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## MOLECULAR SIEVE CHARACTER OF CARBONS DERIVED FROM CELLULOSIC PRECURSORS

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**Abstract**—Cellulosic precursors were examined as suitable materials for the production of carbon molecular sieves to separate straight from branched-chain hydrocarbons. The amorphous and crystalline contents of the precursors, as determined by water adsorption, proved to be important in determining sieve character. For example, cellulose having amorphous and crystalline contents of ~50% yielded a 530°C carbon having negligible capacity for iso-butane and a substantial capacity for n-butane and CO<sub>2</sub>.

**Key Words**—Cellulose, carbon, molecular sieves, n-butane, iso-butane, CO<sub>2</sub>.

### 1. INTRODUCTION

Molecular sieves first gained prominence with their ability to separate straight from branched-chain hydrocarbons. In particular, the 5A zeolite, with its 0.42 nm apertures leading into 1.14 nm cavities, became of considerable commercial importance [1,2]. Since it was thought that carbon molecular sieves may have some advantages over inorganic molecular sieves, such as stability at higher temperatures and in acidic media and lower affinity to water, interest in developing such materials commenced. It was appreciated that thermosetting polymers and coals offered considerable promise as precursors. Such has turned out to be the case. In particular, poly (vinylidene chloride) or PVDC and Saran, the copolymers of PVDC and poly (vinyl chloride), have proved to be excellent precursors for the production of sieves to separate straight from branched-chain hydrocarbons [3-5]. Walker and co-workers [6,7] have also shown that composites consisting of activated carbon and poly (furfuryl alcohol) have great flexibility for hydrocarbon separation.

There has also been much interest in the production of microporous carbons from the carbonization of cellulosic precursors [8,9]. In particular, studies have been conducted on enlarging the micropore surface area of cellulosic chars by their gasification in CO<sub>2</sub> or steam, and on producing mesopore surface area by the addition of inorganic species to the cellulose prior to its carbonization [10-14]. In most cases the microporosity has been characterized by measuring the uptake of CO<sub>2</sub> between -78°C and 25°C, and N<sub>2</sub> at -196°C. In this study, chars produced from diverse sources of cellulose have been charac-

terized, particularly for their adsorption selectivity to n-butane and iso-butane.

### 2. EXPERIMENTAL

#### 2.1 Precursors

The precursor materials used in the present study were of diverse origin and general morphology. Information concerning the various precursors is shown in Table 1. All samples had an ash content of <1% by weight. Table 2 consists of a glossary of terms used in Table 1. Each sample (carbon or precursor) referred to in the present study has been identified by a series of code letters, which may be prefaced by one to three other letters indicating a specific sample preparation given to the precursor (these treatments are identified whenever the sample is mentioned in the text). The code letters are followed by an O for uncarbonized samples or a number indicating the carbonization run for the particular precursor.

Cellulose, as a crystalline polymer, exhibits polymorphism with no less than five accepted crystalline structures [15]. The most common of these, Cellulose I, is the structure exhibited by most natural cellulose materials. It is a monoclinic crystal with the following unit cell dimensions:  $a = 0.82$  nm,  $b = 1.03$  nm,  $c = 0.79$  nm,  $\beta = 84^\circ$ . The second most common structure is Cellulose II, a monoclinic crystal:  $a = 0.79$  nm,  $b = 1.03$  nm,  $c = 0.91$  nm,  $\beta = 63^\circ$ . It occurs in regenerated cellulose materials [15]. The other forms of cellulose have been produced by mechanical and/or chemical treatment of these two basic forms. During such treatments, the amount of crystalline phase present is usually altered.

A sample of rayon viscose yarn UCR (trade name, Villwyte) was supplied by the Union Carbide

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Table 1. Pertinent data on precursors

Sample	UCR	AMVR	WT-B	CP	CS
Material	Villwyte	Tire cord	Filter paper	Cellulose	Coconut shell
Cellulose type	Viscose	Viscose	Natural	Natural	Natural
Form	Yarn	Yarn	—	Powder	Chunks
Stretch (%)	—	110	—	—	—
Twist	2	5	—	—	—
Fibers/yarn	1440	1550	—	—	—
Fiber diameter	~15 $\mu\text{m}$	~10 $\mu\text{m}$	~10 $\mu\text{m}$	<10 $\mu\text{m}$	—
Denier	3300	1875	—	—	—
Crystal type	II	II	I	I	I

Corp. A viscose tire cord rayon AMVR was supplied by the American Viscose Div. of FM Corp. Whatman number 41 filter paper discs (WT-B) 11.0 cm in diameter were cut into small strips before carbonization. A chromatographic cellulose powder (CP) was obtained from Applied Science Labs.

## 2.2 Sample preparation

**2.2.1 Cleaning of rayon and coconut shells.** A 10-g sample of rayon yarn was soaked in warm distilled water. The sample was then immediately rinsed several times with each of the following reagents to remove any soluble surface treatment that may have been applied to the yarns: acetone, benzene, methyl alcohol, and water. It was air dried prior to use.

Coconuts were first cleaned by filing their surfaces to remove all fiber and to produce a smooth finish. After washing this surface with water, the coconut was split open and dried in an oven at 85°C for 1.5 h. Upon removal of the coconut meat the shell was crushed into 0.5 cm  $\times$  1.5 cm diameter pieces.

