

COMBUSTION OF AGRICULTURAL BIOMASS: MASS BALANCE OF PRINCIPAL ELEMENTS

Stéphane Godbout^{1*}, Joahnn Palacios¹, Patrick Brassard¹, Jean-Pierre Larouche¹, Frédéric Pelletier¹, Stéphane P. Lemay¹, Denis Bussièrès² and Matthieu Girard¹

¹*Research and Development Institute for the Agri-Environment (IRDA), Quebec City, Quebec, G1P 3W8, Canada*

²*Department of Basic Sciences, Université du Québec à Chicoutimi (UQAC), Chicoutimi, G7H 2B1, Canada*

*Corresponding author. E-mail: stephane.godbout@irda.qc.ca

Abstract

Interest for the use of biomass from agricultural activities and energy crops as biofuels has risen in recent years. Recently, many studies have concentrated efforts to analyse and characterise gaseous and particulate emissions from biomass thermochemical conversion systems. However, element balances from such processes are poorly documented. With mass balances, it is possible to determine the element distribution in solid and gaseous outputs. Thus, action mechanisms against environmental pollution and human health risks could be strategically targeted.

The objective of this study was to carry out a complete mass balance of the principal elements (C, N, S, Cl, Ca, Si, K, and P) included in a direct combustion process of different agricultural biomass fuels: dried solid pig manure (DSPM), switch grass and willow. Experiments were carried out in a 17 kW commercial biomass pellet stove. The chemical characteristics of biomasses, flue gases and ashes were determined.

The carbon balance showed a normal reaction process. In fact, almost all carbon from each biomass was measured as CO₂ emissions. Ashes contained only 0.2 to 2.1% of carbon input by the biomass. On the other hand, 15 to 60% of the nitrogen content of the biomass fuels could be measured in the solid and gaseous outputs. For sulphur, even if the balance was different for each biomass, at least 50% of the sulphur content of the biomass was converted to gaseous form (SO₂). Around 40% of chlorine in the biomasses could be measured. Cl was retained principally in the ash outputs. The mass balances of minor elements (Ca, Si, P and K) showed similar results. Under an absolute mass basis, minor elements were found principally in ashes. The total mass value of each element is discussed in detail in this paper.

The mass balance closure was nearly 100% in most cases. However, in this study, the mass balance closures of N and Cl were not achieved properly. It is suspected that the main factors affecting the mass balance closure were the very low element concentration and the low velocities at the stove's chimney, which might have caused inaccuracies in gas flow rate measurements. These factors should be considered in future works.

Keywords: Agricultural biomass, combustion, mass balance, elements, emissions

1. Introduction

Rising energy costs and climate change push toward the development of new sustainable green energy. In this context, biomass combustion could be an interesting way to produce environmentally friendly heat or electricity. In fact, biomass is a renewable energy source that could contribute to reduce greenhouse gas emissions, replace fossil fuels, add value to organic wastes and marginal lands. The province of Québec (Canada) is developing a feedstock supply chain for energy production based on woody materials. However, the use of agricultural biomasses as potential solid biofuels has been rising over the last years. Agricultural biomasses targeted with an interesting calorific value include (1) organic-based

waste from agricultural activities e.g. cereal straws and cereal seeds; (2) energy crops e.g. switchgrass, *miscanthus* and fast growing willow; and (3) animal manure e.g. poultry litter and the solid fraction of pig manure. Besides energetic and environmental advantages of using agricultural and livestock waste as bioenergy feedstock, it would allow farmers to take advantage of new markets for traditional waste products (Cantrell et al., 2008),

However, the combustion of biomass fuels in small-scale combustion appliances causes some health, environmental and technical concerns, e.g. emissions of NO_x, N₂O, HCl, SO₂ and dust, corrosion, ash utilization/disposal and ash melting. Many studies about combustion of agricultural biomass fuels include fuel gas and ash analysis. However, in most of cases, the element mass balance is poorly documented. A mass balance analysis of thermochemical conversion systems could provide a better understanding of the final disposition of compounds in the solid and gas wastes.

