

Ash related problems with high alkali biomass and its mitigation - Experimental evaluation

Problemas relacionados a cenizas de biomasa con alto contenido de sales alcalinas y su mitigación: Evaluación experimental

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Resumen.- La biomasa está considerada como una fuente renovable de energía y está jugando un papel muy importante en la búsqueda de nuevas fuentes de energía. La reciente tendencia a consumir cultivos energéticos del tipo herbáceo ha causado problemas en los sistemas industriales, debido principalmente a la composición de su ceniza rica en Potasio, Sodio, Cloro y Fósforo. Dichas sales forman eutécticos de bajo punto de fusión formando zonas líquidas que aglomeran partículas sólidas (fouling) o fundiendo por completo (slagging). Este trabajo resume las investigaciones de los últimos años en este tema, discutiendo la importancia del análisis de laboratorio. Los métodos para evitar dichos problemas en las calderas son evaluados, principalmente el baño del combustible con agua (leaching) y el agregado de sales estables a la ceniza en el quemador. Tomando el caso de la Caña Común (Arundo Donax) como un potencial combustible de alto rendimiento por hectárea, se presentan resultados de la evaluación de su ceniza y se estima su potencial de daño en calderas, como producto de nuestra investigación experimental. Se investiga en el laboratorio el efecto del baño de agua en la consecuente ceniza y el impacto que tiene mezclar su ceniza con la de corteza de Eucalyptus en cuanto a su comportamiento en fusión.

Palabras clave: biomasa; ceniza; calderas; corrosión; fusión

Summary.- Biomass is regarded as a renewable source of energy and is playing a role in future fuel supply trend, with great acceleration. However, due to the chemical composition of the ash of certain types of biomass (particularly short rotation crops like grasses, canes and straws), boiler related problems have occurred systematically in the past. These fuels are rich in alkaline metals (potassium, phosphorus, chlorine and sodium) which form complex eutectic salts that effectively lower the melting point of the ashes during combustion and cause fouling and slagging problems, especially in superheater tubes. This work reviews the latest investigations regarding the prediction of these problems through the evaluation of the ashes in the laboratory and discuss their mitigation by fuel leaching and blending. As a means to demonstrate the methodology, experimental data related to the evaluation of the Common Cane are presented, resulting from our own laboratory tests. These include fusion/sintering tests of ashes sampled from canes in the as-is and water-leached condition and the comparisons with other more traditional biomasses. The results show that the as-is state would be unacceptable to burn, but leaching with water and/or blending with more stable ashes reduces the detrimental effects on boiler components to a tolerable level.

Keywords: biomass ash; alkali; leaching; fusion; fouling

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1. Introduction.- Biomass is a carbon neutral source of energy because when fully combusted the amount of carbon dioxide produced is equal to the amount which was taken from the atmosphere during the growing stage. Therefore, biomass is regarded as renewable energy resource and can play an important role in the future fuel supply trends. Biomass is a very promising source of energy in boilers. In this work, several aspects related to the problems that arise when burning high alkali-content biomasses are presented. Results from investigations in these areas from the last three years are presented, highlighting its current focus around the world. The direct connection between the laboratory tests that can be performed on an ash sample and the future behaviour on an industrial system reveals the importance of evaluating each case in separate and studying mitigating alternatives in the lab, which predict with acceptable accuracy the future behaviour in terms of fouling, fusion, corrosion and deposition in boiler tubes.

Clean wood materials, either in chip or in pellet form, are utilized as a fuel for a wide range of combustors for small domestic stoves and boilers, for commercial and industrial scale boilers and for co-firing in large coal-fired utility boilers. They have a relatively low ash content (less than 2%) and this is largely dependent on the level of bark in the fuel. Clean white wood materials have a very low ash content, generally less than 1%.

Straw and grass materials and the solid residues from the vegetable oil producing industries are utilized in substantial quantities as fuels for industrial-scale boilers and have ash contents in the 4% to 7% range. Poultry litter is utilized in significant quantities as an industrial boiler fuel in Britain and there are a number of new projects, particularly in Northern Europe and North America. It is an example of a high ash fuel, with particularly difficult ash behaviour.

One of the key properties of fuel ash materials in combustion systems is their behaviour at elevated temperatures and, in particular, their fusion behaviour. The sintering and fusion of the ash particles on the grates in stoker-fired combustors, and the sintering, fusion and agglomeration of the ash particles in fluidized bed-fired combustors, are important processes.

