

Reduction of Ash Sintering Precursor Components in Rice Straw by Water Washing

Noha Said,^{a,b,*} Mahmoud M. Abdel daiem,^b Angela García-Maraver,^a and Montserrat Zamorano^a

The thermal conversion of rice straw is an attractive option for recovering its energy, but the process requires exhaustive control because of ash-related problems. Straw washing is one method of reducing ash-related problems and improving combustion behaviour. In this study, the ash of washed and unwashed rice straw samples was chemically characterized, tested using thermogravimetric analysis and environmental scanning electron microscopy (ESEM), and subjected to higher combustion temperatures in a muffle furnace. Results showed that silicon was the most important component in the ash. Furthermore, a reduction in undesirable inorganic compounds related to ash problems, such as chlorine and potassium, was achieved by washing the straw samples. This practice could improve thermal behaviour and decrease the sintering formation of ash.

Keywords: Rice straw; Ash; Thermal analysis; Electron microscopy; Sintering

Contact information: a: Civil Engineering Department, Area of Environmental Technology, Granada University 18071, Granada, Spain; b: Environmental Engineering Department, Faculty of Engineering, Zagazig University 44519, Zagazig, Egypt; *Corresponding author: nsaid_2020@ugr.es

INTRODUCTION

Given the excessive use of fossil fuels and concerns over environmental protection, the utilization of biomass resources, including agricultural residues, has attracted increasing worldwide interest (Fu *et al.* 2009). Rice straw is one of the main agricultural residues in countries such as Egypt, Thailand, China, and especially Japan, where it comprises the largest amount of unused agricultural residue by far (Matsumura *et al.* 2005; Delivand *et al.* 2011; Liu *et al.* 2011; Said *et al.* 2013a). Its energy can be recovered directly through a combustion process, or it can be converted to a valuable energy product through indirect techniques such as gasification and biochemical conversion, after which the products can be burned (Ewida *et al.* 2006).

The combustion of rice straw to directly produce thermal energy not only saves energy, protects the environment, and reduces field-burning pollution; it also increases the income of farmers (Ewida *et al.* 2006; Yu *et al.* 2008). There are, however, some technical limitations involved in thermal conversion systems, such as high ash content, sintering, slag formation, and corrosion problems (Jenkins *et al.* 1996; Baxter *et al.* 1998; Fu *et al.* 2009; Said *et al.* 2013b). Washing rice straw with water is a feasible option for reducing these problems (Jenkins *et al.* 1996; Bakker *et al.* 2002). Previous work (Said *et al.* 2013b) describes the effects of water-washing on the chemical and thermal characteristics of rice straw, indicating enhanced thermal behaviour. This included a higher heating value and a reduction in ash content and sintering formation compared

with the unwashed samples. Also, an improvement in the alkali index value was observed for the washed samples.

Ash analysis based on thermogravimetric analysis and electron microscopy provides more details about its behaviour through combustion processes (Skrifvars *et al.* 2005; Fang and Jia 2012) and the effects of washing samples before combustion. Such studies are rare, however. Against this background, the main objective of the present study is to investigate the effect of washing rice straw on the chemical composition and thermal characteristics of its ash by using X-ray fluorescence (XRF), thermogravimetric analysis (TGA/DSC), and environmental scanning electron microscopy (ESEM).

EXPERIMENTAL

Materials

Sampling procedure

Samples of rice straw approximately 1 m tall were collected from El Sharkia Government, Egypt. They were cut to a size of 10 cm, washed with flushed tap water, and dried in air dry oven at 105 °C to a constant weight in the laboratory; the particle size for the dried washed and unwashed straw samples was reduced to less than 0.5 mm with a cutting mill. Finally, unwashed and washed samples of rice straw were subjected to combustion at 550 °C in a muffle furnace for 5 h to obtain ash samples used for this research, according to UNE-EN 14775 (2010). Moreover, the ash samples were subjected to temperatures of 700, 800, 900, and 1000 °C in a muffle furnace for 2 h to investigate changes in colour and in physical states.

