

THE PRODUCTION OF CHARS BY SUPERCRITICAL FLUID EXTRACTION

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ABSTRACT

Novel techniques were explored for developing larger micropore structure in the chars prepared by supercritical fluid extraction of low-rank coals. Extractions were carried out with 2-butanone at various temperatures and pressures above the critical point, and experiments were performed to maintain the high-surface-area char structure as the pressure was released. The temperatures and pressures were then brought down close to the critical point, and then the pressure was released very slowly while keeping the temperature constant. This aerogel method gave higher surface areas than the method in which temperature or pressure was abruptly lowered, but ultraporous materials were not obtained. The introduction of pillaring reagents under supercritical conditions to preserve the expanded pore structure was also attempted. These experiments were again only partially successful in increasing the surface area of the char.

INTRODUCTION

Supercritical fluid extraction (SFE) of volatile material from coal offers an alternative to coal pyrolysis for production of chars. Previous efforts with low-rank coals at the University of North Dakota gave chars with relatively low surface areas. However, x-ray scattering experiments in an aluminum-beryllium high-pressure high-temperature extraction cell showed that very large surface areas ($>2000 \text{ m}^2/\text{g}$) are present during SFE of Wyodak subbituminous coal with an organic solvent, but the pores collapse during the reversion back to subcritical conditions (1).

New techniques were explored to attempt to maintain the ultraporous structure that develops in the low-rank coals under supercritical conditions. Following supercritical solvent extraction of some of the coal material, attempts were made to stabilize the highly porous structure so that it did not undergo the collapse normally observed when the pressure is brought back to ambient. The techniques involve careful release of pressure at the critical point of the solvent as in the preparation of aerogel precursors and introduction of a stabilizing agent under pressure with a high-pressure liquid chromatograph (HPLC) injection device. The stabilizing agents were boron, silicon, and titanium compounds that could decompose to oxide clusters which could pillar the micropore structure.

EXPERIMENTAL

Wyodak (Clovis Point) subbituminous coal, Gascoyne (Knife River) lignite, and Velve lignite were used for the supercritical extractions. These coals were ground to -60-mesh size and dried in an oven at 110°C for several hours. The samples were then stored under argon in plastic containers until used. 2-Butanone and ethanol were used as solvents. Tetraethyl orthosilicate (TEOS), titanium tetraisopropoxide (TIP), and tributyl borate (TBB) were added to the coal to stabilize the micropores generated during extraction.

An HPLC column (Supelco, 250-mm long, 8.5-mm i.d. \times 12.5-mm o.d.) was used for supercritical extraction of coal because it could withstand the high pressure and temperature (up to 2500 psi and 350°C , respectively). The supercritical fluids (2-butanone or ethanol) were introduced into the stainless steel reactor via an ISCO LC-5000 syringe pump (ISCO, Lincoln, NE, USA), an injector (Rheodyne, Cotati, CA, USA), and a 2-m long (1/16-in.-o.d. \times 0.02-in.-i.d.) stainless steel preheating coil. The reactor and the preheating coil were placed inside a gas chromatograph (GC) oven (Varian, Aerograph series 1400 GC) to control the extraction temperature. A fluid flow rate of approximately 1-2 mL/min (measured at the pump) was achieved using a needle valve and a 1-m \times 0.1-mm silica capillary restrictor attached to the outlet of the extraction tube.

The reactor was packed with 5 g of desired coal and placed in the oven. After the extraction apparatus was assembled, the reactor was filled with 5 mL of the solvent under static conditions (no flow out of the cell) while the oven was heated to desired temperature. The dynamic extraction (constant fluid flow) was then started and was continued for the desired time period. The extract was collected in an Erlenmeyer flask placed in a hood. At the end of the extraction, solvent flow was stopped, and residual solvent in the reactor was slowly released (requiring about 10 min.). Thereafter, the oven was cooled to ambient temperature, and the reactor was detached from the extraction line. The residue from the reactor was collected, dried at 110°C , weighed, and analyzed for surface area using American Society for Testing

and Materials (ASTM)-D4607 (iodine number) and by the percent iodine sorption method used by Sutcliffe Corp.