The work presented in this paper begins with a summary of the cause and effects of alkali salts in ashes, presenting very recent advances in the field, outlining different mitigation methods including leaching of the fuel with water and blending with more stable salts. In order to apply the methodology of analysis, samples of wood and cane were ashed and analyzed in the laboratory furnaces, product of our own experimental setup. Ash fusion behaviour of as-is samples, leached and blended ash samples were tested and their results correlated with their potential problems due to fouling-slagging.

2. Problems Related to Biomass Ash Behaviour at High Temperatures.- Fouling or deposits are commonly known as the layers of materials (ash) collected on the surface of heat transfer equipment. Slagging characterizes deposits on the furnace walls or other surfaces exposed to predominantly radiant heat. Corrosion is the deterioration of intrinsic properties of a material due to reaction with its environment. Corrosion can be caused either directly by gas phase species, by deposits or by a combination of both. In boilers, these problems are regarded as a major issue that can affect the design, life time and operation of combustion equipment, increase the operating cost, decrease boiler efficiency, increase carbon dioxide emissions, deteriorate combustion behaviour with higher combustion temperatures, increase nitrogen oxides and carbon monoxide, reduce heat transfer and causes corrosion and erosion, as evidenced from the work by Li et al (Figure I). The main contributions to fouling, deposit formation, slagging and corrosion come from ash composition together with sulphur and chlorine contents which facilitates the mobility of many inorganic compounds, in particular alkali compounds. [2]

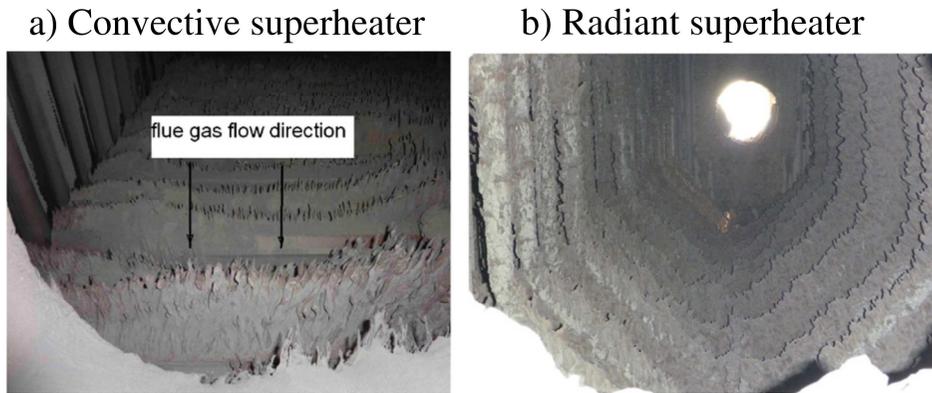


Figure I.- Ash deposition and slagging on heating surfaces of energy power plant in Changchun city, China [1]

Potassium and sodium form alkali silicates that melt at low temperatures (can be lower than 700°C), thus providing a sticky surface for enhanced deposition. Inorganic deposition is less well understood than that of organic materials. Because biomass fuels contain a larger variety of inorganic materials compared to coal, issues of fouling and corrosion need to be explored. This is particularly true for some agricultural residues and new tree growth where the ash can have relatively high alkaline metal contents, particularly sodium and potassium. Sodium and potassium lower the melting point of ash and, hence can increase ash deposition and fouling of boiler tube, as evidenced in Figure II [3].

A comparison of the ash composition between different biomasses is given in Table I, which illustrates the contrast in chlorine and alkali content between herbaceous and woody sources (straw vs bark, for example).

Fuel	Cl	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Mn	MgO	CaO	Na ₂ O	K ₂ O	TiO ₂	P ₂ O ₅	SO ₃
Wood pellets	NA	4.30	1.30	1.50	5.90	8.50	55.90	0.60	16.80	0.10	3.90	1.30
Sunflower pellets	NA	2.90	0.60	0.80	0.10	21.60	21.60	0.24	22.80	0.10	15.20	14.00
Walnut shell	0.10	23.10	2.40	1.50	NA	13.40	16.60	1.00	32.80	0.10	6.30	2.20
Almond shell	0.20	23.50	2.70	2.80	NA	5.20	10.50	1.60	48.50	0.10	4.50	0.80
Olive husk	0.20	32.70	8.40	6.30	NA	4.20	14.50	26.20	4.30	0.30	2.50	0.60
Hazelnut shell	0.1	33.70	3.10	3.80	NA	7.90	15.40	1.30	30.40	0.10	3.20	1.10
Rek Oak wood	0.80	49.00	9.50	8.50	NA	1.10	17.50	0.50	9.50	NA	1.80	2.60
Wheat straw	3.60	48.00	3.50	0.50	NA	1.80	3.70	14.50	20.00	NA	3.50	1.90
Beech bark	-	12.40	0.12	1.10	-	11.50	68.20	0.90	2.60	0.10	2.30	0.80
Tamarack bark	-	7.77	8.94	3.83	-	9.04	53.50	3.40	5.64	0.11	5.00	2.77
Switchgrass	-	66.25	2.22	1.36	-	4.71	10.21	0.58	9.64	0.28	3.92	0.83
Rice straw	-	77.20	0.55	0.50	-	2.71	2.46	1.79	12.59	0.04	0.98	1.18
Olive kernel	-	67.7	20.3	0.05	-	0.05	0.5	11.2	0.15	0.05	-	-