The main objective of this study was to determine, at a laboratory scale, the mass balance of the principal elements (C, N, Cl, S, Si, P, K and Ca) involved in the combustion of three agricultural biomasses (fast growing willow, switchgrass and dried solid fraction of pig manure) in a small-scale combustion appliance (17 kW).

2. Materials and methods

2.1 Mass balance method

Mass balances were determined for the combustion of three agricultural biomasses: fast growing willow (FGW), switchgrass (SG) and dried solid fraction of pig manure (SFPM). In addition, the mass balance for the combustion of commercial wood (a mix of black spruce and grey pine pellets) was included as a control. Equation 1 shows the mass balance used in a thermochemical conversion system. Mass inputs includes the mass contents of an element *i* both in the biomass fuel and in the combustion air. On the other hand, mass outputs include the mass contents of the element *i* in the flue gas and both, fly ash and bottom ash.

$$m_{i_biomass} + m_{i_air} = m_{i_gas} + m_{i_ash} + m_{i_fly\ ash} \quad \text{Eq. 1}$$

Where m_{i_j} is the mass fraction of an element *i* in a constituent *j* (the constituents are the biomass, the combustion air, the flue gas, the bottom ash and the fly ash). In this study, the mass balance of the combustion of the agricultural biomass fuels was determined for four major elements: carbon (C), nitrogen (N), chlorine (Cl) and sulphur (S), as well as four minor elements: potassium (K), calcium (Ca), silicon (Si) and phosphorus (P). Mass balance was performed relative to 1 kg of biomass fuel burned.

2.2 Experimental setup

The combustion tests were carried out in a 17.58 kW nominal output biomass pellet stove (Enviro Omega, Vancouver, Canada). All biomasses used had a pellet shape. Samples of the flue gas were analysed with a Fourier transform infrared spectrometer cell (FTIR) for the measurement of CO, CO₂, NO₂, N₂O, SO₂, HCl, CH₄, NH₃ and H₂O. A zirconium oxide analyser measured O₂ concentrations. In addition, the particular matter (PM) was sampled using two glass fiber filters installed at the entrance of gas sampling probes. Semi-quantitative assessments of PM emissions were made by weighing the filters before and after each combustion test.

A combustion trial involved the combustion of one biomass fuel at three combustion rates: maximum (max.), medium (med.) and minimum (min.). Three repetitions were performed in a completely random arrangement. The appliance controlled automatically the combustion rate

by adjusting the heat output level in the control board. Each combustion test included a 50 min. stabilisation period followed by a 60 min. sampling period. The bottom ashes in the stove and the fly ashes in the chimney were collected and weighed after each combustion trial. The ash produced was compared with the biomass ash content determined by laboratory analysis.

The weight of the pellet stove was continuously measured (Adam scale, GFK 1320a; 600 kg +/- 45 g precision) to determine combustion rate during trials. The combustion rate for each trial was determined using the difference between the initial and the final stove's weight divided by the test duration time.

For each biomass, preliminary experiments were carried out to determine the optimal input air flows. Thus, CO concentrations in the flue gas were analysed for each test. In fact, CO is a product from the incomplete combustion of the fuel and used as a combustion efficiency parameter. Final tests were carried out only with the air flow rates showing the lowest CO concentration at the flue gas for each biomass fuel. Godbout et al. (2011) presented the details of the method and the results of the preliminary tests.

Chemical properties of biomass fuels were determined by the X-ray fluorescence analytical technique (XRF). Other properties analysed included ash content, higher heating value (HHV), humidity and bulk density.

