

REDUCE VOC EMISSION FROM FOUNDRIES BY IN-SITU PYROLYZED COAL

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Abstract

It is hypothesized that a cost efficient adsorbent, namely in-situ pyrolyzed coal, can be produced by utilizing the wasted cupola heat from foundries; and that this pyrolyzed coal can sorb VOC emissions from the exhaust gas within bag house collectors at foundries. In this study, several coals were pyrolyzed as raw materials in an apparatus simulating full scale systems which utilize the wasted heat from a foundry cupola as the energy source. An array of pyrolysis and raw material conditions were studied to investigate their effects on pore structure development in the carbon micro-crystallites. The objective was to achieve a relatively uniform product over a broad range of temperatures and thermal treatment times; and in the foundry, this is more important than achieving as high an adsorption capacity as could be achieved with a commercial activated carbon. The underlying principle is that if we can robustly achieve a uniform sorbent over a broad processing condition, and achieve this with no extra energy cost, this would be of great benefit to the foundry industry. The pore volume distributions and surface areas of different in-situ pyrolyzed coals were analyzed by an accelerated surface area and porosimetry (ASAP) system. Other physical and chemical properties of the in-situ pyrolyzed coals were also tested. It was found that lignite may be a better raw material for in-situ pyrolyzed coal than bituminous coal and anthracite. The in-situ pyrolyzed coals contain mainly micro-pores. Therefore, comparing with commercial lignite-based activated carbon, the lignite-based in-situ pyrolyzed coal contains much less pore volume but considerable amount of surface area, and showed a good adsorption capacity of BTX in adsorption test. Pyrolysis of lignite also made it more basic; and this is desirable in the green sands of a foundry.

Introduction

Air pollution is one of the most important environmental issues in iron foundries, and volatile organic compounds (VOCs) represent a major component of air pollutants. VOCs can be produced from both the coal and the phenolic urethane cores that are included in the green sand mold during the process (Wang et al., 2005; Wang et al., 2006). Foundries are required by EPA to diminish air pollution. Activated carbon can be used to adsorb these emissions (Benkhedda et al., 2000; Cal et al., 1996, 1997; Chiang et al., 2001a; Chiang et al., 2001b; Lillo-Rodenas et al., 2005) in the foundries, but using commercial activated carbon would pose a prohibitively high cost to the foundries. In conventional iron foundries, in order to melt the iron, high temperatures are required in the cupola. The exhaust gas from the cupola travels through a drop-out box, and then cools in an air-to-air heat exchanger followed by a wet scrubber system. Commonly these extra heat sources in the foundries are wasted. The temperature in the drop-out box is 815-1150°C, and this compares favorably to the 800-1000°C temperature at which activated carbon is commercially manufactured (Bansal et al., 1988). Furthermore, in foundries, nitrogen gas is used to provide a gas blanket to protect the molten metal against oxidation during iron pouring. This operation heats the nitrogen temperature to 1300°C. This nitrogen gas flow could also be valuably reclaimed for protecting the coal during carbon pyrolysis. One objective of this research is to investigate the feasibility of reclaiming this commonly wasted heat and nitrogen gas, and use them to produce in-situ pyrolyzed coal from raw coals that are robustly uniform over a broad range of temperature and thermal duration. Coals with different ranks can be used as raw materials for activated carbons (Bansal et al., 1988; Carrasco-Marin et al., 1996; Lozano-Castello et al., 2001; Lyubchik et al., 1997; Murty, 1979; Toles et al., 1996). Thus, in this study, anthracite, bituminous coal, and lignite were tested as raw material. This in-situ pyrolyzed coal could be used to treat air pollution in foundries. In field scale, a heat exchanger tube (HEX) can be protruded through the drop box, and then pass coal, and wasted hot nitrogen gas through this tube. In our lab-scale experiments, a thermogravimetric analyzer (TGA) was used to simulate the proposed situation of a drop-out box with a heat exchange tube. The experiments in the TGA appraised the proper raw coal which provides the most robust product in the pyrolysis system and also investigate effect of different pyrolysis conditions, such as temperature, time, grain size and moisture content, on the development of pore structure.

Experimental Procedure

Raw Material

Three types of coal were studied, anthracite, bituminous and lignite. The anthracite was obtained from Jeddo Coal Company (Hazleton, PA). The bituminous coal we tested is the sea coal that has been used at Neenah Foundry (Neenah, WI). Both of these two coals were received in the form of powder. Two lignite resources from Mississippi Lignite Mining Company (Ackerman, MS), one from Red Hills mine and the other from Sabine mine, were tested. These lignites were received as chunks. They were crushed; and the grains that passed the mesh 40 sieve were kept for the pyrolysis test.

