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(DE96000622)

Development of an Advanced, Continuous Mild Gasification Process for the Production of Co-Products

Quarterly Report
April - June 1995

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Work Performed Under Contract No.: DE-AC21-87MC24116

For
U.S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Morgantown, West Virginia

By
Coal Technology Research Corporation
Bristol, Tennessee

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103 Thomas Road
Bristol, Tennessee 24201

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EXECUTIVE SUMMARY

Two tons of CTC/DOE continuous coke of 6" x 5" x 4" size was produced in the Pilot Demonstration Unit. This coke was tested under actual foundry conditions in a 96" diameter commercial cupola. The test was run on the first shift on April 19, 1995. The coke sample was used as a direct replacement for 25 percent of the coke charge. A total of 51 scrap iron charges were run with the CTC/DOE continuous coke. Results of the test were excellent. The two main indicators improved. Tap temperature increased from an average of 2846°F to 2890°F. Carbon pickup improved from 3.49 percent C to 3.59 percent C when the CTC coke hit the bed. These results are very meaningful because they cannot be measured in the lab.

This test is significant because it proves CTC/DOE coke will replace conventional coke in a working commercial cupola. Further testing is planned with a larger sample which will be run and tested next quarter. This test will be longer and may use a percentage of CTC/DOE coke of 50 percent.

In parallel with the foundry cupola test, a sample of CTC/DOE continuous coke was sent to the Energy & Environmental Research Center at the University of North Dakota. This sample was compared to conventional coke as well as other formed coke from around the world. The coke was tested for chemical and physical qualities. A composite of all this testing indicates that CTC/DOE continuous coke is acceptable and could be a direct replacement for conventional coke.

Work on making acceptable metallurgical grade coke from weakly coking coal was explored. A test matrix using nine raw material compositions and heating profiles was conducted and analyzed. The results do not as yet meet the requirements of metallurgical coke but are promising. Work will continue next quarter on making coke from weakly coking coals.

ChemChar Research, Inc. in Columbia, Missouri, is evaluating CTC chars as potential agents for removing pollutants from gas streams. Composite CTC char treated with the ChemChar activation process resulted in promising results. A 11.8 percent toluene adsorption and 13.4 percent monochlorobenzene adsorption were achieved with CTC char after activation. Additional studies that demonstrate similar degrees of activation achieved under simple and inexpensive process conditions would be very encouraging.

INTRODUCTION

Work on this contract began on October 1, 1987. In the elapsed time since inception of this work, there have been 34 changes of scope, amendments and modifications to the original contract. From start to finish of this contract, the objective of this research and development effort was to develop an advanced, continuous "mild gasification" process. The relative quantities and properties of the products are appropriate for making the concept economically and environmentally viable. In "mild gasification," coal is converted under relatively mild conditions of temperature and pressure in the absence of air into products which include a high heating value gas, high aromatic condensibles, char and coke all with physical and chemical properties suitable for the anticipated end uses.

The program moved forward with four specific tasks: Task 1 was a literature survey of mild gasification processes and product upgrading methods and also a market assessment of markets for mild gasification products. Based on the literature survey, a mild gasification process and char upgrading method was identified for further development. Task 2 was a bench–scale investigation of mild gasification to generate design data for a larger scale reactor. Task 3 was a bench–scale study of char upgrading to value added products. Task 4 was implemented by building and operating a 1000–pound per hour demonstration facility. Task 4 also included technical and economic evaluations based on the performance of the mild gasification demonstration facility.

By June 1994 the experimental work on the 1000 pound per hour demonstration facility was essentially complete. The unit became highly useful for testing the performance of different types of coal from time to time. At this same time, the contract was modified to provide for the design, construction, and operation of a continuous cokemaking facility. This was termed Task 5 in December 1994. Construction and shake–down of the continuous coke plant was completed in early 1995. A one ton quantity of coke was produced and was successfully tested in a 24" diameter cupola in Alabama. Later another one ton test of foundry size coke 4"x5"x6" was successfully completed in a major commercial foundry in Virginia. At the present time (August 1995), larger quantities are being produced for further foundry testing. Several steel companies have expressed interest in testing relatively large quantities of CTC/CLC® coke in their blast furnaces.

From the very start of this work until now, the objective at all times was to develop a continuous commercial coke process. A proposal was submitted in Clean Coal IV and another in Clean Coal V in hopes that Department of Energy funding would be obtained for the building of a larger demonstration plant. That hope was not realized. For almost a year and a half, intensive efforts have been undertaken to privately finance a plant to be built at West Virginia. This effort is now close to realization.

