DEVELOPMENT OF FLY ASH DERIVED SORBENTS TO CAPTURE CO_2 FROM FLUE GAS OF POWER PLANTS

FINAL TECHNICAL PROGRESS REPORT

Reporting Period Start Date: *September 1, 2002*

Reporting Period End Date: *December 31, 2003*

Principal Authors: *Dr. M. Mercedes Maroto-Valer (PI)*
Dr. John M. Andrésen (co-PI)
Dr. Yinzhi Zhang (Research Associate)
Ms. Zhe Lu (Graduate Student)

Date Report Issued: *March 15, 2004*

CBRC Project Number: *01-CBRC-E9*

Submitting Organization: *The Energy Institute*
The Pennsylvania State University
405 Academic Activities Building
University Park, PA 16802-2398
Phone: (814) 863 8265
Fax: (814) 865 3248

ABSTRACT

This research program focused on the development of fly ash derived sorbents to capture CO_2 from power plant flue gas emissions. The fly ash derived sorbents developed represent an affordable alternative to existing methods using specialized activated carbons and molecular sieves, that tend to be very expensive and hinder the viability of the CO_2 sorption process due to economic constraints.

Under Task 1 “Procurement and characterization of a suite of fly ashes”, 10 fly ash samples, named FAS-1 to –10, were collected from different combustors with different feedstocks, including bituminous coal, PRB coal and biomass. These samples presented a wide range of LOI value from 0.66-84.0%, and different burn-off profiles. The samples also spanned a wide range of total specific surface area and pore volume. These variations reflect the difference in the feedstock, types of combustors, collection hopper, and the beneficiation technologies the different fly ashes underwent.

Under Task 2 “Preparation of fly ash derived sorbents”, the fly ash samples were activated by steam. Nitrogen adsorption isotherms were used to characterize the resultant activated samples. The cost-saving one-step activation process applied was successfully used to increase the surface area and pore volume of all the fly ash samples. The activated samples present very different surface areas and pore volumes due to the range in physical and chemical properties of their precursors. Furthermore, one activated fly ash sample, FAS-4, was loaded with amine-containing chemicals (MEA, DEA, AMP, and MDEA). The impregnation significantly decreased the surface area and pore volume of the parent activated fly ash sample.

Under Task 3 “Capture of CO_2 by fly ash derived sorbents”, sample FAS-10 and its de-ashed counterpart before and after impregnation of chemical PEI were used for the CO_2 adsorption at different temperatures. The sample FAS-10 exhibited a CO_2 adsorption capacity of 17.5mg/g at 30^oC, and decreases to 10.25mg/g at 75^oC, while those for de-ashed counterpart are 43.5mg/g and 22.0 mg/g at 30^oC and 75^oC, respectively. After loading PEI, the CO_2 adsorption capacity increased to 93.6 mg/g at 75oC for de-ashed sample and 62.1 mg/g at 75oC for raw fly ash sample.

The activated fly ash, FAS-4, and its chemical loaded counterparts were tested for CO_2 capture capacity. The activated carbon exhibited a CO_2 adsorption capacity of 40.3mg/g at 30^oC that decreased to 18.5mg/g at 70^oC and 7.7mg/g at 120^oC. The CO_2 adsorption capacity profiles changed significantly after impregnation. For the MEA loaded sample the capacity increased to 68.6mg/g at 30^oC. The loading of MDEA and DEA initially decreased the CO_2 adsorption capacity at 30°C compared to the parent sample but increased to 40.6 and 37.1mg/g, respectively, when the temperature increased to 70°C. The loading of AMP decrease the CO_2 adsorption capacity compared to the parent sample under all the studied temperatures.

Under Task 4 “Comparison of the CO_2 capture by fly ash derived sorbents with commercial sorbents”, the CO_2 adsorption capacities of selected activated fly ash carbons were compared to commercial activated carbons. The CO_2 adsorption capacity of fly ash derived activated carbon, FAS-4, and its chemical loaded counterpart presented CO_2 capture capacities close to 7 wt%, which are comparable to, and even better than, the published values of 3-4%.

TABLE OF CONTENTS

1. PROJECT INTRODUCTION

1.1. Background

1.1.1. CO_2 capture for fossil fuel combustion units.

The emissions of anthropogenic CO_2 have increased the CO_2 concentration on the atmosphere with over 30% compared to preindustrial levels (Keeling and Whorf, 1998). Furthermore, it is estimated that future global CO_2 emissions will increase from ~7.4 GtC (billion tons of atmospheric carbon)/year in 1997 up to ~ 26 GtC/year in 2100 (DOE, 1999). Although there is a passionate debate regarding the impact of increasing CO_2 emissions on global climate change and global warming, there is a general agreement in the scientific community that doubling the CO_2 emissions will have a serious detrimental effect on the environment. Most of these anthropogenic emissions caused by fossil fuel utilization, where around one third of these emissions is due to electricity generation from fossil fuel combustion. Furthermore, fossil fuel electricity generation units rank as the first target to reduce anthropogenic emissions due to their stationary nature.

Fossil fuels have been the main energy supplier in the US for over a century. However, the current US fossil energy scenario is undergoing significant transformations, especially to accommodate stringently increasing environmental challenges. The US Department of Energy's Vision 21 Program does in fact represent a paradigm shift from traditional power plants by proposing a 21st Century Energy Plant that integrates multiple technologies with unprecedented efficiency and no environmental impact, while using a diversified fossil fuel portfolio and opportunity feedstocks to generate electricity, transportation fuels and chemicals

(DOE/NETL, 1999). The greatest challenge to achieve no environmental impact or zero emissions is probably greenhouse gases, especially CO_2 emissions that are inevitably associated with fossil fuel burning. Furthermore, CO_2 issues are closely scrutinized by the public opinion who may demand carbon reductions as a priority for the continuation of large scale utilization of fossil fuels. Carbon management can be achieved by (i) increasing the efficiency of energy conversion; (ii) using low-carbon or carbon-free energy sources; and (iii) capturing and sequestering CO_2 emissions. It is generally accepted that the first two alternatives will only provide incremental improvements, and therefore, carbon sequestration technologies must be developed to achieve zero emissions.

Although coal is the most abundant fossil fuel in the US, the reduction of CO_2 emissions from coal-fired units is an imperative to mitigate global climate change, and consequently, to guarantee the key role of coal in the 21st century. The costs of separation and capture of CO_2 are estimated to be about 75% of the total cost of ocean or geological sequestration, including the costs for compression to the required pressure for subsequent sequestration (Herzog, 1998). For instance, for a pulverized coal power plant, the estimated capture costs are \$35-\$264/ton of CO_2 with a power cost increase of 25-215 mills/kWh (IEA, 1999; Herzog, 1998). CO_2 separation and capture technologies aim to isolate the CO_2 into a form suitable for transport and subsequent sequestration, such as in the ocean, geological forms or in permanent mineral carbonates (Maroto-Valer et al, 2001a; and 2002a). Capture of CO_2 at low and moderate pressures from gaseous streams is a commercial practice by many industries, such as for hydrogen production and purification (DOE, 1999). These industries use chemical absorption technologies, that react the CO_2 with alkanolamines, such as monoethanolamine

(MEA), diethanolamine (DEA) and methyldiethanolamine (MDEA), to produce liquid species that can be regenerated upon heating:

$$C_2H_4OHNH_2 + CO_2 + H_2O \leftrightarrow C_2H_4OHNH_3^+ + HCO_3^-$$

However, chemical absorption processes are very energy intensive, and the amine solutions used in the process have very limited lifetimes due to substantial losses during stripping (DOE, 1999). Physical and chemical adsorption processes for CO_2 capture using high-surface area solids have also been proposed. Materials like zeolites and activated carbons have high surface areas (>1,000 m^2/g) and adsorb selectively different gases depending on their surface area, pore size, pore volume and surface chemistry. They operate in pressure-swing-adsorption (PSA) or temperature-swing adsorption (TSA) modes to desorb the adsorbed gases either by reducing the pressure or increasing the temperature, respectively. However, an International Energy Agency study has reported that physical adsorption on zeolites systems may not be attractive for gas- and coal-fired power plants due to these adsorption processes being energy intensive and expensive, particularly the PSA and TSA processes (IEA, 1998). Recently, new solid based sorbents are being investigated, where the amine groups are bonded to a solid surface, resulting in an easier regeneration step (Birbara et al, 1996). However, the supports used thus far, including commercial molecular sieves and activated carbons, are very expensive and hinder the economic viability of the process. Therefore, there is a need to find cost-effective precursors that can compete with the expensive commercial sorbents. For these new precursors to compete effectively with commercial sorbents, they must be inexpensive, and be easily converted into high-surface materials. The unburned carbon in the fly ash meets satisfactorily all these conditions (Maroto-Valer et al, 2000a). Firstly, it can be easily obtained from the utility industries as a byproduct. Secondly, the conventional production of activated carbons consists of a two-step process, that includes a devolatilization of the raw materials, followed by an activation step, while for unburned carbon only a one-step activation process is required, since it has already gone through a devolatilization process while in the combustor, as shown previously by the authors (Maroto-Valer et al, 2001a).

1.1.2. Challenges for increasing utilization of combustion byproducts.

A two-phase strategy to reduce NOx emissions from coal-fired utility boilers was issued by the Environmental Protection Agency (EPA) under Title IV of the 1990 Clean Air Act Amendment. Phase I of this strategy took effect on January 1996 and promulgated that emissions levels from Group-1 boilers should be reduced by over 400,000 tons/year between 1996-1999 (DOE, 1996). One of the more extensively used approaches for meeting the Title IV of the 1990 Clean Air Act-Phase I has been the installation of low-NOx burners, that change the flame-temperature profile as well as the flame chemistry since, in essence, a hot oxygen-rich flame is replaced by a cooler and longer, fuel-rich flame. While these modifications have proven effective in reducing NOx emissions, they have also resulted in a lower combustion efficiency, leading to an increase in the concentration of unburned carbon in the fly ash (Maroto-Valer et al, 1998). In 1999, the combustion of around 1,045 million tons of coal also generated ~107 million tons of coal combustion byproducts (CCBs), including around 62 million tons of fly ash (American Coal Ash Association, 1999). It is estimated that around 6 million tons of unburned carbon were also generated. One third of the fly ash is currently used, with the largest specialized application being in the cement industry. The remaining fly ash, currently over 40 million tons, is placed in landfills. Furthermore, Phase II of Title IV, that began January 2000, will strive to achieve an additional reduction of ~900,000 tons of NOx annually and it is expected that facilities in 19 states could be affected by the implementation of this regulation. It is also anticipated that Phase II will cause a further rise in the concentration of unburned carbon in fly ashes.

The increasing concentration of unburned carbon, usually referred to as LOI (loss-on-ignition), in fly ash has restricted the principal use of ash in the cement industry. This is mainly linked to the tendency of unburned carbon to adsorb air-entrainment agents that are added to the cement to prevent crack formation and propagation. Fly ashes with LOI higher than 6% are generally rendered unsuitable for the cement industry. Consequently, the carbon-rich ash is either placed in holding ponds or landfilled. In 1999 around 40 million tons of fly ash were disposed. However, this landfill practice results in rising costs for the utility companies in addition to the loss of revenue from ash sales. For instance, it has been estimated that in the US, the disposal of the 25 million tons of fly ash that are being marketed will entail an additional cost of over $450 million to the utility industry. Moreover, the increasingly severe regulations on landfill and the limited access to new disposal sites with the subsequent rise in the cost of disposal will demand the utility industry to seek suitable alternatives to this problem. Three possible alternatives have been identified: (i) begin offsetting coal combustion with natural gas; or (ii) require additional coal cleaning to remove the ash prior to combustion; or (iii) simply use the unburned carbon. The first two alternatives could compromise the coal industry, since the utilities could potentially reduce the NOx emissions and the ash disposal problem by using gas instead of coal as fuel, or require additional coal cleaning, which would increase the cost of the coal as fuel and reduce its competitive advantage. Consequently, the third alternative, concerning the use of fly ash carbon, will benefit both the coal and utility industries, and accordingly, environmental and cost-effective strategies need to be established for the use of these high-LOI fly ashes.

