Task 5.10 - Value-Added Coproducts

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TABLE OF CONTENTS

LIST OF FIGURES	ii
LIST OF TABLES	ii
1.0 INTRODUCTION	2
2.0 OBJECTIVES	2
3.0 Accomplishments	2
3.1 Steam Activation	2
3.2 Thermal Activation	3
3.3 KOH Activation	3
3.4 Evaluation of CCV KOH-Treated Lignite as Gasoline Vapor Control Sorbent	3
4.0 FUTURE WORK	7
5.0 REFERENCES	7

LIST OF FIGURES

1	Sorbent test system	5
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LIST OF TABLES

1	Commercial Sorbent	5
---	--------------------------	---

TASK 5.10 - VALUE-ADDED COPRODUCTS

1.0 INTRODUCTION

Future economic growth in the coal industry can be realized with little growth in tonnage by recognizing the importance of coal as a versatile raw material. Research focused on end-use products is needed to integrate value-added coproducts with power generation (the coal refinery concept) and to reduce escalating waste disposal costs by developing profit centers from recycling. Substantial public benefits can be derived from by-products utilization through conservation of energy and resources, reduction in gaseous emissions, and prevention of solid waste pollution. Continued research on carbon products under the base Cooperative Agreement addresses the central question of whether uniquely cost-effective activated carbons can be produced by taking advantage of the inherently porous and reactive structure of low-rank coals (LRCs).

Carbon products will be evaluated in reference to their potential use in air toxics control and other applications.

The Energy & Environmental Research Center (EERC) designated value-added carbon as a product line, with the goal of developing superior carbon products at competitive prices for a range of applications, including SO_x/NO_x /air toxics adsorption, wastewater treatment, molecular sieves, catalyst supports, metallurgical and foundry carbons, and clean-burning solid fuels using EERC processes previously developed under the U.S. Department of Energy (DOE) Mild Gasification program. The approach to be used in meeting specifications for marketable activated carbon products is to develop a fundamental understanding of the extent and quality of the porous surface needed to achieve rapid, high-capacity adsorption of pollutant gases or toxic metals and the processing conditions needed to transform coal and other raw materials into products possessing these superior properties.

2.0 OBJECTIVES

The goal of this product line is to develop superior carbon products at competitive prices for a range of applications, as listed above. The approach that the EERC will use in meeting specifications for marketable carbon products will be to develop a more fundamental understanding of the carbon properties that are required to achieve superior performance in various applications.

3.0 ACCOMPLISHMENTS

3.1 Steam Activation

Initial work in the char development project (4354) and earlier work at the EERC and elsewhere showed that chars and activated carbons from North Dakota lignite and subbituminous coals gave mediocre to poor iodine values. To complete this survey of coals, the carbonization and steam activation (750°C for 30 min) of Velva lignite was performed. This lignite has a somewhat different mineral content that leaves a soft ash. The iodine number for the 400°C char was 267, which was similar to that found for other lignite chars, such as Gascoyne (283). The iodine number

for the activated carbon was lower (252), as expected for high-ash coals. The lower area for the activated carbon is attributed to excessive burnout of the coal catalyzed by the high calcium content associated with the organic structure. As with other high-ash coals, it is unlikely that activation for longer periods would increase the area.

3.2 Thermal Activation

Thermal activation at higher temperatures (900°C) in an inert atmosphere was explored for several chars prepared at the EERC. The 400° char prepared from acid-washed Gascoyne lignite was heated in a nitrogen stream at 900°C. The iodine number for the resulting carbon decreased to 119. A char prepared from an acid-washed Spring Creek subbituminous coal gave an iodine number of only 86. It is clear that even these low-ash carbons from the low-rank coals cannot withstand the higher temperatures without excessive gasification.

