# Pretreatment of biomass pellets by acid washing in order to reduce alkaline components

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Keywords: biomass, pellet, washing techniques, alkali, leaching. Due to the limited availability of wood, as the highest quality raw material for the production of biomass pellets, increasing attention is being paid to the production and use of pellets from low-quality materials such as different types of agricultural waste. However, the complex chemical composition of these types of biomass often leads to various problems during their combustion. One of the biggest problems when it comes to burning biomass pellets is related to the low melting temperature of the resulting ash and its tendency to sintering. By modifying the chemical composition of biomass, it is possible to influence the method of combustion and the characteristics of residual ash. Modification of biomass composition can be carried out by chemical pretreatment with acids, which reduces the concentration of alkali metals and alleviates ash adhesion and the tendency to form slag.

Pellets made from wood biomass, soy straw and chamomile waste from the process of processing medicinal plants were used for the tests in this work. Chemical pretreatment, which consisted in washing the pellet samples with a diluted solution of hydrochloric acid, resulted in mass loss in all cases. The amount of ash, after treatment in hydrochloric acid solution, was reduced by 72.15% -93.27%, depending on the concentration of acid and the type of biomass.

#### INTRODUCTION

Pellets made from the remains of primary or secondary wood processing have become an important renewable energy source used in low-power boilers for household heating, but also in industrial boilers and power plants for the production of electricity and heat. However, due to the numerous technical advantages of wood as a material, as well as the development of consumer awareness of a healthy lifestyle, there has been a disproportionately large demand for this natural resource compared to the quantities available in forests and plantations. It was estimated that in the period 1990-2020 the total area covered by forests decreased by 31% (Wong, 2020). In order to meet the increased needs for pellets, as an energy source based on renewable raw materials, the level of utilization of other non-wood forms of lignocellulosic biomass for its preparation has increased. All over the world, extensive research has been carried out on the burning of pellets prepared from different types of herbaceous and agricultural

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Tatjana Botić, University of Banja Luka, Faculty of Technology, Stepe Stepanovića 73, Banja Luka, RS, B&H; email: tatjana.botic@tf.unibl.org wastes, aquatic biomass and animal biomass wastes, such as different grasses, straws, stalks, leaves, shells, peels, grains and their mixtures (Vassilev et al., 2017).

By using biomass as a raw material for energy production, ash is mostly left behind as a residue. Due to the diverse composition of available biomass, the composition and amount of ash remaining after burning is very different. After wood burning, a minimal amount of ash remains, which can be only 0.1%, depending on the type of wood and the amount of bark. After burning different types of non-woody biomass, a larger amount of ash remains, which is very different and mainly depends on the type and origin of the biomass. For example, only 1.1% of ash remains from walnut shells, while 16–23% of ash can be produced from rice husks (Munawar et al., 2021).

The main problems and challenges in the use of nonwoody biomass as fuel are related to the amount and chemical composition of the ash produced in the combustion process. Due to presence of diverse metal oxides and less base to acid ratio in biomass feedstock, biomass ash often has a low melting temperature leading to slagging and fouling. Slagging is associated with the fusion and sintering of ash particles in the high temperature sections of the boiler.

It is known in general that elements that form the biomass ash are Al, Ca, Cl, Fe, K, Mg, P, Na, S, Mn, Si and Ti, and they contribute to various technological and environmental aspects of biomass combustion (Bostroom et al., 2012; Vassilev, 2017). Some types of biomass, such as agricultural and herbaceous residues, as well as some parts of wood such as bark, have a high content of alkaline oxides and salts. Alkali metals form less stable oxides than Ca, Mg, Si and P, so it can be said that these elements are mainly responsible for the formation of ash (Davidsson et al., 2002). Their presence in the ash affects unwanted processes, such as lowering the melting temperature, agglomeration, and sintering, which can lead to various problems during combustion (Mlonka-Mędrala et al., 2020; Werther et al., 2000). Modification of the biomass composition can be performed by chemical pretreatment with acids, which reduces the concentration of alkali metals and alleviates the adhesion of ash and the tendency to form slag (Namkung et al., 2019; Yu et al., 2014). The second method is based on the idea of using cheap, safe and available additives, such as different types of clay, which can affect alkali metals in biomass ash during combustion (Mack et al., 2019; Wang et al., 2012).

