Analysis of Paper Sludge Pellets for Energy Utilization

Radovan Nosek,* Michal Holubcik, Jozef Jandacka, and Lucia Radacovska

The pulp and paper industry in Europe produces over 11 million tons of waste per year. Given high landfill operational costs, thermal co-processing with biomass may be a viable management and valorisation option for such wastes. In this work, the analysis of biomass (wood sawdust), mixture of primary and secondary pulp mill sludge and their respective blends (50 wt.%, 60 wt.%, 70 wt.% of sludge) was assessed by thermogravimetric analysis. One of the possibilities to ensure valorisation of paper pulp mill sludge is its combustion in the form of pellets containing a different amount of sludge. Production of pellets samples was realised on laboratory experimental device. The measurements showed that increasing the content of paper sludge in the produced pellets reduced the calorific value and increased the ash content. This research deals also with the effect of paper sludge on the ash melting temperatures. The results indicated that a higher content of paper sludge in the pellets increased the ash melting temperatures. This advantage of paper sludge can be utilized in co-combustion of biomass with a low ash melting temperature.

Keywords: Waste sludge; Paper; Pellets; Combustion heat; Ash

*Contact information: Department of Power Engineering, Faculty of Mechanical Engineering, University of Zilina, Univerzitna 1, 010 26 Zilina, Slovakia; *Corresponding author: radovan.nosek@fstroj.uniza.sk*

INTRODUCTION

Sludge is unavoidably generated and its management is a key issue for the pulp and paper industry. Paper sludge management and disposal involve economic, environmental, and social costs that will likely increase in the future. Therefore, several waste recovery options may be considered for sludge from the pulp and paper industries, which include thermal processes such as combustion. Ash is the solid product of combustion, which allow for an important reduction of volume of sludge from the pulp and paper industries. Furthermore, valorisation of such wastes is possible by energy recovery with power and steam generation during combustion (Elliott and Mahmood 2005; Monte *et al.* 2009). On the other hand, and from an economic and practical point of view, the possibility of a joint processing of sludge from the pulp and paper industry with biomass in existing plants may be an interesting option, since it allows for the use of existing infrastructures already equipped with appropriate devices for emission control, reducing at the same time fossil fuels consumption (Vamvuka *et al.* 2009).

Thermal valorisation of pulp mill sludge has been analysed in the research of Coimbra *et al*. (2016). The aim was to assess and compare the thermal behaviour during combustion of primary pulp mill sludge, secondary pulp mill sludge, a bituminous coal, and their respective blends (10 wt.% of either primary or secondary pulp mill sludge). For this purpose, thermogravimetric analysis was carried out, and the Flynn, Wall, and Ozawa non-isothermal kinetic model was applied in order to determine the apparent activation energy associated to the single combustion as well to that related to the co-

combustion of primary and secondary pulp mill sludge with coal. The results obtained in their work showed the potential of thermal valorisation of pulp mill sludge by co-processing with coal, which means an increase of coal reactivity and a decrease of the associated activation energy. In any case, from a practical point of view, for co-processing in existing plants, it must be taken into account the large volatiles content of secondary and, especially, of primary pulp mill sludge (Coimbra *et al.* 2016).

Similar work was done by Coimbra *et al*. (2015) as well, where the effect of adding a low percentage (10 wt.%) of primary or secondary pulp mill sludge on the combustion of coal and its kinetics was evaluated. The results point to co-combustion of coal with primary and, especially, with secondary pulp mill sludge as a feasible management option for such wastes (Coimbra *et al.* 2015).

In China, research has been conducted on mixing paper sludge and rice straw. Investigations were focused on mixtures of sludge and straw that ranged from 10% to 95% straw. The mixtures did not undergo any processing and no pellets or briquettes were produced (Zeqiong and Xiaoqian 2013).

It was found that paper sludge and rice straw display very similar behaviour during high temperature combustion. The results showed lower ash, sulphur, and nitrogen contents for the straw. It has also been discovered that the sludge contains a large amount of non-combustible particles, and thus it contains a higher amount of ash in comparison to rice straw. Results of the experiments showed the ignition temperature and temperature for complete combustion of the individual samples and the mixtures.