3.3 KOH Activation

The effects of inorganic materials on carbonization/activation were investigated for the high temperature range using several potassium and sodium salts, mainly KOH. A rotating kiln was constructed, and several experiments with Gascoyne lignite in KOH gave carbons with rather low areas. The problem appeared to be that the tars coming off the coal were carbonizing in the upper part of the tube and forming a low-area carbon black, which subsequently mixed with the coal in contact with the KOH. Iodine numbers ranging from 200 to 700 were obtained. Plugging of the reactor also occurred. A tube was assembled that could be stirred at 900°C by a mechanical stirrer.

Utilizing the stirred high-temperature reactor, several coals were activated with varying amounts of KOH. Three methods were used to prepare the Gascoyne coal-KOH mixtures. In the Australian method, the coal is treated with aqueous KOH solution to form a paste, which is then dried (1). In the second method, the powdered coal is simply mixed with the powdered KOH. Finally, the dried paste was mixed with additional powdered KOH. The paste method gave the lowest iodine number (302). The powder mix with a ratio of KOH/coal = 3 gave 930; the ratio = 4 gave 708, and the ratio = 2 gave 628. A repetition of the ratio = 3, but without stirring above 850°C, gave 1105. The combined paste powder method gave 636. Acid-cleaned Gascoyne gave 1033 in the powder method and 719 in the paste-powder method. The conclusions from the Gascoyne-KOH activation experiments are that the powder method results in higher surface areas, and the resulting carbons are very good but not ultraporous carbons.

Other coals also gave high-surface carbons: Beluga subbituminous gave 858, and Spring Creek subbituminous gave 949. It was not possible to stir the NaOH mixture, and K_2HPO_4 also did not work. Further work with KOH-coal mixtures in an unstirred reactor is in progress.

3.4 Evaluation of CCV KOH-Treated Lignite as Gasoline Vapor Control Sorbent

Testing was performed to compare Coal Corporation of Victoria (CCV)-prepared sorbent with sorbent removed from a canister purchased from an auto parts store (specified for use in a 1994 Ford) on the basis of modified gasoline working capacity (GWC). GWC is the capacity of a used canister (one that has been through several load-and-purge cycles) in grams of gasoline vapor adsorbed per unit volume of canister sorbent. GWC is a more valid indication of real-world sorbent performance

than the total amount of vapor that a fresh (brand new) canister adsorbs, because of "heel" effects. The heel is the amount of fuel vapor that is too tightly adsorbed to be removable from the canister sorbent by air purging. Because each component of the heel takes up an adsorbing site on the sorbent, the effect of the heel is to decrease GWC. Heels usually account for about 25% to 50% of the total adsorbing capacity of a new sorbent. For the purposes of the lab-scale testing described here, modified GWC refers to grams of gasoline vapor adsorbed per grams of sorbent.

Design of the EERC evaporation canister sorbent test system (Figure 1) was based on published designs of Westvaco Corporation and Dow Chemical Company sorbent test systems. As shown in Figure 1, the test system is built around a gasoline vapor source that supplies vapors to a sorbent bed. A calibrated mass flow controller (MFC) is used to meter nitrogen flow to the gasoline vapor source, and calibrated mass flow detectors (MFDs) are used to monitor nitrogen plus fuel vapor flow into the sorbent bed, and nitrogen plus vapor flow out of the sorbent bed. The output of the sorbent bed is passed through a 10-cm-path-length, 50-cc gas cell mounted in the sample compartment of a Bomem Model MB-100 Fourier-transform infrared (FT-IR) spectrometer, which is used to detect and analyze breakthrough vapor emissions. The volume of the "U-tube" sorbent bed, which is approximately 25 cm³, can contain about 7–10 g of sorbent, depending on sorbent density. Temperatures of the gasoline vapor source and the sorbent bed are maintained by controlled temperature baths that use ethylene glycol and Dowtherm as circulating heat-transfer fluids, respectively.

