CHEMICAL ENGINEERING TRANSACTIONS

VOL. 39, 2014

A publication of AIDIC
The Italian Association of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong

ISBN 978-88-95608-30-3; **ISSN** 2283-9216

DOI:10.3303/CET1439081

Ashes Characterization for Biogas Cleaning from Landfill

Rosa-Hilda Chavez*[a], Javier J. Guadarrama[b]

[a]Instituto Nacional de Investigaciones Nucleares, carretera Mexico-Toluca s/n, La Marquesa, Ocoyoacac, 52750, Mexico, Mexico

[b]Instituto Tecnologico de Toluca, av. tecnológico s/n, Metepec, 52140, Mexico, Mexico

rosahilda.chavez@inin.gob.mx

This paper presents the ashes characterization generated from different incineration processes such as: a) coupled kilns b) conventional kiln and c) wood, in order to set which is best for the biogas purification from landfill. The techniques employed were scanning electronic microscopy (SEM), and X-ray diffraction (DRX). This was evaluated through its micro-structural properties as carbon dioxide reduction efficiency through chemical reaction with calcium oxide found in the ashes. Calcium carbonate mineral was got as highly stable and insoluble salt. The results indicate the ash from wood is the most appropriate to reduce the carbon dioxide due to its high calcium content.

1. Introduction

In recent years, the continuing increases in the prices of fossil fuels and energy demand have driven the development of government policies (Kropač et al., 2013) based on sustainable development (Niesner et al., 2013), through which the proper handling and disposal is promoted and research into renewable energy alternatives (Kostevšek et al., 2013) among which the landfill gas, the product generated from the decomposition of organic matter by anaerobic metabolism of microorganisms (Ryckebosch et al., 2011).

The biogas generated in a landfill is mainly composed of methane (45-55%) and carbon dioxide (30-40%) (Savery and Cruzon, 1972), the latter considered an undesirable compound (Cebula et al., 2009) and others (Fujino et al., 2005) as lesser extent those identified: oxygen and nitrogen (5 - 15%), hydrogen sulfide and other sulfur compounds, siloxanes, aromatic compounds and halogenated volatile organic chlorinated (Ravena and Gregersen, 2007). The presence of these compounds influences the calorific value of biogas (Gelegenisa et al., 2007). Corrosion and abrasion problems caused during its application in power systems such as internal combustion engines, microturbines and fuel cells (Rasi et al., 2007)

The biogas cleaning technologies commonly used for the removal of undesirable compounds correspond to the absorption of water or some chemical and pressure swing adsorption (PSA) (Ryckebosh et al., 2011) or activated carbon (Favre et al., 2009). The use of biological filters, membranes and cryogenic separation (Persson and Wellinger, 2007) represent alternative whose application has failed to be competitive for the high costs involved in its implementation, complexity, production of hazardous substances, specificity with respect to the removal of a certain type of substance and / or high methane losses recorded during the process (Ryckebosch et al., 2011). Recently in Europe have been proposed to exploit technologies ash (Baciocchi et al., 2011) generated in the incineration of municipal solid waste (Mostbauer et al., 2012) for biogas purification (Lin and Wang, 2012). These technologies are based on the principle of accelerated carbonation, wherein the calcium oxide in the ash, reacts with the existing carbon dioxide in a gas flow, leading to the formation of a more stable compound, carbonate calcium Eq. (1), (Starr et al., 2012). So far investigations concerning the efficiency of removal of carbon dioxide to the particle sizes have been reported: 0-2 mm (Lin and Wang, 2012), < 20 mm, < 100 mm (Mostbauer et al., 2012) y 4 mm (Rendek et al., 2006); however, there is no information regarding the evaluation of the microstructure characteristics of the ash employed in these processes.

$$CaO_{(s)} + CO_{2(g)} \leftrightarrow CaCO_{3(s)} + \text{heat} \quad (1)$$

Please cite this article as: Chavez R.-H., Guadarrama J.J., 2014, Ashes characterization for biogas cleaning from landfill, Chemical Engineering Transactions, 39, 481-486 DOI:10.3303/CET1439081

