Generating electricity from spent activated carbon: Life cycle environmental benefits

MARIA THERESA ISLA-CABARABAN^a, GUNNAR MARC SHANE CABARABAN^b ^a Department of Chemical Engineering, ^b Department of Electrical Engineering Xavier University – Ateneo de Cagayan Corrales Avenue, Cagayan de Oro City 9000 PHILIPPINES mtcabaraban@xu.edu.ph gcabaraban@xu.edu.ph

Abstract: Coal-fired power plants generate around one-third of the electricity used in the Philippines, and therefore play a significant role in any discussion of energy and the environment. The fuel potential of spent activated carbon can be used to generate power and potentially offset the burning of coal, while making it possible to avoid the cost of SAC disposal. By cofiring SAC with coal, currently operating power plants might have an opportunity to reduce their impact, but of as yet unknown degree and trade-offs. A life cycle assessment is presented that characterizes the environmental performance of spent activated carbon-to-electricity. The assessment covers only the operation of the power plant, and excluded such processes as SAC transportation, feed preparation, and waste disposal and recycling. Cofiring was found to reduce the environmental footprint of the average coal-fired power plant. At a rate of 10% by heat input, cofiring reduces global warming potential by 40%. NOx, SOx, and particulate emissions are also reduced by cofiring. Consumption of nonrenewable resources and solid waste generation were found to be less for a system that cofires SAC. However, more water than is usually needed for flue gas cleanup is likely to be employed for scrubbing the hazardous Na₂O fumes generated from the direct burning of SAC containing Na₂SO4.

Key-Words: Spent activated carbon, Energy from waste, Co-firing with coal, Life cycle inventory

1 Introduction

Active, or activated, carbons are widely used to adsorb odorous or colored substances from gases or liquids. It is also good at trapping other carbonbased impurities, as well as chlorine. In oleo chemical plants, for example, activated carbons are used for the decolorization and deodorization of glycerin, and the purification of fatty acid and fatty acid derivatives. However, once contaminants concentrate on the active bonding sites and the activated carbon becomes saturated, it is replaced with fresh activated carbon and the spent activated carbon (SAC) usually incinerated.

Restoring the adsorption capacity, referred to as activated carbon regeneration or activated carbon reactivation, might involve heating in steam or in nitrogen (N_2) at a given temperature for an adequate length of time or the use of stirred electrochemical reactors. Depending on the substances adsorbed that need to be removed, a number of solvents, acids, and alkalis might be employed, which includes carbon tetrachloride, hydrochloric acid, hydrogen peroxide, potassium hydroxide, and sodium hydroxide. Regeneration is therefore an energyintensive and a relatively expensive option. Regeneration efficiency, however, decreases after a number of cycles and results in the deterioration of the regenerated adsorbent's porosity and serious carbon weight losses [1-3].

The burning of coal in power plants often generates emissions that have adverse effects on the environment. Cofiring with biomass offers coalfired plants an opportunity to reduce the environmental impacts associated with their operations [4]. On the other hand, cofiring of the SAC with coal can be an economical method for waste disposal while recovering energy from the heat of combustion. In waste cofiring technology, waste materials are usually fired as an alternate fuel rather than blended with the conventional fuel [5–6].

SAC used as fuel is very different from other renewable energy sources. Strictly speaking, it is not a true renewable because it is a by-product of modern civilization and, being waste, it ultimately represents a non-sustainable resource. In addition, its exploitation is dominated by non-energy related considerations (*i.e.* waste disposal practices), with the actual use of the waste for energy recovery being of secondary concern. Using the SAC for fuel has many environmental benefits (such as displacing conventional fossil fuel sources, reducing the volume of waste for landfilling, etc.), but it might also have environmental effects.

This paper presents potential favorable and adverse environmental effects of the use of SAC generated from an oleo chemical plant as an alternative feedstock for power generation. Life cycle inventory (LCI) models were developed using a spreadsheet program and were used to describe, quantify, and compare environmental performance of a thermal power generation facility (1) firing only coal and (2) cofiring coal with SAC. An inventory of energy requirements and selected environmental emissions was performed. Primarily, the goal was to analyze the environmental consequences of the mass burning (i.e., burning "as is," without chemical or physical treatment) of SAC as fuel are known before irrevocable decisions are made.

The paper is structured as follows. Section 2 describes the processes leading to the generation of SAC. Electric power production and the system perspective used are elaborated upon, and the lifecycle models and the data used in the lifecycle modeling are explained. The obtained results are presented and discussed in Section 3. The paper concludes by summarizing key implications of this work, and identifying directions for future research along these lines.