Table I.- Composition of biomass ashes [3]

The corrosion mechanisms in biomass fired boilers can be broadly classified into three classes: (1) Corrosion associated with gas species (active oxidation). (2) Solid phase corrosion. (3) Molten phase corrosion. A general sketch of potassium, sulphur, and chlorine chemistry in a biomass fired boiler is given in Figure III. Complete description of corrosion processes and further literature due to Alkali can be found in [3].

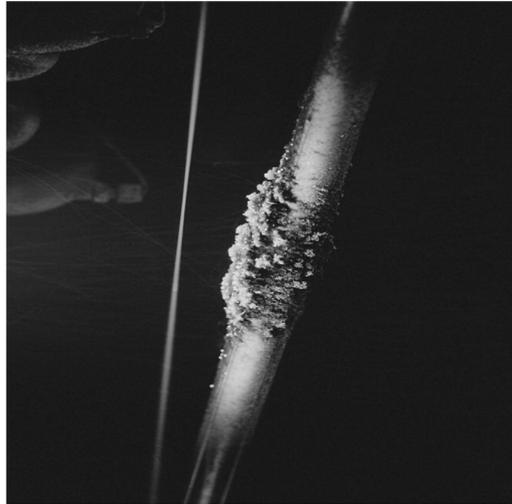


Figure II.- Photograph of deposit forming from wheat straw on a simulated boiler tube [3]

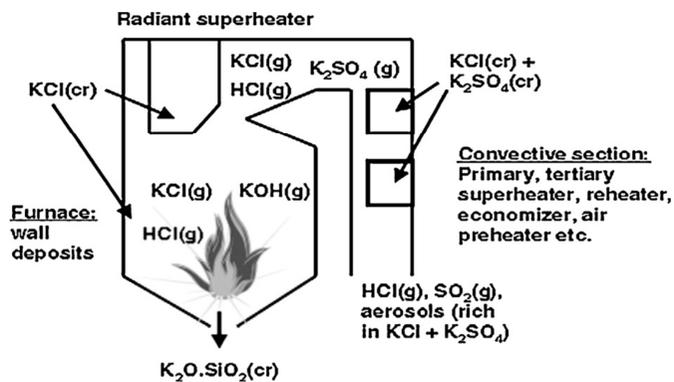


Figure III.- Principal pathways of K, P and Cl in a biomass fired boiler [3]

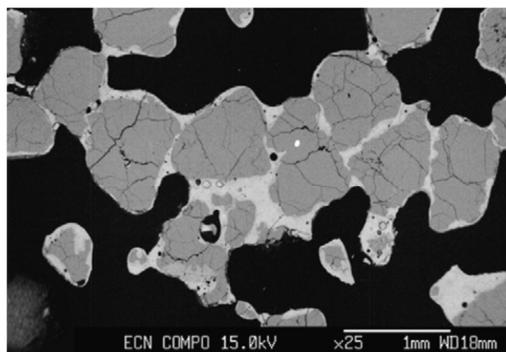


Figure IV.- Agglomeration of solid ash particles due to lower melting point salts [3]

Agglomeration can occur as a result of two phenomena: (i) accumulation of low-temperature-melting salts of potassium and phosphorous, and (ii) in the presence of silica from sand and

calcium from fuel, potassium phosphate can react with silica forming low-temperature-melting silicates of potassium and calcium while phosphorous binds with calcium. Agglomeration is responsible for causing defluidization in boilers [2]. *Figure IV* shows a micrography of a system with solid particles agglomerated by low melting slag salts [3].

