Kinetics of Fly Ash Beneficiation by Carbon Burnout

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I. ABSTRACT

OBJECTIVE
To investigate the kinetics of beneficiation of fly ash by carbon burnout. The project is a joint venture between Delmarva Power, a power generating company on the eastern shore of Maryland, and the University of Maryland Eastern Shore. The studies have focused on the beneficiation of fly ash by carbon burnout.

WORK DONE AND CONCLUSIONS
This summer our efforts were directed toward collecting more Kinetic data and investigating oxidation behavior using varying oxygen concentration. We began to put together an interim report of the project activity to date. The interim report is arranged in a presentation format and is to be used as educational material for our graduate students. The full report will take the usual format when completed. The presentation format is enclosed with this report.

SIGNIFICANCE TO FOSSIL ENERGY PROGRAM
Project is related to Advanced Environmental Control Technology for Coal and coal residue.

PLANS FOR NEXT QUARTER
Our efforts will continue in the direction of investigating the carbon burnout of the fly ash and establishing a lower limit for the carbon remaining after burn out. We expect that the different concentrations of reactant gas will assist in this endeavor.

II. HIGHLIGHT OF ACCOMPLISHMENTS

- Introduction of a number of minority students to research experience in fossil energy.
- Successful application of Proportionality Law to kinetic data.
- Development of fossil energy instructional material for the class room.
KINETICS OF FLY ASH BENEFICIATION BY CARBON BURNOUT

Joseph N.D. Dodoo and Joseph M. Okoh, Co-PI's
and
Adria Diaz, Graduate Student
The material presented here provides information on the kinetics of coal fly ash as it is heated under a controlled environment. Fly ash is the residue that is produced when coal is burned. Typically, the coal is pulverised and burned in very large industrial burners. Massive amounts of heat is converted during the process and the ash that flies off the chute is generally collected by means of an electrostatic separator. As heat is applied to any carbon containing substance the substance loses weight as the carbon burns off. One could be forgiven for assuming that when large quantities of heat have been extracted from coal particles as small as 30 - 50 μm, the fly ash resulting from this process should be carbon free. Not so. There still remain measurable amounts of carbon. The carbon still remaining in the coal when all useful heat has been extracted from it is referred to as residual carbon. Amounts of residual carbon up to 12% are possible and in the present work we had analysis carried out which indicated that some of our samples did contain this amount of carbon. The fact that flash can be burned is proof of the presence of carbon, for during combustion it is the carbon in a material that is burned. How much of the residual carbon is ultimately burned depends on such factors as, pressure, oxidizing medium and the temperature inside the combusting chamber. The physical and chemical changes that a substance experiences when undergoing combustion is referred to as kinetics. We have presented the results of our experiment as view graphs. As such several of the materials are in abbreviated form. However, more details will be given during presentation. Quite naturally, the full report will contain the complete text. We hope that at the end of the seminar series the student will have gained some fundamental knowledge of the nature of coal fly ash and the process of reducing the residual carbon in the fly ash.

Dr. Joseph N.D. Dodoo
Principal Investigator
Abstract

Oxidation Studies of coal fly ash have been carried out at partial pressures in the range 1 atmosphere down to 400 torr. The studies have also been carried out at 1 atmosphere for different temperatures in the range 500 to 750 oC. The equipment used was a state of the art Cann Theromogravimetric analyzer having sensitive microbalance that permitted measurements to .1 µg. The analyzer is part of a GC/MS/TG setup in our laboratory. The fly ash was supplied by Delmarva Power Indian River Plant, DE. The samples were dried and stored in a desiccator to ensure that they remained dry prior to combustion. The combustion process inside the TGA is continuous and the heat released can be related to the percent of carbon consumed. Our setup provided easy identification of the elements in the fly ash. The elemental analysis was also augmented by use of an energy dispersive X-ray analyzer. In the X-ray analysis the carbon in the fly ash was compared with that in a dolomite {CaMg(CO3)2} standard obtained from the U.S. Bureau of Mines (USBOM). Preliminary data show encouraging results in the rate of reduction of the residual carbon. Both analyses show reduction of carbon after burning.
FLY ASH PRODUCTION AND DISPOSAL

