties. In addition, a steam activated, pecan shell-based GAC was added based on the premise that steam activation produces GAC with surface properties distinct from those carbons made by carbon dioxide or phosphoric acid activation. This distinction may result in GAC with improved adsorption of sugar colorants.

GAC with the same designation in both Phase I and Phase II were made at different times but under the same pyrolysis and activation conditions. Phase II GAC were produced in larger batches in a larger furnace and may have somewhat different physical, chemical and adsorption properties.

### **Physical and chemical properties**

GAC prepared from sugarcane bagasse and corn syrup had relatively low bulk density, low hardness, similar pH, and high ash contents when compared to the reference carbons (Table 3). Sugarcane with coal tar as binder had similar bulk density and hardness but lower pH and higher ash content than the reference GAC. Physical activation of pecan shells produced carbons with physical and chemical characteristics (bulk density, hardness, pH, and ash) that were generally similar to the reference carbons. Chemical activation of pecan shell (PS10) appeared to reduce bulk density and hardness. As discussed in Phase I, the observed differences in physical and chemical characteristics among the experimental carbons are attributable to the precursors and activation conditions used in their manufacture. For instance, the low ash and high hardness values of pecan shell-based carbons can be explained by high lignin and low ash contents of the shells in comparison to sugarcane bagasse and the absence of high ash binders.



**Table 3: Select physical and chemical properties of experimental granular activated carbons developed for Phase II<sup>1</sup>**

Carbon	Bulk Density (g/cm <sup>3</sup> )	Hardness (%survival)	pH	Ash (%)
<b>SBCS21</b>	0.25±0.01 <sup>g</sup>	74.25±4.99 <sup>cd</sup>	8.26±0.22 <sup>a</sup>	26.96±1.14 <sup>a</sup>
<b>SBCS11</b>	0.25±0.01 <sup>g</sup>	70.00±10.60 <sup>d</sup>	8.07±1.16 <sup>a</sup>	26.88±2.87 <sup>a</sup>
<b>SBCT11</b>	0.47±0.01 <sup>bc</sup>	93.25±2.75 <sup>ab</sup>	6.60±0.24 <sup>c</sup>	17.79±1.37 <sup>c</sup>
<b>SBCT21</b>	0.47±0.01 <sup>b</sup>	83.25±1.50 <sup>bc</sup>	6.44±0.25 <sup>c</sup>	23.39±0.62 <sup>b</sup>
<b>PS23</b>	0.42±0.01 <sup>d</sup>	91.50±1.29 <sup>ab</sup>	8.10±0.53 <sup>a</sup>	7.33±1.49 <sup>d</sup> <sup>e</sup>
<b>PS9</b>	0.44±0.01 <sup>cd</sup>	91.50±1.29 <sup>ab</sup>	8.11±0.22 <sup>a</sup>	3.61±1.41 <sup>f</sup>
<b>PS63</b>	0.38±0.02 <sup>e</sup>	92.00±1.15 <sup>ab</sup>	7.74±0.13 <sup>ab</sup>	1.70±0.27 <sup>f</sup>
<b>PS10</b>	0.34±0.02 <sup>f</sup>	70.75±2.75 <sup>d</sup>	7.66±0.41 <sup>ab</sup>	3.30±1.72 <sup>f</sup>
<b>CCAL<sup>2</sup></b>	0.48±0.01 <sup>b</sup>	83.25±3.59 <sup>cb</sup>	8.25±0.15 <sup>a</sup>	9.08±0.52 <sup>d</sup>
<b>CPG-LF<sup>2</sup></b>	0.54±0.01 <sup>a</sup>	94.00±1.41 <sup>a</sup>	7.38±0.19 <sup>b</sup>	4.70±0.45 <sup>ef</sup>

<sup>1</sup> = Means with different letters are significantly different at 5% significance level.

<sup>2</sup> = Commercial Carbons, manufactured by Calgon Corp.

## Surface Properties

### *Surface area and pore size distribution*

In comparison to the reference carbons, sugarcane bagasse-based carbons, especially with coal tar as binder, exhibited limited surface area, while the GAC derived from pecan shells showed relatively larger surface area (Table 4). The highest surface area (1200 m<sup>2</sup>/g) among pecan shell-based carbons was achieved by chemical activation (PS10), and the lowest surface area (522 m<sup>2</sup>/g) by carbon dioxide activation (PS9). Steam activation yielded a carbon (PS63) with the closest surface area (852 m<sup>2</sup>/g) to the reference carbons. The proportion of meso- and macropores to the total surface area ranged from 8% to 50%. Pecan shells activated with carbon dioxide (PS9, PS23) were predominantly microporous, while carbons from sugarcane bagasse and coal tar had the highest amount of meso- and macropores. Both the type

**Table 4: Surface properties of experimental and commercial GACs\***

Activated Carbons g)*	TSA <sup>1</sup> (g/m <sup>2</sup> )	MSA <sup>2</sup> (g/m <sup>2</sup> )	MMSA/TSA <sup>3</sup>	TSC <sup>4</sup> (meq H <sup>+</sup> /g)
<b>SBCS21</b>	314	261	0.17	0.29
<b>SBCS11</b>	337	267	0.21	0.19
<b>SBCT11</b>	78	39	0.50	0.07
<b>SBCT21</b>	180	120	0.34	0.12
<b>PS23</b>	641	588	0.08	0.34
<b>PS9</b>	522	477	0.09	0.22
<b>PS63</b>	852	645	0.24	0.31
<b>PS10</b>	1203	942	0.22	1.12
<b>CCAL<sup>5</sup></b>	920	783	0.15	0.47
<b>CPG-LF<sup>5</sup></b>	904	802	0.11	0.49

\* Values are means of duplicate determinations where the standard deviations are less than 10% of the mean values.