Pyrolysis Process

Coals were pyrolyzed in the thermogravimetric analyzer (TGA) from THERMO Electron Corporation (Newington, NH) with a 2 inch (in diameter) x 8 inch (length) furnace reactor tube. The coals were pyrolyzed in the reactor tube, where they were exposed only to N₂ and inert gas. The temperature was increased from room temperature to the desired final temperature (treatment temperature) at a rate of 50°C/min and maintained at the final temperature for a prescribed duration. This duration is defined as pyrolysis time in later sections. After the pyrolysis duration, nitrogen gas was provided until the temperature dropped to room temperature.

Analysis of the Pore Volume Distribution

The character of the pyrolyzed carbons such as surface area and pore volume distribution were measured by the Accelerated Surface Area and Porosimetry System (ASAP) 2010 (Micromeritics, Inc, Norcross, GA). Argon was used as the analysis gas in the ASAP to measure the surface area and pore volume distribution of the pyrolyzed coals. These tests employed 0.3-0.5 g of pyrolyzed coal.

Results and Discussions

Effect of Raw Materials

At first all the raw coals were pyrolyzed in a TGA at 800 °C for 1hour. The TGA balance records show the anthracite only lost 7% of its weight during pyrolysis. For bituminous coal and the lignites, the mass loss was 30% and 55-60% respectively. It is also noticed that for all the coals, most of the mass was lost before the temperature reached 600 °C. The pore volume distributions of these pyrolyzed coals are shown in Figure 1.

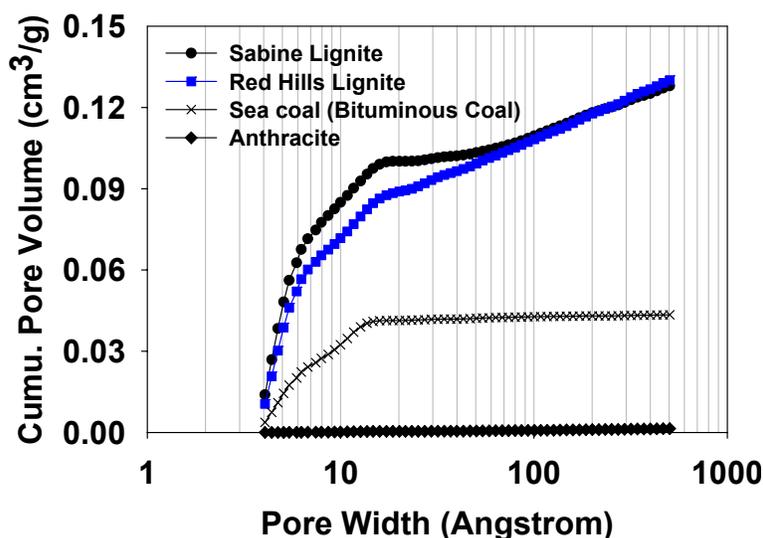


Figure 1. Pore Volume Distributions of Different Raw Coals Pyrolyzed in TGA at 800 °C for 1 Hour

It can be seen that anthracite is not acceptable as a raw material for the in-situ pyrolyzed coal because the simple pyrolysis process can not open any pore structures in anthracite. It is known that anthracite lacks volatile matter and has considerable carbon-carbon linkage between the graphene layers (Green et al., 1982). Simple pyrolysis is not strong enough to open the pore structures among the layers. Furthermore, mild activation at high temperature can not produce significant pore volume in anthracite either (Gergova et al., 1993; Lyubchik et al., 1997; Lyubchik et al., 2002). In contrast, the looser structure in bituminous coal and lignite makes it possible to open those pore volumes by a simple pyrolysis process. The micro-pore volume developed in pyrolyzed lignite is about twice of that of the pyrolyzed bituminous coal.

Effect of Pyrolysis Temperature

Temperature plays an important role during coal pyrolysis. During coal pyrolysis, there is little change in structure below a certain temperature T_d (decomposition temperature) and the value of T_d increase with the rank of the coal from about 350 °C to 450 °C. Active decomposition which leads to generation and discharge of the bulk of the coal's volatile matter will occur between T_d and ~550 °C (Berkowitz, 1985). These statements are confirmed by the mass loss profiles of coals during pyrolysis, since most of the mass was lost before the temperature reached 600 °C. Therefore bituminous coal and lignite were pyrolyzed at different temperature from 600 °C to 900 °C. The pore volume distributions of these pyrolyzed coals are shown in Figure 2. The results show that temperature variation will have much more significant effect on the pore volume distribution of bituminous coal than on that of lignite. As the temperature increases to 900 °C, this bituminous coal lost