RESULTS AND DISCUSSION

Effects of Process Variables

Supercritical extraction of Wyodak coal with 2-butanone at 350°C (980 psi) for 5 min followed by extraction at 265°C for 25 min (640 psi) gave a char with a relatively low iodine number (IN) of 177 mg/g, when the temperature and pressure were dropped to ambient immediately after the extraction time. This value is just a little higher than that of the original coal (162), and indicates that the pores collapse rather quickly as a result of capillary movement of metaplast material, even at this relatively low temperature. Only 10% of the coal was extracted or volatilized in the experiment. The experiment performed under similar conditions, but with a very slow pressure release at constant temperature (265°C), gave a char with significantly higher area (IN = 243), although the amount of material extracted was about the same (8%). Further improvements in the surface area were obtained by increasing the initial extraction period at 350°C to 20 and 40 min before dropping the temperature and pressure to 265°C and 640 psi. By maintaining the temperature while slowly releasing the pressure, chars with INs of 267 and 309, respectively, were obtained, and extraction yields of 12% for both runs were obtained. The 30-min extraction at 350°C (1000 psi) followed by slow pressure release at 265°C gave a char with an intermediate surface area (IN = 283) and the same yield of 12%. Thus, the surface area appears to be directly related to the extraction time at 350°C, but the time at 265°C prior to slow pressure reduction may not be important. At a somewhat higher pressure (1250 psi) and higher solvent flow rate (2 mL/min), the 350°C, 30-min experiment gave a higher extraction (16%), but a lower area (IN = 254) was obtained. Although SFE yields are usually greater at the higher pressures (1), the surface area generated in the char is not directly related to the extract yield.

Experiments conducted with Gascoyne lignite gave chars with generally higher surface areas than those from the Wyodak subbituminous coal. When Gascoyne was extracted for 30 min at 350°C and subjected to rapidly decreasing temperature and pressure, the resulting char had an IN of 256. The corresponding experiment at 350°C (1250 psi) with slow pressure release gave a char with the IN = 361 and a similar extraction yield (12%). Increasing the pressure during the extraction (2500 psi) gave a higher extraction as expected (19%), and the IN of the char was again lower (301).

Another solvent, ethanol, was also investigated. Extraction with ethanol at 350°C (1500 psi) with slow pressure release gave a low extraction (8%) and a low surface area (IN = 137). Previous work demonstrated that the char surface is highly alkylated during SFE in alcohol (2). The alkylated metaplast may have a lower viscosity and undergo more extensive collapse.

A trial with the high-calcium Velve lignite gave a lower-area char (IN = 323) than the Gascoyne lignite under similar conditions (350°C, 1250 psi), although a higher extraction yield was obtained (25%). This could be attributed to increased solubility of the decomposing coal materials (metaplast) because of calcium-catalyzed decarboxylation. Normally, only partial decarboxylation occurs at 350°C.

Effects of Pillaring Additives

To stabilize the high surface areas that develop during SFE, solutions of various alkoxides were introduced under supercritical conditions following the extraction. It was anticipated that the alkoxides would decompose on the coal surface to form metal oxide clusters that would serve as stabilizing pillars to keep the pores from collapsing. Three of these organometallic agents were investigated for their effects in modifying the porosity of the supercritical chars.

Addition of TEOS to char produced by SFE of Wyodak coal at 350°C for 5 min (1050 psi) gave a modified char with a higher surface area (IN = 293) than that produced without the TEOS (IN = 243). Titanium isopropoxide addition under the same conditions gave a slightly lower area char (IN = 238). Addition of TEOS to the char obtained by extraction of Wyodak at 350°C for 20 min also gave a modified char with higher area (IN = 281), but this showed less of an increase. When less TEOS (1/3 of the previous amounts) was added to the 20-min SFE char, the increase in area was greater (IN = 297). When TEOS and TIP were added to Wyodak extracted for 30 min, the INs were similar to those for the 20-min runs. Addition of TBB to the 30-min char gave a significantly higher area char (IN = 328).