1.1.3. Synergistic utilization of fly ash carbons for CO_2 capture

The utilization of unburned carbon can bring enormous economic and environmental benefits to both the coal and utility industry. Although several technologies have been successfully developed and commercialized to separate the unburned carbon from the fly ash, only a few power plants have installed a beneficiation process on their sites. This is due to the low value of the resultant separated materials, since a ton of fly ash is generally sold for as little as $10-20, and the unburned carbon is simply disposed or rerouted to the combustor. However, the economics of a given separation process could be greatly enhanced if both separated materials could be used as precursors for high-value products. In this way, the added value generated from the utilization of both fly ash and unburned carbon would potentially offset the cost of the separation process. For instance, alternative high-value markets for the utilization of fly ash have been widely investigated and include the production of glass ceramics, synthesis of zeolites and use of cenospheres (Querol et al, 1997). However, significantly less attention has been paid to the potential utilization of unburned carbon, which is generally viewed as a liability and is either disposed or rerouted to the combustor. Nonetheless, this carbonaceous material is a very attractive precursor for the production of carbon products, like activated carbons, since it consists basically of elemental carbon and it has gone through a devolatilization process while in the combustor at temperatures well above 1300°C (Maroto-Valer et al, 2001b; and 2001c). Therefore, the added value generated from the unburned carbon utilization as a precursor for premium carbon products, like activated carbons, could offset the cost of the separation process. It is envisioned that the utilities could potentially produce two high-value streams after fly ash beneficiation: (i) a low-carbon stream (<6% LOI) that could be used as an additive for the cement industry; and (b) a high-carbon stream (>50%LOI) that could be used as precursor for CO_2 sorbents. Furthermore, the cement industry is indeed interested in continuing and even increasing its fly ash demand as a cement additive, since this is the only strategy that they have to reduce their CO_2 emissions, where the cement industry is responsible for ~10% of the anthropogenic CO_2 emissions. Clearly, utilizing the activated unburned carbons from fly ashes as support for amine capture of CO_2 would provide the utilities with a unique strategy to reduce their CO_2 emissions, and simultaneously increase their combustion byproducts utilization.

1.2. Program Objectives

The overall objective of this research program is to develop fly ash derived sorbents to capture CO_2 from flue gas of power plants. A selection of high-carbon fly ashes from a sample bank established previously by the authors, and that comprises samples from different combustor types, including pulverized units, fluidized beds and cyclones was conducted for this study. The chemical and physical properties of the suite of fly ash samples investigated were characterized towards their use as sorbents. The fly ash carbon samples were activated using the protocols previously developed by the authors and that include a one-step activation process. The activated fly ash samples were amine impregnated at loadings 20-65 wt% using alcohol amines by immersing them in an amine solution. The porous structure of the activated and impregnated fly ash carbons were systematically characterized using conventional adsorption techniques, like N_2 and CO_2 adsorption isotherms. The produced fly ash sorbents were tested for CO_2 capture. The CO_2 sorption capacities and regeneration of the produced sorbents were compared to those of commercial activated carbons. Finally, a comparison between the produced sorbents and commercial activated carbons was conducted to assess the potential of the proposed CCBs utilization route.

2. EXECUTIVE SUMMARY

The costs of separation and capture of CO_2 are estimated to be about three-fourths of the total cost of ocean or geological sequestration, where the processes involved are very energy intensive and the amine solutions used in the process have very limited lifetimes. Recently, new solid based sorbents are being investigated, where the amine groups are bonded to a solid surface, resulting in an easier regeneration step. However, the supports used thus far, including commercial molecular sieves and activated carbons, are very expensive and hinder the economical viability of the process. Therefore, there is a need to find cost-effective precursors that can compete with the expensive commercial sorbents. For these new precursors to compete effectively with commercial sorbents, they must be inexpensive, and be easily converted into high-surface materials. The unburned carbon in the fly ash meets satisfactorily all these conditions. Firstly, it can be easily obtained from the utility industries as a byproduct. Secondly, the conventional production of activated carbons consists of a two-step process, that includes a devolatilization of the raw materials, followed by an activation step. In contrast, for unburned carbon only a one-step activation process is required, since it has already gone through a devolatilization process while in the combustor, as shown previously by the proposers. Accordingly, this research program focuses on the development of fly ash derived sorbents to capture CO_2 from flue gas of power plants.

In this research project, fly ash carbon samples collected from different combustion systems were activated using the protocols previously developed by the authors, and the resultant activated fly ash samples were amine impregnated. The activated and treated fly ash samples were tested for CO_2 capture and release, and their capacities were compared to those of commercial activated carbons.

Under Task 1 “Procurement and characterization of a suite of fly ashes”, 10 fly ash samples, named FAS-1 to –10, were collected from different combustors with different feedstocks, including bituminous coal, PRB coal and biomass. These samples presented a wide range of LOI value from 0.66-84.0%, and different burn-off profiles. The samples also spanned a wide range of total specific surface area and pore volume. These variations reflect the difference in the feedstock, types of combustors, collection hopper, and the beneficiation technologies the different fly ashes underwent.

Under Task 2 “Preparation of fly ash derived sorbents”, the fly ash samples were activated by steam. Nitrogen adsorption isotherms were used to characterize the resultant activated samples. The cost-saving one-step activation process applied was successfully used to increase the surface area and pore volume of all the fly ash samples. The activated samples present very different surface areas and pore volumes due to the range in physical and chemical properties of their precursors. Furthermore, one activated fly ash sample, FAS-4, was loaded with amine-containing chemicals (MEA, DEA, AMP, and MDEA). The impregnation significantly decreased the surface area and pore volume of the parent activated fly ash sample.

Under Task 3 “Capture of CO_2 by fly ash derived sorbents”, sample FAS-10 and its de-ashed counterpart before and after impregnation of chemical PEI were used for the CO_2 adsorption at different temperatures. The sample FAS-10 exhibited a CO_2 adsorption capacity of 17.5mg/g at 30^{o}C, and decreases to 10.25mg/g at 75^{o}C, while those for de-ashed counterpart are 43.5mg/g and 22.0 mg/g at 30^{o}C and 75^{o}C, respectively. After loading PEI, the CO_2 adsorption capacity increased to 93.6 mg/g at 75oC for de-ashed sample and 62.1 mg/g at 75oC for raw fly ash sample.

The activated fly ash, FAS-4, and its chemical loaded counterparts were tested for CO_2 capture capacity. The activated carbon exhibited a CO_2 adsorption capacity of 40.3mg/g at 30^{o}C that decreased to 18.5mg/g at 70^{o}C and 7.7mg/g at 120^{o}C. The CO_2 adsorption capacity profiles changed significantly after impregnation. For the MEA loaded sample the capacity increased to 68.6mg/g at 30^{o}C. The loading of MDEA and DEA initially decreased the CO_2 adsorption capacity at 30°C compared to the parent sample but increased to 40.6 and 37.1mg/g, respectively, when the temperature increased to 70°C. The loading of AMP decrease the CO_2 adsorption capacity compared to the parent sample under all the studied temperatures.

Under Task 4 “Comparison of the CO_2 capture by fly ash derived sorbents with commercial sorbents”, the CO_2 adsorption capacities of selected activated fly ash carbons were compared to commercial activated carbons. The CO_2 adsorption capacity of fly ash derived activated carbon, FAS-4, and its chemical loaded counterpart presented CO_2 capture capacities close to 7 wt%, which are comparable to, and even better than, the published values of 3-4%.

3. EXPERIMENTAL

The experimental procedures and methodologies used for this work are described below.

3.1. Procurement and characterization of fly ash samples

This task included the selection of high-carbon fly ashes from a sample bank established previously by the authors, and that comprises samples from different combustor types, including pulverized units, fluidized beds and cyclones. These samples derived form different feedstocks (bituminous, PRB, biomass). The chemical and physical properties of the suite of fly ash samples investigated were characterized towards their use as sorbents by using the state-of-the-art analytical techniques available at The Pennsylvania State University. A battery of tests, previously designed by the authors was used to characterize the suite of samples assembled, including LOI, thermogravimetric analysis (TGA), and porosity analysis.

3.1.1. Loss on ignition analysis (LOI)

The loss-on-ignition (LOI) contents of the char samples were determined according to the ASTM C311 procedure. Around 1 g of sample was oxidized in air for 3 hours at 800^{o}C to constant weight in a muffle furnace. The LOI content was then calculated from the weight loss of the sample after oxidation. The LOI analyses were conducted in duplicate.

3.1.2. Thermogravimetric analysis (TGA)

The thermogravimetric analyses were conducted on a Perkin Elmer TGA7 from room temperature to 900°C under air flow (100ml/min), and the samples were heated up to 850°C in air at a rate of 10°C/min.

3.1.3. Porosity analysis

The porous texture of the fly ash samples was characterized by conducting N_2 adsorption isotherms at 77K using a Quantachrome adsorption apparatus, Autosorb-1 Model ASIT. The pore volume was calculated as the volume measured in the nitrogen adsorption isotherm at a relative pressure of 0.95 ($V_{0.95}$). The total specific surface area, S_t, was calculated using the multi-point BET equation in the relative pressure range 0.05-0.35. The Density Functional Theory (DFT) method was used to calculate the pore size distribution. The pore sizes 2nm and 50nm were taken as the limits between micro- and mesopores and meso- and macropores, respectively, following the IUPAC nomenclature (Sing et al., 1985).

3.2. Preparation of fly ash derived sorbents

3.2.1. Activation of fly ash samples and characterization of activated carbons

Firstly, the samples were activated using the protocol previously developed by the authors (Maroto-Valer et al, 2001c). This protocol includes a one-step steam activation process. The activation experiments were carried out in a stainless steel reactor that was placed inside a vertical furnace, as previously described (Maroto-Valer et al., 1999c; and 2002b). The versatility of the design allows the use of different particle size, activating agent, heat treatment, residence time, flow rates and amount of sample. Typically around 3g of sample were placed into a reactor and a flow of steam passed through from the bottom of the bed. The reactor was then heated under nitrogen flow to the desired temperature before steam was introduced in the reactor.

The properties of the carbons that were activated under controlled conditions were systematically characterized, including a detailed description of the micro- and meso-porous structur,e using conventional adsorption techniques, like N_2 and CO_2 adsorption isotherm, as previously described (Section 3.1.3).

3.2.2. Impregnation of activated fly ash samples

The activated carbons from fly ash were modified in order to introduce chemical adsorption sites towards CO_2 capture. Monoethanolamine (MEA), diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA) are among the most commonly used solvents for CO_2 absorption processes (Smith, 1999; Yeh et al, 2001). Alcohol amines have previously been used to impart an amine functionality to activated carbons, and therefore, to enhance their CO_2 capacity (Zinnen et al, 1989). Furthermore, it has been found polyetherimine (PEI) can significantly increase the CO_2 adsorption of molecular sieve materials MCM-41 (Xu et al, 2002). Therefore, all the above compounds were used to modify the activated carbons produced from fly ash.

The activated fly ash carbons can be impregnated by immersing them in an amine solution of the desired amine compound. A desired amount of activated carbon samples are saturated by the solution of chemicals (MDEA, MEA, DEA, AMP and PEI). The resultant slurry was continuously stirred for about 20 minutes, and then dried in air at 120°C until constant weight. The activated carbons before and after chemical loading were characterized by conducting N_2 and CO_2 adsorption isotherms at 77K and 273K, respectively, using a Quantachrome Autosorb-1 apparatus. The BET surface area, DR surface area, total pore volume and mean pore size of the adsorbens were obtained by analyzing the isotherms.