almost all the pore volume that it had developed at lower temperature. It was noticed that the bituminous coal powders used in these tests congealed together after being pyrolyzed under all the temperatures. This indicates the bituminous coal experienced its plastic state during pyrolysis and the temperature needed to reach the state is less than 600 °C. However it seems the loss the pore structure in bituminous coal is not caused by the plastic effect since the pores volumes were increased when the temperature increased to 800 °C. It is most possible that when the temperature increased to about 900 °C, graphitizing occurred, and this eliminated all the space between the parallel graphite-like crystallites in bituminous coal. As a result, the pore volume that had been developed at lower temperature was lost. Thus, this sea coal would not be a good candidate for making a robust in-situ pyrolyzed coal material, because adding accurate temperature control to the heat exchange tube is not what foundry personnel want to be concerned with when a foundry's mission is to make metal castings.

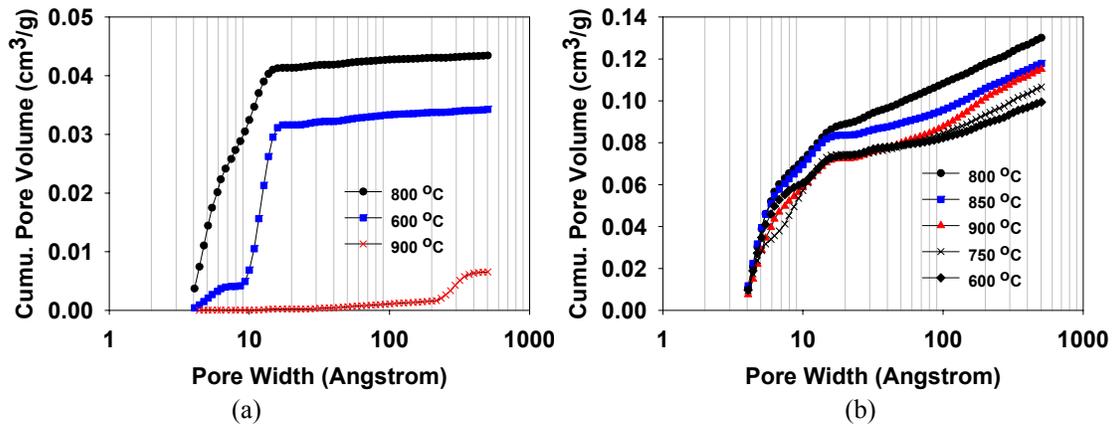


Figure 2. Pore Volume Distributions of Bituminous Coal (a) and Red Hills Lignite (b) Pyrolyzed in TGA at Different Temperatures for 1 hour

In contrast, the pore structure in lignite was more stable under variable temperature conditions. Although lignite is known as a non-graphitizing material, it still lost a small portion of its pore volume when temperature increased from 800 °C to 900 °C. Perhaps there were a few of the random oriented graphite-like crystallites in lignite that were parallel to each other, and these could have undergone partial graphitizing at high temperature. One similar trend observed for both coals is that the pore volume reaches its highest value at about 800 °C. As discussed above, almost all the mass loss was achieved before the temperature reached 600 °C, so it is most possible that the increase in pore volume was contributed by the breaking of oxygen-containing functional groups and cross-links at temperature over 600 °C. The information from TGA-MS test (to be presented at the Carbon Conference) may support this statement. The peaks of CO_x and H₂O evolved at temperature beyond 600 °C, which inferred the break-up of oxygen containing groups.

Effect of Pyrolysis Time

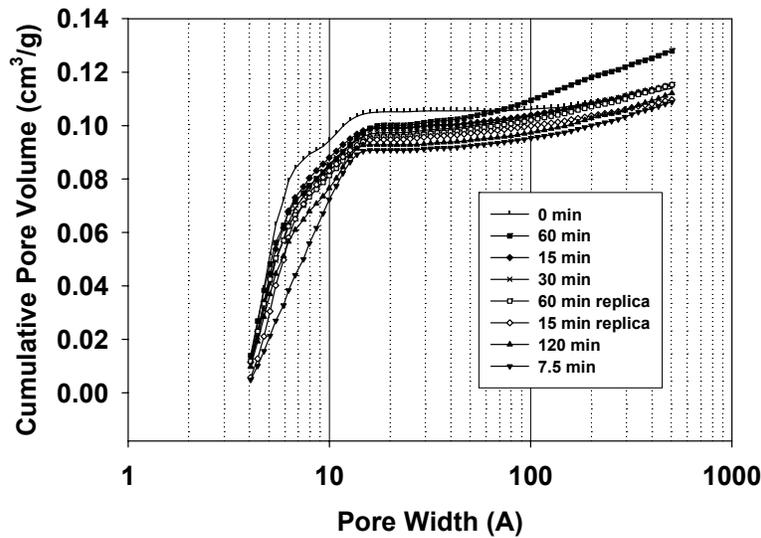


Figure 3. Pore Volume Distributions of Sabine Lignite Pyrolyzed in TGA at 800 °C for Different Times