The presence of rice straw in the mixture reduces the ignition temperature, but also increases the flammability index. In general, combustion of the mixture improves the thermal decomposition of the mixture at high temperatures. The best results achieved for the mixture were 80% straw and 20% sludge.

The effect of the paper sludge weight percentages on the overall combustion characteristics was analysed at the South China University of Technology. The paper sludge was obtained from a paper mill in Guangzhou, China that produces 120 tons of paper sludge daily at full power. As in the previous case, given the high moisture content of approximately 70% to 80%, the sample of sludge was dried at 90 °C for 5 h. Subsequently the sludge was crushed and sieved to achieve a maximum particle size of 250 μm. Three sludge-coal samples were produced containing 10%, 20%, and 50% of dried paper sludge. The differences between coal and paper sludge combustion were significant, but samples with a low weight percentage of paper sludge, such as less than 10 wt.%, resulted in combustion profiles similar to that of coal (Liao and Xiaoqian 2010; Lazar *et al.* 2011).

It was found that paper sludge and anthracite have very different properties; in particular, sludge has a much higher ash content and lower carbon concentration than coal. However, the sludge contains a higher amount of volatile matters and oxygen. These two materials are essential for inducing ignition (Liao and Xiaoqian 2010).

Based on the review on pulp and paper mill sludge management practices, one can recommend there to be research focused on isolating the GHG emission contribution of paper sludge within the fuel mixture when combustion is practiced. The measurement of these emission assessments is essential if such combustion practices are to be compared with landfilling practices in order to determine if GHG emissions are avoided and/or decreased when considering the whole processes (Fauber *et al.* 2016).

Landfilling tends to be reduced or banned, with the passage of time, and therefore paper sludge management practices have to be identified. The objective of this work was to study the combustion of different paper sludge ratios (50, 60 and 70%) with wood sawdust, which will reduce the amount of landfill. Due to the lack of information, this work dealt with an experimental investigation of pellets containing sludge and wood sawdust, and an analysis of the features and characteristics of the produced samples. Thermogravimetric analysis was employed for the study of the thermal processing of samples.

The combustion of mixed pellets and measurement of the emissions and particulates matters will be investigated in further research.

EXPERIMENTAL

Materials

For this research, recycled paper with cellulose content was used. This material comes from a paper producer in Zilina, Slovakia. At present, the company is a global producer of wood and paper products. Production is mainly focused on paper products used every day in homes, and wooden components used in the construction industry. The production consists of two paper machines: PS1 (with a capacity of 30000 tons per year in the width of 285 cm) and PS2 (with a capacity of 54000 tons per year in a width of 528 cm). The average production of paper sludge is approximately 50,000 tons per year. This is higher ratio in comparison with work of Balwaik and Raut (2011) which have reported that about 300 kg of sludge is produced for each 1 ton of recycled paper. The amount of waste generated in paper production varies greatly within different regions, because of different recycling rates.

The investigated paper sludge can be seen in Fig. 1. This paper sludge comes from two sources: primary sludge collected in an initial clarifier, and biological sludge generated in a second clarifier. Primary sludge is generated in the clarification of process water by such operations as dissolved air flotation. The sludge consists of mostly fines and fillers depending on the recovered paper being processed. Secondary sludge sometimes can be recycled to the product (board industry) or thickened, dewatered, and then incinerated or disposed of in landfill. Secondary sludge volumes sometimes are lower than those corresponding to the primary sludge, since most of the heavy, fibrous, or inorganic solids are removed in the primary clarifier. Secondary sludges are often difficult to handle (due to a high microbial protein content), and such solids need to be mixed with primary sludge to permit adequate dewatering (Bajpai 2015). Based on the results of the works Elliot and Mahmood (2005, 2006) it can be estimated that in tested paper sludge approximately 70% is primary sludge and 30% is secondary sludge. The primary sludge can be dewatered relatively easier. Compared with the primary sludge, the secondary sludge is very difficult to dewater. The secondary sludge consists mostly of excess biomass produced during the biological process (Ramalho 1983). Experiments were carried out to find the essential features and characteristics of the sludge. In the first phase, the moisture of sludge was measured. In total, five measurements were performed and the average moisture (w) content was $w = 51\%$.

The production of pellets from paper sludge was also analysed. Pellets were produced from sludge with the moisture content to approximately 51% (Fig. 1 a), and 12% (Fig. 1 b).