<sup>1</sup> = Total Surface Area

<sup>2</sup> = Micropore Surface Area

<sup>3</sup> = Ratio of Macro- and Mesopore Surface Area over Total Surface Area.

<sup>4</sup> = Total Surface Charge

<sup>5</sup> = Commercial carbons, manufactured by Calgon Corp.

of precursor and the method of activation appear to affect pore size distribution. Carbon dioxide activation produced larger meso- and macropore surface area when applied to sugarcane bagasse chars (17%-50%) than when used to activate pecan shell chars (8%-9%). The latter showed more meso- and macropore development when activated with either steam or phosphoric acid. These observations can be explained by the fact that steam is more reactive than carbon dioxide at a given temperature (Rodriguez-Reinoso and Molina-Sabio, 1992). The water molecule has a smaller molecular dimension than carbon dioxide, which leads to faster diffusion into the porous structure of the char. Phosphoric acid, on the other hand, is impregnated into the raw material to influence the pyrolysis such that the tar formation and

volatilization are kept to a minimum (Pollard et al., 1992). The bubbling of phosphoric acid through the by-product matrix and the reduction of tar formation result in a well-developed surface area. The total surface charge did not appear to significantly affect sugar decolorization efficiency of GAC. However, the charge contributed by dissociation of the most acidic groups (groups ionizable at neutral pH) lowered the sugar decolorization efficiency of GAC. This is probably due to charge repulsion between predominantly negatively charged sugar colorants and carbon surface.

### ***Surface chemical groups***

The titration method revealed that many, but not all, of the carbons evaluated contained four classes of surface oxides: carboxyls, lactones, phenols, and carbonyls (Figure 5). The concentration of surface groups varied, depending on the precursor and activation conditions. Among the 10 carbons investigated, chemically activated pecan shell (PS10) showed the highest concentration of surface groups. In contrast, GAC prepared from sugarcane bagasse and coal tar exhibited the lowest concentrations. Phenols and carbonyls were the dominant surface oxides for most of the GAC. Carboxyls were absent in one of the commercial carbon (CCAL) as well as in the steam activated pecan shell-based carbon. The results of FT-IR studies were generally consistent with those of the titration method as shown by FT-IR spectra given in Figures 6 and 7. For instance, the carbon derived from pecan shells through chemical activation (PS10) had the most intense peaks among all the experimental carbons (Figure 7).

These peaks covered the absorption bands corresponding to all the functional groups revealed by titration. The two commercial carbons (Figure 6) and the steam activated pecan-based carbon (Figure 7) exhibited relatively weak FT-IR absorption peaks, indicating a low concentration of oxides on their surface. Approximate FT-IR band assignments indicated the presence of carbonyls, carboxyls, lactones, and phenols. The  $1800\text{-}1540\text{ cm}^{-1}$  band (band 1) was associated with the C=O stretching mode in carbonyls, carboxylic acids, and lactones, while the  $1440\text{-}1000\text{ cm}^{-1}$  band (band 2) was assigned to the C-O stretching and O-H bending modes, such as in phenols and carboxylic acids, (Morterra and Low, 1983; Morterra and Low, 1985; Zawadski, 1981; Laine et al.,