- Fly ash byproduct of coal combustion
- Major constituents of fly ash
  - Quartz (SiO$_2$)
  - Mullite (3Al$_2$O$_3$ · 2SiO$_2$)
  - Hematite (Fe$_2$O$_3$)
  - Magnetite (Fe$_3$O$_4$)
  - Lime (CaO)
  - Gypsum (CaSO$_4$·2H$_2$O)
- ASTM-Class C and Class F fly ash
# Chemical Requirements of Fly Ash

<table>
<thead>
<tr>
<th>Chemical Component</th>
<th>Class C Fly Ash</th>
<th>Class F Fly Ash</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$-min %</td>
<td>50.0</td>
<td>70.0</td>
</tr>
<tr>
<td>SO$_3$ - max %</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>Moisture content - max %</td>
<td>3.0</td>
<td>3.0</td>
</tr>
<tr>
<td>Loss on ignition - max %</td>
<td>6.0</td>
<td>6.0</td>
</tr>
</tbody>
</table>
- Structural configuration of fly ash- thin-walled spheres made of SiO₂
  - Cenospheres
  - Plerospheres

- Annual fly ash production
  - 25% is utilized while the rest is stored in landfills.
Structural configuration of fly ash

Cenosphere

Plerosphere
USE OF FLY ASH IN CONCRETE

Replacement of Portland Cement

- Hydraulic cement that contains various proportions of four primary compounds: Ca$_3$SiO$_5$, Ca$_2$SiO$_4$, Ca$_3$Al$_2$O$_6$ and Ca$_4$Al$_2$F$_2$O$_{10}$.

$$2\text{Ca}_3\text{SiO}_5 + 6\text{H}_2\text{O} \rightarrow \text{Ca}_3\text{Si}_2\text{O}_7\cdot3\text{H}_2\text{O} + 3\text{Ca(OH)}_2$$
Fly ash as a pozzolan

Siliceous or siliceous and aluminous material that in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties.
Advantages of use of fly ash in concrete

- Permeability reduction

Consumption of water-soluble calcium hydroxide by pozzolanic reaction creates additional calcium silicate gel, resulting in slower transport rates for water.
Sulfate resistance
Consumption of calcium hydroxide and decreased permeability reduces the expansive formation of ettringite and gypsum compounds.

Resistance to freezing and thawing
Reduction in permeability reduces water permeability, which is critical in freeze-thaw damage.
Requirements for use of fly ash in concrete

- Chemical composition
  -(SiO$_2$ + Al$_2$O$_3$ + Fe$_2$O$_3$) > 70%
- Pozzolanic activity
  - Strength > 75% of control
- Particle size
  - Fly ash retained in sieve = 34%
- Residual Carbon content
  - Loss on Ignition (LOI) value
Carbon content and air entraining admixture

- Air-entraining admixtures-organic materials that entrain a controlled quantity of air in uniformly dispersed microscopic bubbles and increase the ability of concrete to withstand freeze-thaw cycling.

- Carbon in fly ash adsorbs a portion of the air-entraining admixture, making it unavailable for creating the needed conditions for stable air bubbles.
- Maximum allowable levels of residual carbon in fly ash used in concrete
  - ASTM Low on Ignition value - 6%
  - Levels not higher than 3% demanded by industry

- Need to find an effective method of beneficiation of fly ash to render it adequate for large scale commercial application
<table>
<thead>
<tr>
<th>Processes of carbon oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>✤ Mass transfer of gaseous reactants from the bulk gas phase to the carbon surface</td>
</tr>
<tr>
<td>✤ Adsorption of reactants on the surface</td>
</tr>
<tr>
<td>✤ Occurrence of chemical rearrangements</td>
</tr>
<tr>
<td>✤ Desorption of products</td>
</tr>
<tr>
<td>✤ Mass transport of the gaseous products away from the carbon surface</td>
</tr>
</tbody>
</table>
Temperature zones for gasification processes