In Mexico, the annual potential production of biogas from 186 landfills available is estimated at 1,629 to 2,248 tons of methane per year, which themselves could be used to produce 652-912 MW (SENER, 2012). The application of biogas cleaning process using ash landfill is restricted due to the incineration of municipal solid waste is not implemented in Mexico. However, as ashes features promising, it is obtainable from processes such as incineration of wood (including some municipal solid waste), from conventional kilns for brick production and power plants. The present work evaluated by applying analytical techniques of scanning electron microscopy (SEM), and ray diffraction (XRD), micro-structural properties of elemental and chemical composition and in the form of calcium carbonate ash generated from incineration processes of wood (including some municipal solid waste) and brick manufacture by conventional and coupled kilns (Chavez, 2008) in order to determine the one that will prove to be the most appropriate to use for the capture and removal in the first instance, carbon dioxide of a landfill biogas.

2. Materials and Methods

The ashes used in this study were generated from the following processes:
a) Wood burning (including some municipal solid waste), W&MSW;
b) Conventional kilns, ConvK (Chavez, 2008);
c) Coupled kilns, CoupK (Chavez, 2008).
To evaluate the micro-structural properties was carried out the following procedure:
1. Elimination outside the sample: nails, grass, stones material;
2. Ash homogenization using: a) a mortar with pestle technique for scanning electron microscopy (SEM) and b) using an agate mortar, to X-ray diffraction (XRD);
3. Particle size classification using meshes of 10, 20, 40, 60 and 80. The fraction of size particles is presented in Table 1.
4. Ash washing. Patent: WO 02/18069 A1 (Sander, 2002), the procedure is: a) 2 g of ash placed in a container, add 10 mL of distilled water, b) mixing (15 min) and centrifugation (10 min), c) the ash is removed and dried in an oven at a temperature of 70°C for 15 min.

3. Results and Discussion

3.1 Scanning Electron Microscopy

The Scanning Electron Microscope JEOL JSM-5900LV, low vacuum mode with a maximum accelerating voltage of 20 kV and magnifications to 100X, 1,000X and 2,000X was used. Elemental analysis (Table 2) and the corresponding micrograph for each ash sample is obtained.
The ashes taken from the conventional and coupled kilns contain the same elements: C, O, Na, Mg, Al, Si, O, S, K, Ca, Ti and Fe, but there is significant variation with the existence of Ca, Ti, and P. Wood ash has Cl additionally; ash from conventional coupled kilns has significant variation: sodium (1.49_{ConvK}, 1.19_{CoupK}), magnesium (0.71_{ConvK}, 0.53_{CoupK}), aluminum (5.69_{ConvK}, 5.22_{CoupK}), silicon (16.64_{ConvK}, 16.88_{CoupK}), phosphorus (0.79_{ConvK}, 0.16_{CoupK}), potassium (0.89_{ConvK}, 1.04_{CoupK}), calcium (5.77_{ConvK}, 3.52_{CoupK}), titanium (0.71_{ConvK}, 0.38_{CoupK}) and iron (3.66_{ConvK}, 3.57_{CoupK}).
The morphology of the samples are shown in Figures 1-3, ash produced by incineration process of wood and municipal solid waste are composed of smaller particles, with tendency to form agglomerates and more porosity than ashes from conventional and coupled kilns, which presents greater stony and smooth surface due to presence of silicon compounds (Fernandez et al., 2004), produced during the bricks manufacture (Wang et al., 2010). A residue with high content of calcium oxide and silica, allows carrying out a carbonation process optimally, considering the percentage of elemental calcium in each one of the

Table 1: Ash fraction depending on its particle size

Mesh	Particle size (mm)	Fraction (%)
> 10	> 1.73	23.2
10 - 20	= 1.73 - > 0.86	8.5
20 - 40	= 0.86 - > 0.38	8.9
40 – 60	= 0.38 - > 0.229	26.7
60 - 80	= 0.229 - > 0.18	25.6
< 80	< 0.18	7.2

analyzed samples, wood and municipal solid waste ash are the most suitable (16.59 %) for using in the process of removing carbon dioxide of a landfill biogas. The percentage is 2.87 and 4.71 times higher than conventional and coupled kilns ashes.