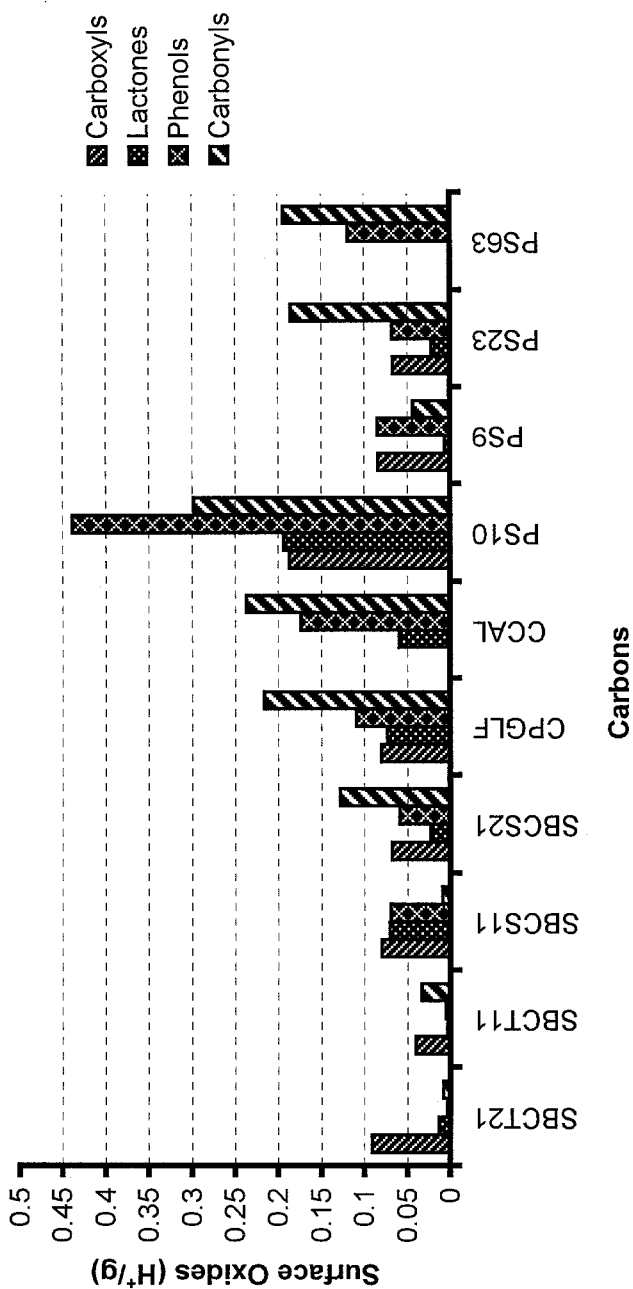


Figure 5. Concentration of surface oxides for GAC. SBSC11 and SB-CT11=Sugarcane Bagasse with Corn Syrup and Coal Tar in a ratio of 1 to 1, respectively; and PS=Pecan Shells; CCAL and CPGLF are the commercial reference carbons. SBSC21 and SBCT21=Sugarcane Bagasse with Corn Syrup and Coal Tar, in a ratio of 2 to 1 respectively; and PS=Pecan Shells (see Table 1 for PS based carbons identification); CCAL and CPGLF are the commercial reference carbons. Bars represent the means of two replications where the standard error for each measurement was less than 5%.

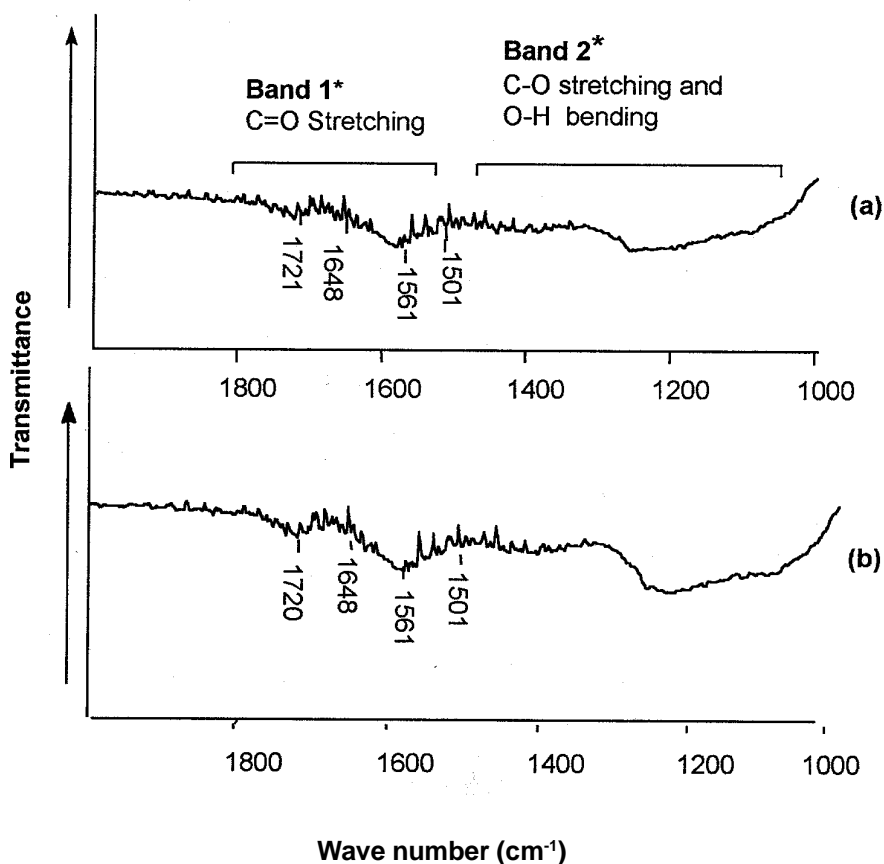


Figure 6. FT-IR spectra of the reference carbons (a) CPG-LF and (b) CCAL.

Band assignments;

**Band 1:** Stretching of C=O in carbonyls (aldehyde and ketones), carboxylic acids, and lactones.

**Band 2:** C-O stretching and O-H bending in alcohols (phenols, lactones) and carboxylic acids.

\*Absorption of each group may shift within each band depending on molecular structure and environment.