A paper was presented in the Clean Coal Conference in Pittsburgh in September 1994 which described the CTC/CLC® process. The paper attracted much interest and opened some doors. This contains an accurate summary of this work up to that time.

TASK 5: CONTINUOUS BRIQUETTING AND COKING

Objective

The objectives of Task 5.1 are to design and construct a 1000 lbs/hour continuous briquetting and coking facility interfaced to the existing twin screw reactors.

In Task 5.2, the facility will be operated at steady state to produce coke for actual testing by industry.

Summary

The design of the facility was done by CTC personnel with a small amount of outside help used only as needed. The basic plan was to use equipment available at CTC and used equipment was purchased wherever possible. The equipment installation was done by CTC personnel with a minimum of outside contractor help.

TASK 5.2: STEADY STATE TEST OF CONTINUOUS FORMED COKE PILOT PLANT

Work focused on preparing and testing a formed coke sample at a working commercial foundry. This foundry produces castings for many industries including the automotive industry. The test went well and was successful.

The test was run on first shift on April 19, 1995. The coke sample was used as a direct replacement for 25 percent of the coke charge in a 96" diameter cupola. Testing started at 8:00 a.m. and was completed at 10:20 a.m. A total of 51 gray iron charges were run with the CTC continuous coke. Results for the test were excellent. The two main indicators improved. Tap temperature increased from an average of 2846°F to 2890°F. Carbon pickup improved from 3.49 percent C to 3.59 percent C when the CTC coke hit the bed. These results are very meaningful because they can't be measured in the lab.

This test is significant because it proves CTC coke will replace conventional coke in a working commercial cupola. Further testing is planned with a 20 ton sample which will be started on next month. The 20 tons will allow a 24 hour test using 50 percent CTC coke, one full day of gray iron production. This full day test will further prove acceptance of the CTC continuous coke and further reduce risk for investors in a commercial plant.

In parallel with the foundry cupola test a sample of CTC continuous coke was sent to the Energy & Environmental Research Center at the University of North Dakota. This sample was compared to conventional coke as well as other formed coke from around the world. The coke was tested for chemical and physical characteristics:

Ultimate composition
Proximate composition
Heating value
High–temperature ash (HTA) composition
Ash fusion temperatures
Apparent specific gravity
True specific gravity
Total pore volume
Surface area
Reactivity
Strength after reaction
Tensile strength
ASTM drop shatter
ASTM stability
ASTM hardness

A composite of all this testing indicates that CTC continuous coke is acceptable and could be a direct replacement for conventional coke.

Process enhancement continued in April. Lifters were installed in the cold portion of the calciner. These lifters will cause the briquettes to move through the cold sections of the calciner tubes quickly. It was decided to add the pitch to the raw material mix at the mixer instead of before the raw material mixture was heated. The pitch in the mix caused a build up in the heating screw and stalled the screw rotation. With the pitch added after heating this build up will be eliminated.

Refinements to the continuous coke PDU continued last quarter. A grate platform was fabricated to allow the coke feed into the calciner to be monitored. This area is a nuisance area and it was difficult to safely monitor the green coke feed. In the same area a fume and gas vent and fan were installed. This system will put a very slight negative pressure on the calciner. Small gas leaks will leak into rather than out off the calciner. These fumes that are collected are diverted to the flue gas stack where they burn. Local start / stop controls were added to the kiln, calciner, bucket conveyor and briquetter. Controls in the central control room are still operative but additional local control is necessary. Spray nozzles were added above the metal quench tank conveyor. Cracking of briquettes is a problem, the thermal shock of dropping a 2000°F briquette into water would contribute to cracking somewhat. It is planned to compare briquettes dropped into a quench tank with briquettes sprayed with water. The data learned from this analysis will be applied to the cooling system in a commercial plant as well as the cooling system in the PDU.

A feed screw was installed and the volumetric screw feeder reactivated to allow the pitch to be introduced into the mixer separately. As previously discussed, with the pitch heated along with the other raw materials it built up in the heating screw and caused it

to stall. With the pitch introduce in the mixer the other raw materials can be heated with no build up. This modification will greatly improve reliability of the raw material feed system.