Methods

Laboratory tests

To determine ash composition, ash samples of washed and unwashed straw were analysed using a Philips Magix Pro PW-2440 sequential spectrometer with a dispersive wavelength and an X-Ray generator of 4 KW. The ESEM analysis for the ash samples was performed using an FEI Quanta 400 ESEM (The Netherlands) equipped with a SAPPHIRE Si(Li) SUTW detector operating at an accelerating voltage between 0.20 to 30 kV to obtain the image, particle size, and composition of the ash analysed in the selected spots. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on the ash of both types of straw samples using a Shimadzu TGA-50H thermo analyser (Japan) in an oxidative atmosphere. The initial mass of the ash samples was kept between 2 and 5 mg and heated from 30 °C to 1000 °C at a heating rate of 5 °C/min and a constant airflow rate of 50 mL/min.

RESULTS AND DISCUSSION

Ash Composition

The chemical composition of the ash obtained from the washed and unwashed straw samples is summarized in Table 1. For unwashed straw samples, the highest ash component was silica (SiO₂), which constituted 65.4% of the total content, followed by K₂O, Cl, Na₂O, MgO, CaO, SO₃, and P₂O₅. In washed samples the silica content was as high as 72.6%, followed in order by K₂O, CaO, Cl, Na₂O, MgO, P₂O₅, and SO₃. Washing

proved very efficient for removing over half the SO₃ and chlorine (respective removal ratios of 59.5% and 59.1%). For Na₂O, K₂O, MgO, and P₂O₅, the removal ratios were 35.7%, 26.1%, 21.9%, and 8.82%, respectively. Calcium oxide and SiO₂ removal were substantially higher, reaching 41.3% and 11%, respectively. Both SiO₂ and CaO appear to reside largely in the plant cell wall of rice straw (Miles *et al.* 1996; Soest 2006); therefore, the washing practice did not effectively remove them. However, washing the straw does serve to extract large amounts of alkali metals such as potassium, which dissolved very well in water, and chlorine, which is highly leached by water (Lee *et al.* 2005; Skrifvars *et al.* 2005). In addition, washing removes varying amounts of sulphur, phosphorus, and other elements caused by soil contamination of the straw (Jenkins *et al.* 1996; Bakker *et al.* 2002; Skrifvars *et al.* 2005); while their percentages are reduced, the relative contents of SiO₂ and CaO are seen to increase.

Table 1. Composition (%) of Ash Elements in Washed and Unwashed Samples

Samples	SiO ₂	K ₂ O	Cl	Na ₂ O	MgO	CaO	SO ₃	P ₂ O ₅	Others
Unwashed	65.43	13.01	5.40	3.11	2.24	2.13	1.26	0.68	6.74
Washed	72.59	9.61	2.21	2.00	1.75	3.01	0.51	0.62	7.70

Environmental Scanning Electron Microscopy Inspection

Figure 1 shows the ESEM results for ash of the unwashed straw samples and the chemical analysis of selected spots. Supporting the results expounded in the previous section, high amounts of chlorine and potassium were detected by ESEM. Additional elements such as Na and Mg were detected in spot 1, and similarly in spot 3, which were observed with a lighter appearance compared to surrounding area. Silica was the predominating element in spot 2, though similar constituents were observed at spot 4. These findings are in line with the results reported by Skrifvars *et al.* (2005) for rice straw ash samples.

Figure 2 shows the ESEM results for the ash of the washed straw sample and the chemical analysis of selected spots. While washing did not have a considerable effect on ash microstructure, it did cause changes in chemical composition. As shown in Fig. 2, all the selected spots consist primarily of silica. Small amounts of other elements including carbon, oxygen, magnesium, and sodium were also present. A considerably high amount of Ca was detected at spot 1. In turn, a considerable loss in chlorine and potassium from washing was observed by ESEM, supporting the results obtained for ash composition (higher SiO₂ and CaO). Meanwhile, markedly lower contents of Cl and K₂O were observed for the washed samples when compared with unwashed ones.