**2.2.2 Precursor modification.** Three techniques were used to modify the crystallinity of the cellulose powder: (a) ball-milling using a rolling motion, (b) ball-milling with vibration, and (c) treatment with ethylenediamine. A steel ball-mill five inches in diameter and three inches in height was used for both milling procedures.

For the first technique, the open ball-mill, containing 10 g of cellulose powder and 60 stainless steel balls (40  $\frac{3}{4}$ -inch balls and 16  $\frac{1}{2}$ -inch balls), was placed in a plastic bag along with Drierite. After two hours, the mill was closed without opening the

bag and then removed from the bag before being continuously rolled for eight hours. The sample was separated from the balls with a number 5 Tyler mesh sieve and stored in a desiccator. The vibratory-milling technique employed the same sample size and procedure as above, but 3.42 kg of  $\frac{3}{8}$ -inch stainless balls were used in place of the previous balls. The mill was vibrated for two hours.

Two systems were constructed for treating rayon yarn with ethylenediamine under nonoxidizing conditions. In system A, a 12-g sample of rayon was placed in the reactor and dried by passing  $\text{N}_2$  through the reactor for three hours. During this period the reactor was maintained at 80°C by a water bath. While maintaining the  $\text{N}_2$  flow, the sample was cooled to 4°C; and approximately 80 ml of ethylenediamine was added to the reactor. After a two-hour soak period, the ethylenediamine was transferred to a collection trap under  $\text{N}_2$  flow. Continuing the flow of  $\text{N}_2$ , the sample was heated at 80°C for two hours, after which the sample was removed and immediately immersed in hexane. Then the sample was rinsed three times with 150 cc of hexane, stored overnight, dried in a stream of  $\text{N}_2$  for eight hours, and finally stored under an atmosphere of  $\text{N}_2$ .

Samples to be treated using system B were first oven dried for 22 hours at 103°C, Soxhlet extracted with acetone for 48 hours, and oven dried for 48 hours at 103°C. With these samples in the extractor, the system was evacuated and filled with  $\text{N}_2$  twice to remove air. While continuing the  $\text{N}_2$  flow, ethylenediamine was introduced from a reservoir until the samples were completely immersed, and then allowed to soak at room temperature for 0.5 hour. Sufficient ethylenediamine was then added to cause

Table 2. Glossary of terms

1. Viscose	Relating to, or made from viscose, a golden-brown solution made by treating cellulose with alkali solution and carbon disulfide, used in making rayon.
2. Rayon	Fibers of cellulosic origin made by the viscose, cupriammonium, or acetate process. All rayons in the present study are viscose rayons.
3. Villwyte	Fiber trademark for a rayon produced commercially.
4. Yarn	A continuous strand composed of fibers assembled or held together by twist.
5. Stretch	Increase in length relative to the initial length.
6. Twist	Number of turns per inch.
7. Denier	The weight expressed in grams of either a single fiber or yarn 9,000 m long.

Table 3. Compounds used as molecular probes

Compounds	Adsorption temperature °C	Pressure (MPa)		Critical cross section (nm)	Molecular area (nm <sup>2</sup> )	Relative pressure (P/P <sub>0</sub> )
		P	P <sub>0</sub>			
Carbon dioxide	-78	0.05	0.10	0.33	0.17	0.50
n-butane	28	0.10	0.28	0.43	0.47	0.36
iso-butane	28	0.10	0.39	0.50	0.51	0.26

the extractor to empty into a flask. This was followed by acetone to wash the bulk of the ethylenediamine from the extractor. The flask was then replaced with another, half-filled with clean acetone. The samples were Soxhlet extracted for 21 hours with a cycle time of 8–10 min. Following removal of the acetone, samples were evacuated with a rotary vacuum pump until dry, and then further dried in an oven with an atmosphere of N<sub>2</sub> at 75°C for a period of 45 min before storing over Drierite.

**2.2.3 Water treatment.** Cellulose powder, treated as described in Section 2.2.2, was placed in a Petri dish and moistened with distilled water until saturated. It was kept wet for 24 hours, and then allowed to air dry. Rayon treated with ethylenediamine was treated with distilled water in the same manner as the cellulose powder.

### 2.3 Carbonization

Cellulose fibers and powders were carbonized using a standard horizontal tube furnace fitted with a 2 1/8 inch quartz tube. Samples to be carbonized were held in a Coors combustion boat. Prepurified N<sub>2</sub> was passed through the quartz tube at 75 to 125 cc/min. The N<sub>2</sub> was further purified by passing it over copper turnings at 400–425°C. Soak temperature and heating rate (7°C–8°C/min) were maintained by a Leeds and Northrup temperature programmer. A soak time of 1.5 hours at the maximum temperature was used prior to cooling in N<sub>2</sub>. Coconut shells were carbonized as 0.5 cm × 1.5 cm pieces, and then ground to pass a 400 mesh sieve for static adsorption measurements. Carbonized cellulose powders were crushed (not ground) to pass a 400 mesh Tyler sieve for adsorption measurements, whereas all other samples were used directly as obtained from carbonization.