- Zone I-Low reactions temperatures, rates chemically controlled over the accessible surface

- Zone II-Rates partially controlled by diffusion in pores, gaseous reactant concentration falls gradually to zero within the pore system

- Zone III- Rates controlled only by diffusion of the gas to the external carbon surface.
Reaction rate evaluated in terms of rate of mass loss

\[ R = -\frac{dm}{dt} = k_{\text{air}}(O) P^n \]

Temperature dependence of carbon gasification evaluated from Arrhenius equation

\[ k = A e^{-\frac{E_a}{RT}} \]

Frequency factor

\[ AN_o = k_B T f^* \]
\[ h f_a \]
Application of Proportionality Law of Processes

- Reaction rates calculated from linear portion of sigmoid curves are not representative of the physical events of the reactions.

- Proportionality Law of Processes: for certain natural phenomena, the change of variable $Y$ with respect to change of variable $X$ ($\frac{dY}{dX}$) is proportional to the difference between a reference value $Y_i$ (asymptote) and of $Y$ at a given $X$ and inversely proportional to $X$
\[ \begin{align*}
\diamond \quad & \text{d}Y/\text{d}X \text{ is proportional to } (Y_i - Y) \\
\diamond \quad & \text{d}Y/\text{d}X \text{ is proportional to } 1/X \\
\diamond \quad & \text{d}Y/\text{d}X = K(Y_i - Y)/X \\
\diamond \quad & \log[1/(Y_i - Y)] = K \log X + C
\end{align*} \]
OBJECTIVE

To determine the kinetics of the reactions of carbon present in fly ash with air as the reactant gas (oxygen) at various reaction temperatures, partial pressures of reactant gas and total surface area.
EXPERIMENTAL PROCEDURES

FLY ASH SAMPLES

- Collected from landfill-Delmarva Power Indian River Plant
- Size-fractioned using sieves with openings of 44, 74, 149, and 250 micrometers
- Dried at 200 °C under nitrogen for 3 hours using a Lindberg furnace
## Fly ash samples

<table>
<thead>
<tr>
<th>Particle diameter (micrometers)</th>
<th>Fly ash sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>149-249</td>
<td>s#100</td>
</tr>
<tr>
<td>74-148</td>
<td>s#200</td>
</tr>
<tr>
<td>44-73</td>
<td>s#325</td>
</tr>
</tbody>
</table>
Surface Area Measurements

-Surface area determinations based on the physical adsorption of gases on solids

- Adsorption isotherm-relationship between the amount adsorbed and the pressure, for a given gas adsorbed on a given solid at a fixed temperature.
- Monolayer capacity: quantity of the adsorbate which can be accommodated in a completely filled, single layer of molecules on the surface of solid

- Surface area is directly proportional to the monolayer capacity
Brunauer-Emmett-Teller (BET) Theory

Describes multilayer adsorption of gases on a wide range of porous and non-porous solids.

\[
\frac{1}{V[(P_o/P)-1]} = \frac{1}{V_m c^1} + \frac{(c^1-1)P}{V_m c^1 P_o}
\]

where \( V \) is the volume adsorbed, \( V_m \) is the monolayer capacity, \( P \) is the pressure of the adsorbate, \( P_o \) is the normal vapor pressure of the gas, and \( c^1 \) is a constant.
- Micropore Area and Micropore Volume (t-plots)

- BJH Adsorption/Desorption Cumulative Surface Area and Pore Volume of Pores.
Surface Area and Porosimetry System-ASAP 2000

<table>
<thead>
<tr>
<th>Analysis Adsorptive</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>77.35 K</td>
</tr>
<tr>
<td>Molecular cross-sectional area</td>
<td>0.162 nm²</td>
</tr>
<tr>
<td>Non-ideality factor</td>
<td>0.000066</td>
</tr>
<tr>
<td>Equilibration interval</td>
<td>5 secs</td>
</tr>
</tbody>
</table>
## RESULTS