2 Methods

The goal of this study is to estimate the environmental effects of the mass burning of SAC from an oleo chemical plant. In order to quantify the magnitude of the benefits offered by cofiring, a life cycle assessment (LCA) was used to evaluate a system that cofire SAC at 10% by heat input, compared with a baseline operation firing only coal. For each emission and resource used, an improvement is said to have been made if cofiring has a smaller environmental impact than the coalonly operation.

Figure 1 shows the LCI system boundaries for the thermal power generation system considered in the study. As shown, the assessment covered only the operation of the power plant, and excluded such processes as SAC transportation, feed preparation, and waste disposal and recycling. Fuel combustion is the principal source of the life cycle emissions. Emissions to water were not treated in this paper. Heavy metal amounts in the flue gas, ash, and other waste streams were not included in the analyses. Avoided stressors are emissions or resource consumption that do not occur if SAC is not cofired with coal at the power plant. Avoided stressors are subtracted from the total inventory of the cofiring operation.

2.1 SAC Production

Oleo chemicals can be found in almost every branch of chemistry due to its wide range of applications. Coconut oil undergoes pre-esterification with methanol (CH₃OH), in the presence of an acid (H_2SO_4) catalyst, to convert the free fatty acids to coco methyl ester and water. A second-stage transesterification, methanolysis, converts the triglycerides to CME with the addition of an excess of CH₃OH and in the presence of an alkaline catalyst NaOCH₃, which is produced by reacting soda (NaOH) with caustic CH₃OH. The methanolysis of the triglycerides produces a crude glycerin stream containing more than 90% glycerin. Glycerin is also produced from the saponification of the coconut oil with NaOH. This process of saponification produces soap (RCOONa) and spent soap lye, containing around 8 to 12% glycerin. Coconut oil is also hydrolyzed to produce corresponding fatty acids and crude "sweet water," which contains around 16 to 20% glycerin.

Crude glycerin thus obtained from these three processes undergoes further processing in a downstream purification stage. Conventionally, it is acidified with H₂SO₄ to split any dissolved soap and release it as fatty acid, which is skimmed off, and produce a sodium sulfate (Na₂SO₄) byproduct. A flocculant, ferric chloride (FeCl₃), is added to entrap the impurities. The flocs thus formed are separated from the glycerin soap lye by filtration, before being fed to the evaporator. Crude glycerin from the evaporator is distilled, and controlled condensation of the vapor separates the glycerin from the water vapor. The condensed glycerin, with up to 99% purity, is deodorized by blowing steam into it, then bleached with activated carbon and filtered to produce the glycerin product [7]. The bleaching process potentially generates 180 kg of SAC per day from an oleo chemical plant processing around 150 tons per day of coconut oil. Typically, arising from the processes described above, it contains around 45 percent C (by mass), 40 percent H₂O, 7 percent glycerine, 6 percent Na₂SO₄, and less than 1 percent each of NaOH and RCOONa.

2.2 Power plant feedstock

The power plant is assumed to use bituminous coal with a higher heating value (HHV) of around 27,113 kJ/kg and 11.12% moisture [8]. Coal is cofired with SAC, which is generated from the bleaching process



Figure 1. Life-cycle inventory system boundary of a power plant cofiring spent activated carbon and coal

described in Section 2.1. Waste-to-energy (WTE) conversion offers a viable means of reducing the volume of SAC produced. Since this energy recovery process essentially uses feedstock that must be disposed of anyway, the burning of SAC may offer low-cost benefits.

2.2.1 SAC as a fuel

The proximate and ultimate analyses of a representative sample of the partially dried SAC are presented in Table 1. The material, having been stored for some time prior to the analyses, contains notably lower moisture content than when it is immediately discharged from the process. Drying of the SAC was necessary to improve the combustion results. When burned wet, a sizeable fraction of the heat of combustion will be used in evaporating the water content, hence, energy is wasted.

From the standpoint of coal classification, the SAC exhibits analyses closest to that of high volatile bituminous coal. The HHV of the SAC (around 28,500 kJ/kg) is slightly greater than the 27,113 kJ/kg (gross) for this type of coal, accounting to a combustible carbon content that is around 10% higher. This means that around 5% less SAC would be needed to produce the same amount of energy from burning coal. Its combustion will also potentially contain lower levels of the oxides of sulfur (SO_x) due to S content that is 96% lower than that of the bituminous variety.