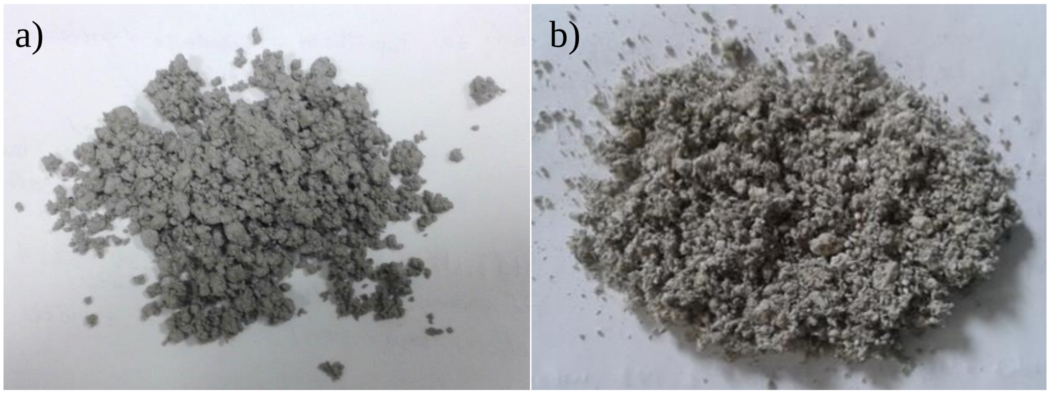

Fig. 1. Paper sludge with a moisture content to approximately 51% (a) and 12% (b)

Production of pellet samples was realised on a laboratory experimental device for pelletizing. The equipment includes an input material tank (storage of material for pellets production), crusher (crush material to fractions of size max. 6 mm), crushed material tank (where the crushed material is temporarily stored), dryer (wet material is dried to optimal humidity), mixing machine with capacity of 50 dm^3 (dried material is mixed with water), pellet mill with capacity of 50 to 70 $kg.h^{-1}$ (material is pressed to pellets), cooler and duster with fan (final product - pellets are cooled to ambient temperature), and produced pellets tank (where pellets are temporarily stored before packing) (Jandacka *et al.* 2016).

There were 5 types of pellet samples produced:

- wood pellets – made from pure wood sawdust,
- 50:50 – made from 50% of paper sludge and 50% of wood sawdust,
- 60:40 – made from 60% of paper sludge and 40% of wood sawdust,
- 70:30 – made from 70% of paper sludge and 30% of wood sawdust,
- sludge pellets – made from pure paper sludge.

Methods

The measurements were made on following equipment: calorimeter LECO AC 500, thermogravimetric analyzer LECO 701 TGA, elemental analyser LECO CHN 628, LECO 628 S, and fusibility temperature analysis device LECO AF 700 (LECO Corporation, Saint Joseph, France).

Subsequently, the higher calorific value was measured by the calorimeter LECO AC 500 (LECO Corporation, 3000 Lakeview Ave, Saint Joseph, France). The measurement of gross calorific value (GCV) is based on the law of conservation of energy, which states that the heat released by the investigated substance shall be equal to the heat that is absorbed by water and the calorimeter.

The lower calorific value (LCV) of sludge was calculated based on the GCV obtained from the calorimeter, H_2 content from elemental analysis and the measured moisture content.

The LECO 701 TGA (LECO Corporation, 3000 Lakeview Ave, Saint Joseph, France), which measured the weight loss, moisture content, ash content, and volatile matter as well as the concentration of various organic, inorganic, and synthetic materials. Thermogravimetric analysis (TGA) is one of the major thermal analysis techniques used to study the thermal behaviour of carbonaceous materials. The rate of the weight loss of the sample as a function of temperature and time was measured to predict the thermal behaviour of the material. The TGA provides a semi-quantitative understanding of the thermal degradation processes occurring during thermo-chemical conversion under various atmospheres (Mansaray and Ghaly 1998).

The carbon, hydrogen, and nitrogen contents were determined using a LECO CHN 628 model (LECO Corporation, 3000 Lakeview Ave, Saint Joseph, France). The device works on the principle of a two-stage furnace where the temperature reaches 1,050 °C. The analysis of the samples was performed at a constant temperature of 949 °C. The combustion was performed with pure oxygen to ensure the complete combustion of all organic samples without the addition of the necessary additional oxidizing metal or other gases.