### Surface Area Measurements

<table>
<thead>
<tr>
<th>Fly ash sample</th>
<th>BET Surface Area (m²/g)</th>
<th>BJH Adsorption Cumulative Surface Area of Pores (m²/g)</th>
<th>BJH Adsorption Average Pore Diameter (Angstrom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>s#100</td>
<td>5.54</td>
<td>2.62</td>
<td>115.75</td>
</tr>
<tr>
<td>s#200</td>
<td>3.99</td>
<td>2.21</td>
<td>116.17</td>
</tr>
<tr>
<td>s#325</td>
<td>3.00</td>
<td>1.83</td>
<td>115.16</td>
</tr>
</tbody>
</table>
ADSORPTION-DESORPTION ISOThERM OF FLY ASH S#100.

[Graph showing volume adsorbed vs. relative pressure]
Results from surface area measurements

- Surface area increases as particle size increases.

- Adsorption-desorption isotherms show hysteresis loops, indicating porosity

- t-plots confirm porosity of fly ash

- Average pore diameters for fly ash samples are similar
Carbon Oxidation Reactions

- 50-mg fly ash samples

- Temperature range: 550 °C - 750 °C

- Partial pressures of reactant gas: 0.213 atm, 0.168 atm, and 0.126 atm
## Thermogravimetric Analyzer - Cahn TG-121

<table>
<thead>
<tr>
<th>Feature</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Balance capacity</td>
<td>1.5 grams</td>
</tr>
<tr>
<td>Maximum Temperature</td>
<td>1100 °C</td>
</tr>
<tr>
<td>Maximum Heating Rate</td>
<td>100 °C/min</td>
</tr>
<tr>
<td>Automatic Gas Switching</td>
<td>4 gases</td>
</tr>
<tr>
<td>Temperature Program Segments</td>
<td>60</td>
</tr>
<tr>
<td>Type of Segments</td>
<td>Isotherms, Ramps</td>
</tr>
</tbody>
</table>


TRACE OF WEIGHT LOSS VS. TIME

Para que se vea bien la letra debe ser al menos 18
PROPORTIONALITY PLOT FOR CARBON OXIDATION
RESULTS

Reaction rates for carbon oxidation at 0.213 atm
(Rates are in mg/g.m²·sec)

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>s#100</th>
<th>s#200</th>
<th>s#325</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>0.0188</td>
<td>0.0069</td>
<td>0.0035</td>
</tr>
<tr>
<td>650</td>
<td>0.0736</td>
<td>0.0219</td>
<td>0.0290</td>
</tr>
<tr>
<td>750</td>
<td>0.1520</td>
<td>0.1586</td>
<td>0.1462</td>
</tr>
</tbody>
</table>
Reaction rates for carbon oxidation at 0.168 atm
(Rates are in mg/g.m²/sec)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>s#100</th>
<th>s#200</th>
<th>s#325</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>0.0302</td>
<td>0.0100</td>
<td>0.0265</td>
</tr>
<tr>
<td>650</td>
<td>0.1036</td>
<td>0.0213</td>
<td>0.1296</td>
</tr>
<tr>
<td>750</td>
<td>0.1830</td>
<td>0.1629</td>
<td>0.2252</td>
</tr>
</tbody>
</table>
Reaction rates for carbon oxidation at 0.126 atm (Rates are in mg/g.m².sec)

<table>
<thead>
<tr>
<th>Temperature °C</th>
<th>s#100</th>
<th>s#200</th>
<th>s#325</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>0.0345</td>
<td>0.0147</td>
<td>0.0675</td>
</tr>
<tr>
<td>650</td>
<td>0.1710</td>
<td>0.1100</td>
<td>0.2110</td>
</tr>
<tr>
<td>750</td>
<td>0.2320</td>
<td>0.1724</td>
<td>0.2455</td>
</tr>
</tbody>
</table>
Reaction rates for oxidation of carbon in fly ash s#100 at 0.213 atm