Methods of pretreatment of bimass with acids are often disputed due to the generation of wastewater loaded with organic and inorganic substances and an increase in the moisture content of the raw material, which requires additional costs of wastewater treatment and drying of the raw material. Pretreatment costs are not negligible also. However, the advantages resulting from the improvement of raw material properties justify further development of existing and research into new pretreatment methods. Studies that have been done on rice straw, wheat straw and corn straw as well as on grasses like switchgrass and Miscanthus showed that after leaching the calorific value remained largely unchanged although ash concentrations were reduced by 15%-39% (Yu et al., 2014). Gudka et al. (2016) investigated the effects of pretreatment of wood biomass too on problems related to fusion and sintering of ash, although it is known that a minimal amount of ash remains after burning wood. Their research showed that the impact of washing is minimal

on High Heating Value (HHV). However, ash content tends to reduce significantly, hence reducing the tendency of fouling and slagging to occur in boilers.

The actual level of influence of acid pretreatment is specific for each type of biomass. In this paper, the possibility of improving the melting characteristics of the ash resulting from the combustion of biomass pellets in laboratory conditions was investigated. Pellets made from wood biomass, soy straw and chamomile waste from the process of processing medicinal plants were used for the investigation in this work.

### MATERIALS AND METHODS

Three types of pellets prepared from different types of biomass, without the addition of additives, were used in pellet combustion experiments:

- Pellet made of wood, with ENplus certificate. The producer is the company ENSA BH Srbac, and this pellet is available on the market of Bosnia and Herzegovina, as well as the EU market;
- Pellet made of soybean straw (CRO Pellet);
- Pellet made of chamomile waste from medical herbs processing plant Prirodno bilje – Banja Luka.
  Pellet was produced in the company ENSA BH – Srbac for the purposes of these experiments, and it is not available on the market.

Table 1 gives basic data on the types of biomass from which the tested pellets were made and fundamental pellet quality parameters.

## Assessment of the ash affinity to ash slagging

For the assessment of the ash affinity to ash slagging and its behaviour at high temperatures, some empirical indexes were used calculated by using the following equations (Guo et al., 2020; Liu et al., 2018; Vamvuka & Zagrofos, 2004):

Alkali index

$$AI = Ash \cdot (K_2O + Na_2O) / HHV$$
(1)

Table 1. Biomass composition and fundamental quality parameters of selected pellet types

| Type of pellet  | Producer   | Biomass specific                               | Moisture<br>(%) | Ash<br>(%) | HHV<br>(MJ/kg) |
|---|------------|--|-----------------|------------|----------------|
| Pellets made from wood<br>biomass (industrial pellet) | ENSA B&H   | Spruce 80% (wood pieces with<br>bark), 20% oak | 5.82            | 1.37       | 19.19          |
| Pellet made of soya straw                             | CRO Pellet | Soya straw, dust < 2%,                         | 7.71            | 6.69       | 19.50          |
| Pellets made of the chamomile waste                   | ENSA B&H   | Chamomile waste                                | 10.22           | 6.50       | 14.75          |

Fouling index

$$F_u = R_{b/a} \left( K_2 O + N a_2 O \right) \tag{2}$$

Base/acid ratio

$$R_{b/a} = \frac{\% \left(Fe_2 O_3 + CaO + MgO + K_2 O + Na_2 O\right)}{\% \left(K_2 O + Na_2 O\right)} \quad (3)$$

Total alkali content

$$TA = K_2 O + Na_2 O \tag{4}$$

Bed agglomeration index

$$BAI = \frac{\% F e_2 O_3}{\% (K_2 O + N a_2 O)}$$
(5)

Ca, Mg, Fe and Al oxide content were determined by using of methods induced coupled plasma (ICP). Potassium oxide was determined by using of methods of atomic absorption spectroscopy (AAS). Titanium oxide was determined spectrophotometry and silicon oxide by gravimetric analysis.