Figures 1, 2 and 3 shown scanning electron micrographs of ashes from wood, coupled and conventional kilns, respectively. The scanning electron micrograph of wood ash and municipal solid waste in 2,000 X magnifications (Figure 1b) presents existence of calcium carbonate, as carbonation crystals.

Table 3 shows the results of washed wood ash and MSW (wMSW). There are significant reductions in elemental potassium, sodium, sulfur and chlorine. Therefore, ashes washing the contributed significantly in reducing the elements mentioned above and increase calcium elemental in the sample, allowing accurate material suitable for use in the cleanup of a landfill gas and suitable for the construction industry by reducing the chlorine content (Ito et al., 2006).Figure 4 shows a reduction of agglomerates by ash washing process

Table 2: Elemental ash composition

Element	Wood and MSW %	ConvK %	CoupK %	Element	Wood and MSW %	ConvK %	CoupK %
C	22.41	21.32	26.16	S	0.46	0.41	0.49
O	45.32	41.93	40.85	K	4.60	0.89	1.04
Na	0.66	1.49	1.19	Ca	16.59	5.77	3.52
Mg	2.02	0.71	0.53	Ti	0.18	0.71	0.38
Al	1.65	5.69	5.22	Fe	0.75	3.66	3.57
Si	4.49	16.64	16.88	Cl	0.27		
P	0.61	0.79	0.16				

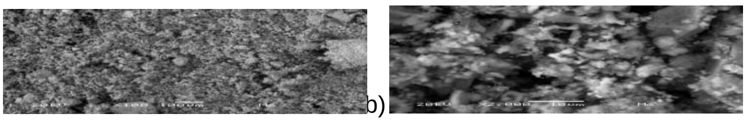
a) b)


Figure 1: Wood ash and municipal solid waste, amplification: a) 100X and b) 2,000X

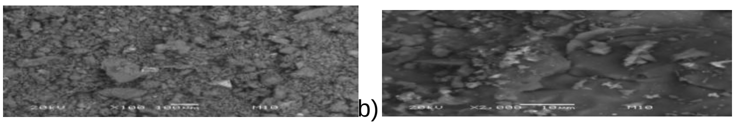
a) b)


Figure 2: Ash coupled kilns amplification: a) 100X and b) 2,000X

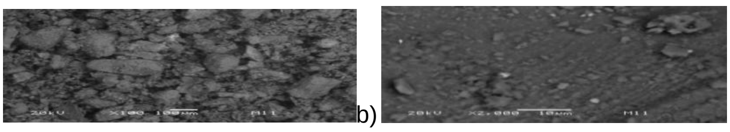
a) b)


Figure 3: Ash conventional kilns, amplification: a) 100X b) 2,000X

Table 3: Elemental ash composition of wood and municipal solid waste, with washing process

Element	%	Element	%	Element	%	Element	%
C	19.03	Al	1.41	S	0.09	Ca	26.12
O	41.47	Si	4.15	Cl	0.03	Ti	0.22
Na	0.32	P	0.93	K	2.43	Fe	1.24
Mg	2.54						

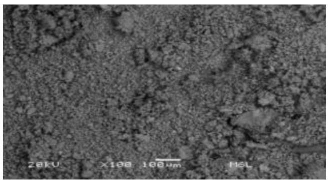
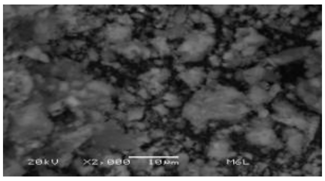
.a)  b) 

