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Corrosive components of nutshells and their chars

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Abstract. Biomass combustion stands among various technologies pointed at fossil fuels consumption decrease. Biomass can be found in very diversified sources spread more evenly across the globe, can be burned with use of traditional combustion solutions and is more CO_2 neutral in combustion than their fossil fuel counterparts. On the other hand biomass has several problems with composition that despite its potential diversity. Problem of excess moisture can be already solved by material selection or by preliminary pyrolysis. The main problem concerns however biomass ash composition. Biomass ashes are more prone to have higher quantities of potentially corrosive components than their coal counterparts. The example of such constituents are alkali metals, sulphur and chlorine. Ash basic composition is also important due to various ash properties like its melting temperature and slagging or fouling tendencies. To address the problem, several indices for fast properties prediction and earlier problem identification can be appointed. This work concentrates on ash quality evaluation for potentially attractive biomass fuel from nutshell materials and their corresponding char obtained by pyrolysis in 300, 450 and 550 °C. Pistachio and hazelnut shells with their chars will be analysed for corrosive compounds and their potential influence on combustion process.

1 Introduction

Biomass solid fuels became increasingly popular source of renewable energy in recent years. The relative low investment cost for implementation and possibility to use seemingly unwanted side products of different processes related to agricultural, industrial or municipal activity were one of the main drives for such trend. There are also significant advantages over conventional coal fuels like lower sulphur and nitrogen content, similar qualitative composition for coal and reduction in waste storage scale [1-5].

On the other hand, there are many drawbacks connected with its use. Most of potential biomass fuels possess large quantities of water in its content, an unfavorable constituent that lowers calorific potential of given fuel and increases its volume needed to substitute conventional solid fuels, effectively increasing the transportation cost [6]. One of possible solution is selection of low-moist biomass materials like nutshells [7]. Among other possible operations, pyrolysis as pretreatment method seems to be most promising. Treating fuel with high temperature in lack of oxidant leads to water evaporation and to release of volatiles due to temperature induced breaks in fuel structure. Removal of both constituents results in noticeable increase in carbon content and fuel quality.

Although pyrolysis allows for better fitting of biomass fuels for existing coal combustion technologies, the biomass inorganic constituents are largely unaffected by its influence. Various studies on the topic of biomass utilization agree that biomass ash pose much bigger of a challenge in process handling. Due to very diversified ash composition between various biomass types and often different quantities than that found in coal ashes. [8,9].

Chlorine is one of the examples of unfavorable ash constituent. In biomass that is generally scarce in sulphur many alkali metals are present in a form of alkali chlorides. Alkali chlorides can act as a catalysts in a process of iron oxidation in the structure of pipes [8]. If there is also sulphur present in ratio at least twice as low as chlorine concentration the corrosion of equipment might even worsen due to complex hydrochloric acid-based corrosion reactions [10,11]. Abundance of alkali metals is also important in this process, as they are needed for creation of salts with sulphur and chlorine, thus increasing their deposits in the system and form various eutectic with corroded steel e.g. KCl-NaCl-$FeCl_2$, further developing the damage of its structure [12] and is also suspected for catalysts deactivation [13]. Apart from corrosion caused by certain ash constituents, the combustion can be influenced by general ash properties. Biomass ash is susceptible for slagging, agglomeration and fouling[14,15] as a result of its lowered ash-fusion temperatures due to presence of elements like Ca, Cl, K, Mg, Na, P, Al, Fe, Ti, Si and S in certain ranges [16]. Several indices were proposed to predict biomass ash properties among which

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Nomenclature

A	ash yield	SP	slagging possibility
a	analytical basis	ST	ash softening temperature
AI	alkali index	ppm	parts per million
BSEI	biomass slagging evaluation index	PS	pistachio shells
daf	dry, ash free basis	PSC	pistachio shell chars
db	dry basis	$R_{b/a}$	base-to-acid ratio
HS	hazelnut shell	UHS	untreated pistachio shells
HSC	hazelnut shell char	UPS	untreated hazelnut shells
Y	Yield	V	volatile matter
M	moisture	%	percent by weight

Cl and S ratios [8,17] e.g. Cl/S ratio [18,19], Biomass slagging evaluation index [20] and Alkali index [16].

More on index calculations can be read elsewhere [21,22]. Given the importance of biomass ash composition, a complex analysis needs to ensure biomass fuel quality. In this work the ash composition of raw hazelnut and pistachio nutshells and their chars were evaluated in order to ensure their potential as a biomass material for combustion and co-combustion processes. The materials were analyzed for corrosion-related constituents and various indices will be used to state the potential behavior of their ashes during the process.