The calorific value was determined using a calorimeter type Parr 6400 Automatic Isoperibol Calorimeter.

#### **Pre-treatment of biomass**

Approach of modification of the biomass chemical composition by using chemical treatments offers the possibility to influence on combustion process and ash melting characteristics. There are different methodologies of the biomass chemical treatment, which could be used according to the quantity and type of agent used, number of treatment repetitions, temperature, duration, way of leaching and way of mixing (Mlonka-Mędrala et al., 2020; Namkung et al., 2019).

In these experiments, chemical treatment of biomass was performed once, without repetitions, by using 3% and 5% hydrochloric acid (HCl) solution in duration of 2 hours, at room temperature ( $22\pm1$  °C), with mixing with a propeller mixer (150 min<sup>-1</sup>). Treatment was performed in 10 mL of HCl solution on 1 g of biomass. After the treatment, the solid sample has been washed by using deionized water to a neutral pH value. After that samples have been dried 24 hours in drier at 105±2 °C.

In order to examine the influence of biomass fineness on the amount of extracted material during treatment with hydrochloric acid, the following treatment was performed in parallel:

- pellet, diameter ~ 6 mm and length 10 mm,
- crushed pellet, after which the crushed biomass was sieved through a 0.25 mm diameter sieve, and

for further processing with hydrochloric acid the fraction <0.25 mm was used.

Combustion of the untreated and treated biomass samples, for estimation of mass losses and ash quantities, have been performed in a laboratory muffle oven at 550 °C. Wight losses were calculated by using the following equations:

% Weight loss = 
$$\frac{m_1 - m_2}{m_1} \cdot 100$$
 (6)

 $m_1$  – mass of biomass sample before chemical treatment (g),

 $m_2$  – mass of biomass sample after chemical treatment (g).

% Ash reduction = 
$$\frac{A_1 - A_2}{A_1} \cdot 100$$
 (7)

 $\rm A_1$  – percentage of the ash before chemical treatment biomass (% m/m),

 $A_2$  – percentage of the ash after chemical treatment biomass (% m/m).

#### Determination of metal concentrations in ash

The concentration of metals in the ash remaining after the combustion of the untreated pellet, as well as the pellet treated with HCl, was determined by using atomic absorption spectroscopy (AAS).

#### **RESULTS AND DISCUSSION**

It is proven that deposition melting characteristics are in correlation with the content of produced metal oxides in the ash. For the assessment of the ash affinity to ash slagging and predict its behaviour at high temperatures, some empirical indexes were calculated and presented in Table 2. The results of determining the content of metal oxides in the ash remaining after the combustion of untreated pellets, which are shown in Table 3, were used to calculate the prediction indexes.

According to all deposition criteria, that is, based on obtained values of prediction indexes, ash from soya pellet has a higher affinity to agglomeration, fouling and slagging. Prediction indexes for the ash from chamomile pellet are a bit lower, but with high probability for fouling and sintering. Ash from wooden pellet has increased  $R_{b/a}$  index, which indicates to high risk of forming deposits but low risk from agglomeration and sintering (Guo et al., 2020).