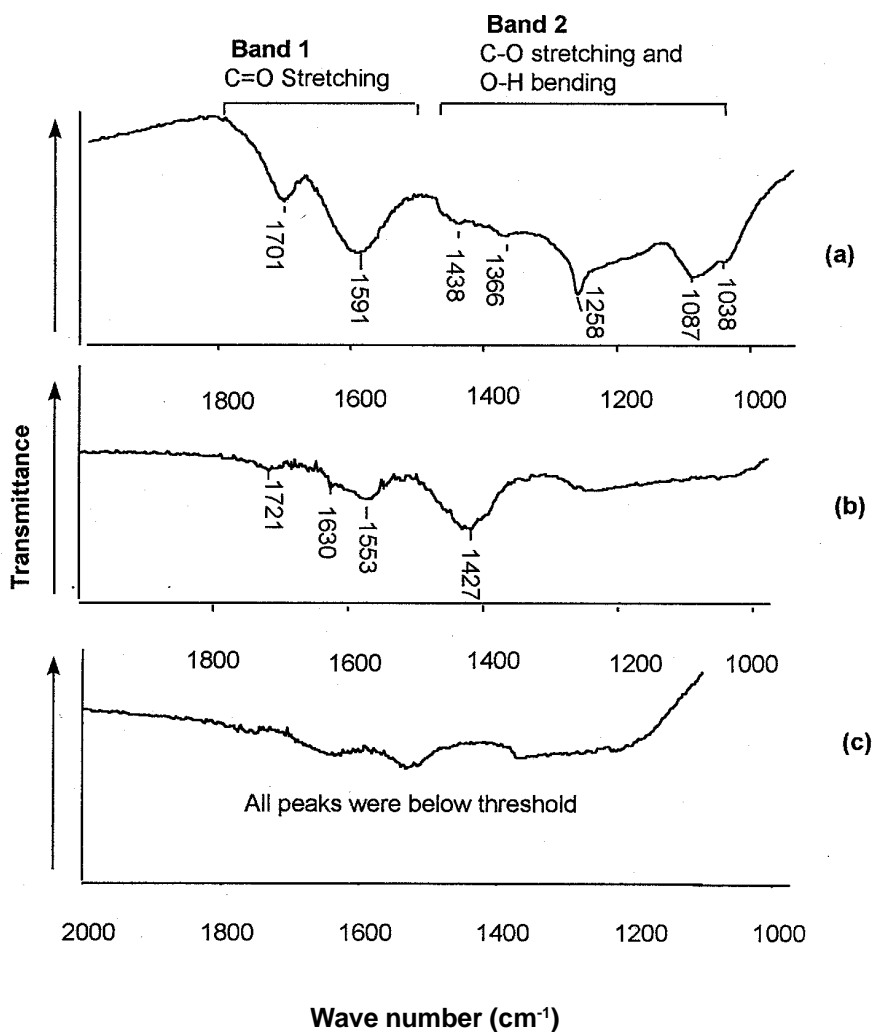


Figure 7. FT-IR spectra of granular activated carbon from pecan shells produced by (a) chemical activation (PS10), (b) carbon dioxide activation (PS23), and (c) steam activation (PS63).

1989). The assignment of a specific wave number to a given functional group was not possible because the absorption bands of various functional groups overlap and shift, depending on their molecular structure and environment. Shifts in absorption position may be caused by factors such as intramolecular and intermolecular hydrogen bonding, steric effect, and degree of conjugation. For instance, within its given range, the position of C=O stretching band (common to carbonyls, carboxylic acids, and lactones) is determined by many factors. These include: (1) the physical state, (2) electronic and mass effects of neighboring substituents, (3) conjugation, (4) hydrogen bonding, and (5) ring strain (Kendall, 1966; Smith, 1979). The IR absorption bands of oxygen groups on the surface of solid GAC are likely to be affected by some or all of the factors listed above.

The presence of peaks in Band 1 is indicative of the presence of carbonyls and/or lactones. Coexistence of peaks in both Band 1 and Band 2 is indicative of carboxylic acids (C=O, C-O stretching and O-H in-plane bending), phenols (O-H bending), lactones, and carbonyls (C=O stretching). The absence of distinct peaks in one or two bands indicates absence of the corresponding surface oxides. Most of the carbons activated at high temperature (800-900 C) showed absorption peaks in Band 1 and no peaks in Band 2, suggesting a predominance of carbonyls and lactones. Chemical activation of pecan shells (PS10) showed strong absorption peaks in both bands, indicating the presence of carboxylic acids and phenols along with carbonyls and lactones. The same pattern was also revealed by titration (Figure 5). These results are in agreement with the findings of many investigators (Bansal et al., 1988; Molina-Sabio et al., 1991; Zawadski, 1981) who reported that carbons produced at lower temperature have a variety of surface oxides, including carboxylic acids, but the majority of these surface structures, especially carboxylic acids and lactones, decompose in the temperature range 600-800 C.

### **Adsorption properties of GAC and their relationship to surface properties**

Based on both molasses color removed and sugar decolorization, GAC made from sugarcane bagasse using corn syrup as a binder (SBCS 21 and 11) and two pecan shell-based carbons (PS63, steam activated and PS10, chemically activated) were as effective

as the commercial carbons in removing sugar colorants (Figures 8 and 9). GAC produced from sugarcane bagasse with coal tar as a binder and those prepared from pecan shells using CO<sub>2</sub> activation were the least effective decolorizers. The superior decolorization efficiency of the carbons produced with corn syrup is probably due to their relatively well-developed surface area compared with carbons made with coal tar. The limited surface area of coal tar carbons may be attributed to the fact that coal tar has a higher carbon content than corn syrup and, therefore, would be volatilized to a much lesser extent (Pendyal et al., 1999a), yielding less developed surface area.

Overall, three characteristics of activated carbon can be used to explain the observed differences in molasses and raw sugar color adsorption among the carbons. These properties are: 1) total surface area, 2) pore size distribution (relative proportion of micro-, meso-, and macropores), and 3) chemical reactivity, which depends on the types and concentrations of the surface oxides on the carbon surface (Mattson and Mark, 1971; Dubinin, 1987). Since percent molasses color removed and percent sugar decolorization did not seem to be directly proportional to surface area, pore size distribution as well as total surface charge may have played a role in the observed differences.

