OPTIMIZING THE USE OF UNBURNED CARBON FOR THE PRODUCTION OF ACTIVATED CARBONS

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Introduction

The U.S. Energy Information Administration has forecasted that only in the first two decades of the 21st century, the energy demand in U.S. will increase by 35% compared to the levels at the end of the 20th century. Fossil fuels have been traditionally the major primary energy source providing with over 85% of the total energy demand and their role is expected to continue growing for the forecasted period due to their inherent cost competitiveness compared to non-fossil fuel energy sources. During 2002, around 900 million metric tons (Mt) of coal was burned, and about 107 Mt of coal combustion by-products were generated, including around 57 Mt of fly ash, that contain uncombusted coal, also referred to as unburned carbon [1]. Unfortunately, over two thirds of this material was disposed. However, the increasing role of coal as a source of energy in the 21st century will demand environmental and cost-effective strategies for the use of carbonaceous waste products from coal combustion. This carbonaceous residue or unburned carbon, is a potential precursor for the production of activated carbons (ACs), since it has gone through a devolatilization process while in the combustor, and therefore, only requires to be activated [2, 3].

The authors previous studies have shown that unburned carbon is a good feedstock to produce vale-added materials, such as activated carbon, where the generated activated carbons have surface areas up to 1,000 m^2/g [3]. However, the microporosity of the produced activated carbon only can be increased by extended activation times and high activation temperatures at the expense of the solid yield. It has been shown that various pretreatments (e.g. oxidation) applied to cokes and anthracites can improve, to some extent, the porosity of the activated products after subsequent activation by steam [4,5]. Nitric acid is a typical oxidizing agent used in aqueous solutions to introduce oxygen surface complexes on carbon, including activated carbons, and carbon fibers. Accordingly, the present paper reports the effect of using a pretreatment process, combined de-ashing and nitric acid oxidation, on the steam activation of unburned carbon.

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Experimental

The sample used for this study, FA1 was collected from the electrostatic precipitators of Penn State University pulverized coal-fired suspension firing research boiler (2 MM Btu/hour), which use high volatile bituminous coal as feedstock. The sample was deashed with a mixed acids ($HCl/HNO_3/HF$) solution at room temperature for 24 hours or at 75^oC for 4 hours, and the resultant samples were labeled as FA1-RDEM and FA1-TDEM, respectively. The deashed samples were treated with 5N nitric acid at boiling conditions for 1 or 5 hours and washed with distilled water till pH of the filtrate reached 7. The obtained samples were labeled as FA1-N1hr and FA1-N5hr for the 1 or 5 hours treatment, respectively. The samples were then activated by placing them into a horizontal furnace and quickly heated (40^oC/min) under nitrogen flow to 850^oC, then steam was introduced in the reactor and kept isothermally for 1 hour.

The loss-on-ignition (LOI) content (generally equaled to total carbon content) of the samples were determined according to the ASTM C311 procedure. The samples were also characterized by a Leeman Labs PS3000UV inductively coupled plasma spectrophotometer (ICP). Prior to the ICP analysis, the samples were ashed at 900^oC, and then the ash was dissolved by a lithium metaborate fusion process and analyzed.

The porous texture of the samples was characterized by conducting N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. From the adsorption isotherm, the total specific surface area, S_t, micropore volume, V_{mi}, and external surface area, S_{ext}, were calculated, as reported elsewhere [3,6]. X-ray photoelectron spectrometer (XPS) analyses were conducted using a Kratos Analytical Axis Ultra unit. A monochromatic Aluminum (1486.6eV) X-ray source was used. The samples were pressed into Indium foil and carefully mounted on a spectrometer probe tip by means of double-sided adhesive tape. The takeoff angle was 90° with respect to the sample plane, and charge neutralization was accomplished using low energy (<2eV) electron flood gun. All binding energies were referred to the carbon 1s peak at 284.4eV. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFs) for the Kratos instrument to the integrated peak areas. The approximate sampling depth under these conditions was 25Å.

Results and Discussion

    1. ICP analysis studies
The ash analysis results of the samples are listed in Table 1, where the results are reported in weight percent on ash basis. The LOI of the parent sample is 40.9%. The chemical characteristics of the unburned carbon samples are dependently largely on the inorganic constituents of the parent coal and the combustion conditions [7]. As expected from a Type F fly ash, around 92% of the total weight of the ash of the FA1 sample is comprised of SiO_2, Al_2O_3 and Fe_2O_3.