3. Analytical and Experimental Methods of Predicting Ash Behaviour.- Llorente et al compare the suitability of five laboratory methods for predicting the ash sintering occurring during the combustion of biomass. The studied methods have been the following: fusibility under DIN norms, measurement of the compression strength of ash pellet previously heated at different temperatures, manual disintegration of biomass ash obtained at different temperatures, relation alkaline earth oxides to alkaline oxides, and representation in a ternary phase diagram $\text{SiO}_2\text{-CaO-K}_2\text{O}$. The two last theoretical methods are based on the analysis of biomass ash elements. [4] The ash sintering behaviour results obtained with these methods for different biomasses have been compared with the ash sintering results obtained in combustion tests of the same biomasses in a 1MWth bubbling fluidised bed combustion (BFBC) pilot plant, with silica as initial bed material. The disintegration and fusibility methods predict with success the sintering behaviour of most of the tested biomasses. Both theoretical methods have been less reliable to predict the ash sintering behaviour than disintegration and fusibility test methods, as evidenced in *Figure V*. [4]

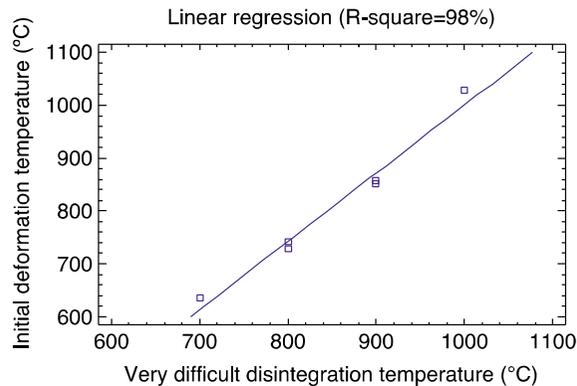


Figure V.- Correlation between initial deformation temperature and sintering test evaluation [4]

3.1. Indexes based on the chemical composition.- Mineralogical analysis and microscopic techniques are increasingly employed for the characterization of mineral materials in fuels, fuel ashes and deposits. X-ray diffraction is commonly used for the identification of the major crystalline phases in these materials. Computer controlled scanning electron microscopy (CCSEM) with energy dispersive X-ray spectrometry is a particularly powerful analytical technique for the examination of the microstructure and chemistry of ashes and deposits. □ These techniques are most commonly employed for fundamental research on the characteristics of ashes, and for investigative work on the microstructural characteristics of ashes and deposits. □ A number of slagging and fouling indices are available for the assessment of the propensity of fuel ashes to form deposits in combustors or furnaces of the technical basis and use of these indices is presented in [5]. These are based either on the fuel ash content and the ash chemical composition, or on the results of laboratory tests that can be performed on small samples of the fuel. In the main, these indices have been developed for the assessment of coals, and are applied, with appropriate modifications, to other solid fuels, including wastes and biomass materials, and to the mixed ashes produced by the co-firing of biomass materials with coal [6].

The majority of the coal slagging indices are concerned with the fusion behaviour of the ash, and the traditional indices are based either on the results of the ash fusion test or on the chemical composition of the ash, commonly the ratio of the acidic metal oxides, (SiO_2 and Al_2O_3) to the basic oxides (Fe_2O_3 , CaO , MgO , Na_2O and K_2O). These indices provide a general assessment of the ash fusion temperature, which is then employed to rank the ash in terms of its propensity to form fused slag deposits. Despite the technical limitations of both of these approaches, these are still used widely in the industry for fuel specification, boiler design and plant operational purposes. [6].

For most biomass materials, potassium tends to be the dominant alkali metal and, as is the case for the sodium, is generally in a form that is available for release by volatilization. The fouling indices for biomass materials tend, therefore, to be based on the total alkali content of the fuel [7].

3.2. Ash Fusion Test.- The fusion behaviour of the ashes is also an important factor in determining the propensities of the fuels to form fused or partly fused slag deposits on the furnace wall surfaces in all combustion systems, and may have an influence on the nature of the fouling deposits that can occur on the heat exchanger and other surfaces in boiler plants.

The standard ash fusion test, which has been applied for the characterization of the fusion behaviour of coal ashes for many decades, is based on the determination of three or four key temperatures on the melting curve. This procedure has been developed, and has been widely applied, for alumino-silicate, coal ash systems, which have complex melting behaviour and tend to produce relatively viscous melts. The results of the application of this test to biomass ashes, which are not alumino-silicate systems in the main, and many of which do not behave in the same way, can provide useful information, but should always be treated with caution. [8][9]

4. Mitigation of Ash Fusion Problems in Industrial Boilers.- In the power generation industry, the most common biomass combustion technologies fall into three categories: stoker/grate firing, fluidized bed combustion - including circulating fluidized bed and bubbling fluidized bed boilers - and suspension firing or pulverized fuel firing.