Multiple regression analysis of the removed color as a function of total surface area and pore ratio showed that it followed a curvilinear relationship (Figure 10). Such a curvilinear relationship predicts that optimal decolorization by GAC would occur around a macro- and mesopore area to total surface area (MMSA/TSA) ratio of 0.25 and a total surface area exceeding of about 1000 m<sup>2</sup>/g. The low MMSA/TSA ratio of 0.08-0.09 for carbons made from pecan shells activated with CO<sub>2</sub> (PS9 and PS23) may, in part, explain why they failed to achieve good decolorization efficiency, despite their relatively high surface area. The high microporosity of these carbons would make adsorption of larger molecules, as found in sugar colorants, problematic. These large molecules would have difficulty entering and navigating through the micropores with the possibility that the micropores could become clogged, thereby effectively stopping further adsorption (Pendyal et al; 1999b). According to Wigmans (1989), an activated carbon with a high percentage of micropores will tend to adsorb low



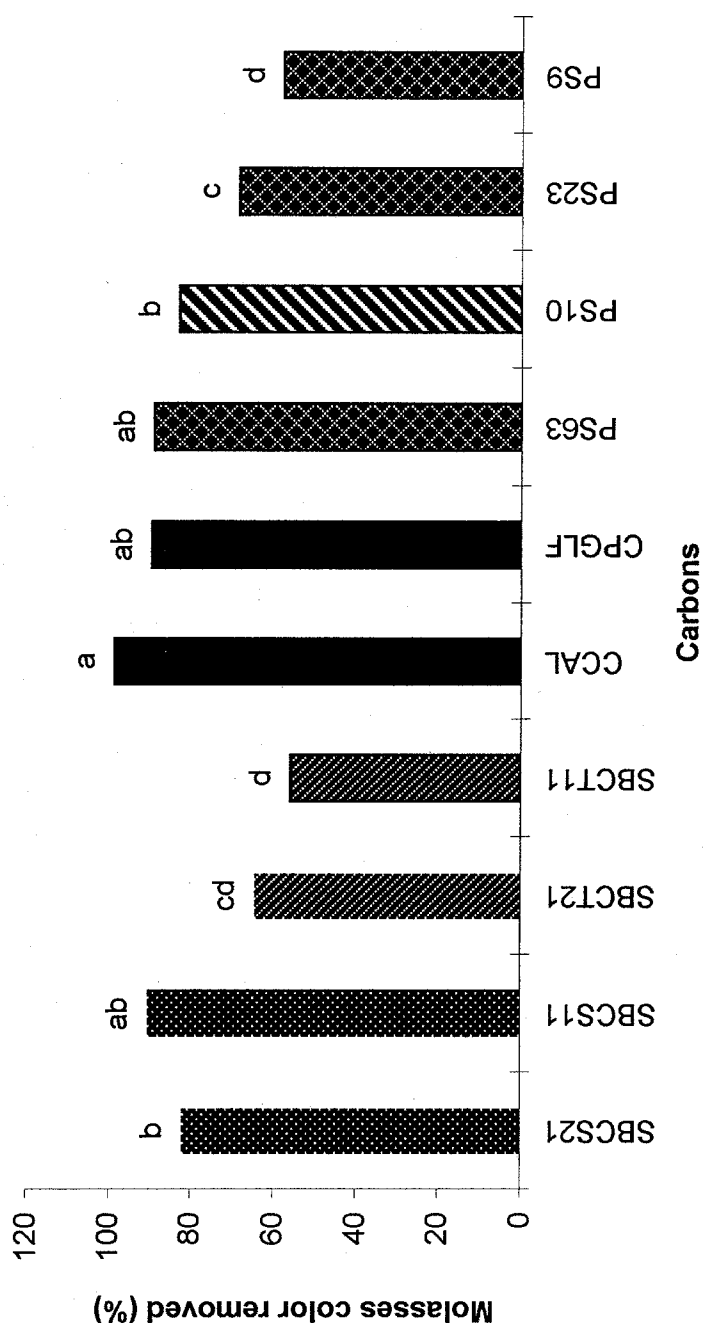


Figure 8. Percent molasses color removed for experimental and commercial carbons. See Figure 5 for carbon identification. Bars represent the means of four replications where the standard error for each measurement was less than 5%. Bars with different letters are significantly different at  $p < 0.05$ .