Figure 4: Washed wood ash and municipal solid waste washed in amplification: a) 100X and b) 2,000X

Table 4: Elemental composition of the different fractions of wood ash and municipal solid waste (mm)

Element	> 1.73	= 1.73 - > 0.86	= 0.86 - > 0.38	= 0.38 - > 0.229	= 0.229 - > 0.18
C	56.60	25.49	17.91	16.46	14.29
O	24.30	37.49	40.68	40.05	39.83
Na	0.70	0.68	0.74	0.73	0.42
Mg	0.23	0.93	1.66	1.83	2.10
Al	2.24	2.18	2.06	2.20	1.24
Si	6.88	7.53	6.55	6.70	3.45
S	0.12	0.29	0.54	0.45	0.61
K	1.09	3.81	7.27	6.95	7.67
Ca	6.57	18.44	19.21	21.06	27.79
Fe	1.29	2.07	1.82	2.00	1.03
Cl		0.16	0.28	0.24	0.31
Ti		0.51	0.57	0.53	0.31
P		0.41	0.73	0.81	0.95

Table 4 shows the analysis of particle fractions obtained by the sieving wood ash sample and municipal solid waste.
Figure 5 shows the morphology of wood ash and municipal solid wastes that are larger than 1.73 mm, is constituted mainly of metal, and opaque irregular elongate appearance and thin structure.
Figure 6 a-d, shows wood ash, and municipal solid waste, with decreasing size (equal to or less than 1.73 mm), it presents more homogeneous formation of aggregates decreases.

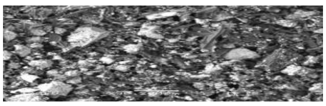


Figure 5: Fraction of wood ash bigger than 1.73 mm

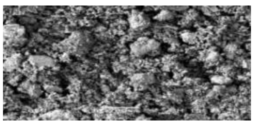
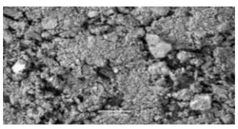
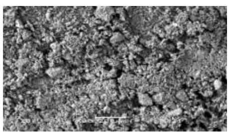
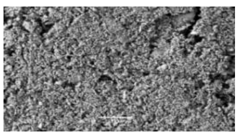
a)  b)  c)  d) 

Figure 6: Wood ash and municipal solid waste fraction: a) =1.73 mm - >0.86 mm, b) = 0.86 mm - > 0.38 mm, c) =0.38 mm - > 0.229 mm, d) = 0.229 mm - > 0.18 mm

3.2 X ray Difraction

Table 5 shows the mineral phases of the analytical technique using X-ray diffraction using an X ray diffractometer D5000 SIEMENS. Figure 7 shows X-ray diffraction pattern corresponds of the incinerated ash, predominantly in CaO.

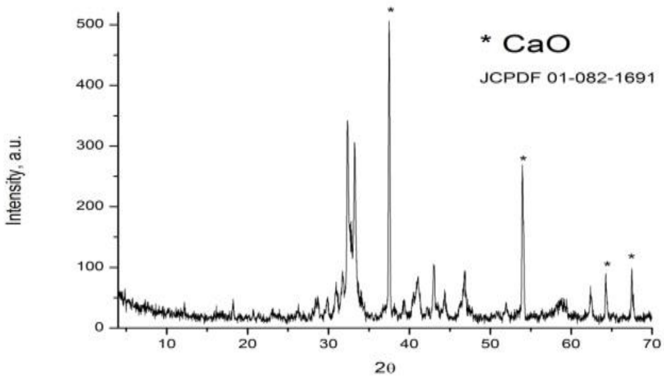


Figure 7: X-ray diffraction pattern corresponds of the incinerated ash, predominantly in CaO