Similar experiments with Gascoyne lignite were inexplicably not effective in promoting the surface area and, instead, decreased it substantially. Tributyl borate gave a char with IN = 266, compared with the original at IN = 361. Addition of a thiol to capture radicals generated during thermal reactions of the coal also gave a low-area char.

The chars produced by this treatment still contain substantial amounts of coal "volatile" material that can be released by further heating at higher temperatures. Devolatilization of the supercritical chars at 750°C and 30 min gave carbons with very low surface areas, however.

CONCLUSIONS

Several modified chars were prepared by SFE of low-rank coals to develop a large micropore structure. Pressure was released slowly at the supercritical temperature to maintain a more porous structure. Tetraethylorthosilicate, titanium isopropoxide, and tributyl borate were introduced under the supercritical conditions to attempt to stabilize the micropore structure by forming pillaring clusters.

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Table 1. Extractions of Wyodak

Coal	Yield, % ¹	Solvent	Reaction Conditions				PD ²	IN
			Flow, mL/min	Temp., °C	Time, min	Pressure, psi		
Wyodak	10	2-Bu ³	1	350	5	980	Fast	177
				265	25	640		
Wyodak	8	2-Bu	1	350	5	920	Slow	243
				265	25	620		
Wyodak	12	2-Bu	1	350	20	980	Slow	267
				365	10	630		
Wyodak	12	2-Bu	1	350	40	1000	Slow	309
				365	20	640		
Wyodak	16.2	2-Bu	2	350	30	1250	Slow	254
Wyodak	8	EtOH ⁴	1	246	30	1000	Fast	137

¹ Extraction wt. coal (mf) - wt. char (mf)/wt. coal (mf) × 100. mf refers to moisture free.

² Pressure drop.

³ 2-Butanone.

⁴ Ethanol.

Table 2. Extractions of Gascoyne

Coal	Yield, % ¹	Solvent	Reaction Conditions				PD ²	IN
			Flow, mL/min	Temp., °C	Time, min	Pressure, psi		
Gascoyne	13.5	2-Bu ³	1	350	30	1250	Fast	256
Gascoyne	13.2	EtOH ⁴	1	350	30	1500	Slow	280
Gascoyne	11.6	2-Bu	1	350	30	1250	Slow	361
Gascoyne	19.3	2-Bu	1	350	30	2500	Slow	301

¹ Extraction wt. coal (mf) - wt. char (mf)/wt. coal (mf) × 100. mf refers to moisture free.

² Pressure drop.

³ 2-Butanone.

⁴ Ethanol.

Table 3. Extractions of Wyodak with Stabilizer Addition¹

Coal	Yield, %	Conditions				IN
		Temp., °C	Time, min	Pressure, psi	Additive (μL)	
Wyodak	8	350	5	920	None	243
		265	25	620		
Wyodak	13.4	350	5	1050	TEOS (300)	293
		265	25	620		
Wyodak	8	350	5	920	TIP (300)	238
		265	25	650		
Wyodak	12	350	20	980	None	267
		265	10	630		
Wyodak	12	350	20	1000	TEOS (300)	281
		265	10	620		
Wyodak	12	350	20	980	TEOS (300)	297
		265	10	640		
Wyodak	12.5	350	30	1000	None	283
Wyodak	13	350	30	1000	TEOS	299
				500		
Wyodak	13.8	350	300	1200	TIP	281
Wyodak	9	350	30	1250	TBB	328

¹ Solvent = 2-butanone, flow rate = 1 mL/min, pressure drop = slow.

Table 4. Extractions of Gascoyne with Stabilizer Added¹

Coal	Extraction, %	Reaction Conditions				IN
		Temp., °C	Time, min	Pressure, psi	Additive (μL)	
Gascoyne	11.6	350	30	1250	None	361
Gascoyne	14.4	350	30	1250	TBB (300)	266
Gascoyne	10.2	350	30	1250	<i>p</i> -Thiocresol (300)	259

¹ Solvent = methylethyl ketone, flow rate = 1 mL/min.