3.3. Capture of CO_2 by fly ash derived sorbents

The ability of CO_2 capture and release for the activated fly ash sorbents was investigated. The adsorption and desorption properties of the activated carbon and chemical loaded activated carbon were characterized using PE-TGA 7. Around 10 mg of adsorbents were placed in a platinum crucible, heated up to desired temperature in 100ml/mim pure N_2 flow, and held at this temperature till the weight of sample was stable (10-20 min.). The gas flow was switched from N_2 to 99.8% bone-dry CO_2 at a flow rate of 100ml/min to measure the CO_2 adsorption performance, and was then changed back to a 100 ml/min N_2 flow at the same temperature for the desorption test. It is anticipated that some operational problems may arise from the low-thermal stability of the amines that can decompose at temperatures below the stack temperatures, and this will be addressed during the present study by selecting heat resistant amines.

4. RESULTS AND DISCUSSIONS

4.1. Task 1 "Procurement and characterization of a suite of fly ashes"

A total of ten fly ash samples, named FAS-1 to -10 were collected from different combustors with different feedstocks, including bituminous coal, PRB coal and biomass. A series of analysis were conducted to characterize their properties, including loss-on-ignition (LOI), thermogravimetric analysis (TGA) and porosity analysis.

FAS-1, and -2 were obtained from PCCs located in Pennsylvania with a net capacity of 243MW and 180MW, respectively. Both units use high-volatile bituminous coals from different seams. FAS-1 was obtained from the cool-side hoppers, while FAS-2 was collected from the silo.

FAS-3 was collected from the Penn State University pulverized coal-fired suspension firing research boiler (2 MM Btu/hour) that uses a high volatile bituminous coal from the Middle Kittanning seam. FAS-5 was obtained from a utility cyclone unit, and the sample was crushed, ground and sieved, and the fraction between 100-200 mesh was collected and used for AC generation studies.

FAS-4 was collected at Penn State University, University Park, from a 2 MW pulverized-coal-fired suspension-firing research boiler equipped with a low-NO_x burner, using Middle Kittanning seam bituminous coal with high volatile matter content.

FAS-5 came from a cyclone unit located in Willoughby, Ohio with a net capacity of 216 MW using a low-volatile bituminous coal, and this unit was retrofitted with a fly ash beneficiation technology, which comprised multi-staged electrostatic precipitation.

The three fly ash samples FAS-6 to –8 were collected from a boiler at Plant Miller (Georgia) burning PRB coal.

FAS-9 was provided by Dr. James Hower, University of Kentucky-Center for Applied Energy Research. This sample comes from Shawnee power plant in Kentucky and the coal feed is PRB-western bituminous blend, roughly 50:50. This sample was selected because of its high Ca content compared to other class F ashes, although it is not a class C.

FAS-10 was procured from a gasifier using subbituminous coal.

4.1.1 LOI analysis

The results of the LOI analyses for fly ash samples FAS1-10 are reported in Table 1. The LOI of the samples collected for the study present a wide range of values from 0.66%-84.0%. The LOI values of some of the samples reported here (FAS-3 to -5) are higher than those typically for PCC systems of <15wt% (FAS-1 and FAS-2).

Previous studies conducted by the authors have shown that the LOI values of fly ashes change significantly within the hoppers of the same unit at a power plant, where fly ashes from cool-side hoppers have generally higher LOI values than those from the hot-side hoppers. This is the case for the sample FA-3 that was collected from the cool-side hoppers of a PCC unit. Other source of high carbon content fly ashes is from power plants that have installed a beneficiation unit to obtain a high carbon stream and a high ash content stream. This is the case for the sample FAS-5 that has the highest LOI value of 84wt%, since it was beneficiated at the plant, and therefore, has a very high LOI value that is not typical for fly ashes that have not been beneficiated.

Table 1. LOI values of the fly ash samples investigated in this study.

Sample	Feedstock Used	System	LOI Wt %
FAS-1	HvB	PCC	10.0
FAS-2	Bit.	PCC	12.0
FAS-3	HvB	PCC	50.8
FAS-4	SubB	PCC	62.7
FAS-5	n.d.	Cyclone	84.0
FAS-6	PRB	Boiler	0.66
FAS-7	PRB	Boiler	0.83
FAS-8	PRB	Boiler	1.03
FAS-9	Biomass	Boiler	22.3
FAS-10	SubB	Gasifier	38.0

For the three fly ash samples collected from PRB coal-fired boilers, although their color was dark, all their LOI values are quite low (<1.03 wt%). The LOI of FAS-6 is only 1.03%, both LOI values of the other two samples, FAS-7 and FAS-8, are below 1%. The fly ash sample collected from a biomass-fired utility (FAS-9) has a LOI value of 22.3%, and the sample is the mixture of black chips with woody texture.

4.1.2. Thermogravimetric analysis (TGA)

The TGA profiles for three fly ash samples (FAS-2, FAS-4, and FAS-9) are shown in Figure 1. For these three samples their TGA profiles are quite different due to the different feedstock (bituminous for FAS-2, sub-bituminous for FAS 4 and biomass for FAS-9). For FAS-2, its weight loss begins at around 470°C till around 680°C and then almost levels off, remaining around 88% ash after the carbon completely burns off. For FAS-4, its weight loss occurs in the temperature range of 430-660°C and the ash remaining after the carbon burns off is ~63%. However, the biomass fly ash FAS-9 starts losing weight at much lower temperatures, around 300°C, with a second weight loss step beginning at around 634°C, and containing ~78% ash (i.e., 22% carbon) at the end of the test.

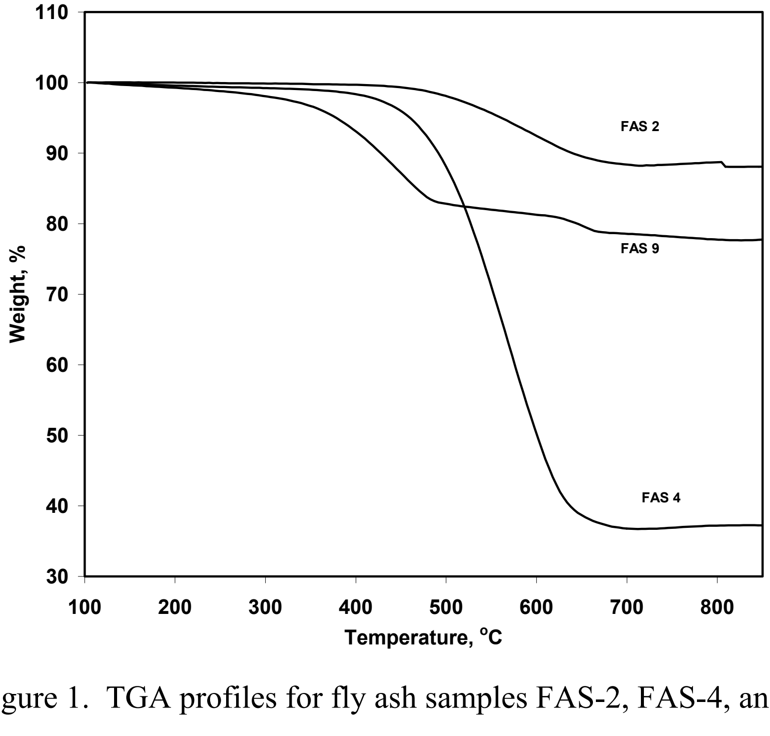


Figure 1. TGA profiles for fly ash samples FAS-2, FAS-4, and FAS-9.

4.1.3. Porosity studies

Figure 2 shows the isotherms of samples FAS-3 to –9 (the isotherm for sample FAS-10 is not included since it presents much higher adsorbed volumes). The sample from biomass, FAS-9 presents the biggest hysteresis loop, which is usually associated with the filling and emptying of mesopores by capillary condensation. Besides the steep rise at the low relative pressure, which corresponds to the micropore filling, the isotherm keeps rising with increasing relative pressure, even near saturation pressure, indicating that there are mesopores and macropores in the sample.

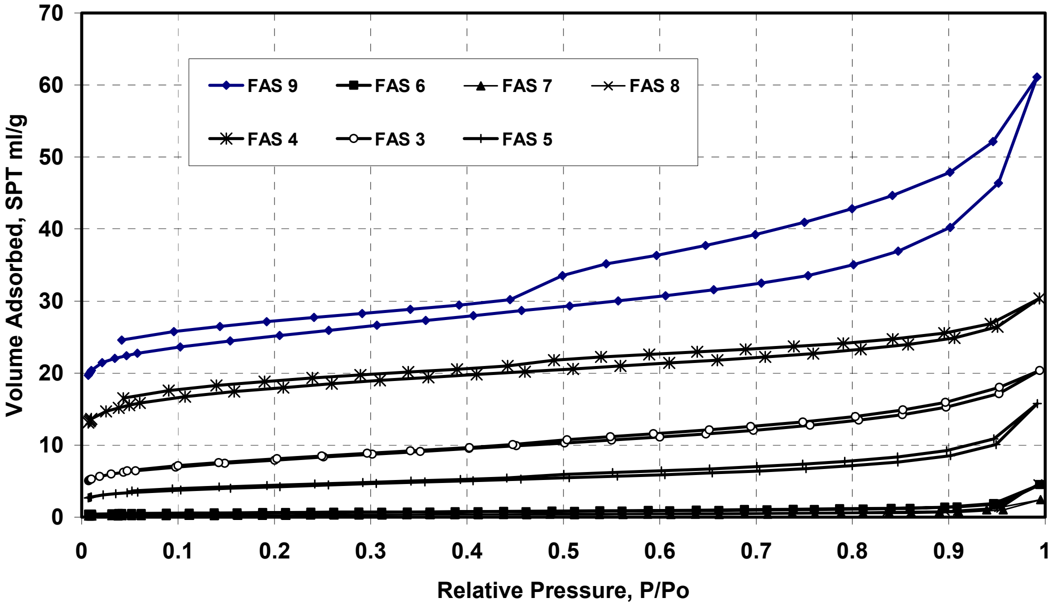


Figure 2. N_2-77K isotherms of samples FAS 3-9.

Table 2 presents the surface area and pore volume for samples FAS-3 to –10.The samples collected have a wide spread surface area, from less than 1 m^2/g for FAS-6 up to 284

m^2/g, for FAS 10, where the latter was collected from a gasifier. The fly ash sample FAS-4 collected from a biomass burning utility has the next highest surface area, 78 m^2/g.

Table 2. Surface area and pore volume of the samples investigated.

Sample	Surface Area m^2/g	Pore Volume ml/g
FAS-3	81.5	0.087
FAS-4	120.0	0.081
FAS-5	8.7	0.008
FAS-6	0.9	0.002
FAS-7	1.1	0.002
FAS-8	2.1	0.003
FAS-9	77.4	0.072
FAS-10	284.0	0.277

The pore size distribution of FAS-4 and FAS-9 was calculated within 0.4-60 nm by applying the Density Theory Function (DFT), as shown in Figure 3. Due to the nonlocal or smoothed density theory approximation, which is superior to the BJH method that only calculates the mesopore size distribution, the DFT method can calculate the pore size distribution for micropores, mesopores, and even to macropores.

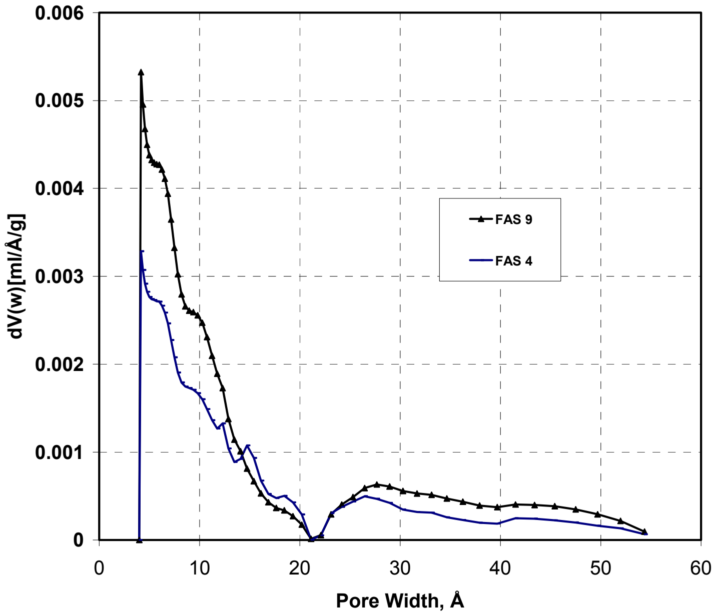


Figure 3. Pore size distribution of FAS-4 and FAS-9 calculated by DFT

According to the recommendation of IUPAC, a micropore is a pore with width less than 2nm (20 Å), a macropore is a pore with width larger than 50nm (500 Å) and a mesopore is a pore with width between 2-50nm (20-500 Å). In Figure 3, it should be noted that there are basically two peaks in the pore size distribution curve for these two samples. The first one in the micropore range and centered at around 0.4nm (4 Å) corresponds to the steep rise at low relative pressure of the isotherm (Figure 2). The other peak ranges from 2nm (20 Å) to 5.5nm (55 Å), corresponding to the slow climb at high relative pressure in the isotherm (Figure 2). Due to the small size of the micropores and the overlapping of the fields of opposite walls of the micropores, the micropores are the major active site for most adsorbates, while the mesopores act especially as adsorption sites for larger molecules. For the case of chemical impregnation of sorbents for CO_2 adsorption, it was postulated that the mesopores play an important role, since the chemical impregnation may completely blocks micro-pores and reduce openings of meso-pores.