### 2.4 Static adsorption—molecular probe technique

Each of four adsorption tubes was a McBain balance containing a fine quartz spring (0.6 cm diameter) with a sensitivity of 0.18 mm/mg, an aluminum bucket, and two thin Pyrex hooks. The end of a hook was used as a reference point for measuring the spring extension with a Gaertner M-911 cathetometer (±0.005 cm precision). Assuming an average sample weight of 0.17 g, the precision in measuring the surface area was estimated to be 4 m<sup>2</sup>/g to 9 m<sup>2</sup>/g. Vacuum was provided by a two-stage mercury diffusion pump backed by a mechanical pump. A

capillary bypass was used for slow evacuation and addition of gases. Furnaces were placed around the loaded adsorption tubes and heated to 200°C and held for two hours under a vacuum of better than 10<sup>-2</sup>Pa. After out-gassing, the samples were allowed to cool to room temperature before again reading the cathetometer. The adsorption baths (Dewar flasks) were then put into place. Before adsorption, the adsorbate was flushed through the apparatus. Unless it is indicated otherwise in the text, the pressures given in Table 3 were used for static adsorption studies. The cathetometer was read at several intervals; but unless specified otherwise, data are reported for a one-hour equilibration time. The various molecules used in the present study, estimates of their kinetic diameters calculated from the minimum equilibrium cross-sectional diameter, and the molecular areas used to calculate surface areas are listed in Table 3. Since volume uptake of adsorbate is almost entirely in the micropores of cellulose chars (that is, the chars contain negligible mesoporosity[16]), uptake is essentially independent of relative pressure in the range used in this study.

Purification of the adsorbates was achieved in two traps. Carbon dioxide was dried by passing it through magnesium perchlorate, and iso-butane was passed through a 5A zeolite trap to remove normal hydrocarbons. N-Butane was used as received.

## 3. RESULTS AND DISCUSSION

### 3.1 Water adsorption by cellulosic precursors

The difference in crystal type between natural cellulose and regenerated cellulose[17] has been shown to be accompanied by a variation in their fractional crystallinity[18]. Such variations among cellulosic materials have been extensively investigated, and a number of methods used to quantify them. Valentine[19] has suggested that completely amorphous cellulose adsorbs 19.3 wt% water at a relative pressure of 0.65. This value was based on a comparison of the moisture adsorption of several different types of cellulose and the amorphous fraction determined by deuterium exchange. A linear relationship between the two techniques was obtained which, upon extrapolation to 0% amorphous content, indicated that no moisture was adsorbed. Caulfield and Steffes[20] confirmed these results by examining the 0.65 relative pressure moisture adsorption and density of cellulose ball-milled for

Table 4. Crystallinity of precursors by water adsorption

Sample designation	Type of cellulose	Adsorption of water (g/g)	Amorphous content (wt%)
CP-O	Cellulose powder	0.051	26
UCR-O <sup>a</sup>	Viscose rayon	0.089	46
AMVR-O <sup>a</sup>	Viscose rayon	0.099	51

<sup>a</sup>Washed rayons; see Section 2.2.1 for clarification.

various lengths of time. Moisture adsorption approached a limiting value of 19.3 wt%. Expressing the moisture adsorption as a ratio relative to 19.3 wt% and plotting the specific volume (cc/g) versus this ratio, a value of 0.633 cc/g for the specific volume of 100% crystalline cellulose was obtained. This was only slightly above the value of 0.628 cc/g that was calculated for the unit cell. Thus it was assumed that 19.3 wt% was an appropriate value to use for a 100% amorphous cellulose.

The amorphous contents of three cellulosic precursors are given in Table 4. Moisture adsorption was measured at 28°C and a 0.65 relative pressure. These materials have quite different amorphous contents. The effect that this variation in precursor amorphous content has on the pore structure of carbons derived from them will be discussed later.

In order to obtain samples with intermediate degrees of crystallinity cellulose powder was ground using either a rolling action or a vibratory action. As seen in Table 5, the milled cellulose was less crystalline; and the two-hour vibratory milling was more effective than eight-hour roll-milling. Although the crystallinity was changed, the material did not appear to be physically altered, except for a slight discoloration of the roll-milled samples.

A portion of the ground cellulose was placed in a Petri dish and moistened until just saturated. It was covered and kept moist for 24 hours, after which it was allowed to dry by evaporation. This recrystallization process significantly decreased the amorphous content of the milled samples and provided a series of samples with varying amorphous contents for carbonization.

Another technique for modifying the crystallinity of cellulose was attempted, which involved exposure to ethylenediamine. Although this has been shown to form a complex with cellulose, which upon acetone extraction does alter the crystallinity[21],

a quantitative measure of this alteration was not possible by water adsorption. The incomplete removal of diamine by 21 hours of Soxhlet extraction with acetone or washing with three 150 cc aliquots of hexane precluded the determination of crystallinity with the adsorption technique. Although some amine was retained in these samples, they were carbonized to determine what effect the treatment may have had on the porosity of the carbon produced.