Qualitative Analysis of Ash

Unwashed samples

The ash obtained from the unwashed samples at 550 °C has a dark grey colouring (Fig. 3a). This colour could result from residual carbon compounds that require a higher temperature or longer time to completely burn the straw samples (Wattanasiriwech *et al.* 2010). The combustion of ash samples at 700 °C resulted in a grey colour, and they were easy to remove. Nevertheless, when the combustion temperature was increased to 800 °C, light ash sintering was observed, and the sintering increased with increasing combustion temperature (up to 900 °C). Severe sintering and slag formation of a dark brown colour was observed when the combustion temperature reached 1000 °C, making it impossible

to remove the ash from the crucibles (Fig. 3b). This may be caused by the fact that silica in combination with alkali and alkaline earth metals, especially potassium, can lead to the formation of compounds that readily slag and foul at normal furnace temperatures (Miles *et al.* 1996; Skrifvars *et al.* 2005). Moreover, chlorine could be an important facilitator in fouling and in the vaporization of alkali species, leading to the formation of more severe deposits (Miles *et al.* 1996).

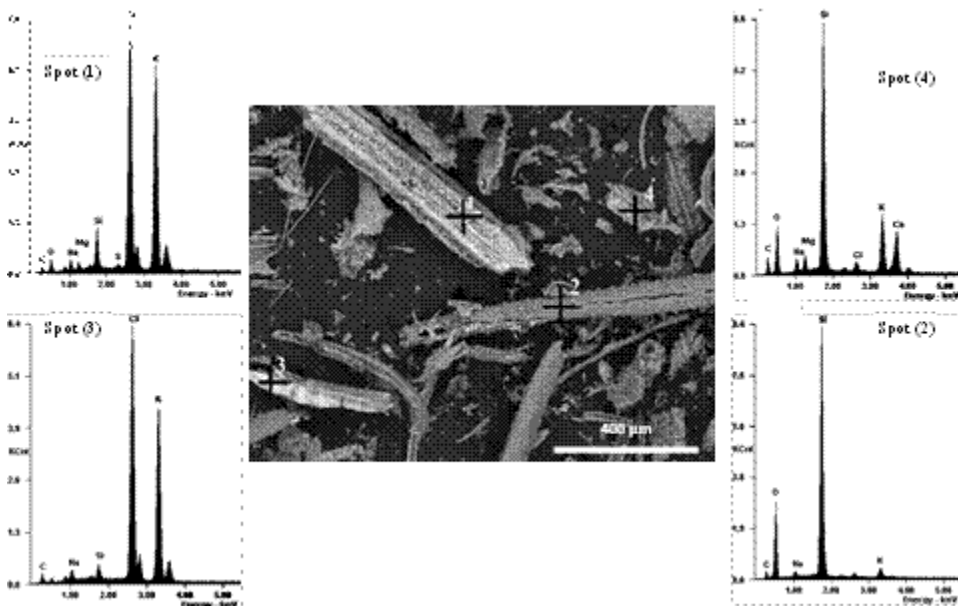


Fig. 1. ESEM analysis of ash (unwashed samples)