The sulphur content was measured on a LECO 628 S model (LECO Corporation, 3000 Lakeview Ave, Saint Joseph, France), which provided independent determination of sulphur in a small sample (350 mg). A sulphur analysis was detected by combustion at 1,450 ° C with very short analysis times (less than 2 min).

Ash fusion temperatures are a critical quality control parameter for predicting the performance of a specific fuel and evaluating the tendency of a fuel to slag. The ash melting temperature of produced samples was determined on the basis of the STN ISO 540 (2008) standard. The meltability of ash is characterized by the physical state of the ash, which occurs during the heating process under well-defined conditions in a furnace. During the melting of ash, the following four temperatures were monitored (Holubcik 2013):

- Shrinkage temperature (ST), the temperature at which first symptoms occur, rounded edges or the edges of the test specimen due to melting;
- Deformation temperature (DT), the temperature at which the edges of the test specimen become completely rounded, without changing the amount;
- Hemisphere temperature (HT), the temperature at which the test specimen creates a hemisphere, the amount of which is equal to about half the base; and
- Flow temperature (FT), the temperature at which the ash pitch on a base in such a layer, the amount of which is approximately one third of the test specimen at the melting temperature.

Ash in boilers could cause various problems and decrease the heat transfer in heat exchangers, which could cause corrosion of the heat transfer surfaces.

RESULTS AND DISCUSSION

The produced pellets of the raw paper sludge were too soft and broke up easily. The structure of the produced pellets can be seen in Fig. 2 a and b.

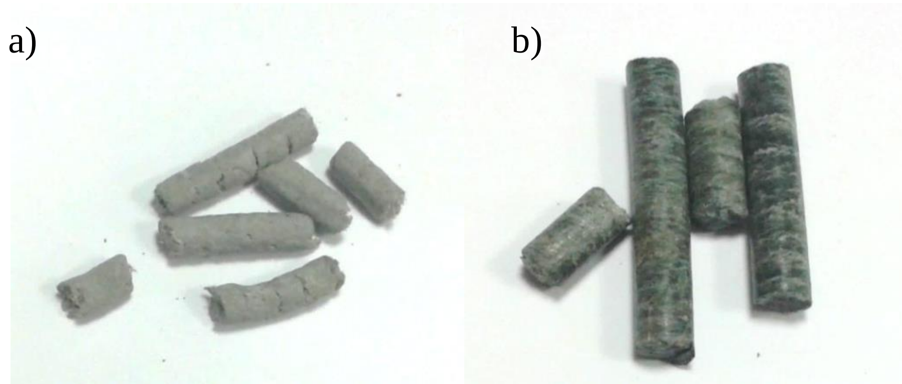

Fig. 2. Pellets from paper sludge with moisture content of approximately 51% (a) and 12% (b)

Experimentally it was found that the moisture content of the input material must be between 20% and 25% to produce high quality samples and to ensure problem-free compression of the pellets with the LCV of approximately 12 MJ.kg^{-1}.

The GCV was measured by calorimeter and five measurements were taken for each sample of undried paper sludge, and the average gross calorific value was 5.84 MJ.kg^{-1}. The average value of LCV was 4.03 MJ.kg^{-1}. After drying and pressing in pellet mill the GCV of paper sludge pellets was 6.72 MJ.kg^{-1} and LCV was 5.87 MJ.kg^{-1}. For proper evaluation, the measured results were compared with the properties of the wood pellets samples made from pure wood sawdust. The LCV of wood pellets was higher in comparison to the produced samples of pellets, as expected. Sawdust was found to have a higher LCV and thus the increase of calorific value in the samples produced from the mixture was noticed. Table 1 shows average values of moisture, GCV and LCV of the produced samples.