One common problem related to grate firing is melting of the biomass ash on the grate. Combustion temperatures may reach 1400C. Ash melting problems have been reduced or eliminated by using water-cooled grates and reducing combustion air preheat temperatures. [10]

High steam temperature increases the risk of high temperature corrosion when exposed to the corrosive flue gas. Studies indicate that with steam temperatures above 550C, the lifetime of superheaters is unacceptably low, although problems start to occur at even lower temperatures. [11] Fluidized bed technology is the most flexible for firing a wide range of fuels and fuels that are variable, including biomass. Adequate heat transfer surface is provided to maintain bed temperature in the range of 815 to 925C, within prime temperature range of sorbents to react with bed contaminants and this is at the lower end of the potential ash softening and contaminant agglomeration temperature range. [11]

4.1. Bed Composition Control.- In grate or fluidised-bed burners it is possible to change the composition of the ashes by adding stable metallic salts. Different additives including kaolin, dolomite, limestone, lime, alumina etc. are other solutions that can reduce agglomeration and slagging by coating sand particles, thus preventing reactions between silica and potassium phosphate. [2]

These additives are meant to increase the melting point of the ash formed during combustion. However, with the use of most of these materials, chlorine is released in gas phase, thus not totally eliminating the corrosion effect [3].

Other recent studies suggest the use of materials such as bauxite, kaolinite, limestone and magnesium oxide and other additives to produce high melting point alkali compounds relative to alkali chlorides. [10][11]

4.2. Effect of Leaching on Ash Chemistry.- The removal of these detrimental elements has been tested by leaching biomass fuel with water. In general, leaching reduces the volatilization of inorganic species at ashing temperature higher than 575C. Leaching leads to a notable decline in the alkali index which leads to reduce fouling. [12-13]

Combustion tests were carried out with an atmospheric lab-scale fluidized bed reactor by Vamvuka *et al* [14]. Control methodologies for mitigating ash problems were applied, such as leaching the raw fuels with water and using different mineral additives during combustion tested in a fluidised bed burner. The ashes and the bed material were characterized in terms of mineralogical, chemical and morphological analyses and the slagging/fouling and agglomeration propensities were determined. A comparison between the as-is and leached condition is presented in *Figure VI*. [14]

The results showed that fly ashes were rich in calcium, silicon and iron minerals and contained substantial amounts of alkali, falling within the range of ‘‘certain or probable slagging/fouling’’. Leaching of the raw fuels with water resulted in a significant reduction of the problematic elements potassium, sodium, chlorine and sulphur in the fly ashes. The use of fuel additives decreased the concentrations of alkali and iron minerals in the fly ashes.

Fuel additives or water leaching reduced the slagging/fouling potential due to alkali. Under the conditions of the combustion tests, no signs of ash deposition or bed agglomeration were noticed. [14]

Overall, the results imply that problematic operation and maintenance problems in biomass power systems, caused by the release of alkali compounds from the agricultural by-products of this study, may be significantly reduced by straight forward, fast and low cost methods. The conversion of these biomass materials by thermochemical processes could reduce the volume of wastes, allowing for energy recovery, economic and environmental benefits. [15][16]

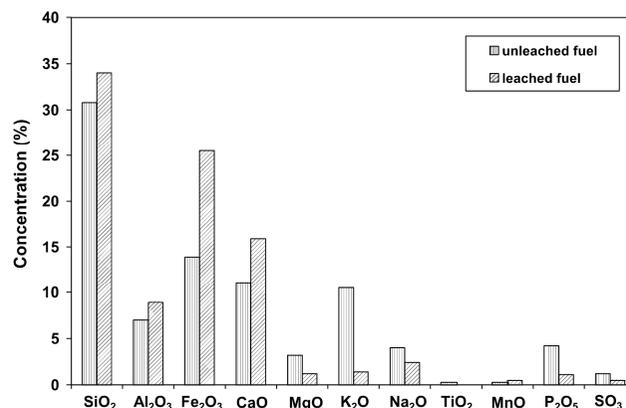


Figure VI. Main components of fly ashes of leached and unleached olive kernels [14]

5. Latest Investigations in Biomass Ash and its Relation with Fusion Related Problems.- The issues regarding biomass ashes are of enormous relevance, where new energy sources are

investigated at every research centre in the world. From the last few years, a summary of the advances regarding research activities in ash behaviour follow.