3. Results and discussion

3.1 Biomass fuels analysis

Table 1 summarises chemical and physical biomass fuel properties. C, N, Cl, S, Si, P, K and Ca were the elements analysed in this study. The carbon (C) content in FGW and SW (45.1 and 43.5 % w.b.) are similar to wood (47.1 % w.b.). SFPM had a lower C content (40.5 % w.b.) than other biomass fuels. On the contrary, SFPM had the highest N, Cl, and S content (2.26, 0.305 and 0.834 % w.b., respectively) while wood had the lowest content for the same elements (0.108, 0.001, and 0.008 % w.b., respectively). Regarding minor elements, SW had the highest Si content (2.405 % w.b.) and SFPM had the highest P, K and Ca contents (1.464, 1.321, 1.945 % w.b.).

TABLE 1 : Chemical and physical properties of biomass fuels

Element or property	Units	FGW	SW	SFPM	Wood
Chemical properties					
C	% (w.b.)	45.1	43.5	40.5	47.1
N	% (w.b.)	0.584	0.624	2.26	0.108
Cl	% (w.b.)	0.003	0.013	0.305	0.001
SO₃	% (w.b.)	0.145	0.089	0.834	0.008
SiO₂	% (w.b.)	0.716	2.405	0.986	0.041
P₂O₅	% (w.b.)	0.215	0.157	1.464	0.006
K₂O	% (w.b.)	0.588	0.229	1.321	0.047
CaO	% (w.b.)	1.367	0.624	1.945	0.153
Physical properties					
Bulk density	g/ml	590	509	769	686
% humidity	% (d.b.)	12.66	14.14	10.52	6.57
% ash (750 °C)	% (d.b.)	2.76	3.65	8.80	0.54
Gross calorific value	MJ/kg	18.0	18.7	15.6	17.9

Wood had the lowest ash content (0.5% d.b.) among evaluated biomass fuels. On the other hand, the ash content of SFPM was significantly higher than other biomasses (8.8 % d.b.). Ash content in the SW and FGW were slightly different (2.8 and 3.7% respectively).

Literature reports similar values for wood: 0.6% (Samson et al, 2007); switchgrass: 2–5.2% (Alexander, 2008; van der Berg and de Visser, 2003 and Samson, 2007), and willow (1–5%) (biofuelsb2b, 2007). FAO (1980) documented the ash content of SFPM from 10% to 28%. Humidity was lower in the wood pellets (6.6%) than other biomasses (10.52–14.14 % d.b.).

3.2 Operational results

Average combustion rates were similar: 1.83, 1.50, 1.81 and 1.97 kg(d.b.)/h for the combustion of FGS, SW, SFPM and wood, respectively. Average O₂ concentration in flue gas ranged from 14.7% to 19.3%. The range of the averaged flue gas flow rates was from 0.66 to 0.8 m³/min. The temperatures at the chimney were on average 128, 109, 125 and 135 °C for FGS, SW, SFPM and wood, respectively. As expected, the total ash produced after the combustion trials (4.6, 4.7, 11.3 and 0.1 % on average for FGW, SW, SFPM and wood, respectively) was proportional with the ash content obtained by laboratory analysis (2.76, 3.65, 8.80 and 0.54 %, respectively).

3.3 Mass balance

Figure 1 summarises the recovered mass of major elements (C, N, Cl and S) in the gas, ash and fly ash from 1000 g of biomass fuel burned. Even if air input was not included in the figure, it was in the analysis. However, the C content in combustion air is very low (0.02 g/kg_{biomass}) relative to the C content in biomass fuels (405 - 471 g/kg_{biomass}). As shown in figure 1, the carbon presented an expected reaction. In fact, almost all C was recovered in the flue gas (302 – 326 g/kg_{biomass}), largely in the CO₂ emissions (294 – 310 g/kg_{biomass}). Ash and fly ash from SFPM combustion produced the highest quantities of recovered C content, (up to 8.41 and 0.67 g, respectively, of the initial C content in the biomass fuels).