4.2. Task 2 "Preparation of fly ash derived sorbents"

4.2.1. Activation and characterization of activated carbons produced.

The activation experiments were carried out in a stainless steel reactor that was placed inside a vertical furnace, as previously described (Maroto-Valer et al., 1999c; and 2002b). Nitrogen adsorption isotherms were used to characterize the resultant activated samples and Table 3 lists the surface area and total pore volume of some of the studied samples. The specific surface areas for the parent fly ash samples prior to activation range from 9 to 120 m^2/g. FAS-4 has the highest surface area and pore volume of 120 m^2/g and 0.08 ml/g, respectively. This suggests that the sample FAS-4 has already generated some porosity while in the combustor prior to the activation process. On the other hand, FAS-5 has the smallest surface area and pore volume of 9 m^2/g and 0.01ml/g, respectively. This could be due to the higher temperature experienced in the cyclone for FAS-5 compared to the other samples studied here that were procured from PCC units. Such a temperature effect has been observed for other carbons, with an extreme case being for carbons produced from poly(furfuryl alcohol) in which the adsorption capacity approaches zero for heat-treatment temperatures of about 1000°C (March et al., 2000). Microporosity in carbons is well known to be dependent on heat treatment temperature (Marsh et al., 1964) and the heating rate experienced by the coal particles in the different furnaces. Heating rate affects porosity and reactivity of the resulting carbons (Marcilla et al., 1996). In addition to temperature and heating rate, another factor that could influence the porosity development in the unburned carbons is the inorganic impurities composition, which may have a catalytic effect on carbon gasification reactions (McEnaney, 1991). The other sample reported here, FAS-3, comes from PCC utility boilers and has a surface area and pore volume similar to other samples previously investigated at the authors' laboratory (Maroto-Valer et al., 2001b; and 2001c).

Table 3. Surface area and total pore volume of the FAS-3, -4, and -5 samples and their activated counterparts.

Sample	Activated carbon	Surface area, m^2/g	Total pore volume, cc/g
FAS-3	FAS-3	82	0.09
	FAS-3-60	163	0.12
	FAS-3-120	307	0.22
FAS-4	FAS-4	120	0.08
	FAS-4-30	372	0.23
	FAS-4-60	538	0.33
	FAS-4-90	825	0.54
	FAS-4-120	1075	0.77
FAS-5	FAS-5	9	0.01
	FAS-5-60	87	0.08
	FAS-5-120	79	0.08

The surface area and total pore volume values for the steam-activated samples are also listed in Table 3. The activation times are given in minutes for each sample. For example, FA-5-60 corresponds to the FA-5 sample after 60 minutes activation. For all the samples, the steam activation process has successfully increased the surface area and pore volume. Since the parent samples have significantly lower surface areas and pore volumes than their activated counterparts, it can be concluded that the one-step activation process used here is sufficient to increase the surface area and pore volume of fly ash samples. However, the activated samples present very different surface areas and pore volumes, where FAS-4 has the highest surface area after activation. For FAS-5, its surface area and pore volume only increase from 9 m^2/g and 0.01 ml/g to 87 m^2/g and 0.09 ml/g, respectively, after steam activation.

4.2.2. Impregnation of activated fly ash samples

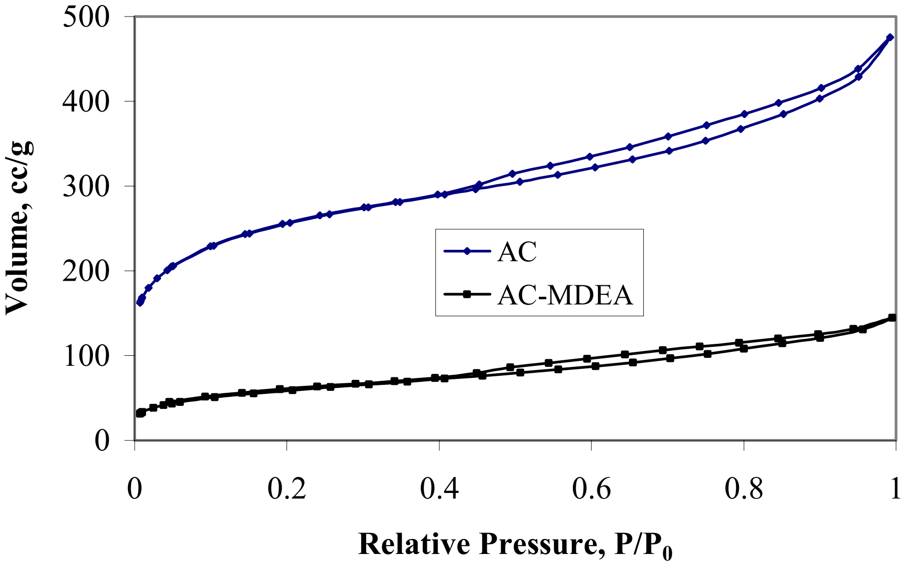
The activated carbons from fly ash have been modified with loading of chemicals in order to introduce chemical adsorption sites towards CO_2 capture, these chemicals including MEA, DEA, AMP, MDEA and MCM-41, as described in Section 3.2.2. The activated carbon investigated here was generated from FAS-4 at 850^oC for 90 minutes by steam activation.

The amount of chemicals loaded on the activated carbons is calculated by the weight difference of activated carbons before and after chemical impregnation, as presented in Table 4. It can be seen that the highest loading was achieved for MDEA (46%), while the loading levels for DEA, MEA and AMP were 34, 29, and 17 wt%, respectively.

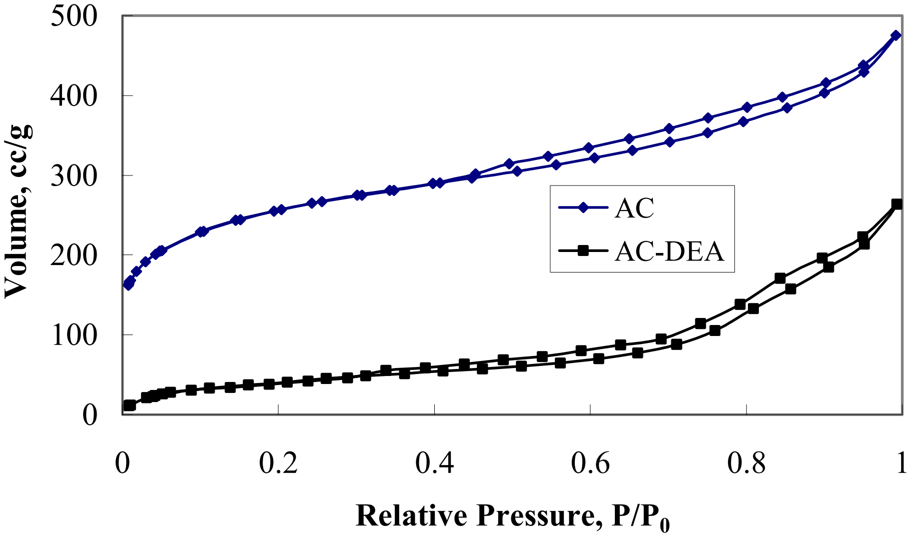
Table 4. Amount of chemicals loaded on the activated carbons.

Chemicals	Loading amount, wt%
MDEA	46
DEA	34
MEA	29
AMP	17

The N_2 adsorption isotherms at 77K on the parent activated carbon (AC), as well as the impregnated samples AC-MDEA, AC-DEA, AC-MEA, and AC-AMP are presented in Figures 4 (a)-(d), respectively. All the isotherms are Type IV of the BDDT classification, where the distinct hysteresis loops are associated with the filling and emptying of mesopores. The isotherm of the impregnated samples present lower adsorbed volumes than the parent activated sample. This indicates that the chemically loaded activated carbons have smaller micropore and mesopore volumes than AC. This decrease is probably due to the pore filling effect of the impregnated chemicals.

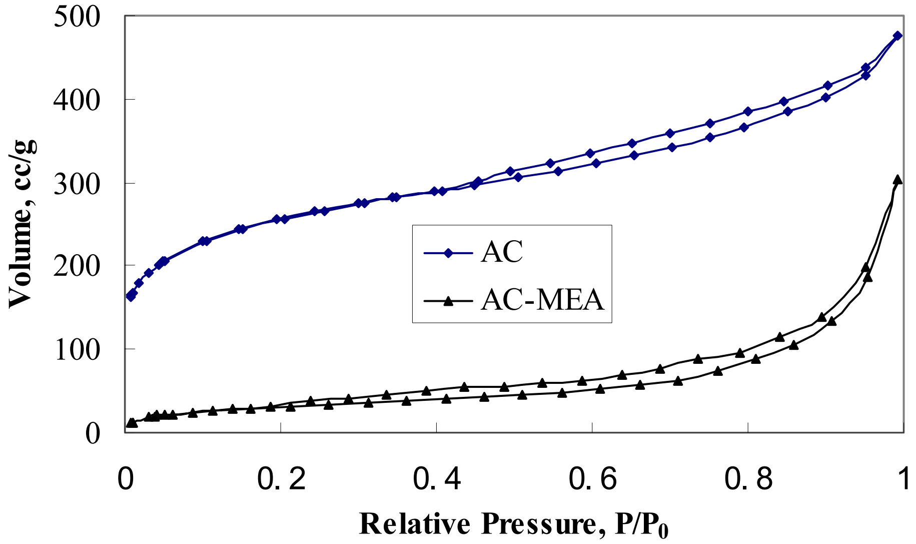


(a)



(b)

Figure 4 (a)-(b). N_2 (77K) adsorption/desorption isotherm for activated carbon and activated carbon loaded with (a) MDEA; and (b) DEA.