The Dulong formula [9], which is used to estimate the HHV of fuels, was used to estimate the amounts of C and NH (hydrogen in the material that requires air oxygen for its combustion, and whose oxidation with oxygen contributes to the heating value of the fuel) present in the SAC. Based on the measured HHV, calculations would show that around 73.1% of the SAC is combustible carbon. NH is 2.61% of the SAC. Around 17.5% and 15.37%, respectively, of the carbon and hydrogen are assumed to be part of the molecular structure of free moisture and combustible soap, RCOONa, in SAC. Around 12.93% of SAC is carbon in the volatile matter, whose effect in the combustion process is to produce smoke [10].

2.3 Thermal power generation life cycle models

The thermal power generation life cycle models were developed for the combustion options considered in this study. The options developed represent the burning of feedstock through the generation of electrical energy. Comparison using the LCI models was conducted for 1 kWh of electrical energy produced.

SAC is co-milled and pulverized with the coal in the existing coal milled, hence an additional dedicated SAC mill is not required.

Combustible carbon as obtained from the analyses is converted to carbon dioxide (CO_2) after

Duovimata Analyzia	I In:4	"As Received"		
Proximate Analysis	Umt	SAC Samples	Bituminous Coal ^c	
Moisture	% by mass	4.26^{a}	11.12	
Volatile Matter	% by mass	15.68 ^a	34.99	
Ash	% by mass	4.38 ^a	9.70	
Fixed Carbon	% by mass	75.68 ^a	63.75	
Ultimate Analysis				
С	% by mass	88.61	63.75	
Н	% by mass	3.08	5.74	
0	% by mass	3.79	16.76	
Ν	% by mass	0.03 ^b	1.25	
S	% by mass	0.11 ^a	2.51	
Ash	% by mass	4.38	9.70	
Higher Heating Value	Kcal/kg	28,500 ^a	27,113	

Table 1. Characteristics of SAC and bituminous coal

^a QAD-012. "Quality Test Certificate for Solid Fuels." June 2005. Holcim, Inc. Lugait, Misamis Oriental.

 ^b Results of "Analysis and Recommendations." Soil and Plant Tissue Testing Laboratory. June 2005. Central Mindanao University. Musuan, Bukidnon.
 ^c [7]

the combustion is complete. Similarly, NH and sulfur are converted to moisture and sulphur dioxide (SO₂), respectively.

 $\begin{array}{l} C+O_2 \rightarrow CO_2 \\ H_2+\frac{1}{2} O_2 \rightarrow H_2O \\ S+O_2 \rightarrow SO_2 \end{array}$

Non-fuel CO_2 emissions are those that result from the limestone scrubbing reaction during subsequent flue gas clean-up (FGC).

The oxides of nitrogen $(NO_x = NO + NO_2)$ are formed during combustion. Ninety-five percent of the total NO_x in the combustion products is NO, which is subsequently oxidized to NO₂ in the atmosphere. Fuel NO_x is produced from the oxidation of fuel-bound nitrogen, which is the major source of NO_x emissions from combustion [11]. The rate of NO formation is known to increase exponentially with temperature. NO is subsequently oxidized to NO_2 in the atmosphere. Thermal NO_x results from the reaction between O_2 and N_2 from the air at high temperatures. Prompt NO_x is formed by the reaction of hydrocarbon fragments in the fuel with atmospheric N₂ to yield fixed nitrogen. As with pulverized coal flames, about 30 - 35% of nitrogen in SAC (fuel-bound nitrogen) is assumed to be converted to fixed nitrogen species, which are readily oxidized to NO; and remaining nitrogen in the SAC gets converted into atmospheric N_2 .

Flue gas temperatures must be more than about 900 °C to prevent the emission of dioxins, furans, volatile organic compounds, odorous compounds, and other potentially hazardous compounds in the flue gas [12–13]. On the other hand, to ensure good furnace operation, furnace temperatures should not be so high as to increase the formation of NO_x. Combustion temperatures (with bituminous coal) are held at 1,500-1,700 °C. To maintain these temperatures when using SAC, about 30-50% excess air must be supplied. As had been demonstrated in [14], no clear effect of excess air on NOx emissions could be observed, probably because of a balance between the increase in NO formation due to the supply of excess air and the reduction of the formation of fuel-NO due to decrease in gas temperatures.

Only 32% of the energy produced in the thermal power plant is converted to electrical energy. The assumptions for the power plant operations considered in this study were adapted from the dataset on the performance, resource consumption, emissions, and waste generation for an average coal power plant [15]. It was further assumed that, approximately, 10% of the combustible fuel carbon goes in the bottom ash. It was further assumed that 85% of the ash in the fuel goes out through the stack as fly ash after the combustion; 1% of the generated fly ash, which contains 2% soot carbon, is emitted into the atmosphere. SPM was calculated on the basis of the ash contents of the fuel.