### 3.2 Carbonization of cellulosic precursors

Carbonization results are shown in Figs. 1 and 2. A small weight loss occurs below 230°C, followed by the primary degradation process, which is accompanied by a large weight loss between 230–330°C. Essentially all weight loss is completed by 600°C. Total weight loss, upon heating between 800–900°C, ranges between 80–86% for all precursors except the coconut shell.

Bacon and Tang[22], Tang and Bacon[23], Bacon[24], and Brunner and Roberts[9] have been concerned with char yield upon the pyrolysis of cellulose. Pyrolysis is described in terms of four successive stages: (a) desorption of physically adsorbed water up to ~150°C; (b) splitting off of structural water through condensation of hydroxyl groups between 150–230°C; (c) chain scissions, or depolymerization, and breaking of C–O and C–C bonds within ring units between 230–400°C; and (d) aromatization between 400–700°C. In addition to H<sub>2</sub>O, CO, and CO<sub>2</sub>, considerable tar is released between 230–400°C. Figure 3 depicts these steps. Ultimately, four carbon chain residues are suggested to undergo aromatization[23].

As expected, variation in heating rate has a large effect on char yield, possibly for two reasons. First, it affects the extent of secondary tar cracking reactions as the tar molecules diffuse from the pore

Table 5. Effect of grinding on precursor crystallinity

Sample designation	Treatment	Adsorption of water (g/g)	Amorphous content (wt%)
CP-O	None	0.051	26
GCP-O	Roll-milled 8 h	0.071	37
RGCP-O	Recrystallized	0.061	32
VGCP-O	Vibratory-milled 2 h	0.079	41
RVGCP-O	Recrystallized	0.041	21

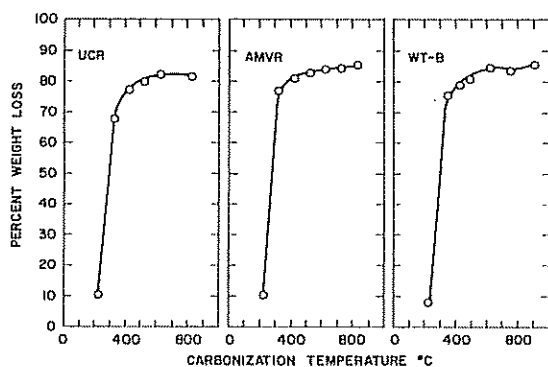


Fig. 1. Weight loss on carbonization of as-received rayons UCR and AMVR and filter paper WT-B.

system. Second, it affects the extent of dehydration prior to the commencement of depolymerization and, hence, the size of the volatiles released[9]. Brunner and Roberts[9] report that the yield of char upon carbonization of cellulose powder (similar to our CP sample) varies from 11% to 28% upon changing the heating rate from 70°C/min to 0.03 C/min. At a heating rate comparable to that used in this study (7–8°C/min), they report a char yield of ~20%. It can be appreciated that the heating rate chosen will have a profound effect on the cellulosic-derived char and, hence, on molecular sieving properties. This variable was not explored in this study. Brunner and Roberts have shown that decreasing the heating rate increased the specific micropore volume of the char accessible to CO<sub>2</sub> uptake at –78°C[9].

### 3.3 Pore accessibility by static adsorption for carbonized precursors

It will be shown later that the porosity of the carbon produced from cellulosic precursors is ini-

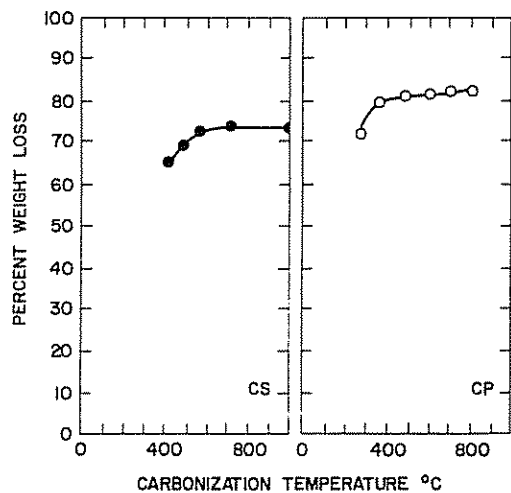


Fig. 2. Weight loss on carbonization of coconut shell CS and cellulose powder CP.

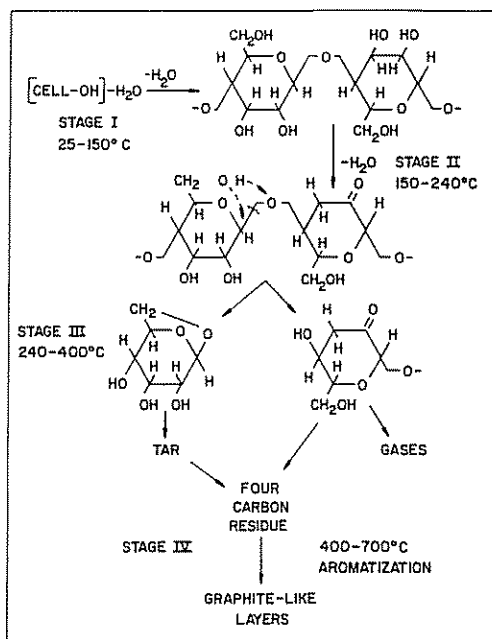


Fig. 3. Mechanism of cellulose degradation[23].

tially formed during the primary degradation process (230°C to 300°C) irrespective of the apparent purity (i.e., coconut shells and cellulose powder). Although the weight loss curves show very little change for heat treatments above 430°C, the adsorption results, to be discussed later, indicate that the accessibility of this porosity is significantly altered by heat treatment and the precursor fine structure. To visualize these effects, the adsorption data expressed as “monolayer equivalent” surface areas were plotted versus the carbonization temperature. The “monolayer equivalent” surface area, as defined by Barrer[25], is the area occupied by the same quantity of sorbate if it were spread as a close packed monolayer on a smooth surface.