Table 1. Experimental Results for Moisture, GCV, and LCV of the Produced Samples

Tested sample	Moisture wt.%	Gross Calorific Value Q_s (MJ.kg^{-1})	Lower Calorific Value Q_i (MJ.kg^{-1})
Wood pellets	8.21	18.29	16.76
50:50	5,40	13.26	12.15
60:40	5.22	12.18	11.10
70:30	4.69	11.12	10.10
Sludge pellets	12.04	6.72	5.87

The results of produced pellets measured by TGA are presented in Table 2. Moisture content depends mainly on initial moisture of input material before the process in pellet mill. The moisture of input material was between 18 and 25%, depending on the pellet process. The highest moisture content was measured in paper sludge pellets and the lowest in the 70:30 pellets sample. During pellets production it was observed that paper sludge increase the quality of pellets and it is not necessary use so much water in comparison with wood pellets.

The sludge pellets sample contained almost no fixed carbon but they had noticeable contents of volatiles in the combustibles.

The high concentration of ash was caused by the higher content of non-combustible particles in the sludge. This could cause clogging of the burner during combustion and flame suffocation due to deposition of ash in the vicinity of the burner. The high ash content in paper sludge is the highest disadvantage from the point of view of its energy using.

Table 2. Results for the Produced Pellets Measured by TGA

Tested sample	Moisture (%)	Volatiles (%)	Ash (%)	Fixed Carbon (%)
Wood pellets	8.21	74.99	0.49	16.31
50:50	5.40	67.20	22.23	5.17
60:40	5.22	65.13	26.83	2.82
70:30	4.69	63.69	30.89	0.73
Sludge pellets	12.04	43.42	44.33	0.21

Table 3 shows the levels of sulphur, nitrogen, carbon, and hydrogen. As shown, the highest concentrations of carbon and hydrogen were in the wood pellets. It can be seen that all tested samples had very low nitrogen content. All samples also had very low content of sulphur. Biomass itself contains only trace amounts of sulphur in comparison with fossil fuels and paper sludge contains only sulphur from cellulose and not from additives during paper production.

Table 3. Contents of Carbon (C), Hydrogen (H), Nitrogen (N), and Sulphur (S) in the Samples (wet basis)

Tested sample	C (%)	H (%)	N (%)	S (%)
Wood pellets	48.78	6.310	0.017	0.066
50:50	36.021	4.702	0.044	0.046
60:40	34.996	4.533	0.016	0.047
70:30	32.899	4.188	0.034	0.040
Sludge pellets	24.752	2.587	0.189	0.045

The high concentration of ash was caused by the higher content of non-combustible particles in the sludge. The ash melting temperatures of the produced samples are given in Table 4. The measured results indicated that a higher content of sludge in the pellets increased the ash melting temperatures. These positive results can help to avoid the creation of sinter deposits and slags in the boilers. The working temperature of the device was limited up to 1,500 °C, which corresponded to the maximum measured temperatures in Table 4. Therefore, the paper sludge could be utilized as an additive in the combustion of biomass with a low ash melting temperature.

Table 4. Ash Melting Temperatures of Produced Pellets Samples

Sample	DT (°C)	ST (°C)	HT (°C)	FT (°C)
Wood Pellets	1115	1254	1313	1394
50:50	1196	1500	1500	1500
60:40	1235	1500	1500	1500
70:30	1254	1500	1500	1500
Sludge pellets	1270	1500	1500	1500

CONCLUSIONS

The paper sludge had a relatively low LCV after drying. This was attributable to a high proportion of ballast-ash content (51.8% to 41.9%). The differences between LCV of wood and paper sludge pellets were significant 16.76 MJ.kg^{-1} and 5.87 MJ.kg^{-1}, respectively.

Thermogravimetric results obtained in this work showed that co-processing of wood sawdust with paper sludge may be a management route for this waste. Large differences between wood and sludge pellets were plain by their respective TG analysis. These differences are mainly related to the higher fixed carbon and volatile content of wood pellets, as compared with produced mixed samples of pellets and, especially sludge pellets.

Analysis of the results showed that the mixed samples had noticeably higher content of ash in comparison to wood pellets. The samples of pellets with ratios of 50:50 and 40:60 had more than 20 times higher concentration of ash in comparison to wood pellets. In the case of the sample with a ratio of 30:70, the ash content was 30 times higher. This can lead to more frequent maintenance and disposal of ash.

However, results obtained in this work indicate the potential of thermal valorisation of paper sludge by co-processing with sawdust. From a practical point of view, for co-combustion of biomass (with a low ash melting temperature) in existing plants, it must be taken into account the high melting temperature of paper sludge. This can have positive effect on reducing landfill amounts.