2.2.3 Avoided stressors

Activated carbon does not appear on any of the listed hazardous substances. Except for NaOH, which exhibits the characteristics of corrosivity and reactivity, the adsorbed substances for which the activated carbon is used also do not appear on any such list. However, NaOH is present in the SAC in relatively small amounts and is assumed to have negligible effect on the potential fuel's corrosivity and reactivity. It was assumed that all of the cofired SAC would have been landfilled. The resource consumption and emissions that would have occurred during the landfilling of SAC disposal are avoided, and credited in the LCI. Gas emissions from landfilling SAC were calculated over the period of the landfill's active decomposition of 20 years. For this assessment, all of the carbon in the SAC landfilled was assumed to decompose, with 10% of the carbon going to methane (CH_4) and 90% to CO₂. Moreover, the organic carbon in SAC in the form of glycerine and RCOONa was evolved as CO₂ [16]. Conventional landfills have gas collection systems with efficiency of 80% [17]. The inorganic components, Na₂SO₄ and NaOH, are completely soluble in water and are released during conventional landfilling as leachate. It was assumed that 99% of the leachate produced is collected and treated, and the remaining 1% leaks to aquatic recipients.

3 Results

3.1 Air emissions

Table 2 shows the estimated air emissions from the

burning of SAC considered in this study.

The reductions in NO_x and particulate emissions were assumed to be due solely to the lower amount, respectively, of fuel-bound nitrogen and ash in SAC. Similarly, the amount of SO_x emitted is reduced by cofiring with SAC, which contains a lower percentage of sulfur than is present in the average bituminous coal. Consequently, the amount of limestone required for FGC is also reduced. Increasing the share of SAC (i.e. > 10% by heat) could lead to lower concentrations of NO_x, SO_x and N₂O [18]. However, this could result to lower gas temperatures than the average coal burning [14], since SAC has a lower volatile matter content.

Glycerin, which is present in the SAC, is generally transferred to gaseous acrolein (acrylic aldehyde, CH₂CHCHO) by thermal decomposition at temperatures above 290 °C [19]. Although not very persistent in air, acrolein has a very disagreeable odor. Adverse health effects of acrolein are primarily confined to the respiratory and gastrointestinal tracts after inhalation and ingestion, respectively [20]. When SAC is mass burned for power generation, it potentially emits 16.76 g of acrolein per kWh of net electricity generated. However, combustion of acrolein should be complete if the combustion products are allowed sufficient residence time in the combustor.

 Na_2SO_4 , on the other hand, emits fumes of SO_x and disodium oxide (Na₂O) when heated to decomposition to temperatures above 850 °C.

 $Na_2SO_4 \rightarrow Na_2O + SO_3$

NaOH does not burn, nor support combustion, but decomposes to Na_2O when subjected to high temperatures.

$$NaOH \leftrightarrow Na_2O + H_2O$$

Hazardous Na_2O fumes generated from the thermal decomposition of NaOH and Na_2SO_4

Air omissions	Gram per kWh of net electricity generation				
AIT emissions	No cofiring	10% cofiring	% change from no cofiring		
CO_2	749.171	652.202	-13		
NO _x	3.104	2.801	-10		
SO_x	3.589	3.245	-10		
Particulates	8.185	7.718	-6		
Na ₂ O	0.003	0.003	-10		
CH_4	8.825	-4.404	-150		

present in the SAC amounts to 9.90 g/kWh of net electricity generated. Na_2O is highly irritating to skin, damaging to the eyes, and destructive to the mucous membranes. It produces the caustic NaOH when in contact with water, the reaction being accompanied by large amounts of heat. A plant that already invested in scrubbers may therefore remove Na_2O by expediently spraying around 2.30 g more water/kWh of net electricity generated than is required for normal FGC operation.

3.1.1 Global warming potential

The global warming potential (GWP) of the no cofiring and 10% cofiring cases is 935.5 g CO₂-eq/kWh and 560.6 g CO₂-eq/kWh, respectively. Cofiring SAC at 10% thus reduces the GWP of the coal-fired power plant by around 40%. The systems take credit for landfill CH₄ and CO₂ avoided in utilizing SAC in cofiring. Similar reductions in the GWP were obtained in related studies [21–22]. As had been demonstrated, parallel operations of coal-fired power plants with other renewable energy sources result in decreases in CO₂ emissions [23].