(c)

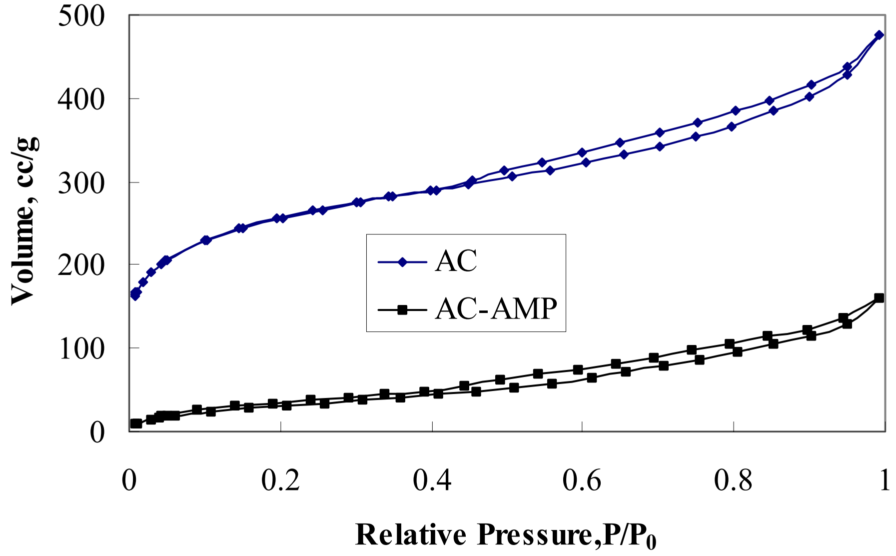
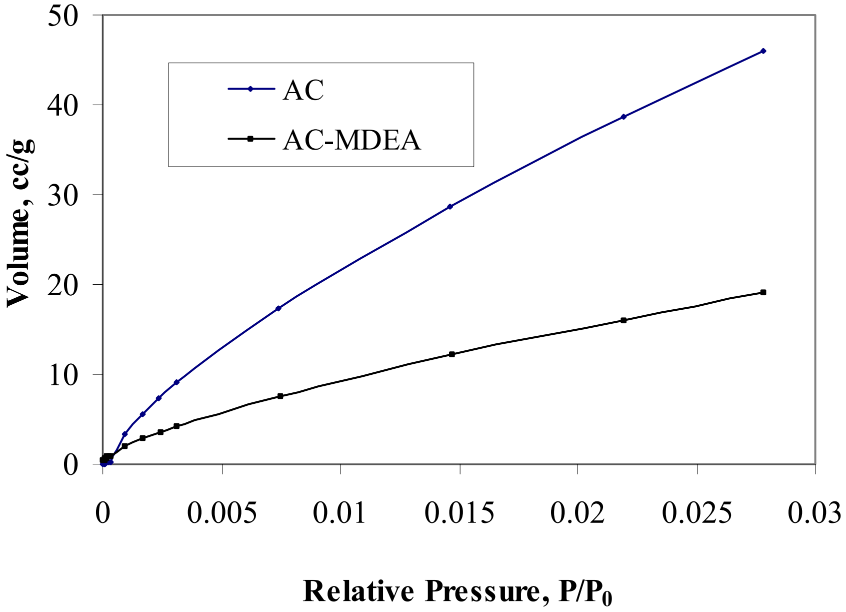


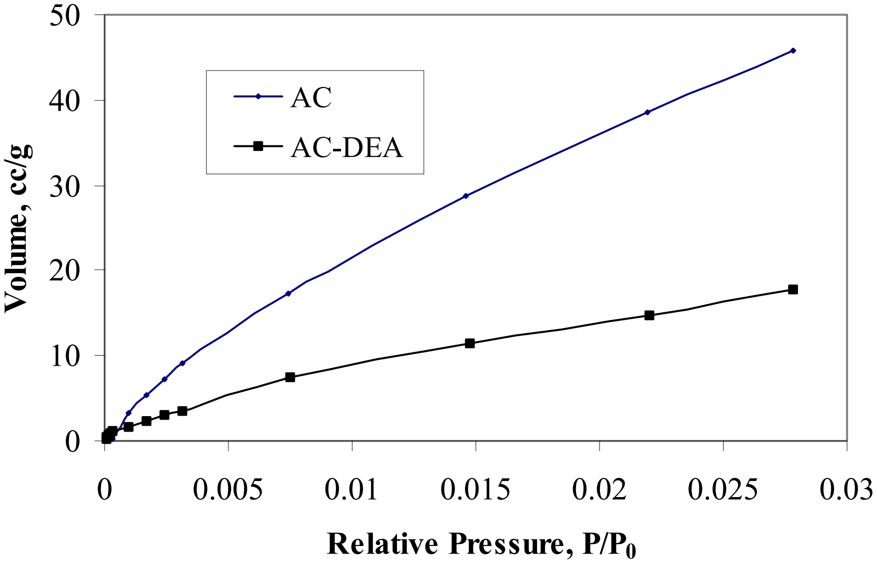
Figure 4 (c)-(d). N_2 (77K) adsorption/desorption isotherm for activated carbon and activated carbon loaded with (c) MEA; (d) AMP.

The CO_2 adsorption isotherms at 273K of samples AC, AC-MDEA, AC-DEA, AC-MEA, and AC-AMP are shown in Figures 5(a)-(d), respectively. Again, the isotherm of the parent activated carbon (AC) presented a larger adsorption volume than that of the chemical loaded activated carbons, indicating its larger extent of microporosity. This confirms that some of the micropores in the activated carbon samples were filled by the impregnation chemicals, as also indicated by the N_2 adsorption isotherms in Figures 4 (a)-(d).

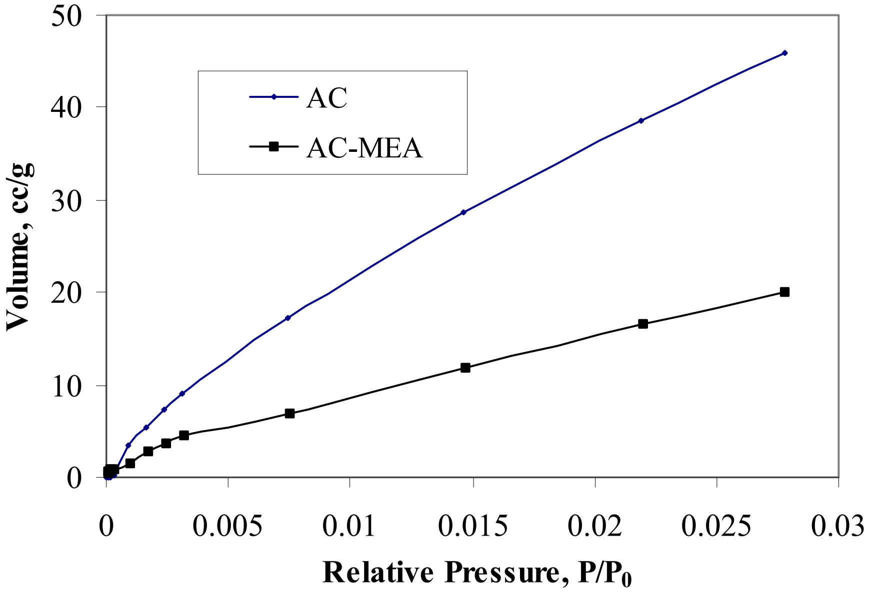


(a)

Figure 5 (a). CO_2 (273K) adsorption/desorption isotherm for activated carbon and activated carbon loaded with: (a) MDEA.

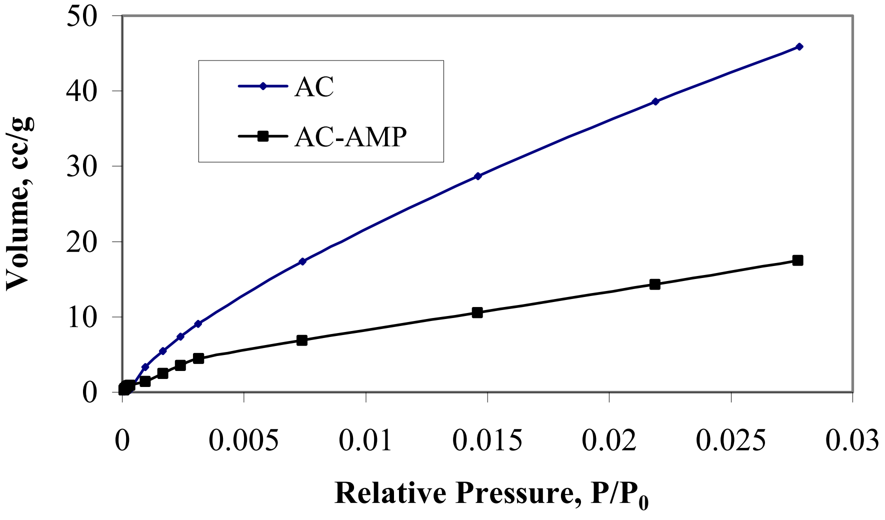


(b)



(c)

Figure 5 (b)-(c). CO_2 (273K) adsorption/desorption isotherm for activated carbon and activated carbon loaded with: (b) DEA; and (c) MEA.



(d)

Figure 5 (d). CO_2 (273K) adsorption/desorption isotherm for activated carbon and activated carbon loaded with: (d) AMP.

Table 5 lists the N_2 BET surface areas and total pore volumes (calculated from the amount adsorbed at relative pressure P/P_0 0.95). The DR surface areas, determined from the micropore volumes, are also presented in Table 5. The BET and DR surface areas, and the total pore volume of the parent AC are 818 m^2/g, 501 m^2/g and 0.665 ml/g, respectively. The chemical impregnation process results in a decrease of BET and DR surface areas of all the chemicals used (Table 5) indicating a blocking of some of the micro- and meso-pore volume. For example, the BET and DR surface areas, and the total pore volume for AC-MDEA have decreased to 204 m^2/g, 96 m^2/g, and 0.203 ml/g, respectively. This is consistent with the N_2 and CO_2 adsorption isotherms presented previously (Figures 4 and 5).

The micropore volumes were calculated from α_s-plot using a nongraphitized carbon black as a reference, and the mesopore volumes were calculated by subtracting the micropore volume from the total pore volume. After the loading of chemicals, the micro- and mesopore volume decrease due to the pore filling effect of chemicals. However, the chemicals investigated here (MDEA, DEA, MEA, and AMP) played different roles on the micropores and mesopores filling of activated carbon. Chemical MDEA had the most significant effect on micropore filling, with a micropore volume decrease of 73%. Chemicals AMP, DEA, and MEA resulted in a decrease of micropore volume of 71%, 69% and 64%, respectively. For the case of mesopore filling, chemical AMP presented the highest ability to decrease the pore volume (68%), followed by MDEA, DEA, and MEA with volume decrease of 65%, 39% and 4%, respectively.

Table 5. Surface area (S_{BET} and S_{DR}) and pore volumes (V_{total}, V_{mic} and V_{mes}) for the parent activated carbon and its chemical loaded counterparts.

	AC	AC-MDEA	AC-DEA	AC-MEA	AC-AMP
S_{BET}, m^2/g	818	204	265	241	245
S_{DR}, m^2/g	501	96	108	120	100
V_{total}, cm^3/g	0.665	0.203	0.288	0.397	0.201
V_{mic}, cm^3/g	0.400	0.110	0.126	0.143	0.118
V_{mes}, cm^3/g	0.265	0.092	0.162	0.254	0.084
Decrease in V_{mic} after chemical loading, %		73	69	64	71
Decrease in V_{mes} after chemical loading, %		65	39	4	68

The mechanism of pore filling using different chemicals is still not well understood, but it is assumed that the different pore filling effect was due to the difference in the molecular size of the chemicals. There appears to be significant differences in the way that the chemicals are filling up the pores of the parent activated sample. On one hand, the MEA is very specific towards filling the micropores and virtually does not accumulate in the mesopores. On the other hand, both MDEA and AMP appear to build up in the mesopores and may block off the micropores without actually filling them.

4.2.3. Deashing of fly ash sample

A conventional acid (HCl/HNO_3/HF) digestion step was conducted to remove the ash from sample FAS-10 and concentrate its unburned carbon. About 50 g of fly ash sample was treated with the above acids at 65°C for 4 hours. The deashed sample was labeled as DEM-FAS10.

Table 6. LOI and pore structure parameters of sample FAS-10 and its desahed counterpart.

Sample	LOI, wt%	Surface area, m^2/g	*Pore Volume, ml/g*
FAS-10	38	284	0.277
DEM-FAS10	97	731	0.740

The LOI and pore structure parameters of sample FAS-10 and its deashed counterpart are listed in Table 6. The deashing step used here can successfully concentrate the unburned carbon, where the deashed sample DEM-FAS10 presents LOI values as high as 97 wt%. Furthermore, the deashed sample DEM-FAS10 has a total surface area as high as 731m^2/g, compared to 284m^2/g for the parent sample FAS-10. This increase in surface area is related to the removal of the inorganic fly ash, which is virtually non-porous.