Professor Vassilev and his team of researchers at the Bulgarian Academy of Sciences have published this year the results of the identification of various biomass ashes and their relationship with subsequent problems in boilers. They have demonstrated that the definitive utilization, technological and environmental advantages related to biomass ash associate preferentially with the ash alkalinity and the fouling behaviour can be predicted based on experimental tests. [17]

Researchers at the University of Leeds in the UK recently studied the ash behaviour of short rotation crops like wheat straw and compared it with woody biomasses like Eucalyptus bark. The fouling behaviour of untreated and leached biomass samples were assessed for fouling related problems. They concluded that the leaching of alkaline metal oxides of sodium, potassium, phosphorus and magnesium influenced the fouling behaviour. Water leaching resulted in a high removal of alkali metal ions and chloride, where up to 92% of sodium and 62% of potassium were removed, together with 100% of the chloride. There was a general trend of higher concentrations of water-soluble species for the herbaceous biomass compared to woody biomass. As a consequence of water washing, the fouling indexes are markedly reduced. The consequent ash melting behaviour changes, increasing the characteristic temperatures during the ash fusion test in 300C to 400C for the herbaceous biomass. [18]

A new image analysis based technique has been developed by Pang et al, and uses image processing techniques to characterise the behaviour of ashes from biomass, coal and coal/biomass blends using a single heating test at elevated temperatures. It is a reproducible test that combines the conventional ash fusion test, dilatometry and sinter strength test by means of image analysis. [19]

An extended overview of the complex phase-mineral and chemical composition and properties of biomass ash was conducted in the work by Vassilev in 2013. They conclude that the knowledge of the minerals involved and it's correlation with the behaviour of its ash at high temperatures has potential applications in prediction of properties and utilisation connected with the innovative and sustainable utilisation of biomass ash. [20]

Butler performed studies on carbonization of various biomasses and concludes that herbaceous materials, despite containing less lignin compared to spruce wood, showed higher char yields as estimated by thermo-gravimetric analysis (TGA), suggesting a greater degree of alkali catalyzed reactions resulting in the production of char, especially for wheat straw [21].

The effects of water washing on fuel properties, pyrolysis/combustion characteristics, and ash fusibility of biomass fuels were reported by Deng *et al.* Their analysis included fuel analysis, thermo-gravimetric analysis and ash fusion temperature measurements. The results show that potassium, sulphur and chlorine contained in biomass, which may be harmful to boiler operation, can be effectively removed by washing. [22]

5.1. Suggestions for industrial application.- Biomass fuels can be washed at the field or at the plant site. Water soaking seems to be a controllable and effective manner. Thus a pool must be constructed, since washing the whole straw with tap water can effectively remove potassium, sulphur and chlorine according to Deng *et al.* Therefore, for industrial application, it is suggested that biomass fuels without grinding should be soaked in ordinary water for 3 hours at a rate of 12.5 grams of fuel per litre of water. [22]

If washing is applied at the field, water can be obtained from a river or lake nearby. The leachate from the pre-treatment process, which contains potassium, sulphur, chlorine and organic compounds, can be used to irrigate the field.

According to Tonn *et al*, the combustion of biodiversity-rich semi-natural grassland biomass no longer needed for forage allows nature conservation to be combined with bioenergy production. Natural leaching by rainfall during the period between biomass harvest and collection can reduce the content of elements detrimental for the combustion of grassland biomass. The study assesses the influence of biomass characteristics on leaching efficiency and the potential effects of leaching on ash melting behaviour and elemental release. [23]

The effect of water leaching is evidenced in *Figure VII*, where potassium and chlorine are the elements most strongly reduced by leaching of semi-natural grassland biomass, with only small site and harvest date effects. Both ash melting behaviour and potassium and chlorine release can be considerably improved by leaching at an intensity that can occur naturally under field conditions.