The alkali index is a measure commonly used for biomass to predict the fouling propensity of a fuel originating from alkali salt deposition. Adelha et al.

|                                      | Type of pellet                                     |                                 |                                   |  |
|--------------------------------------|--|---------------------------------|-----------------------------------|--|
| Deposition-predictive indexes        | Pellets made from wood biomass (industrial pellet) | Pellets made from soya<br>straw | Pellets made from chamomile waste |  |
| Alkali index (Al), kg alkali/GJ      | 0.049  | 0.364                           | 0.384                             |  |
| Fouling index (F <sub>u</sub> )      | 8.253  | 92.514                          | 30.469                            |  |
| Base/acid ratio (R <sub>b/a</sub> )* | 1.421  | 8.63                            | 3.002                             |  |
| Total alkali content (TA)            | 0.058  | 0.107                           | 0.102                             |  |
| Bed agglomeration index (BAI)        | 0.270  | 0.059                           | 0.013                             |  |

Table 2. Indexes for prediction of ash behavior at high temperatures

\*b-indicates the sum of the basic oxides in the ash; a-indicates the sum of the acidic oxides in the ash

Table 3. Ash analysis after combustion experiments in muffle oven

|                                | Type of pellet  |                                 |                                   |  |
|--------------------------------|---|---------------------------------|-----------------------------------|--|
| Ash components (% m/m)         | Pellets made from wood<br>biomass (industrial pellet) | Pellets made from soya<br>straw | Pellets made from chamomile waste |  |
| SiO₂                           | 17.72   | 5.46                            | 7.74                              |  |
| Fe <sub>2</sub> O <sub>3</sub> | 1.57  | 0.64                            | 0.13                              |  |
| Al <sub>2</sub> O <sub>3</sub> | 3.34  | 1.07                            | 2.37                              |  |
| TiO <sub>2</sub>               | 1.08  | 0.74                            | 0.68                              |  |
| K <sub>2</sub> O               | 5.81  | 10.72                           | 10.15                             |  |
| Na₂O                           | 0.00  | 0.00                            | 0.00                              |  |
| CaO                            | 21.45   | 45.92                           | 19.02                             |  |
| MgO                            | 2.62  | 10.79                           | 3.09                              |  |

(2019) in their work present that fouling is probable for an Alkali Index above 0.17 kg/GJ and that fouling virtually certain to occur for an Alkali Index above 0.34 kg/GJ. The Alkali Index is incomplete as a descriptor of fouling behavior, however, it is useful principally as a general guide. The Alkali Index for pellets made from soya straw and chamomile waste are above the value of 0.34 kg/GJ.

From the results of the determination oxide content in the ash of untreated biomass, it is evident that the fast-growing biomass has almost twice bigger potassium content. Biomass with high annual growth is mainly rich in potassium oxides because it takes it from the soil (Werther et al., 2000). High contents of potassium (K), particularly in combination with silicon (Si) increases tendency of the ash sintering (Gollmer et al., 2019). The results of the experiment of chemical pre-treatment of biomass pellet samples with 3% and 5% HCl solution were presented in Figure 1.

In the case of pellet produced from herbaceous rests greater mass loss was achieved, during treatment with 3%- HCl solution than with treatment with 5% HCl solution. In the case of soya straw and wooden pellets, situation is opposite, greater mass loss was achieved



Figure 1. Mass loss of the pellets in function od the HCl concentration in the solution



Figure 2. Mass loss of pellets in function of biomass granulation

|  | Type of pellet                                     |                                 |                                   |
|--|--|---------------------------------|-----------------------------------|
|  | Pellets made from wood biomass (industrial pellet) | Pellets made from soya<br>straw | Pellets made from chamomile waste |
| Ash (% m/m)  | 1.37   | 6.69                            | 6.50                              |
| Ash after the treatment with 3% HCl solutions (% m/m)    | 0.34   | 0.62                            | 1.25                              |
| Ash after the treatment with 5% HCl<br>solutions (% m/m) | 0.31   | 0.45                            | 1.81                              |

Table 4. The proportion of inorganic residues in the pellet before and after treatment with acid

by using 5%- HCl solution. However, all differences are less than 1%, and they are in the range of normal errata. According to that, it can be concluded that the increase of the percentage of HCl from 3% to 5%, had no significant effect on the amount of matter excreted.