Sabine lignite was pyrolyzed in the TGA at 800 °C final temperature for different durations from 0 minutes to 120 minutes; and the pore volume distributions of these pyrolyzed coals are shown in Figure 3. It can be seen from Figure 3 that the pore volume distributions of these pyrolyzed carbons are close to each other. The micro-pore volume (pore width < 20 Å) values of most of these pyrolyzed carbons are within the range 0.095 to 0.10 cm³/g. Also, it is hard to find a trend of pore volume distribution according to pyrolysis time. By considering system errors in the experimental results, it probably can be concluded that longer pyrolysis time will have less effect on the pore volume distribution of the in-situ pyrolyzed coal. Because the coal was pyrolyzed under the protection of the inert gas nitrogen, perhaps no more reaction will occur in the system after releasing the volatile matter and breaking the oxygen-containing groups.

Effect of Grain Size

In order to be reused in a green sand mold, the desired form of the in-situ pyrolyzed coal is powder. The carbon can be crushed into powder form either before or after pyrolysis; and the authors sought to see how grain size affected the thermally-treated product. In order to appraise the effect of raw material grain size on the pore volume distribution of in-situ pyrolyzed coal, raw Sabine lignite was screened; and particles bigger than mesh 50 but less than mesh 20 were kept. Then 1 gram of this coal was pyrolyzed in the TGA at 800 °C for 15 minutes. The pore volume distribution of this bigger-size in-situ pyrolyzed coal was compared with that of a US mesh <40 in-situ pyrolyzed coal which was pyrolyzed under same conditions in Figure 4. It can be seen that the grain size of the raw material affects the pore volume development greatly. If pyrolyzed from dried material the US mesh 20/50 lignite will suffer about 3% less weight loss than the US mesh <40, but the US mesh <40 pyrolyzed carbon contained about 50% more pore volume than the US mesh 20/50 pyrolyzed carbon. It is known that bigger grain size will limit the transfer of volatile matters from coal bulk to the coal surface and increase the possibility of second reaction between volatile matters and carbon. It is also possible that lignite with smaller grain size is more effective in receiving heat energy to break the surface oxygen-containing groups than that with bigger grain size. Therefore in order to achieve more pore volume, it is better to grind the raw material into powder before pyrolysis.

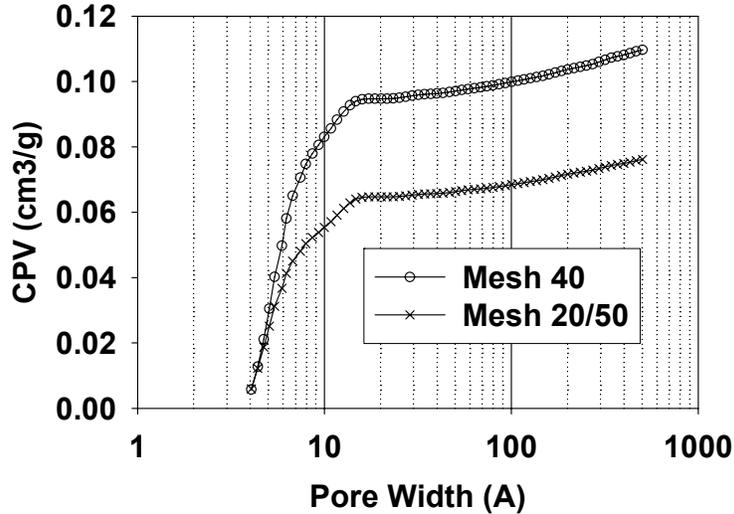


Figure 4. Pore Volume Distributions of Lignite with Different Grain Sizes Pyrolyzed in TGA at 800 °C for 15 minutes