Table 5: Mineral components in wood ash and municipal solid waste

Particle size(mm)	Crystalline species
> 1.73	Calcium-or-deredalbite (Na, Ca)Al (Si, Al)$_3$O$_8$
	Quartz (O$_2$Si)
	Calcite (CaCO$_3$)
	Magnesium-calcite (Mg$_{0.06}$Ca$_{0.94}$)(CO$_3$)
	1M magnesium-muscovite (K$_{0.80}$Na$_{0.02}$Ca$_{0.01}$)(Al$_{1.66}$Fe$_{0.06}$Fe$_{0.02}$Mg$_{0.28}$)(Si$_{3.41}$Al$_{0.59}$)O$_{10}$
	Magnesiohornblende (Ca,Na)$_{2.26}$(Mg,Fe,Al)$_{5.15}$(Si,Al)$_8$O$_{22}$(OH)$_2$
= 1.73 - > 0.86	Plagioclaselabarodita - Ca$_{0.63}$Na$_{0.37}$(Al$_{1.63}$Si$_{2.37}$O$_8$)
	Calcite CaCO$_3$
	Ca$_2$Mg$_5$Si$_8$O$_{22}$(OH)$_2$
	Potassium-magnesium-silicate K$_{1.14}$Mg$_{0.57}$(Si$_{1.43}$O$_4$)
	Talc 3MgO$_4$SiO$_2$2H$_2$O
	Tremolite-calcium-Albite Na$_{0.685}$Ca$_{0.347}$Al$_{1.46}$Si$_{2.54}$O$_8$
= 0.86 - > 0.38	Calcite CaCO$_3$
	Calcium-or-deredalbite (Na, Ca)Al(Si, Al)3O$_8$
	Magnesio-hornblenda (Ca,Na)$_{2.26}$(Mg, Fe, Al)$_{5.15}$(Si, Al)$_8$O$_{22}$(OH)$_2$
	Disorderedalbite Na(Si$_3$Al)O$_8$
= 0.38 - > 0.229	Quartz (SiO$_2$)
	Disorderedalbite Na(Si$_3$Al)O$_8$
	Calcite CaCO$_3$
	1M magnesium-muscovite (K$_{0.80}$Na$_{0.02}$Ca$_{0.01}$)(Al$_{1.66}$Fe$_{0.06}$Fe$_{0.02}$Mg$_{0.28}$)(Si$_{3.41}$Al$_{0.59}$)O$_{10}$
	Magnesio-hornblenda (Ca, Na)$_{2.26}$ (Mg, Fe, Al)$_{5.15}$ (Si, Al)$_8$O$_{22}$(OH)$_2$
	Brownmillerite Ca$_2$((Fe$_{0.922}$Al$_{1.078}$)O$_5$
= 0.229 - > 0.18	Margarite-2M1-CaAl$_2$(Si$_2$Al$_2$)O$_{10}$(OH)$_2$
	Disorderedalbite Na(Si$_3$Al)O$_8$
	Calcium carbonate CaCO$_3$
	Pargasite NaCa$_2$Mg$_4$AlSi$_6$Al$_2$O$_{22}$(OH)

4. Conclusions

According to the results, wood ash, and municipal solid waste has the ability to carry out a process of carbonation as the samples analyzed the presence of calcium oxide with a major intensity peak. It is noted that elements such as aluminum, sodium, potassium and magnesium resulting in the formation of some other mineral species in the ash resulting from incineration processes to which are subjected the raw materials which give rise to their training.

Acknowledgments

For partial funding to carry out this work to the National Council for Science and Technology (CONACyT), Projects: EDOMEX-2009-C02-135728 and SEP-CONACyT-CB-2007-01-82987.

References

Baciocchi R., Corti A., Costa G., Lombardi L., Zingaretti D., 2011, Storage of carbon dioxide captured in a pilot-scale biogás upgrading plant by accelerated carbonation of industrial residues, Energy Procedia, 4, 4985-4992.

Cebula J., 2009, Biogas purification by sorption techniques, Architecture civil engineering environment, The Silesian University of Technology, 2,95-104.