The dependence of surface area on carbonization temperature for the solvent cleaned rayons, filter paper, and cellulose powder is shown in Figs. 4 and 5. As indicated previously, the development of a porous structure occurs in the temperature range of 230°C to 330°C. This resulted in a CO<sub>2</sub> surface area of 300 m<sup>2</sup>/g–400 m<sup>2</sup>/g, irrespective of the precursor. Areas increased with carbonization temperature to 500 m<sup>2</sup>/g–560 m<sup>2</sup>/g at 830°C, indicating an increase in the number of pores and/or the size of the pores. This is most likely due to an increase in the size of existing pores as the carbon rearranges itself into an aromatic layer structure. As discussed, this type of rearrangement has been observed by Bacon and Tang[22] to occur in the 400°C–700°C temperature range.

Although the CO<sub>2</sub> area increases in this temperature range, the n-butane surface area reaches a maximum at 530°C–630°C, and then rapidly decreases from 630°C to 830°C. Since one area is increasing

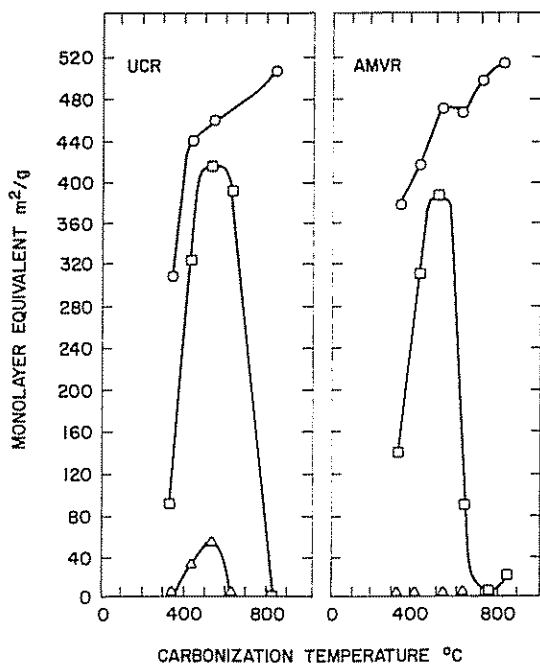


Fig. 4. Change of surface area with carbonization temperature of carbons from washed UCR and AMVR rayons using carbon dioxide (○), n-butane (□), and iso-butane (△).

while the other is decreasing, the carbon re-arrangement must be narrowing the pore entrance size, which results in the hindered passage of n-butane molecules. The effect of carbonization tem-

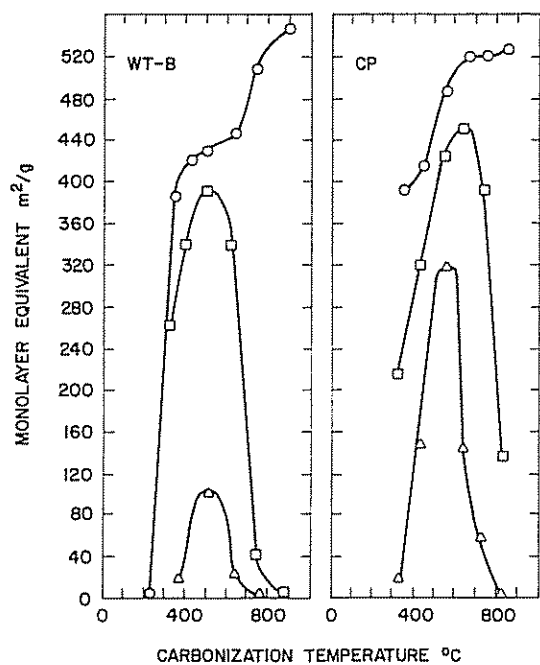


Fig. 5. Change of surface area with carbonization temperature for filter paper WT-B and cellulose powder CP carbons using carbon dioxide (○), n-butane (□), and iso-butane (△).

perature seems to be the creation of porosity at low temperatures, followed by "pore mouth sintering" at higher temperatures. It is the size of the pore mouth that controls the accessibility of the pore system, and it is this parameter that is most affected by the differences in the precursor materials.

Comparison of the iso-butane adsorption by carbons from the different precursors, prepared at the carbonization temperature corresponding to the characteristic maxima of the n-butane adsorption curves, revealed large differences. The iso-butane surface areas ranged from over 300 m<sup>2</sup>/g for the cellulose powder carbon to nil for the washed AMVR rayon carbon. This variation in iso-butane surface area will be shown later to be related to a difference in crystallinity of the precursors.