2 Experimental

2.1 Material preparation

Base material was obtained from food industry residue waste materials from pistachio and hazelnut distribution. The shells were air dried for up to 48h and ground in ring roller mill (EKOLAB LAB-09-200). The resulting powders were the sifted for fractions between 0.5 and 2.0 mm in diameter. In order to obtain chars of respective nutshell, the materials were placed in ceramic containers with lids and put into a muffle furnace (CZYLOK FCF 7 SM/pl) where they were heated to 300, 450 or 550 °C for 30 minutes. Raw nutshell or their respective chars were then characterized.

2.2 Proximate and ultimate Analysis

Nutshells and their chars elemental composition was conducted with Eltra CHS-580 analyser according to polish standard PN-G-04571:1998 and PN-G-04584. The measurement provided information on carbon, hydrogen and sulphur content.

Proximate analysis comprised of moisture, volatile matter ash content and lower heating value was also performed in order to obtain data for indices calculations. Moisture, volatile matter and ash analysis was performed with thermogravimetric analyzer (Eltra Thermostep). The lower calorific value measurement was performed with KL-11 Mikado calorimeter according to polish standard PN-EN 14918:2010.

2.3 Ash constituents determination

For determination of main ash components content Atomic Absorption Spectrometry (Hitachi High Technologies Z-2000) was used. Measurement required conversion of the material into liquid medium.

Table 1 Summarisation of most important fuel constituents and parameters for pistachio and hazelnut shells and their chars obtained from technical analysis, elemental analysis and chlorine spectrophotometric. Some measurement errors was not added due to their neglibility

Sample	C^a [%]	H^a [%]	M^a [%]	A^a [%]	V^a [%]	Cl^{db} [%]	S^a [ppm]	Cl/S [-]	Y^a [%]	LHV^{daf} [MJ/kg]
PS (Raw)	47.4±0.30	6.9±0.30	6.1±0.05	1.1±0.02	76.9±0.01	0.5±0.03	61±5	86.8	-	16.8
PSC (300°C)	59.3±0.30	5.6±0.30	0.5±0.05	1.1±0.02	62.8±0.02	0.8±0.03	73±5	109.1	63.8	21.9
PSC (450°C)	82.5±0.30	3.4±0.30	0.2±0.05	1.6±0.02	18.2±0.02	0.8±0.03	63±5	121.1	26.1	31.0
PSC (550°C)	88.8±0.30	2.6±0.30	0.1±0.05	3.0±0.02	8.2±0.02	0.8±0.03	44±5	179.3	22.4	34.4
HS(Raw)	50.1±0.30	6.9±0.30	8.0±0.05	0.3±0.02	75.8±0.02	0.1±0.03	92±5	3.7	-	16.1
HSC (300°C)	61.2±0.30	5.6±0.30	1.3±0.05	2.3±0.02	61.2±0.02	0.1±0.03	112±5	9.0	63.6	16.9
HSC (450°C)	81.8±0.30	3.4±0.30	0.8±0.05	3.3±0.02	25.7±0.02	0.1±0.03	114±5	8.7	31.7	31.1
HSC (550°C)	88.6±0.30	2.8±0.30	0.2±0.05	3.0±0.02	8.1±0.02	0.1±0.03	39±5	23.7	23.2	34.3

To achieve this, 0.2 g of every sample was moved into separate Teflon tube and treated with mixture of 6 ml HNO_3 (69%, POCH, for spectral analysis) and 2 ml of HF (J.T. Baker, analytical solution up to 60%), closed and placed into microwave digestor (Speedwave Four Berghof) for 2.5 h, in order to react all solid mineral matter. Sample vessels were then cooled, opened and treated with 20ml of saturated boric acid solution and placed in digester for another 40 minutes. Volume of resulting samples was then adjusted to 50ml with deionized water with 50μl addition of cesium solution (100mg/l). Concentrations of Na, Ca, Mg, P, Ti, Si, Fe, Al, K, were then measured on AAS flame atomizer. Phosphorus content was determined by X-ray fluorescence
using EDXRF spectrometer (Panalytical Epsilon 3^{XLE}).

Chlorine content have been evaluated as chlorine anions in water solution with use of direct reading spectrophotometer (DR/2000 HACH). Chlorine present in sample was transferred into liquid solution by burning 0.5 g under 0.5 g layer of chlorine-absorbing Eschka mixture (60÷72% MgO and 30÷36 % Na_2CO_3, POCH) and boiling remaining residue in deionized water with addition of mercuric thiocyanate (99.99%, POCH) and ferric ion solution (POCH), according PN-ISO 587:2000 standard.