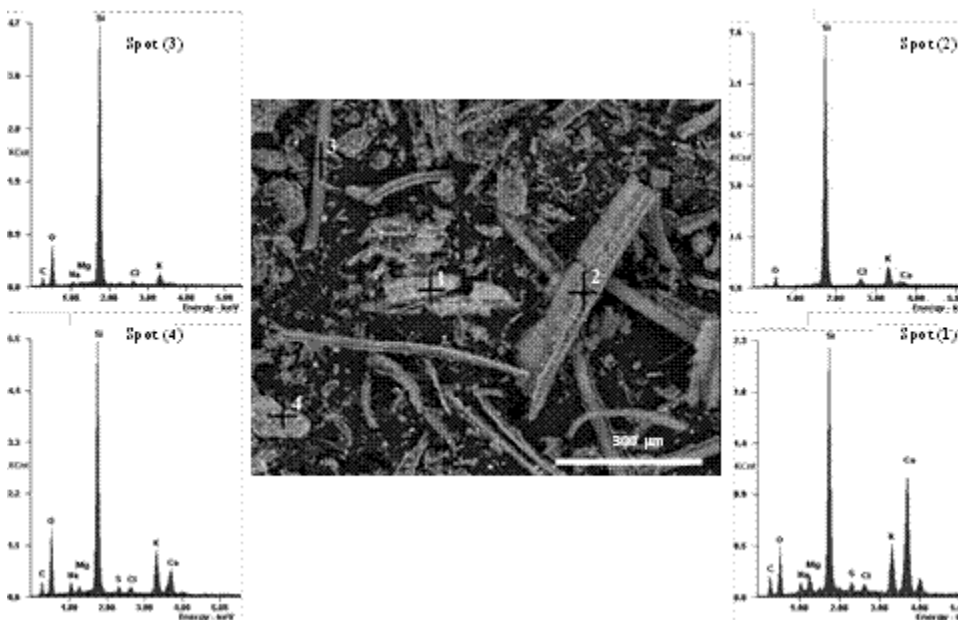


Fig. 2. ESEM analysis of ash (washed samples)

Washed samples

The ash of the washed samples at 550 °C was grey-coloured (Fig. 3c). With increasing combustion temperature (up to 700 °C), the ash had a lighter grey colour and became close to white when the furnace temperature was increased to 1000 °C (Fig. 3d). Unlike the unwashed samples, the ash of the washed samples was easy to remove and did not show sintering or slag formation. This could be explained by the reduction of undesirable compounds, especially potassium, after washing (Table 1). Moreover, the alkali index of rice straw is greatly decreased when washed, as indicated previously (Said *et al.* 2013a). Washing therefore leads to significant changes in inorganic composition and substantially improves combustion behaviour (Jenkins *et al.* 1996; Bakker *et al.* 2002; Lee *et al.* 2005).

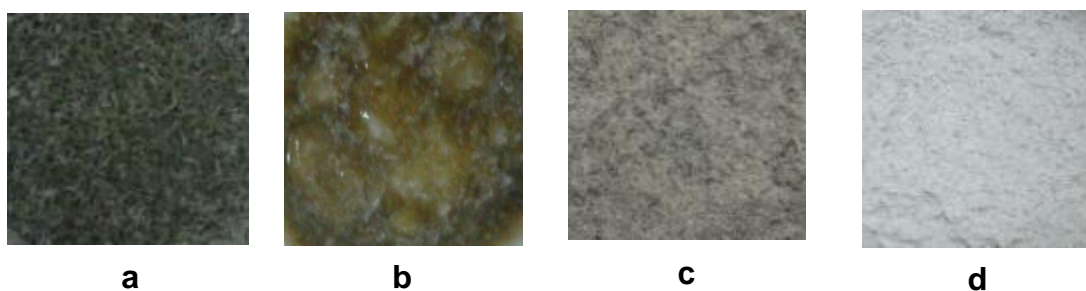


Fig. 3. Ash combusted in a muffle furnace. (a) unwashed sample at 550 °C; (b) unwashed sample at 1000 °C; (c) washed sample at 550 °C; and (d) washed sample at 1000 °C

Thermogravimetric Analysis and Differential Scanning Calorimetry

To consider the combustion behaviour of ash in detail, the thermogravimetric curves of the ash obtained at 550 °C for washed and unwashed straw samples were analysed (Fig. 4).

Thermogravimetric analysis

The TGA curves showed changes in the mass loss of the ash samples with increasing temperature, essentially in the same order as found in previous work (Fang and Jia 2012). An initial mass loss occurred at temperatures lower than 200 °C because of the evaporation of water, which was readily absorbed into the atmosphere by the much smaller ash particles before testing (Fang and Jia 2012). The mass loss at 200 °C in the unwashed samples was higher than that for the washed samples (2.80% *versus* 1.20%). It may be that the moisture in the unwashed samples was absorbed by components such as chlorine and potassium, which were present together in greater concentrations than in the washed samples (Lee *et al.* 2005; Skrifvars *et al.* 2005).