More complex carbonization curves were obtained for the carbons produced from the unwashed (as-received) UCR and AMVR rayons. The carbonization curves, as shown in Fig. 6, are quite different from the results for the washed fibers shown in Fig. 4. The decrease in CO<sub>2</sub> adsorption for the UCR carbons heat treated above 530°C does not reflect a change in available surface area, but a decrease in pore opening size sufficient to result in activated diffusion of CO<sub>2</sub>. This was evidenced by an increase in adsorption at longer equilibration times for the 830°C carbonized sample. Variations in the n-butane adsorption with carbonization temperature are more complex, with two maxima apparent for the AMVR carbon and a shoulder on the curve for the UCR carbon. Negligible surface area was available to iso-butane for samples carbonized between

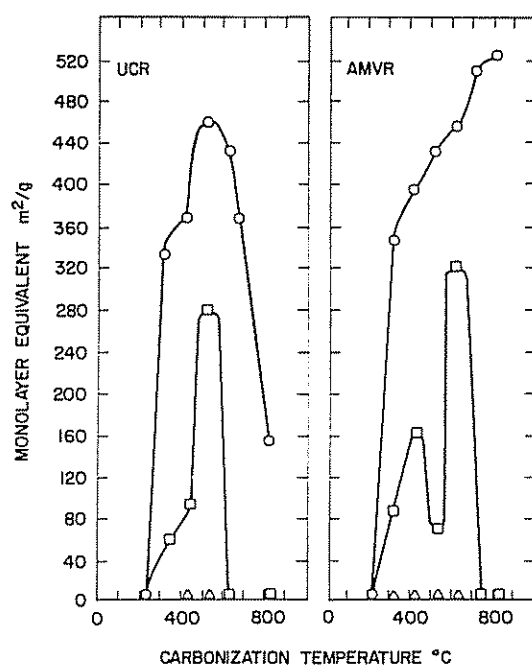


Fig. 6. Change of surface area with carbonization temperature of carbons from as-received UCR and AMVR rayons using carbon dioxide (○), n-butane (□), and iso-butane (△).

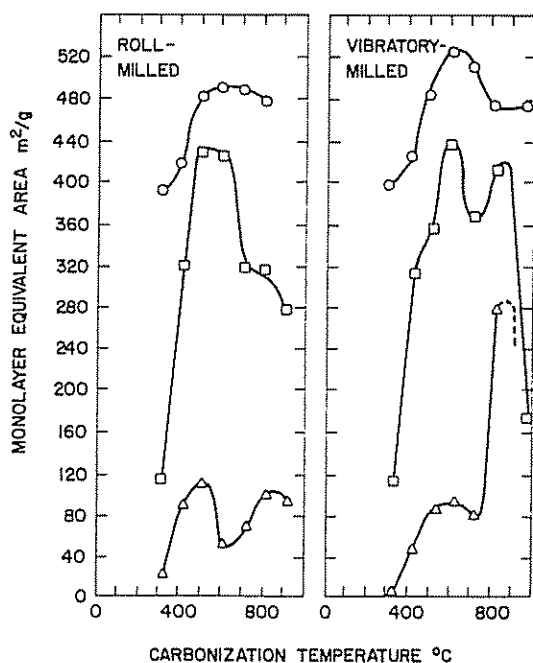


Fig. 7. Change of surface area for milled cellulose carbons with carbonization temperature using carbon dioxide (O), n-butane (□), and iso-butane (Δ).

400°C–630°C. These results emphasize how sensitive uptake of adsorbates on the carbons is to any modification in cellulose pretreatment prior to their pyrolysis.

Grinding of the precursor by a rolling action or

a vibratory action drastically changed the nature of the microporosity in the char derived subsequently from the cellulose powder. Comparison of the curves in Fig. 7 with the results for the unground cellulose powder in Fig. 5 indicates that the iso-butane curve has changed from a simple bell-shaped curve with a maximum at 530°C to a doubly peaked curve. Comparing the surface areas of the 530°C carbons indicated that grinding resulted in a significant decrease in iso-butane adsorption. The decrease in adsorption does not indicate a decrease in available surface area for iso-butane, but a decrease in the rate of adsorption. As indicated in Fig. 8, longer equilibration times resulted in additional adsorption. This effect of equilibration time was observed in all cases when an adsorbate gave a significantly lower surface area than CO<sub>2</sub>.

When the ground materials were exposed to water for 24 hours and then dried, the carbons produced from these materials showed an increase in accessibility. The adsorption curves in Fig. 9 have the same general appearance as the original ground cellulose carbons, but the magnitude of the adsorption was significantly greater. The increased adsorption for the one-hour equilibration times employed indicates a more rapid adsorption, and can be attributed to a larger pore entrance. The slight modification of the precursor crystallinity was the only apparent difference in the starting materials that could have altered the effect of carbonization temperature on the resulting pore structure.