Crushing the pellets increases the percentage of weight loss for 1.74%-4.8% m/m compared to uncrushed pellets, dependence of type of biomass and concentration of the acid solution (Figure 2). The assumption is that chopped biomass swells more easily during treatment in a hydrochloric acid solution, which facilitates the extraction of mineral substances. Based on this, it can be assumed that the effect of biomass pretreatment would be greater if it was performed before biomass pelleting, when it is chopped and loose.

Calcium (Ca), magnesium (Mg), potassium (K) and natrium (Na) compounds, as CaO, MgO, KOH and NaOH, represent basic carriers of the alkali components in the ash. By pretreating the pellets with 5% hydrochloric acid, a high percentage of calcium, magnesium and potassium concentration reduction was achieved in all three types of pellets. The biggest reduction was achieved in the case of pellets made from waste of medicinal plants processing, namely: Ca-99,9%, Mg-96,0% i K-96,9%. In soy straw pellets, a decrease in concentration was measured for: Ca-96.0%, Mg-96.7% and K-95.5%. In the case of wood pellets, a decrease in concentration was measured for: Ca-98.8%, Mg-56.4% and K-81.5%.

However, by pretreating the pellets with 3% hydrochloric acid, a slightly smaller reduction in the concentration of the mentioned elements was achieved than with 5% acid, so treatment with a higher acid concentration is not justified. In the case of treatment with 3% acid, the greatest reduction was also achieved in pellets from the waste of medicinal plants processing, namely: Ca – 99.7%, Mg – 94.9% and K – 94.1%. In the case of soy straw pellets, a decrease in concentration was measured: Ca – 79.2%, Mg – 92.3% and K – 89.2%. In the case of wood



Figure 3. Changes in metal concentrations in the ash after the treatment with HCI

pellets, a decrease in concentration was measured: Ca – 94.0%, Mg – 43.4% and K – 76.8%.

Changes in concentrations of this compounds in the ash after treatment of biomass samples with 3% and 5% HCl is presented on Figure 3a-3c.

Quantity of ash after treatment in hydrochloric acid solution is reduced for 72.15 - 93.27%, depending on acid concentration and type of biomass. Taking into consideration what is ash by definition, the conclusion is that treatment using hydrochloric acid solution, eliminated significant percentage of non-combustible components from biomass samples. High percentage of leaching of non-combustible components indicates confirms the weak connection of oxides, silicates and carbonates of alkali and alkaline earth metals with the raw material. Similar investigation was performed by Davidsson et al. on the wood waste and wheat straw samples (Davidsson et al., 2002). They have concluded that by pre-treatment of biomass with high ash content it is possible to reduce alkaline compounds up to 90%, while in the case of biomass with smaller ash content, like wood, this technique has a limited effect.

Problems that occur in the furnace during the combustion of pellets, especially pellets of poorer quality, do not necessarily occur due to the large amount of ash, but when the melting temperature of the ash is too low. However, the large amount of ash still complicates the problem, in terms of the difficult removal of ash from the furnace, which creates the preconditions for the formation of slag (Botić et al., 2022).

## CONCLUSION

The results of this research showed that the pretreatment of pellets with hydrochloric acid reduces the ash content in the pellets by 72.15%–93.27%, depending on the type of biomass, which reduces the tendency of slag formation in boilers and furnaces.

The leaching effect would be slightly greater if pretreatment of the biomass was carried out before pelleting.

Use of hydrochloric acid solutions in combination with washing deionized water in removal of alkali from raw biomass has shown significant effects, but these effects were not the same for different types of biomass and the process must be investigated in order to determine optimal solutions and parameters. It is noticeable domination of calcium and reduction of its content, already after treatment with 3% HCl for 79% in a case of soya straw samples and over 99% in a case of chamomile samples. **Acknowledgement:** The authors of this work express their gratitude to ENSA d.o.o. Srbac, the company that made pellet samples from the biomass delivered to them.

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