Because the ash samples tested were obtained at 550 °C, a very low rate of mass loss was observed from 200 up to 700 °C; only about a 3.60% loss in the ash mass of the unwashed sample. This loss may be attributed to the oxidation of some organic components that had not completely burned, as well as to the evaporation of some inorganic matter from the ash with further increases in temperature (Fang and Jia 2012). Above 700 °C and up to 850 °C, a markedly increase in mass loss (5.50% and 7.70% for washed and unwashed samples, respectively) was observed. This may be due to the higher deposition rate of char particles of unwashed straw during higher combustion temperatures (Bakker *et al.* 2002), and also to the removal and decomposition reaction of

inorganic components such as chlorine and potassium (Fang and Jia 2012) which are found together and in greater proportions in the unwashed samples, as indicated by the ash composition and ESEM analyses described above.

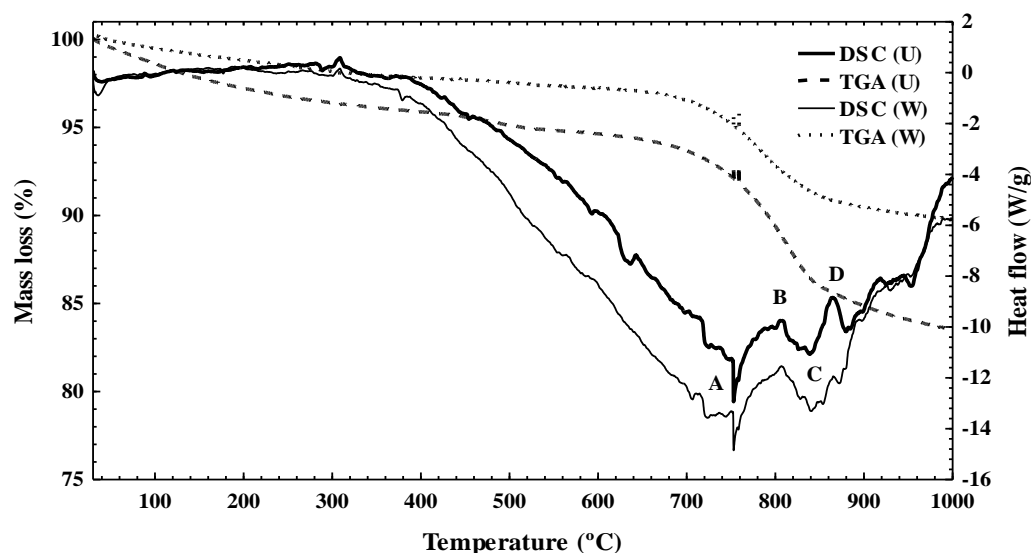


Fig. 4. TGA and DSC for ash of washed (W) and unwashed (U) samples

Potassium starts to be released at a low rate at very low temperatures, but is then more rapidly released as the temperature increases up to 800 °C (Knudsen *et al.* 2004; Skrifvars *et al.* 2005). The potassium absorbed from the soil mainly remains as ions in fresh plants; when the plants wither, the potassium may exist in simple salts such as KCl and K₂SO₄, which have high activity and strong migration characteristics at high temperatures (Yu *et al.* 2010). A high content of potassium salts is retained in ash after the completion of combustion, and at high temperatures these salts may evaporate and volatilise into gas or react with silicon, calcium, or other elements to form complex silicates after 800 °C (Baxter *et al.* 1998; Fang and Jia 2012). The minor mass loss observed from 850 °C up to 1000 °C (1.33% and 2.51% for washed and unwashed samples, respectively) can be attributed to the evaporation of KCl and the reaction between Si and KCO₃, which decomposes after 1000 °C (Masia *et al.* 2007; Szemmelveisz *et al.* 2009).

Differential scanning calorimetry

The DSC curves are important for studying the thermal behavior of ash, representing the melting point as a maximum of the endothermic peaks of DSC trace (Buzarovska *et al.* 2008). As can be seen in Fig. 4, the ash samples recorded a maximum endothermic peak in the range of 700 °C to 800 °C, represented as zone (A). In agreement with Wanger (2009) and as indicated in the figure, the melting peak was followed by an exothermic decomposition reaction represented in zone (B); then, the evaporation of the decomposition product represented at zone (C) was followed by a crystallization exothermic peak represented at (D), which was only observed for the unwashed sample and not detected in the washed one.