In both cases of no cofiring and 10% cofiring, less than 25% of the CO_2 emissions, which make up greater than 95% of all air emissions, come from CO_2 produced from the landfilled SAC. In the 10% cofiring case, FGC operations account for less than 2% of the CO_2 emissions.

3.2 Resource consumption

Table 3 summarizes the resources or inputs that are used and the solid wastes that are potentially produced from the use of SAC as fuel for power generation. Coal is consumed at the highest rate, accounting for around 87% of the non-renewable resources. Water consumption almost doubles in the 10% cofiring case to remove Na_2O fumes emitted when SAC containing Na_2SO_4 and NaOH is burned.

3.3 Solid waste

The wastes resulting from operations of the system needed to cofire SAC with coal can be grouped into (1) FGC waste, and (2) boiler ash. FGC waste is reduced through cofiring due to the lower ash content of SAC. The lower limestone requirement with 10% cofiring results in less FGC waste. The FGC waste is typically dewatered, mixed with ash and lime, and landfilled. Recovery of FGC usually includes asphalt production and wallboard production. The ash may be used in cement production, either as a cementitious material supplement or as a blended addition to the finished cement. Other possible uses for ash include structural fills and waste stabilization.

Known effects of the environmental stressors identified in this study are summarized in Table 4 below. No attempt, however, was made to establish the causal relationship between the identified emission and an environmental impact.

4 Conclusion

As a solid waste, SAC is classified as nonhazardous; NaOH being present in the material in relatively small amounts that it is assumed to have negligible effect on the material's corrosivity and reactivity. WTE is a logical part of the solution for SAC from the oleo chemical industry, burning wastes at extremely high temperatures, and converting the stored internal energy of SAC into usable energy, i.e., electricity. Proximate and ultimate analyses provided conclusive evidence that

Table 3	Resource/ir	nut rea	mirements	and	solid	wastes
Table 5.	Resource/II	iput iet	unements	anu	sonu	wastes

Degeunee/Innut	g/	kWh of net elec	tricity generation
Resource/Input	No cofiring	10% cofiring	% change from no cofiring
Coal	392.6	353.3	-0.5
Spent activated carbon	0	37.3	
Limestone	56.5	52.6	-6.9
Water	0.5	0.7	47.6
Solid wastes			
Bottom ash	29.4	29.4	0.1
Fly ash	32.0	30.2	-5.7
FGD slurry	35.6	34.4	-3.4

H, E
H, E
H, E
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пе
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Table 4. Summary of stressors and stressor categories identified in this study

 Υ H – Human health; E – Ecological health

the SAC has combustibles composition and a heating value that makes it a suitable for cofiring with coal in a large combustion plant for power generation. By generating power, it can potentially offset the burning of coal, as well as emissions from coal-fired facilities, while making it possible for the oleo chemical company to circumvent the cost of SAC disposal.

Cofiring SAC with coal can lead to reductions in the environmental impacts of coal-fired power plants. Nearly all air emissions could be reduced by feeding even a small amount of SAC. Moreover, net GWP is reduced due to the landfilling decomposition emissions avoided when SAC is cofired with coal. Except for water, resource consumption is also reduced from levels required for the no cofiring case. Finally, solid wastes are cut, not only because of decreases in the generation of fly ash and FGC wastes but also because the landfilling of SAC is avoided.

More water than is usually needed for FGC is likely to be employed for scrubbing the hazardous Na_2O fumes, and to douse the exothermic heat of reaction. Potential acrolein release to the atmosphere can be avoided if the residence time for combustion products is adequate for complete combustion.

The focus of this work was on the estimation of the environmental performance of the cofiring of SAC with coal in power generation plants. In future work will be done on the direct burning of the SAC in a circulating fluidized bed combustor for power generation. The technology has shown promising results for cofiring waste biomass with coal [18]. However, the kinetics of burning SAC, as well the particle-to-bed heat transfer coefficient, particle surface temperature, burnout time, and specific burnout rates, need also to be investigated to optimize its utilization as a potential energy resource.

Acknowledgement

The authors would like to acknowledge the Xavier University Faculty Research Unit (now Kinaadman Research Center) for funding this work and for Pilipinas Kao, Inc. for providing resources crucial to the investigation. The valuable contributions of Cyril Fabrea, Sheila Mae Lago, Jay Lou Damaso, Ranilo Opena, and Ric Salva are likewise recognized. Josephine June Yu and Cromwell Basallo also provided extensive technical guidance and review.

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