Chavez R.H., 2008, Pollution reduction and energy savings of a coupled two-kiln system for bricks making, Environmental Progress, 27(3), 397-404.

Favre E., Bounaceur R., Roizard D., 2009, Biogas, membranes and carbon dioxide, Journal of membrane science, 328, 11-14.

Fernandez M., Li X., Simons S.J.R., Hills C.D., Carey P.J.,2004, Investigation of accelerated carbonation for the stabilization of MSW incinerator ashes and the sequestration of CO_2, Green Chem., 6, 428-436.

Fujino J., Morita A., Matsuoka Y., Sawayama S., 2005, Vision for utilization of livestock and residue as bioenergy resource in Japan, Biomass and Bioenergy,29, 367-374.

Gelegenisa J., Georgakakis J.D., Angelidakic I., Mavrisa V., 2007, Optimization of biogas production by codigesting whey with diluted poultry manure', Renewable Energy, 32, 2174-2160.

Ito R., Fujita T., Sadaki J., Matsumoto Y., Ahn J.W., 2006, Removal of chloride in bottom ash from the industrial and municipal solid waste incinerators. Int. J. Soc. Mater. Eng. Resour.,13(2), 70-74.

Kostevšek A., Cizelj L., Petek J., Cucek L, Varbanov P.S, Klemeš J.J., Pivec A., 2013, Use of renewable in rural municipalities´ integrated energy systems, Chemical Engineering Transactions, 35, 895-900, DOI: 10.3303/CET1335149.

KropačcJ., Ferdan T., Pavlas M., 2013, Waste to energy modelling – energy efficiency versus minimized environmental impact,, Chemical Engineering Transactions, 35, 901-906, DOI:10.3303/CET1335150.

Lin W.Y., Wang J.–Y., 2012, Investigation on accelerated carbon of MSW incineration bottom ash for application of biogas purification, 3rd International Conference on Industrial and Hazardous Waste Management,12-14September 2012, Chania, Greece.

Mostbauer P., Olivieri T., Lomabrdi L., Paradisi A.,2012,Pilot-scale upgrading of landfill gas and sequestration of CO2 by MSWI bottom ash, ASH 2012,25-27January 2012,Stockholm, Sweden.

Niesner J., Jecha D., Stehlík P., 2013, Biogas upgrading technologies: State of art review in European region, Chemical Engineering Transactions, 35, 517-522, DOI: 10.3303/CET1335086.

Persson M., Wellinger A., 2007, Report on Technological Applicability of Existing Biogas Upgrading Processes, Part I. <www.biogasmax.eu/media/report_on_technological_2007__041639600_1025_22052007.pdf> accessed on 06.12.2012.

Rasi S., Veijanen A., Rintala J., 2007, Trace compounds of biogas from different biogas production plants, Energy, 32, 1375-1380.

Ravena R.P.J.M., Gregersen K.H., 2007, Biogas plants in Denmark: success and setbacks, Renewable and sustainable energy reviews, 11, 116-132.

Rendek E., Ducom G., Germain P., 2006,Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash, Journal of Hazardous Materials, B128, 73-79.

Ryckebosch E., Drouillon M., Ververen H., 2011, Techniques for transformation of biogas to biomethane, Biomass and bioenergy, 35, 1633-1645.

SanderB., 2002, Process for the treatment of bottom ash from waste incineration plants, International Publication Number: WO 02/18069 A.

Savery W.C., Cruzon D.C., 1972, Methane recovery from chicken manure'. Journal of the Water Pollutants Control Federation, 44(12), 2349-2354.

Starr K., Gabarrell X., Villalba G., Talens L., Lombardi L., 2012, Life cycle assessment for biogas upgrading technologies, Waste Management, 32, 991-999.

SENER, 2012, Biogas <www.renovables.gob.mx/portal/Default.aspx?id=2195&lang=2> accessed 10.09.2012.