4.3. Task 3 “Capture of CO_2 by fly ash derived sorbents”

The adsorption and desorption properties of the activated carbon and chemical loaded activated carbon were characterized using PE-TGA 7. Around 10 mg of adsorbents were placed in a platinum crucible, heated up to desired temperature under a 100ml/mim pure N_2 flow, and held at this temperature till the weight of sample was stable (10-20 minutes). The gas flow was then switched from N_2 to 99.8% bone-dry CO_2 at a flow rate of 100ml/min to measure the CO_2 adsorption performance, and was then changed back to a 100 ml/min N_2 flow at the same temperature for the desorption test.

The CO_2 adsorption/ desorption profiles of the activated fly ash carbon (AC) and the chemical loaded activated carbons are presented in Figure 6-10, and the adsorption capacity results of the CO_2 uptake are also listed in Table 7. Both the adsorption and desorption time was 150 minutes for sample AC and AC-MDEA, and 60 minutes for other chemical samples. The adsorption capacity of the samples was expressed as their weight change in percentage, and the desorption capacity was calculated as the ratio of desorbed CO_2 over the adsorbed CO_2. The samples for CO_2 capture throughout this study were named using the sorbents, followed by the adsorption temperature. As shown in Figure 6, the activated carbon exhibited a CO_2 adsorption capacity of 40.3 mg/g (4.03%) at 30°C. With increasing adsorption/ desorption temperature, the CO_2 uptake on the activated carbon decreased to 18.5 and 7.7 mg/g at 70 and 120^{o}C, respectively. This is probably because the CO_2 adsorption on activated fly ash carbon prior to impregnation is a physical process.

Figures 7-10 show the CO_2 adsorption/ desorption profiles of the activated fly ash carbon loaded with chemicals. The loading of chemicals MDEA, DEA, and AMP resulted in a decrease of the CO_2 adsorption capacity as measured at 30^{o}C, where the CO_2 adsorbed decreased to 17.7 mg/g for AC-MDEA, 21.1 mg/g for AC-DEA, and 22.3 mg/g for AC-AMP. This was probably due to two reasons: (i) the reaction between CO_2 and amino groups could not happen under this low adsorption temperature (30^{o}C); and (ii) CO_2 was physically adsorbed on the surface of chemical loaded activated carbons, as observed for the AC sample. The loading of these three chemicals significantly decreased the surface area and pore volume of the activated carbon due to the pore filling effect, which probably leads to the low CO_2 adsorption capacity compared with AC-30. The loading of MEA led to the an increase of CO_2 uptake compared to that of activated carbon (68.6 mg/g vs. 40.3 mg/g), this could be due to the a result of chemical reaction between MEA and CO_2 under the test conditions.

The loading of MDEA, DEA and MEA increased the CO_2 adsorption capacity at higher temperature (30.4 mg/g vs. 18.5 mg/g, and 16.1 mg/g vs. 7.70mg/g for MDEA at 70^{o}C and

120°C, respectively; 37.1 mg/g vs. 18.5 mg/g for DEA at 70°C, and 49.8 mg/g vs. 18.5mg/g for MEA at 70°C). While the AMP loaded activated carbon did not show the increase of CO_2 adsorption under the temperatures investigated in this study. This indicated that the loading of amine groups on the activated carbon may have potential to increase the CO_2 adsorption capacity under higher temperature that are close to the stack temperature, ~120°C, but it highly depends on the chemical selected.

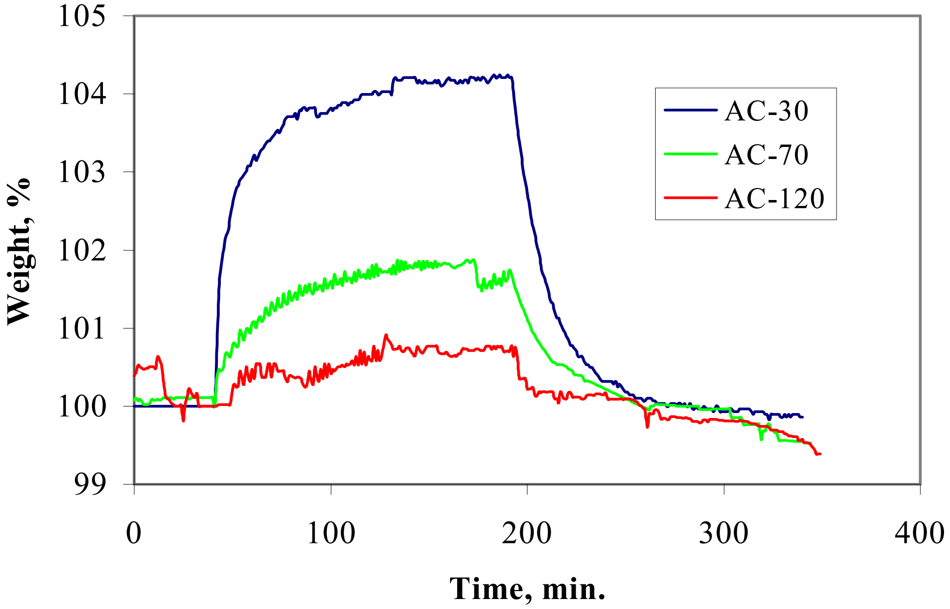


Figure 6. CO_2 adsorption/desorption profiles of the activated fly ash carbon (AC) at 30, 70 and 120°C.

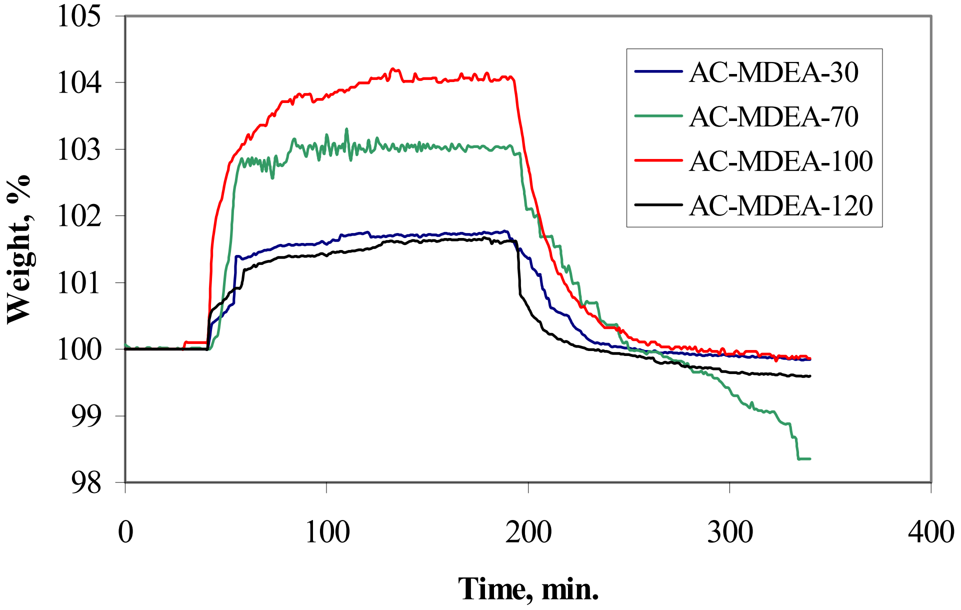


Figure 7. CO_2 adsorption/desorption profiles of the activated and MDEA impregnated fly ash carbon (AC-MDEA) at 30, 70, 100 and 120°C.

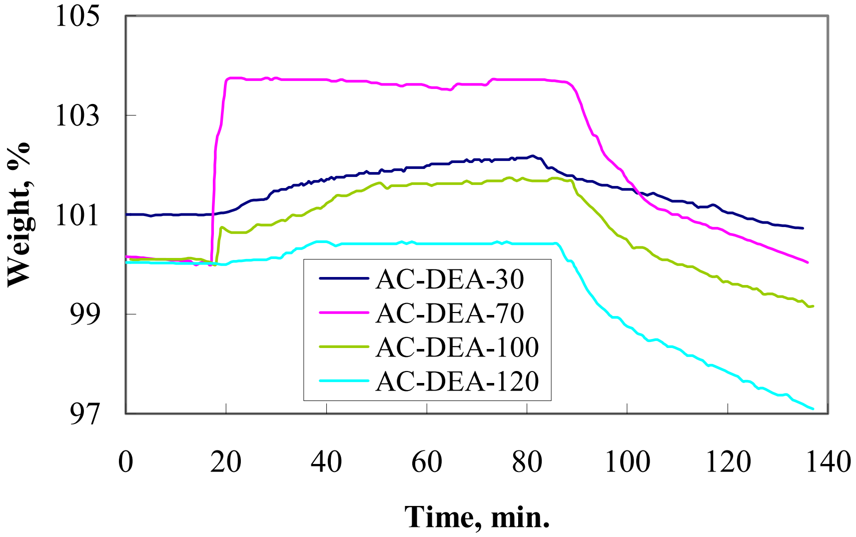


Figure 8. CO_2 adsorption/desorption profiles of the activated and DEA impregnated fly ash carbon (AC-DEA) at 30, 70, 100 and 120°C.

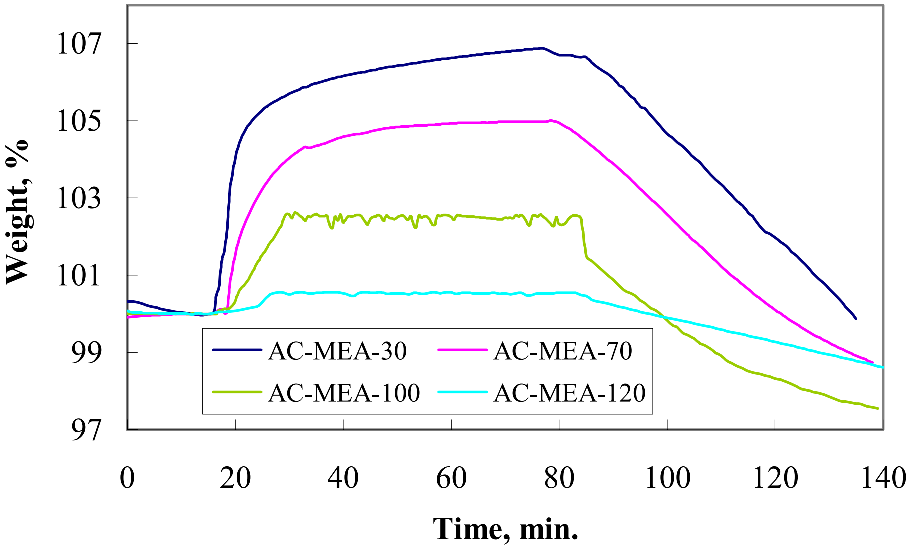


Figure 9. CO_2 adsorption/desorption profiles of the activated and MEA impregnated fly ash carbon (AC-MEA) at 30, 70, 100 and 120°C.

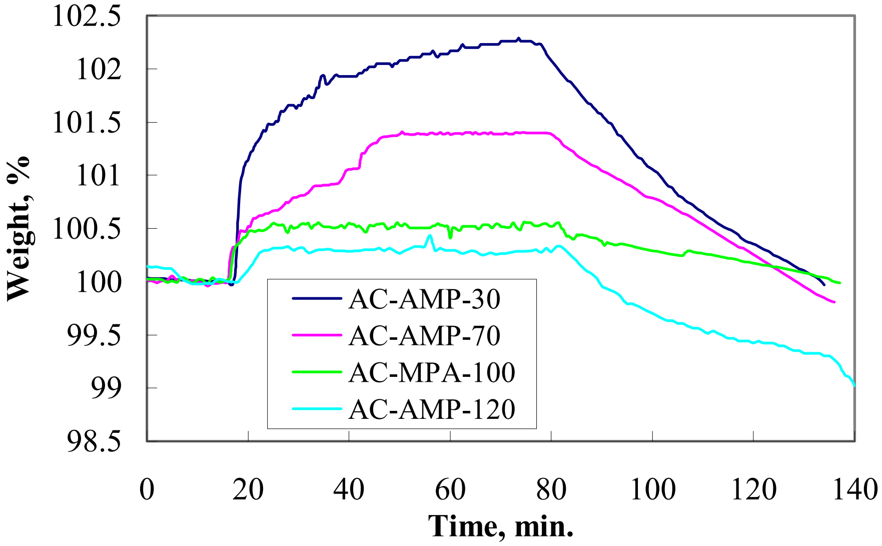


Figure 10. CO_2 adsorption/desorption profiles of the activated and AMP impregnated fly ash carbon (AC-AMP) at 30, 70, 100 and 120°C.