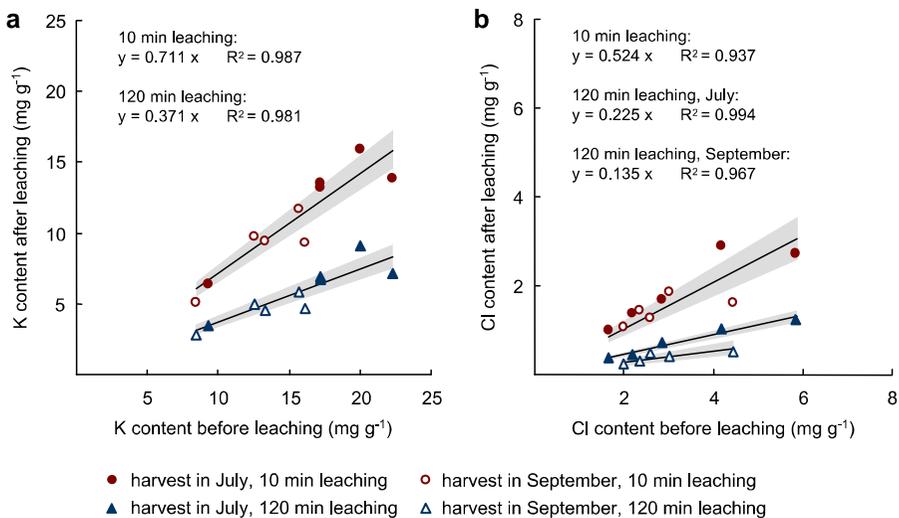


Figure VII.- Potassium and chlorine depletion from water leached grassland [23]

Additionally, the positive effects of leaching on the fuel quality of biomass also offers a utilization alternative for forage hay damaged by rain, thus helping to reduce farmers' economic risks in haymaking.

According to the recent investigation by Li *et al* [1], the problems of ash fouling, slagging and deposition during biomass combustion were identified by the ash fusion characteristics. The results of the ash fusion test for different biomass fuel ashes and simulated ashes can be used in boiler design and operation to determine or control a reasonable combustion temperature.

Based on the ash-related problems during biomass combustion, Nui *et al* studied the evolution of element sulphur, potassium and chlorine and ash fusion characteristics of capsicum stalks, cotton stalks and wheat stalks ashed at 1000, 1200 and 1400°C. The samples are further studied by X-Ray diffraction analyses. The ash fusion characteristics of biomass are mainly dependent on the high-temperature molten material built up by quartz, potassium iron oxide and silicates. [24]

6. Experimental Results: Evaluation of Slagging/Fouling Behaviour of the “Common Cane” Ash.- In order to apply the methodology proposed and evaluate a biomass performance in

slagging/fouling as a product of its ash behaviour at high temperatures, we chose the common cane (*Arundo Donax*), which is found in abundance in Uruguay and elsewhere and shows good promise as a source of biomass fuel due to its yield of up to 50 tonnes/ha of dried biomass (5 times more than woody biomass), with a direct combustion high heating value of 4400 kcal/kg. [25][26]. *Figure VIII* shows an image of the cane species under consideration, which was chopped to 1cm pieces and dried for its ash content and fusion behaviour evaluation.



Figure VIII.- Photograph of “Arundo Donax” (common cane)

6.1. Biomass Fuel Case Study: Common Cane “Arundo Donax”.- Perennial rhizomatous grasses display several positive attributes as energy crops because of their high productivity, low (or none) demand for nutrient inputs consequent to the recycling of nutrients by their rhizomes, exceptional soil carbon sequestration, adaptation to saline soils and saline water, and resistance to biotic and abiotic stresses. Several field studies have highlighted the beneficial effect of this crop on the environment due to its minimal soil tillage, fertilizer and pesticide. Furthermore it offers protection against soil erosion.

The experiments were carried out in labs of the Materials Testing Institute of the UdelaR in Montevideo, Uruguay, in January/March 2014. Ash contents measured based on samples from the stalk and leaves show values between 6% and 7% (dry basis) when ashed at 650C for at least 8hrs until no weight loss was detected.

Ash samples of approximately 2g were placed in a furnace in a cylindrical shape and heated up at 10C/min, until a maximum temperature of 1200C. Every 100C the samples were weighted and examined for signs of sintering or fusion. The different stages during the heating of the samples can be categorized as: L (loose ash, as per the beginning of the test), LS (lightly sintered, able to disintegrate it manually), S: sintered (porous ash block difficult to break it apart manually); M (molten ash, liquid state)

Figure IX shows an image of the cane ash sample in the furnace and then completely sintered when cooled down from 900C. *Figure X* shows a comparison between the Eucalyptus bark and cane ash when subjected to high temperatures: the bark remained as a stable loose powder at 1200C, whereas the cane ash was found completely molten.