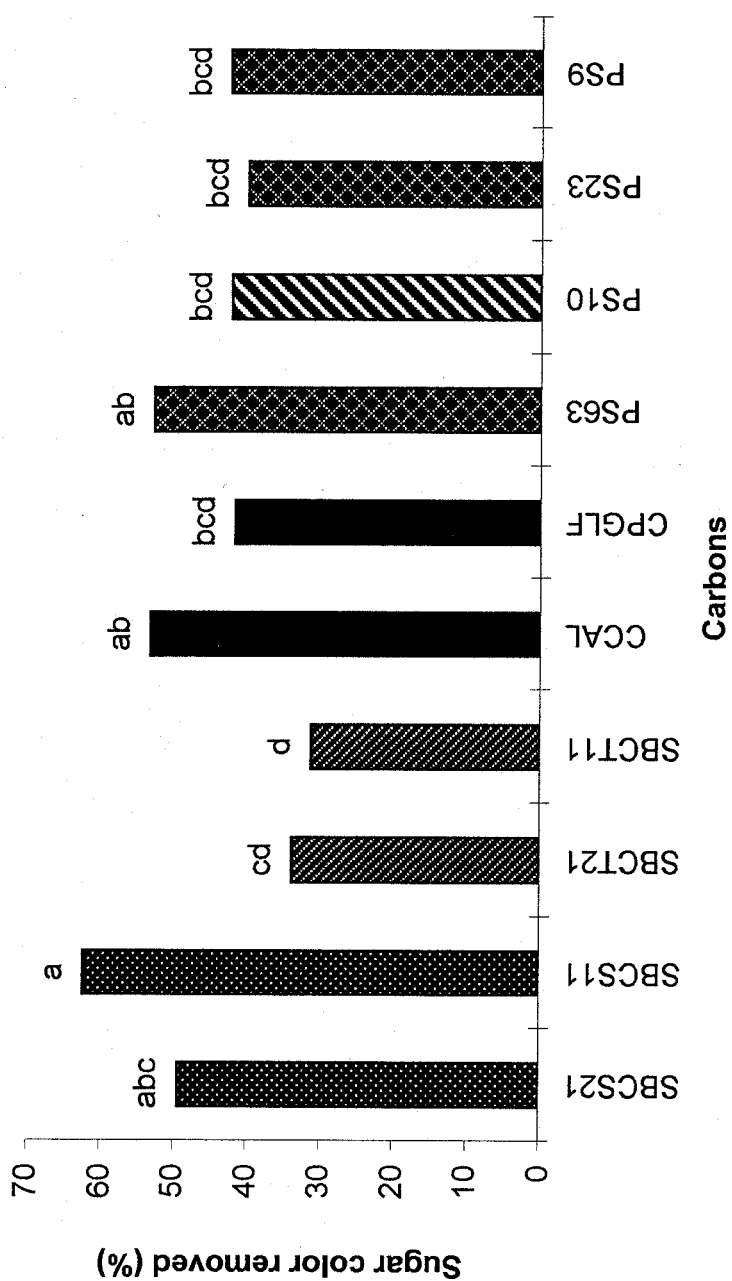


Figure 9. Sugar decolorization efficiency of experimental and commercial carbons. See Figure 5 for carbon identification. Bars are means of four replications where the standard error for each measurement was less than 5%. Bars with different letters are significantly different at  $p < 0.05$ .

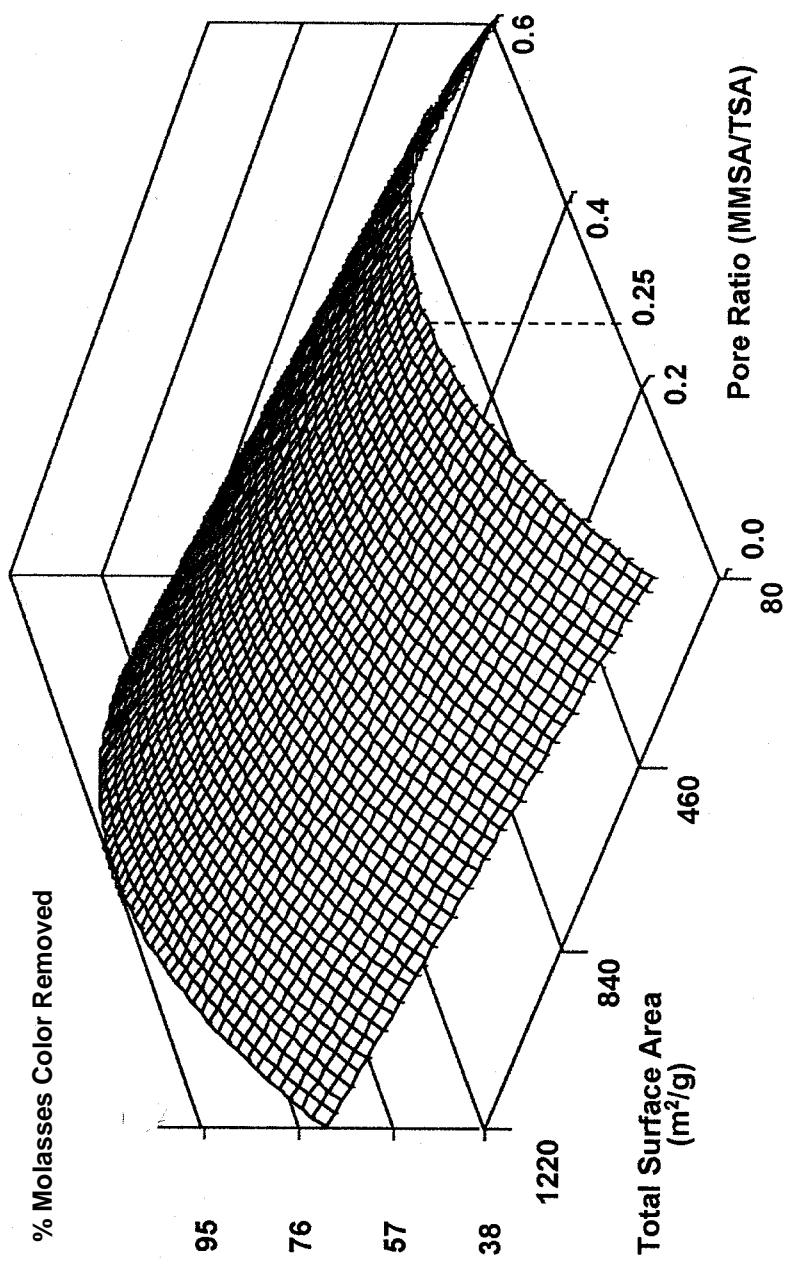


Figure 10. Percent molasses color removed as a function of total surface area and pore ratio

molecular weight compounds and as the percentage of micropores decreases, the carbon can adsorb compounds with a broader range of molecular sizes. The presence of macro- and mesopores may adsorb the larger colorant molecules while allowing the smaller molecules access to the micropores where they are adsorbed.