FIGURE 1: Mass balance of C, N, Cl and S (values in g/kg_{biomass})

As for the N mass balance, since the N₂ concentrations were not measured, it was assumed that N₂ from the combustion air did not react during the combustion process and was emitted under the same composition. Moreover, NO were assumed as 95 % of NO_x emissions (Fowler, 2003). As result, N contents in ash and fly ash were low (up to 0.28 and 0.06 g/kg_{biomass}, respectively) relative to N content in the flue gas (up to 4.37 g/kg_{biomass}) where the major N content was recovered (figure 1). As expected, wood emitted low amounts of N in both gas (0.6 g/kg_{biomass}) and ash (0.03 g/kg_{biomass}). The combustion of SG emitted the highest amounts of N, even if N content in the FSPM was higher (22.6 g/kg_{biomass}) than in the SG (6.24 g/kg_{biomass}). Biomass fuel composition and combustion mechanism should be investigated in order to reduce NO_x emissions in small-scale appliances.

Very low quantities of Cl were measured in the flue gas as HCl emissions (0.01 g/kg_{biomass} in average) and no significant differences between biomass fuels were found. Moreover, larger Cl quantities were retained in the ash and fly ash, particularly from the SFPM combustion (1.21 and 0.14 g/kg_{biomass}, respectively). Based on these results, as proposed by Duong et al. (2009) and Baxter et al (1998), the Cl could be combined with the alkaline elements available and consequently formed alkali chloride compounds different to HCl, such as potassium chloride (KCl) or sodium chloride (NaCl). According with Van Loo et Koppejan (2008), at low flue gas temperatures, alkali chlorides will condense in the boiler section, on fly ash particles or on heat exchanger surfaces. Furthermore, Cl recovered from SFPM reached only 44 % of the Cl input. As opposed, Cl output by wood and FGW were larger than initial Cl content in the biomass. In fact, the method used to measure Cl (titration with silver nitrate (AgNO₃)) does not provide an accurate measurement for very low concentrations such as in these biomass fuels (0.03 and 0.01 g/kg_{biomass}).

S was mainly recovered in the flue gases. SW and SFPM had the highest S quantities emitted as SO₂ (1.13 and 4.15 g/kg_{biomass}). Moreover, total S mass closure was more than 100 % in all mass balances, especially, for SW and wood. This excess may have been due to the lack of precision in the measurement of the gas flow rate at the chimney and/or to the low S content in biomass fuels, such as SW and wood (0.36 and 0.03 g/kg_{biomass}).

Furthermore, the mass balance of minor elements (Si, P, K and Ca) had similar results between themselves. In fact, for all biomass fuels, evaluated minor elements were found primarily in the bottom ash (figure 2). The mass balance closure was near to 100 % in agricultural biomass fuels for Ca, Si and K (78 – 121 %). P content in biomass fuels are lower (0.01 – 3.2 g/kg_{biomasse}) than other elements. However, SFPM presented an important P content (3.20 g/kg_{biomasse}) compared to the other biomass fuels (0.01 – 0.47 g/kg_{biomasse}). After combustion, a large fraction of P remained in the ash. Therefore, even if P is a relevant simple nutrient allowing the use of ash as fertilizer, at the same time, P is not desired as a constituent in biomass because it is one of the major ash-forming elements occurring in combustion. P mass closures were the furthest from 100 % (216, 143, 81 and 568 %, respectively for the FGW, SG, SFPM and wood). This could be due by the low contents hindering accurate measurements. The same applies for the minor element balances in wood. In fact, all evaluated minor elements in wood are very low; consequently, balance closure is always greater than 100 % (140, 184, 112 and 568 % respectively for Ca, Si, K and P). Finally, because of Si output in the ash of SG was high; it is potentially useful for cement based materials (Palacios et al., 2011).