Chemical Property Changes of the In-situ Pyrolyzed Coal

Some chemical properties of the in-situ lignite chars, such as the elemental analysis (Table 1) and slurry pH (Table 2) were also measured. The elemental analysis shows that the in-situ pyrolyzed coal produced from Sabine lignite had the highest carbon content. It probably is the reason why the in-situ Sabine lignite char has the highest pore volume and surface area. From the elemental analysis, it can also be found that there is no oxygen content (by difference) in the ash free part of the in-situ chars. This may suggest that the oxygen-containing function groups at the coal surface were eliminated during the pyrolysis. The elimination of the oxygen-containing groups will favor the in-situ char in application from two aspects. First, the oxygen-containing groups will decrease the VOC adsorption capacity of the in-situ pyrolyzed carbon (Chiang et al., 2002; Chiang et al., 2001a; Chiang et al., 2001b; Lillo-Rodenas et al., 2005; Yun et al., 1999). Second, the oxygen-containing groups will increase the acidity of the in-situ pyrolyzed coal, which limits the use of in-situ pyrolyzed coal in a green sand mold. The slurry pH test of the raw lignite and pyrolyzed lignite confirmed the elimination of these oxygen-containing groups. Without pyrolysis, the slurry pH of the raw Sabine lignite is around 6, while the slurry pH of the in-situ char is about 10.

Table 1. Elemental analysis of pyrolyzed lignites (*O is calculated by difference)

Lignite	C	H	N	S	O*	Ash
Sabine	73.1	0.84	1.28	0.65	0.23	23.9
Red Hills	61.7	0.67	1.13	0.52	0	36.1

Table 2. Slurry pH of raw Sabine lignite and in-situ Sabine lignite char

Material	Slurry pH	
	Raw lignite	6.00
In-situ pyrolyzed coal	10.42	10.45

Preliminary VOC Adsorption Test on In-situ Pyrolyzed Coal

In adsorption experiments, Sabine lignite pyrolyzed at 800 °C for 1 hour was packed in the first section of the column. The objective of this experiment has been to test the feasibility of using the in-situ char as adsorbent for VOC adsorption. Meanwhile, the types of VOCs from the sea coal emission can also be verified (Figure 5). It can be seen from the results that after been pyrolyzed, there were no VOCs left in the lignite. However, after the adsorption experiment, hexane, benzene, toluene and xylene were collected on this pyrolyzed lignite. No BTX was found in the breakthrough check section. The results indicate that the pyrolyzed lignite material offers a feasible means for adsorbing the VOCs from green sand mode emission.

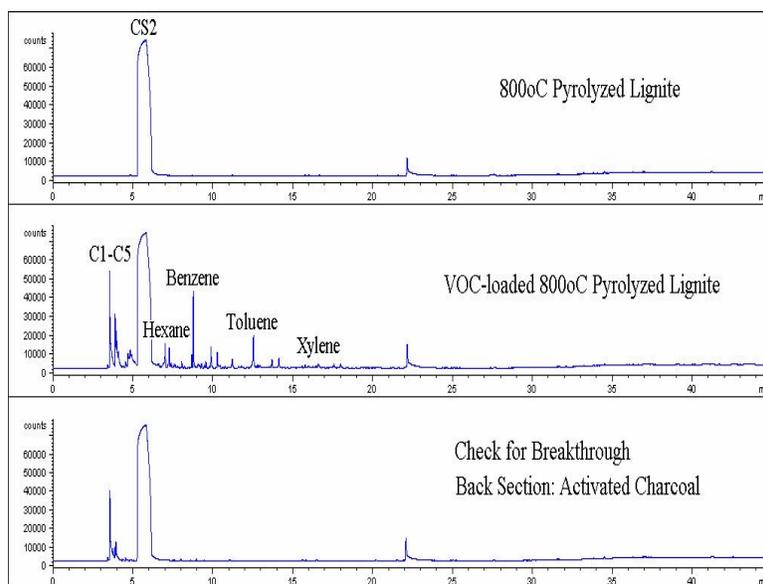


Figure 5. Adsorption of VOC Emission from Sea Coal on Pyrolyzed Sabine Lignite

Conclusion

It is confirmed that by using lignite as the raw material, an in-situ pyrolyzed coal which will robustly contain an adequate amount of pore volume; and this can be produced via the wasted heat from iron foundries. The pore volume distribution of the in-situ pyrolyzed coal will be affected by the pyrolysis temperature and raw material grain size, but pyrolysis time has little effect. The lignite-based in-situ pyrolyzed coal will generate the highest pore volume at a temperature around 800 °C and lose about 10% of this porosity when the temperature yet further increases to 900 °C. TGA-MS, elemental analysis and slurry pH test confirmed the destruction of oxygen-containing groups within the lignite; and this also eliminated the acidity of lignite. Adsorption test shows that the in-situ pyrolyzed coal offers promise for removing benzene, xylene, and toluene-type compounds.

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