The negatively charged surface formed by the dissociation of specific types of surface oxides appears to reduce color removal by GAC. The highest percent color removal was achieved by carbons having no carboxylic groups (or no negative charge at pH 7) (Figure 11). A carbon's efficiency in removing sugar colorants decreased with an increasing amount of negative charges on the surface, probably because of charge repulsion of sugar colorants, which are predominantly negatively charged.

Electrostatic repulsion would explain why the carbon made from pecan shells with chemical activation (PS10) exhibited decolorization capacity lower than expected, despite its extensive surface area ( $1200 \text{ m}^2/\text{g}$ ) and its favorable pore size distribution (0.22). The steam activated pecan shell-based carbon was a good sugar decolorizer because it possessed a good surface area ( $850 \text{ m}^2/\text{g}$ ), an optimal pore size distribution (0.24), and no carboxyls (negligible surface charge). This set of surface properties appears to favor the adsorption of sugar colorants and would, therefore, be recommended for carbons designed for use in sugar refineries.

Carbons prepared from sugarcane bagasse and coal tar exhibited low decolorization efficiency mainly because of their very low surface area ( $78\text{-}180 \text{ m}^2/\text{g}$ ). The combination of sugarcane bagasse and corn syrup yielded GAC with moderate surface area ( $300 \text{ m}^2/\text{g}$ ), good pore size distribution, and a relatively low surface charge, which would explain their good sugar decolorizing capacity.

### **Grouping of experimental GAC based on similarities to the commercial carbon references**

The results of principal component analysis (Figure 12) and cluster analysis (Table 5) revealed that two by-product-based carbons, namely PS10 (chemically activated pecan shells) and PS63 (steam activated pecan shells) were similar to the reference carbons in terms of surface and adsorption properties. The two  $\text{CO}_2$  activated pecan shell-based carbons (PS9 and PS23) did not

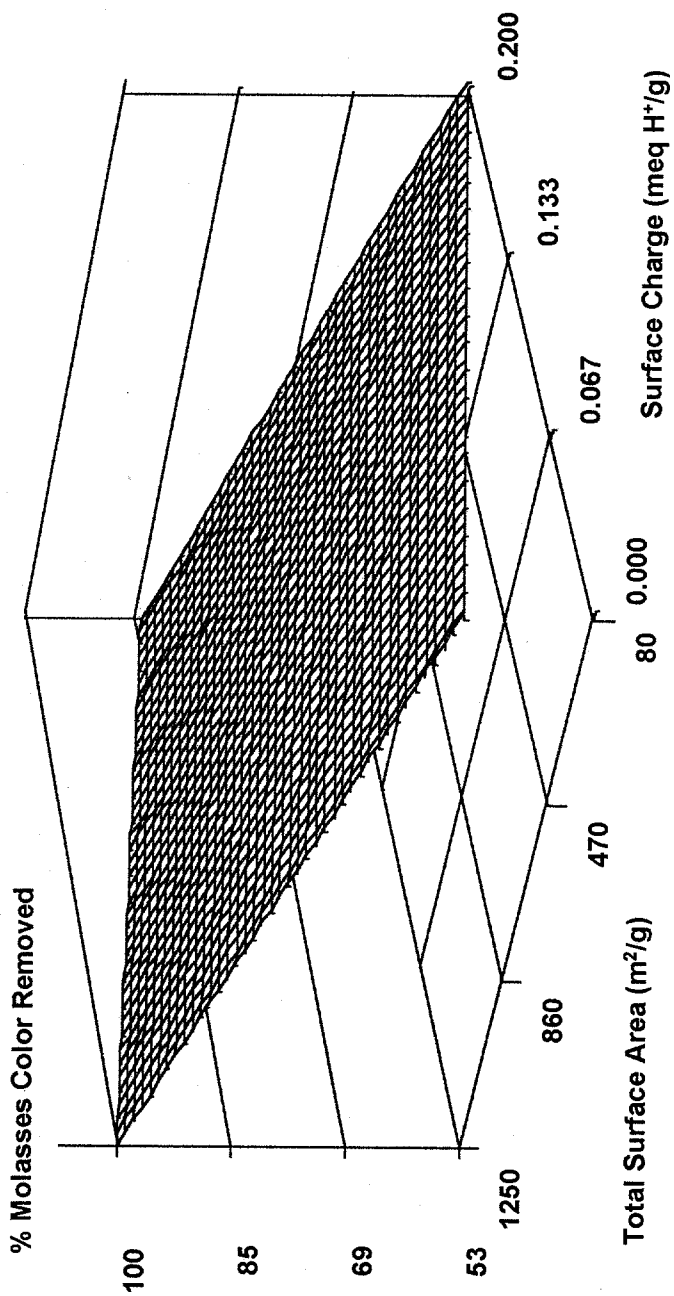


Figure 11. Percent molasses color removed as a function total surface area and surface charge (groups ionizable at neutral pH).