A direct correlation of the iso-butane adsorption results for carbons prepared at 530°C from cellulosic

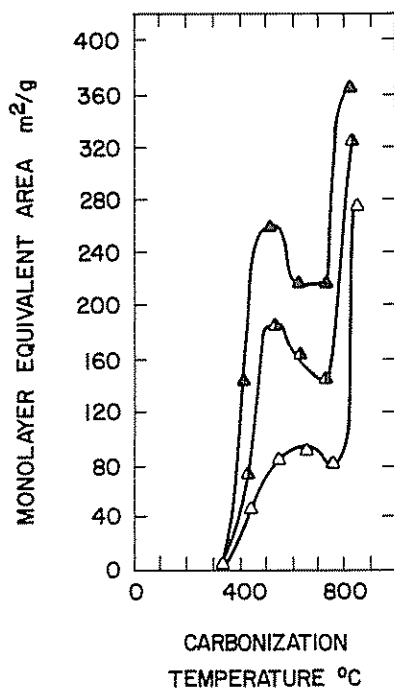


Fig. 8. Change of iso-butane surface area with carbonization temperature for carbons from vibratory-milled cellulose powder at equilibration times of 1 h (Δ), 5 h (▲), and 11 h (▲).

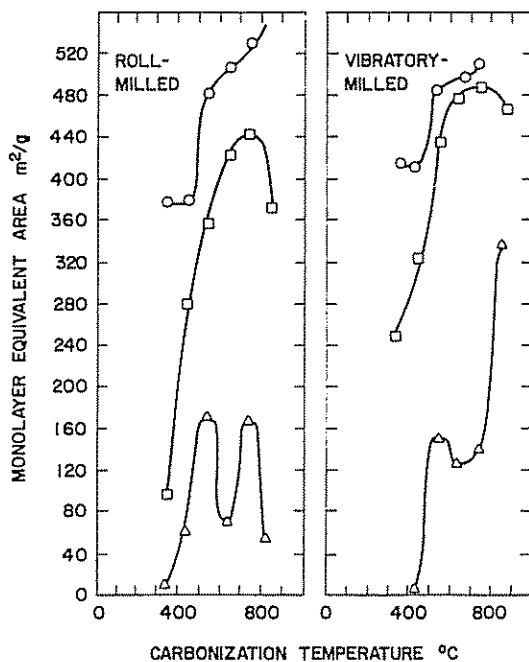


Fig. 9. Change of surface areas with carbonization temperature for carbons from recrystallized roll-milled and vibratory-milled cellulose powders using carbon dioxide (O), n-butane (□), and iso-butane (Δ).

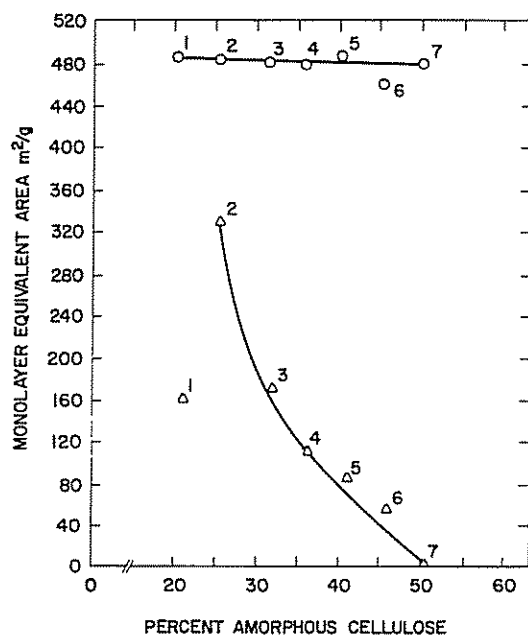


Fig. 10. Effect of precursor crystallinity on surface area of 530°C carbons from RVGCP-O (1), CP-O (2), RGCP-O (3), GCP-O (4), VGCP-O (5), UCR-O (6), AMVR-O (7), using carbon dioxide (○), and iso-butane (Δ).

precursors was obtained with the crystallinity of the precursor, as measured by water adsorption. As discussed previously, water adsorption results were used to calculate the percentage of amorphous cellulose, assuming that 100% amorphous cellulose adsorbs 19.3 wt% water. The decrease in iso-butane adsorption with increasing amorphous content, as shown in Fig. 10, was not accompanied by a significant decrease in CO<sub>2</sub> adsorption. Since the total surface area accessible to CO<sub>2</sub> has not changed, the decrease in iso-butane adsorption must arise from a narrowing of pore constrictions, which limits the rate of diffusion into the pore system. It is also apparent that the amorphous and crystalline material must result in similar specific pore volumes on carbonization, but with different pore constriction sizes.

If common impurities found in natural cellulose had a major effect on the general thermal stability of the pore system or on the effect of heat treatment on the accessibility of the pores, they should be evident in a material such as carbonized raw coconut shell. The adsorption results in Fig. 11 show the typical rise and fall of surface area for coconut shell carbons, as has been found for carbons from rayon, filter paper, and cellulose powder. The same pore closure above 630°C, resulting in exclusion of n-butane and iso-butane, was observed along with the maxima between 430°C and 630°C. From this correspondence in behavior, it appears that the creation of pores and their thermal stability in coconut shells is basically the same as pure cellulose, and unaffected by other components that may be present.