This crystallization peak could indicate sintering formation occurring with the ash of the unwashed sample, as discussed in the section on ash behaviour. No considerable

difference in melting temperature was observed between the washed and unwashed samples. However, the fact that the unwashed sample recorded a lower heat flow rate may be associated with the higher ash-related problems of the unwashed samples; this would result in low thermal conductivity, retarding the rate of heat transfer (Jenkins *et al.* 1996; Zbogar *et al.* 2009).

CONCLUSIONS

1. Chemical analysis and ESEM of rice straw ash samples revealed that silica was the foremost component (65.4%), followed by K₂O (13%), and that these two components are combined at high combustion temperatures and associated with ash sintering problems.
2. Thermogravimetric analysis provided valuable indications of component decomposition, which occurred in stages, and more detailed information about thermal behaviour and related reactions at high combustion temperatures.
3. The washing process resulted in a reduction of some sintering precursor components in the ash samples, such as K₂O and Cl. Lower ash mass losses at greater combustion temperatures and enhanced thermal behaviour were observed after washing.

ACKNOWLEDGMENTS

This research was funded by the Innovation and Science Division of the Andalusian Regional Government (Research Projects P08-RNM-03584 and TIC-02913), the Spanish Ministry of Science and Innovation (Research Project CTM2009-07199), and the Spanish Agency for International Development Cooperation (AECID) of the Ministry of Foreign Affairs and Cooperation (Project AP/045946/11).

REFERENCES CITED

- Bakker, R. R., Jenkins, B. M., and Williams, R. B. (2002). "Fluidized bed combustion of leached rice straw," *Energ. Fuel.* 16(2), 356-365. DOI: 10.1021/ef010197w
- 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 Process. Technol.* 54(1-3), 47-78. DOI: 10.1016/S0378-3820(97)00060-X
- Buzarovska, A., Bogoeva-Gaceva, G., Grozdanov, A., Avella, M., Gentile, G., and Errico, M. (2008). "Potential use of rice straw as filler in eco-composite materials," *Aust. J. Crop Sci.* 2(1), 37-42.
- Delivand, K. M., Barz, M., and Gheewala, S. (2011). "Logistics cost analysis of rice straw for biomass power generation in Thailand," *Energy* 36(3), 1435-1441. DOI: 10.1016/j.energy.2011.01.026
- Ewida, K. T., El-Salmawy, H., Atta, N. N., and Mahmoud, M. M. (2006). "A sustainable approach to the recycling of rice straw through pelletization and controlled burning," *Clean Technol. Envir.* 8(3), 188-197. DOI: 10.1007/s10098-006-0043-x