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( R ) (initial rate law) (mg/g.m(^2)sec)</th>
<th>( R ) (Proportionality Law) (mg/g.m(^2)sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>0.0188</td>
<td>2.267</td>
</tr>
<tr>
<td>650</td>
<td>0.0736</td>
<td>12.165</td>
</tr>
<tr>
<td>750</td>
<td>0.1520</td>
<td>28.630</td>
</tr>
</tbody>
</table>
Arrhenius Plot

\[ \ln R \]

\[ \frac{1}{T}, K^{-1} \times 10^4 \]
### Arrhenius parameters for fly ash samples

<table>
<thead>
<tr>
<th>$P_{O_2}$ (atm)</th>
<th>$s^#100$ Ea (kJ/mol)</th>
<th>$s^#200$ Ea (kJ/mol)</th>
<th>$s^#325$ Ea (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.213</td>
<td>73.85</td>
<td>108.40</td>
<td>131.44</td>
</tr>
<tr>
<td>0.168</td>
<td>68.28</td>
<td>95.78</td>
<td>76.12</td>
</tr>
<tr>
<td>0.126</td>
<td>63.81</td>
<td>88.07</td>
<td>43.92</td>
</tr>
</tbody>
</table>
Weight loss of fly ash sample s#100 at 0.213 atm

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight loss (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>550</td>
<td>9.5</td>
</tr>
<tr>
<td>650</td>
<td>11.4</td>
</tr>
<tr>
<td>750</td>
<td>12.2</td>
</tr>
</tbody>
</table>
Large weight losses observed between 600 °C and 710 °C originating from calcination of limestone and dolomite in fly ash (Brown and Dykstra, 1995)

Limestone and dolomite can be entrained in the gas flow through boilers and can appear in fly ash.
Oxygen dependence of reaction rates

<table>
<thead>
<tr>
<th>Fly ash sample</th>
<th>a</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>s#100</td>
<td>-1.132</td>
<td>0.87</td>
</tr>
<tr>
<td>s#200</td>
<td>-1.437</td>
<td>0.99</td>
</tr>
<tr>
<td>s#325</td>
<td>-5.553</td>
<td>0.93</td>
</tr>
</tbody>
</table>
RATE DEPENDENCE ON OXYGEN CONCENTRATION
FLY ASH S#200

\[ \text{slope} = -1.437 \]
RATE DEPENDENCE ON OXYGEN CONCENTRATION

FLY ASH S#325

\[ \ln R = -5.53 \ln O_2 \]

slope = -5.53
Results from carbon oxidation reactions

- Trend of increasing rates with increasing temperatures under same pressure of reactant gas.

- Reaction rates calculated from the proportionality law were higher than the initial rates calculated from the linear portion of the curve.
- Reaction rates represent total weight loss and not only carbon oxidation

- Evaluation of rate dependence on temperature is not possible based on data collected

- Trend of increasing rates with decreasing concentration of reactant gas
CONCLUSIONS

- Surface area analysis reveal that surface area is controlled by carbon content. The higher surface areas in large particles are due to the presence of highly porous carbonaceous particles.

- Reaction rates at temperatures above 550 °C are not representative of carbon oxidation and, therefore, are not useful in determination of temperature dependence of carbon oxidation in fly ash.
The inverse relationship between reaction rates and reactant gas concentration may be caused by volatilization and easy of transport of products by the action of the vacuum applied to the samples.
RECOMMENDATIONS

- Temperatures below 550 °C should be used for future studies in order to assess temperature dependence of carbon oxidation in fly ash.

- Carbon determinations should be performed on fly ash samples after oxidation reactions to determine whether all carbon present in fly ash is oxidized. This will ensure that reaction rates are representative of the complete oxidation of carbon.
- A more accurate determination of oxygen dependence can be accomplished by use of series of reactant gas mixtures containing different concentrations of oxygen to eliminate the need to apply vacuum to the samples.
EL FIN