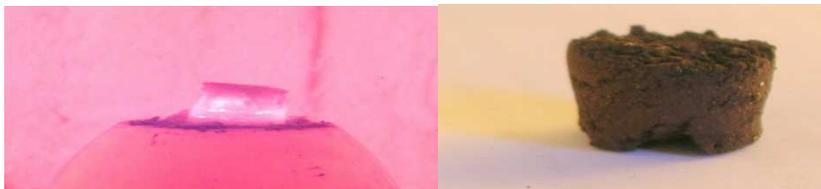


Figure IX.- (a) Ash sample in furnace (b) Sintered sample after exposure to 900C



Figure X.- Ash states of Eucalyptus bark and common cane

Table II shows the results of the fusion tests performed on all samples. The cane ash sintered at 900C and became liquid at 1000C, showing a weight loss of 10% at 1000C which remained invariable for the remainder of the test. Measured ash content of bark, leaves and pulp of the Eucalyptus tree varied quite substantially as expected, but neither showed signs of sintering, fusion or weight loss during the fusion tests.

		STATES: M: Molten; S: Sintered; LS: Lightly Sint.; L: Loose					
		Temperature reached by sample, C					
Ash from biomass:	%Ash	700	800	900	1000	1100	1200
Cane as-is	7%	L	LS	S	M	M	M
weight loss-->					10%	10%	10%
Eucalyptus leaves	4%	L	L	L	L	L	L
Eucalyptus bark	6%	L	L	L	L	L	L
Eucalyptus pulp	1%	L	L	L	L	L	L
Cane leached (2hr@100C)	2%	L	L	L	LS	LS	LS
Cane ash w 33% bark ash	--	L	L	L	LS	LS	LS
Cane ash w 66% bark ash	--	L	L	L	LS	LS	LS

Table II.- Ash fusion evolution of samples tested in the lab. Summary of all tests.

In order to understand possible ways to mitigate the fusion problem of canes when burned in industrial equipment, a 30g sample of canes cut in 1cm pieces was leached in 2lt of boiling water for 2hr. The dissolved solids in the water increased 400ppm during the treatment, meaning that 800mg of matter was extracted from the canes (approximately 3% dry basis)

The ash content of the leached sample dropped to 2% compared to the 7%, implying that the extraction during the leaching process focused on the water soluble content of the ash: i.e.: the alkali salts of K, P and Na. This is further confirmed by the absence of signs of sintering or fusion during the high temperature test. Leached samples at 1200C behaved like unleached samples at 800C, delaying the onset of fusion in approximately 400C.

Another way of estimating possible solutions to the ash fusion of untreated canes is to mix the fuel and/or ashes with stable oxides, which can come from a stable ash on another burner or simply by co-firing a blend of fuels. In this preliminary investigation we mixed two blends with cane ash and contents of bark ash at 33% and 66% and performed ash fusion tests. Both samples remained stable up to 1200C, with no signs of fusion or strong sintering, showing that blending effectively changes the fusion behaviour. This methodology is a possible solution to the burning of canes as-is, and in this regard, it could be a methodology for any problematic biomass in terms of its ash behaviour.

7. Conclusions.

- Due to the chemical composition of the ash of certain types of biomass (particularly short rotation crops like grasses, canes and straws), boiler related problems have occurred systematically in the past. These fuels are rich in alkaline metals (potassium, phosphorus, chlorine and sodium) which form complex eutectic salts that effectively lower the melting point of the ashes during combustion and cause fouling and slagging problems, especially in superheater tubes [3].
- Knowledge of the minerals involved and its correlation with the behaviour of its ash at high temperatures has potential applications in prediction of properties and utilisation connected with the innovative and sustainable utilisation of biomass ash. [17, 20]
- The fusion behaviour of the ashes in the lab is an important factor in determining the propensities of the fuels to form fused or partly fused slag deposits on the furnace wall surfaces in all combustion systems, and have a direct influence on the nature of the fouling deposits that can occur on the heat exchanger and other surfaces in boiler plants.[1][2]
- High steam temperature increases the risk of high temperature corrosion when exposed to the corrosive flue gas. Studies indicate that with steam temperatures above ~550C, the lifetime of superheaters is unacceptably low, although problems start to occur at even lower temperatures. [3]
- The removal of the detrimental elements has been tested by leaching biomass fuel with water, leading to a notable decline in the alkali index which reduced fouling.[14][18][22]
- Problematic operation and maintenance problems in biomass power systems, caused by the release of alkali compounds from the agricultural by-products may be significantly reduced by straight forward, fast and low cost methods. [27]
- The conversion of these biomass materials by thermochemical processes could reduce the volume of wastes, allowing for energy recovery, economic and environmental benefits. [27]
- The common cane showed typical behaviour of herbaceous biomass: high ash content and high tendency to melt.[27]
- Leaching the canes showed a marked improvement in the ash fusion behaviour, as did blending the ashes with stable Eucalyptus bark ashes. The sintering and fusion temperatures were 300C to 400C higher than the canes as-is case.

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9. References.

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