The laboratory coking furnace was redesigned and rebuilt last quarter. The previous heating elements "Starbars" (silicon carbide) were never intended to be used in an atmosphere contaminated with hydrocarbon volatiles and carbon. In fact that was a fatal error. Starbars are electrically live on the surface. If carbon is allowed to deposit on the surface it will electrically short that portion of the hot zone. The remaining part of the hot zone can be over heated because of the additional watt loading. This carbon also caused electrical shorting from phase to phase and phase to ground. This will thermally stress the Starbars and cause failure. In this application the Starbars always are exposed to carbon. One suggestion was to operate the Starbars in a oxidizing atmosphere and burn the carbon off rather than short the Starbars. This couldn't be done because the oxygen would also burn the briquettes. The very high maintenance caused several problems. First the direct cost, the Starbars cost $120 each. Expenditure for replacement Starbars in 1994 was over $4,000. The maintenance was always untimely. Many times before coke testing could be done the furnace would have to be disassembled, repaired, and reassembled. The third problem with this high maintenance was long lead time on the Starbars, four weeks. Efforts were made to keep a reasonable replacement quantity of Starbars but when a spike in repairs were required sometimes the coking program would be halted until replacement Starbars were received.

With the prior design of the lab coke furnace all the heat was from the top. Data acquired and expertise derived from the lab coke furnace was hard to apply to a continuous commercial furnace. Most potential commercial coke furnaces heated from all sides or rabbled the coke product so that in one way or another the coke was heated from all sides. Also, the long ramp times of the furnace and long heat history of the briquettes were hard to relate to a continuous commercial furnace. The time spent ramping up to soak temperature steps is difficult to incorporate into a furnace that runs at a continuous temperature.

For the reasons stated above it was decided to redesign and rebuild the coke furnace. The heating elements chosen were Watlow AOV Multicell Heaters. These heaters are encased in a inconel sheath. This will eliminate any problems with a contaminated atmosphere. Since the surface of the element does not conduct electricity contact with carbon will have no effect. Also, the inconel sheath makes the element reasonably durable. The Starbars were very fragile. The furnace was redesigned to allow heating from both under and over the coke. This will make the heat much more uniform and shorten the required coking time as well as be closer to what a commercial continuous furnace would be. The new heating system has a power capacity of over 30 KW, the old system had a power capacity of 21 KW. This power increase will shorten ramp times and allow the study of how ramp times relate to total heat history. Shorter ramp

times will also be closer to what to expect in a continuous commercial coke furnace.

In May more work was done with a steel producer to make coke from western non–coking coal and with mildly caking coal. The study is focused on changing isotropic carbon to anisotropic carbon by treating the non–coking coal with petroleum pitch. If the carbon form can be changed it would make the coke less reactive. Also, work is being done on blending Western and Eastern coals before char is made. Both of these theories have shown some success but need more study.

TASK 5.5: ENVIRONMENTAL EMISSION REDUCTION STUDIES

ChemChar Research, Inc. located in Columbia, Missouri, is evaluating CTC chars as potential agents for removing pollutants from gas streams. A summary of the initial work taken from the May 1995 report is included below.

Adsorption of Toluene, Chlorobenzene, and Sulfur Dioxide

The char samples examined were those provided by CTC; those prepared by ChemChar cocurrent flow gasification of Rosebud subbituminous coal from Hanna, Wyoming; and Darco®, a commercial activated carbon. The char samples were taken as received and ground to obtain sample sizes in the range of 60–20 mesh (250 μm – 850 μm). The samples were then placed in an oven at 120°C for at least one hour to facilitate the removal of moisture. After being heated in the oven the samples were removed and placed in a desiccator to cool.

Adsorption of Toluene and Chlorobenzene

The adsorption of both toluene and benzene by the chars was examined. These compounds were chosen because toluene is a typical, environmentally important aryl hydrocarbon and chlorobenzene is an important aryl halide (organohalide compound).

For measurement of toluene and chlorobenzene adsorption, the dried samples were first carefully weighed and placed in a drying tube. Nitrogen gas was passed over the samples for a thirty minute period to allow any fine char dust to be removed prior to adsorption analysis. The drying tube and its char sample contents were then weighed, and toluene vapors contained in a gaseous nitrogen stream were passed over the sample for an additional thirty minute period. The apparatus used for the studies is shown in Figure 1.

Adsorption of Sulfur Dioxide

The adsorption of sulfur dioxide was performed by quantitatively producing SO_2 gas and flushing the gas over the char using nitrogen as a carrier gas. The set–up for this procedure is shown in Figure 2.