The mixture with a low weight percentage of paper sludge, such as 10 wt.%, is planned in future research with the assumption of similar combustion profiles to that of wood pellets.

ACKNOWLEDGMENTS

This work has been supported by the projects APVV-15-0790 "Optimization of biomass combustion with low ash melting temperature" and KEGA No. 042ŽU-4/2016 "Cooling by physical and chemical processes."

REFERENCES CITED

Bajpai, P. (2015). *Management of Pulp and Paper Mill Waste*, Springer, DOI 10.1007/978-3-319-11788-1__2

Balwaik, S. A., and Raut, S. P. (2011). “Utilization of waste paper pulp by partial replacement of cement in concrete,” *Int. J. Eng. Res. Appl*. 1(2), 300-309. Available at: http://ijera.com/pages/ v1no2.html

Coimbra, R. N., Paniagua, S., Escapa, C., Calvo, L. F., Otero, M., (2016). “Thermal valorisation of pulp mill sludge by co-processing with coal,” *Waste and Biomass Valorization* 7(4), 995-1006.

Coimbra, R. N., Paniagua, S., Escapa, C., Calvo, L. F., and Otero, M. (2015). “Combustion of primary and secondary pulp mill sludge and their respective blends with coal: A thermogravimetric assessment,” *Renewable Energy* 83, ISSN 0960-148, 11050-1058.

Elliott, A., and Mahmood, T. (2005). “Survey benchmarks generation, management of solid residues,” *Pulp Pap.* 79, 49-55.

Fauber, P., Barnabé, S., Bouchard, S., Côté, R., and Villeneuve, C. (2016). “Pulp and paper mill sludge management practices: What are the challenges to assess the impacts on greenhouse gas emissions?” *Resources, Conservation and Recycling* 108, ISSN 0921-3449, 107-133.

Holubcik, M. (2013). *Possibilities of Increasing Ash Melting Temperature of Biomass*, Ph.D. Dissertation, University of Zilina, Zilina, Slovakia.

Jandacka, J., Jurasekova, L., Nosek, R., and Holubcik, M. (2016). “Using paper sludge in the manufacture of wood pellets,” *Chip and Chipless Woodworking Processes* 10(1), 327-332.

Lazar, M., Brestovic, T., and Schvarzbacherova, E. (2011). “Designing low gas flow meters based on the calorimetric principle of flow rate measuring,” *The Holistic Approach to Environment* 1(4), ISSN 1848-0071, 153-162.

Liao, Y., and Xiaoqian, M. (2010). “Thermogravimetric analysis of the co-combustion of coal and paper mill sludge,” *Applied Energy* 87(11), 3526-3532. DOI: 10.1016/j.apenergy.2010.05.008

Mansaray, K., and Ghaly, A. (1998). "Thermal degradation of rice husks in nitrogen atmosphere," *Bioresource Technology* 65(1-2), 13-20. DOI: 10.1016/S0960-8524(98)00031-5

Monte, M. C., Fuente, E., Blanco, A., and Negro, C. (2009). “Waste management from pulp and paper production in the European Union,” (http://eprints.ucm.es/11900/1/Waste_management_M_C_Monte_2009.pdf), 1 April 2016.

Ramalho, R. S. (1983). “Introduction to wastewater treatment processes,” 2nd Ed., Academic, New York. ISBN 0-12-576560-6

STN ISO 540 (2008), “Hard coal and coke: Determination of ash fusibility,” International Organization for Standardization, Geneva, Switzerland.

Vamvuka, D., Salpigidou, N., Kastanaki, E., and Sfakiotakis, S. (2009). “Possibility of using paper sludge in co-firing applications,” *Fuel* 88, 637-643 (2009).

Zeqiong, X., and Xiaoqian, M. (2013). “The thermal behaviour of the co-combustion between paper sludge and rice straw,” *Bioresource Technology* 146, 611-618, DOI: 10.1016/j.biortech.2013.07.127.

Article submitted: February 3, 2017; Peer review completed: May 15, 2017; Revisions accepted: August 1, 2017; Published: August 7, 2017.
DOI: 10.15376/biores.12.4.7032-7040