3 Results

3.1 The influence of pyrolysis temperature on material properties and content of sulphur and chlorine

General outlook on nutshells properties after thermal treatment shows increase of carbon content followed by decrease of other constituents like moisture and volatile matter, typically for pyrolytic processes. Beside major enhancement of lower heating values with increase of pyrolysis temperature, such loss of carbonaceous compounds is followed by visible loss of sample mass, from around 33-36% on lowest treatment temperature up to around 77% in highest, as pictured by data on char yield (Table 1).

Although the overall quality of fuels is improved that way, some more temperature resistant biomass compounds also increase their mass contribution. One of most important of them is chlorine, which increases its content from 0.52% to around 0.8% in case of pistachio shells and from 0.03% up to 0.1% in case of hazelnut shells, as seen in Table 1 The rapid gain in chlorine content between samples treated in 300 °C and raw sample followed by stable Cl concentration in rest of chars for both materials might suggest some process of weaker bonded chlorine loss, balanced with mass decrease as it declined during higher pyrolysis temperatures. It is important to note that literature data

Table 2 Chemical composition of ash in pistachio and hazelnut shells and their corresponding chars after recalculation for oxides, shown as weight content in percents [%], parts per million [ppm] or mixed in specified order [ppm/%]. The result assumes that detected elements are present in ash in their most stable oxide, presented by weight percent. Literature comparison is marked with asteriks [26,27].

Sample	MgO [%]	Na_2O [%]	K_2O [%]	Fe_2O_3 [%]	SiO_2 [%]	Al_2O_3 [%]	CaO [%]	P_2O_5 [%]	TiO_2 [ppm/%]
UPS (Raw)*	3.3	4.6	18.7	36.3	8.4	2.2	10.3	12.1	0.2
PS (Raw)	3.8±0.20	14.8±0.08	21.7±0.90	28.3±0.42	8.7±0.08	2.1±0.06	12.7±0.28	12.79±0.02	647±1.50
PSC (300°C)	3.9±0.21	12.8±0.08	22.9±0.80	28.5±0.36	8.7±0.06	2.3±0.14	12.8±0.34	10.45±0.01	645±1.50
PSC (450°C)	3.8±0.30	11.0±0.08	20.8±1.25	28.8±0.55	9.0±0.42	2.1±0.09	12.7±0.25	8.47±0.02	645±1.50
PSC (550°C)	3.5±0.30	8.3±0.04	22.0±0.50	28.9±0.73	8.9±0.4	2.1±0.09	12.8±0.19	6.82±0.01	646±1.50
UHS (Raw)*	7.9	1.3	30.4	3.8	33.7	3.1	15.4	3.2	0.1
HSC (Raw)	3.3±0.40	1.6±0.03	34.6±0.32	1.4±0.28	37.9±0.08	3.0±0.1	13.7±0.19	5.98±0.02	0.2±0.02
HSC (300°C)	3.7±0.04	1.4±0.02	34.4±0.54	1.5±0.4	37.7±0.22	3.1±0.07	13.9±0.24	3.31±0.03	0.2±0.02
HSC (450°C)	3.5±0.10	0.9±0.02	34.7±0.25	1.4±0.13	36.9±0.35	2.9±0.31	13.7±0.27	2.05±0.03	0.2±0.02
HSC (550°C)	3.7±0.07	0.6±0.02	33.4±1.47	1.4±0.24	36.7±0.26	3.0±0.14	13.6±0.34	2.00±0.02	0.2±0.02

on pistachio shows lower concentrations of chlorine of up to 0.21%. The difference for hazelnut is much smaller as literature claims it to be around 0.2%, which in comparison with 0.03% might origin from measurement precision. Such differences might result from salt addition to nutshells during their processing. Sulphur content is one of many nutshell virtues as it is present in their structure in amounts as small as 61ppm for pistachio and 92 ppm in hazelnut. What is more, its content, although increasing with pyrolysis temperature up to 450°C treatment temperature, finally decrease with temperatures beyond that mark, up to 44ppm and 39ppm, respectively. Literature data gives much higher sulphur concentrations of around 1,6% and 0.44% for pistachio and nutshell respectively. The reason between such differences can only be explained by growth environment. In order to examine those subsequent processes in respect for their influence on corrosion potential, a ratio of chlorine to sulphur was Cl and S contents. The results shown that slagging intensity would be much lower if the nutshells used by literature data were used rather than pistachio shells post those that have been post-processed.