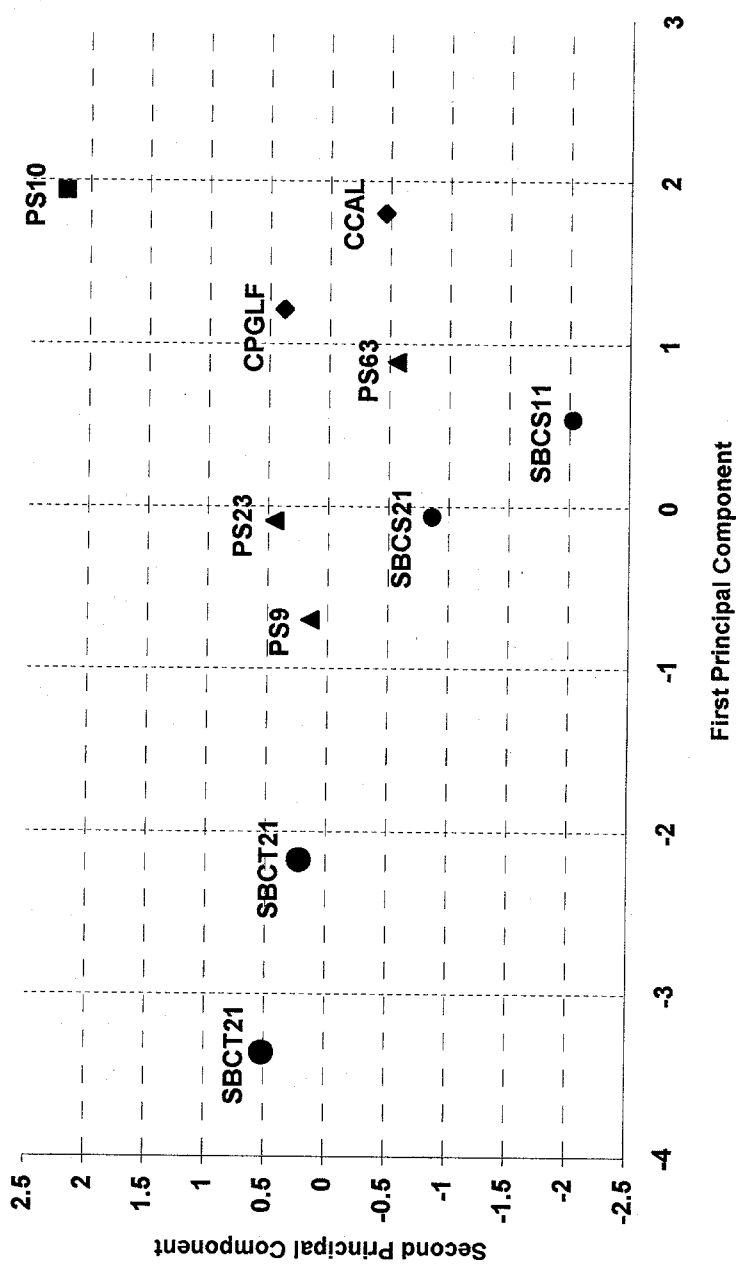


Figure 12. Grouping of GAC based on the first two principal components. See Figure 5 for carbon identification.

**Table 5: Grouping of experimental GACs based on their surface and adsorption properties**

Cluster 1	Cluster 2	Cluster 3
CCAL	SBCS21	PS23
CPGLF	SBCS11	PS9
PS63	SBCT21	
PS10	SBCT11	

cluster with the reference carbons mainly due to unfavorable pore size distribution. Carbons prepared with coal tar (SBCT11, SBCT21), on the other hand, were not classified with the reference carbons because of their low surface area. GAC derived from sugarcane bagasse with corn syrup (SBCS11, SBCS21) were close to being included with the commercial carbons, but were excluded by their relatively low surface area. Otherwise, they showed good sugar decolorization potential.

## SUMMARY AND RECOMMENDATIONS

This work has demonstrated that granular activated carbons produced from group 1 or group 2 agricultural by-products can be as effective as commercial GAC in removing sugar colorants, depending on the conditions of preparation. The type of agricultural by-products and, to a lesser extent, the binder used, influenced the physical, chemical, and surface properties of GAC and thus their adsorptive properties. A combination of sugarcane bagasse (group 1 by-product) and corn syrup produced carbons with the best sugar decolorization capacity but unsatisfactory physical properties. These GAC would be desirable only in “gentle” applications such as filtration through carbon-packed filters (e.g. aquarium filters) and systems designed for purification of gases (e.g. deodorization). In contrast, pecan shells, a group 2

material, were excellent GAC precursors and did not require the use of binders. Physical, chemical, and surface properties of GAC made from pecan shells were, however, dependent on the type of activation.

Multiple regression analysis of sugar decolorization as a function of surface properties revealed that larger total surface area, a well-developed macro- and mesoporosity, along with minimal surface charge (few carboxyl groups), were desirable in GAC designed for sugar decolorization. Steam activation of pecan shells was the only by-product/activation combination that produced a GAC with all three desirable characteristics of a good sugar decolorizer. Chemical activation of pecan shell-derived carbons with phosphoric acid yielded GAC with high surface area and adequate pore size distribution, but with large surface charge. However, the latter can be further improved by subjecting these carbons to higher activation temperature treatment to eliminate some of the surface oxides, especially carboxylic acids.

Since pecan shells produced GAC that were very similar to the reference carbons, they are worthy of further investigation. Future work should focus on ways to optimize the properties of pecan shell-based carbons to meet all the standards of quality required by sugar refineries. Scale up of carbon production from bench-type to pilot plant trials, where conditions in sugar refineries could be simulated, would be the next phase. In such a phase, carbon regeneration, economic analysis, and market potential should also be studied and contrasted with existing alternatives used in sugar refineries. This is expected to lead to successful production of GAC from pecan shells and would offer a cheap and renewable source of decolorizing carbons for sugar refiners.



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