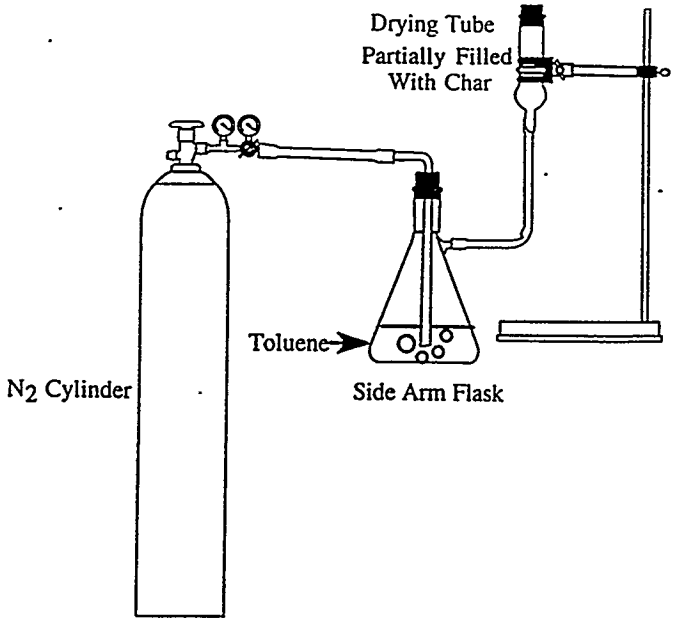

Figure 1. Apparatus for measurement of sorption of organic vapors by char.