Treatment of Villwyte rayon with ethylenediamine followed by hexane extraction and carbonization produced a carbon whose pore system was less accessible to n-butane than a carbon from untreated rayon. The n-butane monolayer equivalent area for one hour equilibration on a 530°C carbonized material decreased from 411 m<sup>2</sup>/g to 59 m<sup>2</sup>/g. As indicated in Table 6, washing and drying the treated rayon with water prior to carbonization resulted in a carbon whose pores were quite accessible to n-butane; the monolayer equivalent area increased to 368 m<sup>2</sup>/g. When a diamine-treated rayon was Soxhlet extracted for 21 hours with acetone prior to carbonization at 530°C, the one-hour n-butane monolayer equivalent area was 339 m<sup>2</sup>/g. Wetting and drying the rayon prior to carbonization gave a carbon with a n-butane area of 314 m<sup>2</sup>/g. The acetone extraction apparently restored the rayon to its original condition, whereas hexane extraction resulted in a modified material.

### 3.4 Final thoughts

It has been shown that the ability to produce a carbon sieve from cellulosic precursors capable of separating straight chain hydrocarbons (like n-butane) from branched-chain hydrocarbons (like iso-butane) is markedly dependent upon the particular cellulosic precursor selected. A variety of precursors are

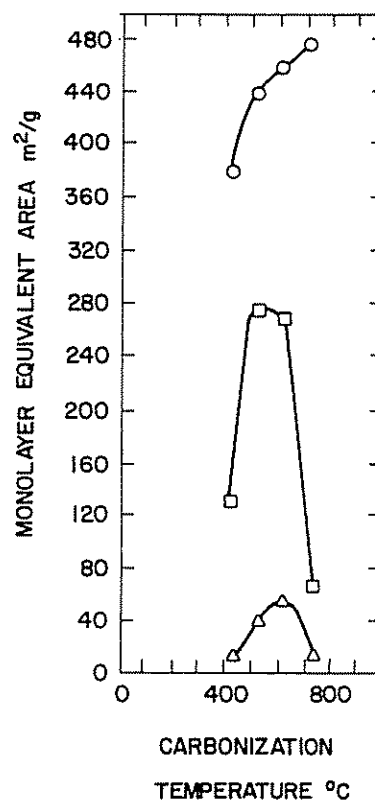


Fig. 11. Change of surface area with carbonization temperature for coconut shell carbons using carbon dioxide (○), n-butane (□), and iso-butane (Δ).



Table 6. Surface areas of 530°C carbons from EDA treated rayon

Sample	Treatment	Monolayer equivalent area (m <sup>2</sup> /g)	
		CO <sub>2</sub>	n-butane
UCR-13	None	455	411
DUCR-1	EDA, hexane wash	380	59
RDUCR-2	Water washed DUCR-1	467	368
DUCR-4	EDA, acetone Soxhlet extracted	408	339
RDUCR-5	Water washed DUCR-4	443	314

available, ranging from regenerated cellulose (viscose) fibers to cellulose powder commonly used in chromatography. It is expected that cellulose molecular orientation is significantly greater in the former precursor. The question is whether this orientation carries over to a similar orientation in the small trigonally bonded carbon crystallites formed upon carbonization. The extent of crystallite alignment will determine the amount of microporosity and its availability in the carbonized cellulose. Bacon and Tang's[22] X-ray orientation studies showed a direct correspondence between cellulose molecular orientation and preferred orientation of the crystallites in the carbonized rayon tire yarn fiber (similar to our AMVR sample). Ruland also studied preferred orientation versus heat treatment temperature for a rayon fiber[26]. He found that preferred orientation in the starting rayon was destroyed with the destruction of the cellulose structure at ~280°C, except for a very slight residual orientation that persisted up to 1000°C. Hence, the importance of cellulose molecular alignment on the character of CMS produced is still an open question. Filaments having varying degrees of molecular orientation can be produced by varying the degree of stretch applied to the cellulose filament during its regeneration in the production of rayon. This should be an important variable to explore in future studies.

It is interesting that carbonized rayon fibers proved to be the preferred precursors for the production of a sieve for n-butane/iso-butane separation. Little surface area was available to iso-butane for fibers prepared between 300°C–800°C, whereas ~300 m<sup>2</sup>/g of surface area was available for n-butane for fibers prepared between 500°C–600°C. By contrast, chars prepared from cellulose powder exhibited large surface areas available to both n-butane and iso-butane upon carbonization at ~550°C.

In addition to the possibility of cellulose molecular alignment being of importance to sieve preparation, it was expected that the extent of amorphous material in the precursor would be of importance. Bacon reports that initial degradation of the cellulose structure occurs in the amorphous regions, and then in the crystalline regions upon pyrolysis[24]. With the exception of sample No. 1, a good correla-

tion is found between iso-butane uptake on 530°C carbons and percentage of amorphous material in a wide variety of precursors, as was seen in Fig. 10.

#### 4. CONCLUSIONS

Cellulosic materials are viable precursors for the production of microporous carbons and, in some cases, molecular sieve carbons for the separation of straight from branched-chain hydrocarbons. Most desirably, the precursor should have a large amorphous content. As the amorphous content approaches 50 wt%, as determined from water adsorption, the uptake of iso-butane in the 530°C carbons becomes negligible. At present, it is not clear whether cellulose molecular orientation plays a role in affecting subsequent sieving properties of carbons produced therefrom.

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