Furthermore, the adsorption capacity of AC-MDEA, and AC-DEA increased with raising operating temperature. Samples AC-MDEA-70 and AC-MDEA-100 presented a CO_2 uptake of 30.4 and 40.6 mg/g, respectively (Table 6); and sample AC-DEA-70 had a CO_2 uptake of 37.1 mg/g. This indicated that chemical adsorption of CO_2 on these two sorbents took place under these temperatures, and the higher temperature is favorable for the chemical reaction of CO_2 and amino-group as opposed to the pure physical adsorption of the parent activated carbon (AC), where an increase in the temperature results in a drastic decrease in the CO_2 uptake. However, a significant decrease of CO_2 uptake was found when increasing the adsorption/desorption temperature to 120°C for AC-MDEA and 100°C for AC-DEA, the adsorption amount of CO_2 was down to 16.1 mg/g for sample AC-MDEA, and 16.3 and 4.20 mg/g for samples AC-DEA-100 and AC-DEA-120, respectively. This is probably due to amine decomposition as well as of CO_2 desorption. MDEA probably presented a higher decomposition temperature compared with that of DEA.

In contrast, with the increasing of adsorption temperatures, the adsorption capacity of samples AC-MEA and AC-AMP decreased continuously. The amount of CO_2 adsorption on AC-MEA decreased from 68.6 mg/g to 5.5 mg/g after increasing the adsorption temperatures from 30°C to 120°C. The highest adsorption capacity at 30 and 70°C was obtained for AC-MEA probably due to a combination of physical adsorption inherent from the parent sample and chemical adsorption of the MEA. As the temperature is increased, the contribution from physical adsorption drops off quickly and probably offsets any gain in the chemical adsorption enhanced by the increase in temperature . For AC-AMP, a decrease of CO_2 adsorption amount from 22.3 mg/g to 2.8 mg/g was obtained when the adsorption temperatures changed from 30°C to 120°C. This could be due to decomposition of the chemicals.

Table 7. CO_2 capture using activated fly ash carbon (AC) and its chemical loaded counterparts at different temperatures.

Sample	CO_2 uptake, mg CO_2/g adsorbent	CO_2 uptake, %	CO_2 uptake, mol CO_2 /mol chemical
AC-30	40.3	4.03	
AC-70	18.5	1.85	
AC-120	7.70	0.77	
AC-MDEA-30	17.1	1.71	0.046
AC-MDEA-70	30.4	3.04	0.82
AC-MDEA-100	40.6	4.06	0.109
AC-MDEA-120	16.1	1.61	0.044
AC-DEA-30	21.1	2.11	0.050
AC-DEA-70	37.1	3.71	0.089
AC-DEA-100	16.3	1.63	0.039
AC-DEA-120	4.20	0.42	0.010
AC-MEA-30	68.6	6.86	0.095
AC-MEA-70	49.8	4.98	0.069
AC-MEA-100	25.3	2.53	0.035
AC-MEA-120	5.50	0.55	0.008
AC-AMP-30	22.3	2.23	0.045
AC-AMP-70	14.0	1.40	0.028
AC-AMP-100	5.20	0.52	0.011
AC-AMP-120	2.80	0.28	0.006

In contrast, with the increasing of adsorption temperatures, the adsorption capacity of samples AC-MEA and AC-AMP decreased continuously. The amount of CO_2 adsorption on AC-MEA decreased from 68.6 mg/g to 5.5 mg/g after increasing the adsorption temperatures from 30^{o}C to 120^{o}C. The highest adsorption capacity at 30 and 70°C was obtained for AC-MEA probably due to a combination of physical adsorption inherent from the parent sample and chemical adsorption of the MEA. As the temperature is increased, the contribution from physical adsorption drops off quickly and probably offsets any gain in the chemical adsorption enhanced by the increase in temperature . For AC-AMP, a decrease of CO_2 adsorption amount from 22.3 mg/g to 2.8 mg/g was obtained when the adsorption temperatures changed from 30^{o}C to 120^{o}C. This could be due to decomposition of the chemicals.

Finally, Table 7 shows that the chemical loaded sorbents only adsorbed up to a maximum of 0.109, 0.089, 0.095, and 0.045 mol CO_2/mol chemical for samples AC-MDEA, AC-DEA, AC-MEA, AC-AMP, respectively. While the corresponding chemicals loaded for these samples are as high as of 46%, 34%, 29% and 17%, respectively, with the chemicals probably forming multilayers on the surface of the activated fly ash carbon. Therefore, large quantities of the chemicals loaded on the activated carbons remained unutilized for capture. This indicates that only the external layer of chemicals impregnated onto the carbon surface is capturing CO_2.

The CO_2 adsorption/ capacities of fly ash FAS10 and its deashed counterpart before and after PEI loading were tested and the results are listed in Table 8. The CO_2 adsorption studies of all these samples were conducted at both 30°C and 75°C. At 30°C, the parent sample FAS-10 can adsorb around 17.5 mg CO_2/g, while DEM-FAS10 can adsorb as much as 43.5 mg CO_2/g. This is consistent with the much higher total surface area of 731m^2/g for the latter compared to 284m^2/g FAS-10 (Table 6). As expected from a physical adsorption process, the CO_2 adsorption capacities of both sample decreased to 10.2 mg CO_2/g and 22.0 mg CO_2/g for samples FAS-10 and DEM-FAS10, respectively, when the temperature was rised from 30 to 75°C.

Table 8. CO_2 adsorption/desorption capacity of FAS10 and its deashed counterpart before and after PEI loading.

Sample	CO_2 uptake, mg CO_2/g adsorbent	CO_2 uptake, %
FAS10-30	17.5	1.75
FAS10-75	10.3	1.03
DEM-FAS10-30	43.5	4.35
DEM-FAS10-75	22.0	2.20
FAS10-PEI-75	62.1	6.21
DEM-FAS10-PEI-75	93.6	9.36

The CO_2 adsorption capacities of PEI loaded fly ash FAS10 and its deashed counterpart were also tested and the results are listed in Table 8. The CO_2 adsorption studies for these two samples were conducted at 75^{o}C. After PEI impregnation, both samples FAS10-PEI and DEM-FAS10-PEI have much higher CO_2 adsorption capacities than their non-impregnated counterparts, especially for sample DEM-FAS10-PEI, which adsorbed as much as 93.6 mgCO_2/g, compared to only 22.0 mgCO_2/g for its non-impregnated counterpart, DEM-FAS10. For the raw FAS10 sample, the PEI modification increased the CO_2 adsorption to 62.1 mg/g at 75°C from 10.3mg/g for unloaded counterpart.

4.4. Task 4 "Comparison of the produced CO_2 by fly ash derived sorbents with commercial sorbents"

The surface porous properties and CO_2 adsorption capacities of selected activated fly ash carbons were compared to a commercial activated carbon (Table 8). It can be seen that some of the activated carbon from fly ash present surface areas similar or higher than the commercial activated carbon F400. Similarly, for these samples, the CO_2 adsorption capacity is within the range reported for the commercial carbon (23.23 and 21.99 mg/g vs. 29,78 mg/g).

Moreover, it has been reported that commercially available sorbents that have surface area of 1000-1700 m^2/g present a CO_2 capture capacity of 3-4% (Gray, 2001). The CO_2 adsorption capacity of AC and chemical loaded activated carbon (AC-MDEA, AC-DEA, AC-MEA, and AC-AMP) presents a CO_2 capture capacity as high as of 2.23-6.86%, which are comparable with the published values.

Table 8. Surface porous properties and CO_2 adsorption capacities of selected activated fly ash carbons were compared to a commercial activated carbon (F400).

	S_t m^2/g	S_{me} m^2/g	V_t mL/g	V_{me} mL/g	CO_2 adsorption mg/g (75°C)
AC-FAS4	387	58	0.213	0.062	14.12
AC-FAS4-N1	1139	86	0.615	0.097	23.23
FAS-5-DEM	731	632	0.740	0.702	21.99
F400	966	146	0.598	0.157	29.78

Further studies are recommended to establish a more in depth comparison of the produced sorbents with a wider range of commercial carbons, and to conduct an economic analysis of the viability of establishing this route as a cost–efficient strategy to reduce the disposal of CCBs.

5. CONCLUSIONS

In this research project, fly ash carbon samples collected from different combustion systems were activated using the protocols previously developed by the authors. The resultant activated fly ash samples were further amine impregnated with amine containing compounds. The activated and impregnated fly ash samples were tested for CO_2 capture properties, and their capacities were compared to those of commercial activated carbons.

Under Task 1 "Procurement and characterization of a suite of fly ashes", 10 fly ash samples, named FAS-1 to -10 were collected from different combustors using different feedstocks, including bituminous coal, PRB coal and biomass. A series of analysis were conducted to characterize their properties, including loss-on-ignition (LOI), thermogravimetric analysis (TGA) and porosity analysis. These samples presented a wide range of LOI value from 0.66-84.0%. Furthermore, these 10 fly ash samples also presented different thermal stability as tested using TGA. The LOI values of some of the samples reported here (FAS-3, -4, –5, -9 and -10) are higher than those typically for PCC systems of <15wt% (FAS-1 and FAS-2). However, this work focuses on the study of high carbon fly ashes as feedstock for activated carbons, and therefore, fly ash samples with high LOI contents, FAS-4 and FAS-10, were intentionally selected for further activation and CO_2 adsorption study. The 10 fly ash samples also presented different thermal burn-off profiles as tested using TGA. The burn-off profiles reflect the difference in feedstock, types of combustors, collection hopper, and the beneficiation technologies the fly ashes underwent. Furthermore, the fly ash samples present various total specific surface areas and pore volumes, which are measured using N_2 adsorption isotherm at 77K. The total surface area and total pore volume of samples FAS-4 and FAS-10 are as high as

120m^2/g and 0.081ml/g, and 284m^2/g and 0.277ml/g, respectively, even prior to any treatment. This indicated that some porosity is developed during the combustion or gasification process.

Under Task 2 “Preparation of fly ash derived sorbents”, the fly ash samples were activated in a stainless steel reactor by steam. Nitrogen adsorption isotherms were used to characterize the resultant activated samples. One-step activation can successfully increase the surface area and pore volume. The activated samples present very different surface areas and pore volumes due to the difference in the physical and chemical properties of their precursors. For example, the 850^C steam activated carbon produced from FAS-3 presents surface area of 163m^2/g after 60 minutes activation, and 307m^2/g after 120 minutes activation. While for the case of FAS-4, the activated carbon has surface area as high as 538m^2/g for 60 minute-activation, and 1075m^2/g for 120 minute-activation. In contrast, the surface areas for the activated FAS-5 after 60 and 120 minutes activation are only 87m^2/g and 79m^2/g, respectively. This is probably due to the difference in the physical and chemical properties of fly ash precursors. Furthermore, the activated FAS-4 was loaded with chemicals MEA, DEA, AMP, and MDEA, where the highest loading was achieved for MDEA (46%), and the loading levels for DEA, MEA and AMP were 34%, 29%, and 17%, respectively. The impregnation of chemicals decreased significantly the surface area and pore volume of the activated fly ash.