- Fang, X., and Jia, L. (2012). "Experimental study on ash fusion characteristics of biomass," *Bioresour. Technol.* 104, 769-774. DOI: 10.1016/j.biortech.2011.11.055
- Fu, P., Hu, S., Xiang, J., Sun, L. S., Yang, T., Zhang, A. C., and Zhang, J. Y. (2009). "Mechanism study of rice straw pyrolysis by Fourier transform infrared technique," *Chinese J. Chem. Eng.* 17(3), 522-529. DOI: 10.1016/S1004-9541(08)60240-2
- Jenkins, B. M., Bakker, R. R., and Wei, J. B. (1996). "On the properties of washed straw," *Biomass Bioenerg.* 10(4), 177-200. DOI: 10.1016/0961-9534(95)00058-5
- Knudsen, J. N., Jensen, P. A., and Dam-Johansen, K. (2004). "Transformation and release to the gas phase of Cl, K, and S during combustion of annual biomass," *Energ. Fuel.* 18(5), 1385-1399. DOI: 10.1021/ef049944q
- Lee, K., Kang, B., Park, Y., and Kim, J. (2005). "Influence of reaction temperature, pretreatment, and a char removal system on the production of bio oil from rice straw by fast pyrolysis, using a fluidized bed," *Energ. Fuel.* 19(5), 2179-2184. DOI: 10.1021/ef050015o
- Liu, Z., Xu, A., and Zhao, T. (2011). "Energy from combustion of rice straw: Status and challenges to China," *Energy Power Eng.* 3, 325-331. DOI: 10.4236/epe.2011.33040
- Masia, A. A. T., Buhre, B. J. P., Gupta, R. P., and Wall, T. F. (2007). "Characterizing ash of biomass and waste," *Fuel Process. Technol.* 88(11-12), 1071-1081. DOI: 10.1016/j.fuproc.2007.06.011
- Matsumura, Y., Minowa, T., and Yamamoto, H. (2005). "Amount, availability, and potential use of rice straw (agricultural residue) biomass as an energy resource in Japan," *Biomass Bioenerg.* 29(5), 347-354. DOI: 10.1016/j.biombioe.2004.06.015
- Miles, T. R., Miles Jr., T. R., Baxter, L., Bryers, R., Jenkins, B., and Oden, L. (1996). "Alkali deposits, A summary report for the National Renewable Energy Laboratory, NREL," Subcontract No. TZ-2-11226-1.
- Skrifvars, B. J., Yrjas, P., Kinni, J., Siefen, P., and Hupa, M. (2005). "The fouling behavior of rice husk ash in fluidized-bed combustion. 1: Fuel characteristics," *Energ. Fuel.* 19(4), 1503-1511. DOI: 10.1021/ef049714b
- Said, N., El-Shatoury, S. A., Díaz, L. F., and Zamorano, M. (2013a). "Quantitative appraisal of biomass resources and their energy potential in Egypt," *Renew. Sust. Energ. Rev.* 24, 84-91. DOI: 10.1016/j.rser.2013.03.014
- Said, N., Bishara, T., García-Maraver, A., and Zamorano, M. (2013b). "Effect of water washing on the thermal behavior of rice straw," *Waste Manage.* 33(11), 2250-2256. DOI: 10.1016/j.wasman.2013.07.019
- Soest, P. J. V. (2006). "Rice straw, the role of silica and treatments to improve quality," *Anim. Feed. Sci. Tech.* 130(3-4), 137-171. DOI: 10.1016/j.anifeedsci.2006.01.023
- Szemmelveisz, K., Szucs, I., Palotas, A. B., Winkler, L., and Edings, E. G. (2009). "Examination of the combustion conditions of herbaceous biomass," *Fuel Process. Technol.* 90(6), 839-847. DOI: 10.1016/j.fuproc.2009.03.001
- UNE-EN 14775 (2010). "Solid biofuels - Determination of ash content," *Spanish Association for Standardisation and Certification (AENOR)*.
- Wanger, M. (2009). *Thermal Analysis in Practice-Collected Applications*, Mettler Toledo Application Handbook, http://cn.mt.com/cn/zh/home/applications/Application_Browse_Laboratory_Analytics/Application_Browse_thermal_analysis/TA_Appl_Handb/TA_in_Practice/_jcr_content/standardpar/1145/file/file.res/Thermal_Analysis_in_Practice.pdf.
- Wattanasiriwech, S., Wattanasiriwech, D., and Svasti, J. (2010). "Production of amorphous silica nanoparticles from rice straw with microbial hydrolysis

- pretreatment,” *J. Non-Cryst. Solids* 356(25-27), 1228-1232. DOI: 10.1016/j.jnoncrysol.2010.04.032
- Yu, Z. S., Ma, X. Q., and Ao, L. (2008). “Kinetic studies on catalytic combustion of rice and wheat straw under air- and oxygen-enriched atmospheres, by using thermogravimetric analysis,” *Biomass Bioenerg.* 32(11), 1046-1055. DOI: 10.1016/j.biombioe.2008.02.001
- Yu, C. J., Qin, J. G., Xu, J., Nie, H., Luo, Z. Y., and Cen, K. F. (2010). “Straw combustion in circulating fluidized bed at low-temperature: Transformation and distribution of potassium,” *Can. J. Chem. Eng.* 88(5), 874-880. DOI: 10.1002/cjce.20321
- Zbogar, A., Frandsen, F., Jensen, P. A., and Glarborg, P. (2009). “Shedding of ash deposits,” *Prog. Energy Combust. Sci.* 35(1), 31-56. DOI: 10.1016/j.pecs.2008.07.001

Article submitted: July 10, 2014; Peer review completed: September 7, 2014; Revised version received and accepted: September 13, 2014; Published: September 23, 2014.