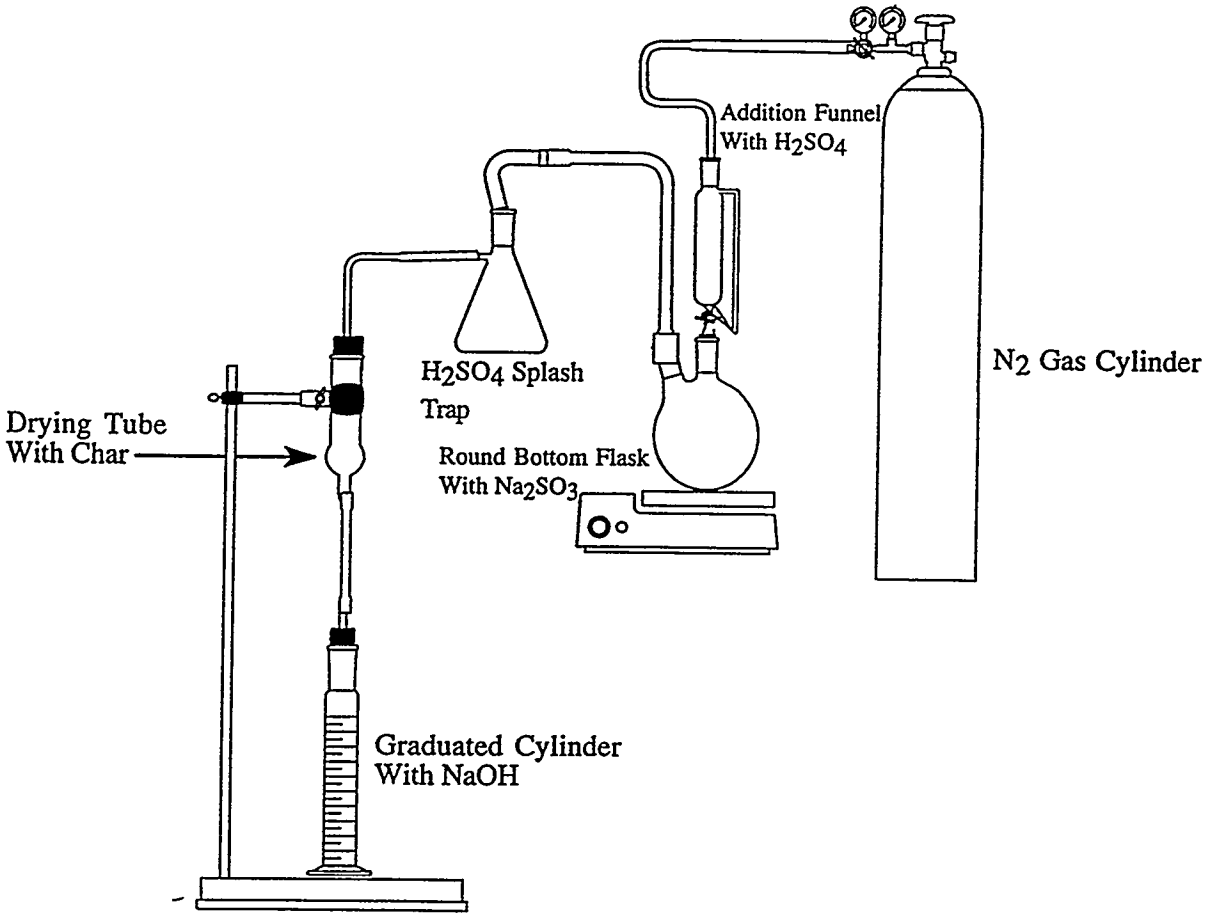

Figure 2. Apparatus for measurement of adsorption of sulfur dioxide by char.

The production of sulfur dioxide in the laboratory was carried out by the reaction of sodium sulfite with sulfuric acid.

$$Na_2SO_3 + H_2SO_4 \rightarrow SO_2(g) + Na_2SO_4 + H_2O$$

In this procedure, the sulfuric acid is added to a weighed amount of sodium sulfite and allowed to react. As the gas is produced it is carried through the char by a stream of nitrogen carrier gas. The sulfur dioxide that is not retained by the char is collected in a sodium hydroxide solution. The reaction and sulfur dioxide collection are allowed to continue for a one hour period of time.

At the end of the one hour time period the sodium hydroxide solution was titrated with a standard HCl solution.
The initial sulfur dioxide studies showed that the CTC char did not absorb sulfur dioxide, so NaOH was added to the char at a level of 5% by wight to increase the SO_2 adsorption.

Results of Char Adsorption Studies

The results of the adsorption studies by various kinds of char are summarized in Table 1 for sorption of organics and in Table 2 for sorption of sulfur dioxide. The weight of sulfur dioxide sorbed by char was calculated from the amount of sulfur dioxide collected in base. Values are reported as weight percentages calculated as follows:

$$\text{Weight percent} = \frac{\text{Weight gained}}{\text{Weight of char}} \times 100$$

Table 1. Sorption of Toluene and Monochlorobenzene by Various Kinds of Char

Char[1]	Percent Sorption Toluene[2]	Percent Sorption Monochlorobenzene[2]
Iaeger, WV	0.094	0.226
Iaeger, WV, 20–8 mesh	0.030	Not Run
Skyline, UT	0.381	0.180
Soldier Creek, UT	0.298	0.169
Southern, UT	0.090	0.156
Sunny Vale, UT	0.257	0.145
Composite CTC Char[3]	0.00	Not Run
Activated CTC Char[4]	11.8, 10.3(1), 10.3(2)	13.4
TRB Stock Char[5]	0.90	Not Run
Activated TRB Char[6]	8.9, 11.6, 15.0, 16.6, 17.2	Not Run
Darco® Activated Carbon	11.9	Not Run

[1]60–20 mesh size unless otherwise designated.

[2]Percent weight gain by char after exposure to organic vapor.

[3]A composite sample of CTC pyrolysis char of unspecified origin.

[4]Composite CTC char freshly gasified by the ChemChar process under activation conditions. The value of 11.8% toluene sorption was obtained within 2 hours of activation; the value of 10.3% designated (1) was obtained 18 hours after activation, and the value of 10.3% designated (2) was from the identical sample equilibrated for an additional 30 min with toluene vapor, showing no additional uptake of toluene; the monochlorobenzene sorption value of 13.4% was obtained on the char 18 hours after activation.

[5]Aged sample of char prepared by three successive gasification runs on Hanna, WY, subbituminous coal with the ChemChar process, designated TRB char.

[6]TRB char freshly gasified by the ChemChar process under activation conditions.

Table 2. Sorption of Sulfur Dioxide by Char

Char	Char as Received	Char Treated with NaOH	Char Treated with NaOH and Gasified
Iaeger, WV	0.033	9.43	0.016
Skyline, UT	0.201	Not Determined	Not Determined
TRB Char	4.73	Not Determined	Not Determined

Discussion and Conclusions from Char Adsorption Studies

The untreated CTC pyrolysis chars exhibit values of a few tenths of a percent less for sorption of toluene and monochlorobenzene. These low values are expected for an unactivated pyrolysis char. It should be noted that aged TRB char is only marginally better than the untreated pyrolysis chars at sorbing toluene, and that gasification of TRB char under activation conditions is necessary to give it a high sorptive ability, ranging from 8.9% to 17.2% of toluene as shown in Table 1. Cocurrent flow gasification of composite CTC pyrolysis char provided a product with good sorptive properties, with values of 11.8% and 10.3% of toluene as shown in Table 1. These values compare favorably to the value of 11.9% by weight toluene obtained with Darco® activated carbon. Demonstration by additional studies that similar degrees of activation can be achieved on other kinds of pyrolysis char by cocurrent flow gasification under conditions of activation would be very encouraging with respect to the possibility of preparing a good activated carbon from pyrolysis char with a simple and inexpensive process. Such studies are currently underway.