FIGURE 2: Mass balance of Ca, Si, K and P (values in g/kg_{biomass})

4. Conclusion

Combustion tests of three agricultural biomasses were carried out in a small-scale appliance (17 kW) in order to determine mass balances of eight principal elements (C, N, Cl, S, Ca, Si,

K and P). Results showed that N and S content in biomass fuel are mainly emitted in the flue gases. However, Cl tends to be retained in ash instead of being emitted in the flue gas as HCl which would potentially increase corrosion in the combustion system. In addition, evaluated minor elements were found primarily in the bottom ash for all biomass fuels. Results will help to target objectives to overcome environmental, health and technical concerns regarding the combustion of agricultural biomass fuels. Finally, it is suspected that the main factors affecting the mass balance closures were the low element concentration and the low velocities at the appliance's chimney, which might have caused inaccuracies in the gas flow rate measurements. These factors should be considered in future works.

5. Acknowledgements

The authors thank the MAPAQ and the IRDA for their financial and in-kind contributions. Authors gratefully appreciate the participation of C. Gauthier, M. Coté, M. Girard and B. Prost in the realisation of this study and the construction of the experimental setup.

Reference list

Alexander, L. (2008). Biomass, Nitrogen and Ash Content in Stands of Switchgrass and Big Blue Stem in Northwestern Pennsylvania. Allegheny College Center for Environmental and Economic Development Publication.

Baxter, L.L., Miles, T.R., Miles Jr., T.R., Jenkins, B.M., Milne, T., Dayton D., Bryers., R.W. and Oden, L.L. (1998). The behavior of inorganic material in biomass-fired power boilers: field and laboratory experiences. *Fuel Processing Technology* 54, 47–78

Biofuelsb2b. (2007). Typical calorific values. On line. Accessed July 2011. http://www.biofuelsb2b.com/useful_info.php?page=Typic

Cantrell B. K., T. Ducey, K. S. Ro, P. G. (2008). Hunt, Livestock waste-to-energy generation opportunities, *Bioresource Technology* 99, 7941-7953.

Duong, D. N.B., D. A. Tillman, F. Wheeler et N.J. Clinton. (2009). Chlorine Issues with Biomass Cofiring in Pulverized Coal Boilers: Sources, Reactions, and Consequences – A Literature Review. On line. Accessed Mars 2012. http://www.fwc.com/publications/tech_papers/files/TP_PC_09_01.pdf

FAO. (1980). Feed from animal wastes: state o knowledge. ISSN: 0254-6019. <http://www.fao.org/DOCREP/004/X6518E/X6518E00.HTM>. On line. Accessed July 2011.

Fowler S. (2003). Principles and Basics of Flue Gas Analysis - madur for our environment and our customers' money. On line, Accessed February 2012 <http://www.habmigern2003.info/PDF/SCHULUN.pdf>

Palacios, J.H., Verma, M., Godbout, S., Pelletier, F., Brassard, P., Larouche, J-P., Bussièrès, D. and Solomatnikova, O. (2011). Value-addition of residual ashes from different biomass origins in cement based materials : a comparative study. 7th International Symposium on Cement Based Materials for a Sustainable Agriculture, Quebec, Canada, September 2011.

Samson R., Ho, C., and Bailey, S. (2007). The potential of Switchgrass as a Commercial Pellet Fuel in Ontario. On line. Accessed July 2011. <http://www.gtmconference.ca/site/downloads/presentations/2A1%20-%20Roger%20Samson.pdf>

Van der Berg, D. and de Visser, P. (2003). Switchgrass (*Panicum virgatum L.*) as an alternative energy crop in Europe Initiation of a productivity network. Chapter 7 : Thermal conversion of switchgrass. On line. Accessed July 2011. http://www.switchgrass.nl/pdf/Sw_FinalRep_full2.pdf

Van Loo, S. and Koppejan, J. (2008). The handbook of biomass combustion and co-firing. Editor: S. Van Loo and Jaap Koppenjan. Sterling, VA. USA. ISBN : 978-1-84407-249-1.