Under Task 3 “Capture of CO_2 by fly ash derived sorbents”, the activated carbon generated from FAS-4 and its chemical loaded counterparts were also selected for the investigation of CO_2 capture capacity. Prior to impregnation, the activated carbon exhibited a CO_2 adsorption capacity of 40.3mg/g at 30°C, and decreases to 7.7mg/g at 120°C. After loading chemicals (MDEA, DEA, MEA, and AMP), the CO_2 adsorption capacity of MDEA loaded sample increased significantly at higher temperatures (40.6mg/g vs. 7.7mg/g at 120^oC). While for other chemicals, they either increased the CO_2 adsorption capacity at low temperatures (37.1 mg/g vs. 18.5 mg/g for DEA at 70^oC; and 68.6 mg/g vs. 40.3 mg/g, 49.8 mg/g vs. 18.5 mg/g for MEA at 30^oC and 70^oC, respectively); or decrease the CO_2 adsorption capacity under the studied temperatures, like AMP. Therefore, chemically attached amino groups in fly ash derived sorbents may have a great potential when used in flue gases and the selection of the chemical is a critical step.

In addition, sample FAS-10 and its de-ashed counterpart before and after impregnation of chemical PEI were used for the CO_2 adsorption at different temperatures. The deashing step using acids can successfully concentrate the unburned carbon, where the resultant deashed sample DEM-FAS10 have LOI values as high as 96.7%, and a total surface area as high as 731m^2/g, compared to 284m^2/g for the parent sample FAS-10. This increase in surface area is related to the removal of the inorganic fly ash, which is virtually non-porous. The raw fly ash sample exhibited a CO_2 adsorption capacity of 17.5mg/g at 30^oC, and decreases to 10.25mg/g at 75^oC, while the de-ashed counterpart exhibited a CO_2 adsorption capacity of 43.5mg/g and 22.0 mg/g at 30^oC and 75^oC, respectively. After loading PEI, the CO_2 adsorption capacity increased to 93.6 mg/g at 75^oC for de-ashed fly ash sample compared to 22.0 mg/g for un-loaded counterpart, 62.1 mg/g at 75^oC for raw fly ash sample from 10.3mg/g for unloaded counterpart.

Under Task 4, “Comparison of the produced CO_2 by fly ash derived sorbents with commercial sorbents”, the surface porous properties and CO_2 adsorption capacities of selected activated fly ash carbons were compared to commercial activated carbons. Some of the activated carbon from fly ash present surface areas similar or higher than the commercial activated carbon F400. Similarly, for these samples, the CO_2 adsorption capacity is within the range reported for the commercial carbon (23.23 and 21.99 mg/g vs. 29,78 mg/g).

Fly ash derived sorbents represent a potential alternative for CO_2 capture to the existing methods using specialized activated carbons and molecular sieves, that tend to be very expensive and hinder the viability of the CO_2 sorption process due to economic constraints. The unburned carbon in the fly ash can be concentrated to carbon contents >97% by using conventional acid digestion methods. This deashing process not only removes the inorganic ash from the unburned carbon, but also changes the porous structure and surface properties of the resultant carbon. Hence, deashed fly ash samples with high surface area, and CO_2 adsorption capacities can be produced from the unburned carbon treated with acid washing. Further, the impregnation of PEI can improve significantly the CO_2 adsorption of unburned carbon and its activated counterparts, where the PEI impregnated deashed FAS10 sample can adsorb as much as 93.6 mg CO_2/g at 75^{o}C.

Furthermore, the one-step steam activation can significantly increased the surface area, and therefore, provide a large chemical uptake for the fly ash samples without deashing. The activated FAS-4 produced at 850^{c}C for 90 minutes activation has a CO_2 adsorption capacity of 40.3mg/g at 30^{o}C. In addition, the impregnation of chemicals MEA, DEA, AMP, and MDEA chemicals on activated FAS-4 can reduce the surface area and the total pore volume of the activated carbons due to the blocking of both micro- and meso-pores. However, the chemical loading impacted to a great extent the CO_2 adsorption capacity of the activated fly ash samples. **T**he MDEA loaded sample presents a CO_2 adsorption capacity of as high as 40.6mg/g at 120°C. While for other chemicals, they either increased the CO_2 adsorption capacity at low temperatures (37.1 mg/g vs. 18.5 mg/g for DEA at 70°C; and 68.6 mg/g vs. 40.3 mg/g, 49.8 mg/g vs. 18.5 mg/g for MEA at 30°C and 70°C, respectively); or decrease the CO_2 adsorption capacity, such as AMP. Therefore, chemically attached amino groups in fly ash derived sorbents may have a great potential when used in flue gases and the selection of the chemical is a critical step.

6. PUBLICATIONS RESULTING OF THIS RESEARCH PROGRAM

M. M. Maroto-Valer, Z. Lu and Y. Zhang, Development of low-cost fly ash derived sorbents to capture CO_2 from flue gas of power plants, Second Annual Conference on Carbon Sequestration, U.S. DOE National Energy Technology Laboratory, Alexandria, VA, May 5-8, 2003, Paper CAPII1.pdf (CD-ROM publication).

M. M. Maroto-Valer, Z. Lu, Y. Zhang and J. M. Andrésen, Using unburned carbon derived sorbents for CO_2 capture, Proceedings International Ash Utilization Symposium, CAER-University of Kentucky and U.S. DOE National Energy Technology Laboratory, Lexington, KY, October 20-22, 2003, Paper 91 (CD-ROM publication).

M. M. Maroto-Valer, Y. Zhang, Z. Lu, and Z. Tang, Microporous activated carbon produced from unburned carbon in fly ash and their application for CO_2 capture, Prepr. Am. Chem. Soc. Div. Fuel Chem., 2004, 49(1), 304-305.

M. M. Maroto-Valer, Y. Zhang, Z. Lu, and Z. Tang, Development of fly ash derived sorbents to capture CO_2 from flue gas of power plants, Fuel Processing Technology, In preparation.

M. M. Maroto-Valer, Y. Zhang, Z. Lu, and Z. Tang, Novel carbon based sorbents for CO_2 capture, *Seventh International Conference on Greenhouse Gas Control Technologies, 2004,* Accepted.

M. M. Maroto-Valer, Z. Lu and Y. Zhang, Development of novel low-cost carbon-based CO_2 sorbents, Third Annual Conference on Carbon Sequestration, 2004, Accepted.

Students supported in this project

Zhe Lu, MS, Fuel Science, Penn State University.

7. REFERENCES

American Coal Ash Association, 1999, CCPs Survey, http://www.acaa-usa.org

American Society for Testing and Materials, C311-00, Book of Standards Volume: 04.02, Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland-Cement Concrete.

Ban, H.; Li, T.X.; Hower, J.C.; Schaefer, J.L. and Stencel, J.M. 1997, Fuel, 76(8), 801-805

Barrett, E.P.; Joyner, L.G. and Halenda, P.P. J. Amer. Chem. Soc. 1951, 73, 373-380.

deBoer, J.H.; Lippens, B.C.; Lippens, B.G.; Broekhoff, J.C.P.; Heuvel, A. van den and Osinga Th.V. J. Colloid & Interface Sci. 1966, 21, 405-414.

Department of Energy, 1996, Clean Coal Technology, Reducing emissions of nitrogen oxides via low-NOx burner technologies, Topic report no. 5.

Department of Energy, Office of Science, Office of Fossil Energy, 1999, US DOE Report: Carbon Sequestration: Research and Development.

Department of Energy/National Energy Technology Laboratory, 1999, Vision 21 Program Plan.

Gray, M.L., Soong, Y., Champagne, k.J., Stevens, R.W., Toochinda, P., and Chuang, S.S.C., In Proceedings of the 11th International Conference on Coal Science, 2001, San Francisco, CA.

Gregg, S.J.; Sing, K.S.W. Adsorption, surface area and porosity. 2nd edition, Academic press: London, 1982.

Groppo, J.G.; Robl, T.L.; Lewis, W.M.; McCormick, C.J. 1999, Minerals and Metallurgical Processing, 16(3), 34-36.

Herzog, H.J., 1998, Proc. Stakeholders' Workshop on Carbon Sequestration, MIT EL 98-002, Massachusetts Institute of Technology.

Hill, R.L.; Sarkar, S.L.; Rathbone, R.F. and Hower, J.C., 1997, Cement and Concrete Research, 27(2), 193-204

International Energy Agency, 1999, CO_2 reduction – Prospects for Coal.

Keeling, C.D., and Whorf, T.P., 1998, Trends: A Compendium of Data on Global Change, Oak Ridge National Laboratory.

Kruk, M.; Jaroniec, M. and Gadkaree, K.P., 1997, J. Colloid and Interface Science, 192, 250-256.

Marcilla, A.; Asensio, M. and Martin-Gullón, I., 1996, Carbon, 34, 449-456.

Marsh, H. and Díaz-Estébanez, M.A.D. Sciences of Carbon Materials. (Marsh, H.; Rodríguez-Reinoso, F., eds.) Universidad de Alicante, 2000, Chapter 10.

Marsh, H. and Wynne-Jones, W.F.K. Carbon. 1964, 1, 269-279.

Maroto-Valer, M.M., Taulbee, D.N., and Hower, J.C., 1998, Conference on Unburned Carbon on Utility Fly Ash, 49-51.

Maroto-Valer, M.M.; Taulbee, D.N. and Hower, J.C., 1999a, Energy & Fuels, 13, 947-953

Maroto-Valer, M.M.; Taulbee, D.N.; Schobert, H.H. and Hower, J.C. Proceedings of the international ash utilization symposium, Lexington, 1999b, 188-194.

Maroto-Valer, M.M.; Taulbee, D.N. and Schobert, H.H. Prepr. Am. Chem. Soc. Div. Fuel Chem. 1999c, 44(1), 101-105.

Maroto-Valer, M.M., Andrésen, J.M., Schobert , H.H., and Morrison, J.L., 2000a, Conference on Unburned Carbon on Utility Fly Ash, 21-24.

Maroto-Valer, M.M.; Taulbee, D.N. and Hower, J.C. Prepr. Am. Chem. Soc. Div. Fuel Chem. 2000b, 45(3), 401-405

Maroto-Valer, M. M., Zhang, Y., Kuchta, M.E., Andrésen, J. M., 2001ca, Proc. 18th International Pittsburgh Coal Conference, CD, 23-01.pdf.

Maroto-Valer, M. M.; Taulbee, D. N.; Hower, J. C., 2001b, Fuel, 80, 795.

Maroto-Valer, M. M., Zhang, Y., Andrésen, J. M.; Jones, A., Morrison, J. L., 2001c, Prepr. Pap. Am. Chem. Soc., Div. Fuel Chem, 46(1), 316.

Maroto-Valer, M.M., (Editor), Song, C., Soong, Y., 2002a, Environmental challenges and greenhouse gas control for fossil fuel utilization in the 21st century, Kluwer Academic / Plenum Publishers, 2002, 1-447.

Maroto-Valer, M.M.; Andrésen, J.M. and Zhang, Y. In Advancing Sustainability through Green Chemistry and Engineering, (Lankey, R.L. and Anastas, P.T., eds). American Chemical Society Symposium Series, Vol. 823, 2002b, Chapter 15, 225-241.

McEnaney, B. Active sites in relation to gasification of coal chars, Fundamental issues in control of carbon gasification reactivity, Eds. Lahaye J. and Ehrburger P., Kluwer academic publishers. 1991. 175-199.

Ranjani, V.S., Shen, M.S., Fisher, E.P.; Poston, J.A., Energy and fuels, 2001, 15, 279-284.

Sing, K.S.W.; Everett, D.H. and Haul, R.A.W. Pure & Appl. Chem. 1985, 57(4), 603-609.

Sloss, L.L. Trends in the use of coal ash IEA coal research, CCC/22, 1999.

Smith, I.M., CO2 reduction-prospects for coal, IEA coal research, 1999.

Querol, X., Plana, F., Alastuey, A., and Lopez-Soler, A. 1997, Fuel, 76, 793.

Yeh, J.T.; Pennline, H.W., Energy and fuels, 2001, 15, 274-278.

Xu, X., Song, C., Andresen, J., Miller, B., Scaroni, A., Energy and Fules, 2002, 16, 1463

Zhang, Y., Lu, Z., Maroto-Valer, M.M., Andresen, J.M., Schobert, H.H., Energy and Fuels, 2003, 17, 369.

Zinnen, H.A; Oroskar, A.R.; Chang, C.H., US Patent 4,810,266, 1989.