During testing, pressure drop across the sorbent bed is monitored (via a computerized data acquisition system) with an electronic differential pressure transducer. The temperatures of the two temperature baths and the ambient temperature in the lab are also monitored throughout each test. The temperature of the FT-IR gas cell is maintained at 25°C using an electronically controlled heater. A floating ball-type flow indicator is used to monitor the outlet gas flow on the downstream side of the FT-IR gas cell. All electronically monitored temperature, pressure, and flow rate readings are converted to digital signals by a data logger. The FT-IR and data logger are connected to and controlled by a personal computer, which is programmed to collect and store data at timed intervals.

In the tests performed, fuel vapors were generated by routing nitrogen carrier gas (at a flow rate of 50 cm³/minute) through a sealed (with a rubber stopper) 150-cm³ Erlenmeyer flask containing 100 cm³ of gasoline. As shown in Figure 1, the carrier gas is bubbled into the gasoline through a stainless steel frit immersed in the gasoline. Before initiation of testing, an appropriate volume of dried sorbent (about 20 cm³) is poured into the U-tube (the empty weight of which has been recorded), the weight of sorbent added is recorded, and the sorbent bed is sealed and immersed in the 25°C temperature bath. The complete flow system minus the gasoline vapor source is purged with nitrogen flowing at 50 cm³/min for 5 minutes. The gasoline vapor source is then prepared as follows. The empty 150-cm³ flask is weighed and the weight recorded; then a 100-mL gasoline sample (prepared in advance) is brought from refrigerated storage and poured into the empty flask. The flask plus gasoline is weighed and the weight recorded. The inlet and outlet lines for the nitrogen carrier gas are connected to the flask and it is placed in the temperature bath. Nitrogen carrier gas flow (which is stopped briefly to enable immersion of the nitrogen supply line fritted end into the gasoline) is accurately reset to 50 cm³/min, and the computerized data acquisition program is initiated to collect data at 2-minute intervals.

Figure 1. Sorbent test system.

Each two-phase test was performed as follows. Gasoline adsorption was allowed to proceed until sorbent saturation, which was determined to have occurred when the FT-IR spectra of the gasoline vapor stream emerging from the sorbent bed was similar to the baseline gasoline vapor FT-IR spectra (obtained through analysis of gasoline vapors generated as described above but routed through an empty sorbent bed). Following saturation, sorbent desorption (purging) was performed by routing nitrogen gas at a flow rate of 150 cm³/min through the sorbent bed (which was removed and reinstalled "in reverse" to more accurately simulate an automobile canister purge operation) until the weight of the sorbent bed stabilized. Table 1 shows the results of the tests performed for comparison of CCV sorbent with commercial canister sorbent using regular unleaded gasoline. Although 12 load-and-purge cycles were performed with the commercial sorbent, only cycles 1, 2, and 12 data are shown because data for cycles 3-11 were essentially identical. Only two cycles were performed with the CCV sorbent.

The data in the table show that the CCV sorbent had a lower initial adsorbing capacity than the commercial sorbent (3.01 g versus 3.32 g-note the higher CCV sorbent weight) and a significantly lower modified GWC, due to its low desorbing capacity. These data indicate that the CCV sorbent, as processed for these tests, may be better suited to applications in which a stronger hold on volatiles is required and higher purge rates can be employed.

TABLE 1

Test Results for Commercial Sorbent vs. CCV Sorbent with Regular Unleaded Gasoline				
	Sorbent Weight, g	Gas Adsorbed, g	Gas Desorbed, g	Modified GWC, %
Commercial Sorbent				
Cycle 1	7.15	3.32	1.66	NA
Cycle 2		1.82	1.70	25.5
Cycle 12		1.90	1.86	26.6
CCV Sorbent				
Cycle 1	8.93	3.01	0.68	NA
Cycle 2		0.85	0.64	9.5

4.0 FUTURE WORK

Since the KOH-activated carbons did not appear to reach the ultraporous state, we need to consider alternative applications other than ultracapacitors. Methods for converting coal-derived liquids to ultraporous carbons need to be explored.

5.0 REFERENCES

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