Table 1. ICP analysis results for the studied samples*.

Sample	FA1	FA1-Rdem	FA1-Tdem	FA1-N1hr
Ash (900°C)	40.9	4.89	2.28	1.44
Al_2O_3	29.4	30.3	31.0	26.4
BaO	0.52	5.11	3.09	0.5
CaO	2.33	25.9	23.3	9.25
Fe_2O_3	9.29	2.83	3.20	11.7
K_2O	1.83	0.51	0.36	0.25
MgO	0.92	8.45	9.95	2.95
MnO	0.04	<0.05	<0.05	<0.05
Na_2O	0.61	1.05	0.43	<0.05
P_2O_5	0.13	<0.05	0.08	0.86
SiO_2	53.8	10.2	11.4	38.0
SrO	0.11	1.19	0.87	0.65
TiO	1.22	3.52	2.62	9.70

* Results are reported in weight percent on ash basis.

The combination of the three acids, $HCl/HNO_3/HF$ can effectively deash the sample even at room temperature to an ash content of 4.89% for FA1-RDEM compared to 40.9% for parent sample FA1. The sample deashed at 75°C for 4 hours has an ash content as low as 2.28%, which suggests that the acids digestion at 75°C is more effective to remove the ash in a much shorter time period, 4 hours compared to 24 hours at room temperature. The nitric acid treatment was intended to introduce oxygen surface complex to the surface (section below). However, it was also effective in decreasing the ash content to 1.44%.

2. XPS studies

X-ray photoelectron spectrometer studies were used to characterize the surface functionality of the samples. The samples were first scanned from 0-1200eV binding energy to survey the various elements on the surface. Then high resolution data was collected for C 1s and O 1s at 278-295 and 525 – 540 eV binding energy, respectively. The parent sample, FA1, contained around 41% ash, and therefore, besides S, various metal atoms, such as Ca, Al, Mg were detected by XPS. As reported by the ICP studies, the XPS data also show that the acid digestion step process can effectively remove ash from the sample. Furthermore, heating during the acid treatment can increase the efficiency of ash removal. The XPS studies indicated that the acid treatment using $HCl/HNO_3/HF$ not only removed most of the ash, but it also changed

the surface chemistry of the sample. The subsequent nitric acid treatment increased significantly the oxygen content, as previously reported [8,9].

In order to obtain more information about the oxygen functional groups of the oxidized samples, the samples were scanned again with high resolution at the C 1s and O 1s binding energies. The resulting high resolution XPS data of C 1s spectrum for the studied samples are shown in Figure 1. The parent sample (FA1) and its deashed treated counterpart at room temperature (FA1-Rdem) only have one main peak at 284.4 eV. However, the sample deashed at higher temperatures (FA1-Tdem) and the nitric treated samples (FA1-N1hr and FA1-N5hr) show a shoulder at higher binding energy besides the main peak at 284.4 Kev, which is ascribed to oxidized carbon. With the longer treatment with nitric acid, the peak corresponding to oxidized carbon becomes more prominent, indicating that the oxidized carbon content increases. Correspondingly, the O 1s spectrum also split into two peaks at around 532 KeV and 531.5KeV that are assigned to single bond C-O and double bond C=O, respectively.
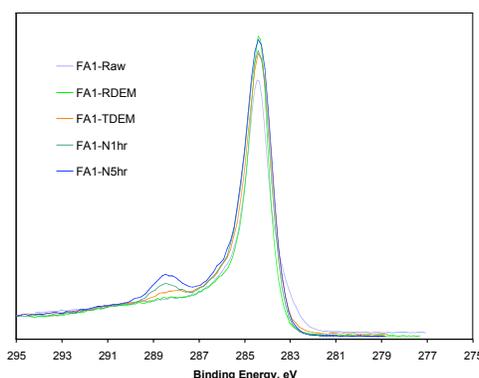

Figure 1. High resolution C 1s spectra of raw and treated samples.

3. Porous structure studies

The porosity data of the studied samples are listed in Table 2, where for the purpose of comparison, all the data are reported on ash-free carbon basis. The parent sample has a surface area and pore volume of 125.4m^2/g and 0.077 ml/g, respectively, with an average pore size of 2.46nm. This is consistent with the authors' previous work that has shown that unburned carbon samples have a relatively low porosity, mainly in the mesoporous and macroporous range [3].