As shown in Table 2, untreated CTC pyrolysis char has little tendency to sorb sulfur dioxide. Impregnating the char with NaOH gave an excellent high value of 9.43% for SO_2 sorption, whereas char impregnated with NaOH, then subjected to cocurrent flow gasification, took up only negligible quantities of SO_2. These results appear to be somewhat inconsistent, and additional studies of SO_2 sorption are being underway.

Electron Micrograph Profiles

The CTC pyrolysis chars were examined by electron microscopy to provide information about the char morphology, particularly the abundance and size of micropores in the char. The procedures and results are presented below.

Sample Preparation

The samples were prepared by randomly picking char pieces and placing these pieces on a sample stage covered with double–sided carbon tape. The samples were then coated with 300 Å of gold to prevent charging of the char surface by the electron beam. The samples were then placed into the analysis chamber and the chamber was pumped down to 10^{-5} mbar.

Instrument Parameters

Accelerating Voltage: 20KeV
Tilt: 45°
Detector: Everheart–Thornley

Results of Electron Micrograph Studies

The attached photomicrographs are of the five CTC chars at magnifications of 20X, 200X and 5000X. At 20X it is seen that the surface porosity varies significantly from one piece of char to the next. At 200X the macroporous nature of the char can be clearly seen, and this magnification was used to compare the pore sizes of the chars as shown in Table 3. The average pore sizes for the Skyline, Soldier Creek, West Virginia and Sunny Vail chars were determined to be 27.7, 23.3, 28.2, and 24.9 μm respectively. The pore size for the Southern Utah char was not determined because of the nonporous surface. At 5000X the char surfaces appeared smooth so that no pores were visible. At this magnification, the pores were too large to appear individually, and the electron micrographs show only the apparently smooth walls of the char pore surfaces.

A photomicrograph of TRB char was also taken at 1000X. The average TRB pore size determined from this photomicrograph was 6.35 μm.

Table 2. Macropore Size of Various Chars (micrometers)

Sample[1]	Skyline	Soldier Creek	West Virginia	Southern Utah	Sunny Vail	TRB
1	5.6	18.7	50.5	—	13.1	11.5
2	31.8	93.5	35.5	—	46.7	6.0
3	13.1	18.7	24.3	—	26.2	6.5
4	46.7	11.2	46.7	—	28.0	2.5
5	41.1	13.01	37.4	—	41.1	6.0
6	18.7	9.4	9.4	—	11.2	11.0
7	9.4	18.7	16.8	—	9.4	3.5
8	3.7	15.0	28.0	—	44.9	4.5
9	93.5	13.1	26.2	—	9.4	5.0
10	13.1	22.4	7.5	—	18.7	7.0
Average	27.7	23.3	28.2	—	24.9	6.34

[1]Ten pores were selected randomly from each electron micrograph and measured at their longest dimension.

Discussion and Conclusions from Electron Micrograph Studies

Electron microscopy does not have sufficient resolution to show the micropores that are involved with sorption of species at the molecular level, but it does reveal information about the size and abundance of larger macropores.

One of the CTC pyrolysis chars, the Southern Utah char, was atypical in that it did not have a significant population of macropores. The other four samples of CTC pyrolysis chars showed a high population of relatively large pores of about 25 μm in size. These pore sizes are significantly larger than those of TRB char, which showed an average pore size of about 6 μm. The pore sizes and populations of the CTC pyrolysis chars other than the Southern Utah char would indicate that these chars should be suitable as a physical treatment medium for wastes, such as for the bulk uptake of sludges and oils. The larger sizes of the pores in the CTC pyrolysis chars are consistent with the absence of very small pores characteristic of activated carbons. Additional electron micrographs will be taken of CTC chars activated by cocurrent flow gasification to see if gasification increases the population of relatively small pores.