The acid/deashing treatment process at both room temperature and 75°C decreased the porosity of the samples to 83.4 m^2/g and 54.5m^2/g, respectively. This also resulted in an enlargement of the pore size (3.13 and 2.99 vs. 2.46 nm). Acid digestion is widely used to demineralize coal, and a decrease of the surface area has been reported [10]. In contrast, the nitric acid treatment resulted in an increase of the surface area (211 and 175 m^2/g) accompanied by a decrease of the pore size (2.25 and 2.34 vs. 2.46 nm for the parent sample). This may be associated the formation of oxidated surface complexes in the pores or pore entrances. Previous studies have reported that the

modification of the surface of activated carbon with nitric acid resulted in a decrease of the surface area of activated carbon, especially for high surface area activated carbon. This decrease in the surface area was probably associated with the destruction of the thin pore wall of highly activated carbons [8].

Table 2. Porous texture properties of the studied samples.

	S_{BET} m^2/g	S_{ext} m^2/g	S_{mi} m^2/g	$V_{0.95}$ ml/g	V_{mi} ml/g	V_{me} ml/g	D_{av} nm	LOI %
FA1	125.4	28.1	97.3	0.077	0.0467	0.030	2.46	63.1
FA1-Rdem	83.4	27.7	55.7	0.065	0.027	0.038	3.13	95.3
FA1-Tdem	54.5	21.6	32.9	0.041	0.014	0.027	2.99	96.4
FA1-N1hr	211.2	20.4	190.8	0.119	0.095	0.024	2.25	98.9
FA1-N5hr	175.5	22.1	156.3	0.103	0.078	0.025	2.34	98.8

4. Steam activation studies

The above samples were activated by steam at 850^oC for 1 hour, and the porosity data from the N_2-77k isotherms of the resultant activated carbons are presented in Table 3. The values are reported in ash-free carbon basis, as described for Table 2.

Table 3. Porosity of the activated carbons.

	AC-FA1-Raw	AC-FA1-Rdem	AC-FA1-Tdem	AC-FA1-N1h	AC-FA1-N5h
Surface Area m^2/g	895	783	972	1174	999
Micropore	765	557	817	1085	931
Mesopre	129	226	155	89	68
Pore Volume ml/g	0.489	0.507	0.552	0.634	0.575
Micropore	0.350	0.249	0.334	0.534	0.498
Mesopore	0.139	0.258	0.218	0.100	0.077
Average Pore Size, nm	2.2	2.6	2.3	2.2	2.3

Table 3 shows that activated carbons with surface area 780~1170m^2/g can be produced from unburned carbon. These surface area values are similar to those reported for commercial activated carbons (>750m^2/g). However, our previous studies have shown that extended activation times and temperatures are needed to obtain a microporous carbon [2, 3]. The activated sample produced from FA1-Rdem (AC-FA1-Rdem) has a lower surface area than the parent activated sample (783 vs. 895 m^2/g). In contrast, the activated sample produced from FA1-Tdem has a higher surface area compared to the

activated parent sample (972 vs. 895m^2/g). This may indicate that the room temperature de-ashing process may have just resulted in the removal of catalytically active inorganic components. In contrast, the heated de-ashing process may be able to oxidize the surface of sample, resulting in activated carbon with a higher surface area and microporosity. Finally, the data shown in Table 3 indicates that the sample from the nitric acid treated unburned carbon AC-FA1-N1h has the highest surface area and microporosity (1174m^2/g and 0.534ml/g).

Conclusions

Unburned carbon is a potential precursor for the production of activated carbons, since it has gone through a devolatilization process while in the combustor, and therefore, only requires to be activated. However, the porosity of the produced activated carbon only can be increased by extended activation times and high activation temperatures at the expense of the solid yield. The work reported focuses on the use of a pretreatment process, combined deashing and nitric acid oxidation, to improve the steam activation of unburned carbon. The combination of the three acids, HCl/HNO$_3$/HF can effectively deash the sample even at room temperature. The room temperature deashing process may result in the removal of catalytically active inorganic components. In contrast, the heated de-ashing process (75°C) may be able to oxidize the surface of sample, resulting in activated carbons with a higher surface area and microporosity. The combination of acid deashing followed by nitric acid treatment oxidizes the surface of the carbon, and decrease the porosity.

Acknowledgements

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