3.2 Influence of ash constituents on corrosive properties

Ashes are the most dangerous solid fuel counterpart due to potential presence of vast range of either metallic of non-metallic origin. The summary of their share in ash composition was presented in Table 2. Data in the table was prepared with assumption that most of ash compounds are present in their most stable oxide forms. Pistachio and hazelnut being in the same category of biomass products, have large similarities in their ash composition. Both nutshells are abundant in potassium and calcium, elements typical for biomass fuels. High concentration of phosphorous and iron with relatively low amounts of aluminium and magnesium are normal

Table 3 Summarisation of calculation results of ash quality indices for pistachio and hazelnut shells and their corresponding chars, with additional explanation of results. The indices present in the table are starting from the left : Cl and S Ratio, Biomass Slagging Evaluation Index, Alkali Index, Base-to-acid Ratio, Slagging intensity based on Cl and S ratio, Slagging possibility based on AI and BSEI and Softening Temperature based on Base-to-acid Ratio. Samples marked with asteriks were calculated basing on literature data [26,27].

Sample	Cl Ratio [-]	S Ratio [-]	BSEI [-]	AI [kg Na_2O + K_2O/ GJ]	$R_{b/a}$ [-]	Slagging	SP	ST [K]
UPS (Raw)*	0.14	1.40	1.87	0.14	6.72	Slight	Low	1000-1200
PS (Raw)	3.05	2.89	1.29	0.23	7.27	Serious	Possible	1000-1200
PSC (300°C)	3.33	3.19	1.43	0.43	7.47	Serious	Certain	1000-1200
PSC (450°C)	2.93	3.34	1.63	0.48	6.94	Serious	Certain	1000-1200
PSC (550°C)	2.83	3.21	1.67	0.49	6.96	Serious	Certain	1000-1200
UHS (Raw)*	0.09	0.45	0.8	0.19	1.59	Slight	Possible	1000-1200
HSC (Raw)	0.98	2.70	0.43	0.35	1.38	Serious/ Severe	Certain	<1000
HSC (300°C)	0.87	2.09	0.48	0.56	1.34	Serious/ Severe	Certain	<1000
HSC (450°C)	0.92	2.24	0.49	0.53	1.39	Serious/ Severe	Certain	<1000
HSC (550°C)	0.79	1.94	0.52	0.50	1.26	Severe/ Slight	Certain	<1000

defined. This parameter seems to be highly exceeded benchmark ratio of 2 for all pistachio materials, suggesting that their potential to dissociate steel is strong. On the other hand the amount of chlorine versus sulphur in hazelnuts is also high but the result is smaller by around tenfold with their pistachio counterparts, suggesting weaken chlorine/sulphur alkali corrosion [10,11] for hazelnuts than for pistachio shells. Cl/S ratio was also calculated for literature data, due to varying for pistachio nutshells, according to literature [26]. Its high sodium content of around 14% that is not confirmed in other works also hints along with high chlorine content to be an effect of salt addition during pistachio processing. Hazelnut has more biomass-proper composition with more corrosion safe compounds like potassium, aluminium and calcium oxides dominating with low presence of potentially corrosive sodium and iron. Its composition is also in agreement with literature data [27].

The important conclusion ash content data is general stability of compounds concentration is ashes for every obtained chars. The only decreases are shown by more stable compounds such as sodium, potassium and phosphorous oxides. Stability of their presence ensures stability of ash properties as they are dependent only on ash composition instead of presence in fuel.

In order to fully evaluate process several indicators were introduced in order to efficiently examine the quality of examined biomass fuel. One of important ash properties is its susceptibility to form alkali-based glass deposits (slag) on the surface of pipes and various combustion equipment. Such ability depends largely on presence of chlorine and sulphur based salts and can be characterized by Cl (1) and S-ratio indexes (2):

$$Cl\ ratio = \frac{\%(Cl + K_2O + Na_2O)}{\%(SiO_2 + Al_2O_3)} \quad (1)$$

$$S\ ratio = \frac{\%(S + K_2O + Na_2O\ )}{\%(SiO_2 + Al_2O_3)} \quad (2)$$

In addition, alkali index was also used as it addresses higher proximity of biomass chars to coal than their raw counterparts and also relates to fuel volume. Alkali index (AI) can be calculated with use of fuel lower heating value LHV:

$$AI = \frac{K_2O + Na_2O}{LHV} \quad (3)$$

Where LHV is a lower heating value of given material in GJ/kg. To evaluate temperature ranges in which ash softens, biomass slagging evaluation index (BSEI) was calculated:

$$BSEI = \frac{\%(MgO + Al_2O_3 + \ Fe_2O_3)}{\%(MgO + \ P_2O_5)} \quad (4)$$

Finally, changes in fouling tendency with pyrolysis temperature of nutshell chars was evaluated with base to acid ratio:

$$R_{b/a} = \frac{\%(MgO + Al_2O_3 + \ Fe_2O_3)}{\%(SiO_2 + Al_2O_3 + TiO_2)} \quad (5)$$

Results of calculations can be found in Table 3. According to Cl and S ratio, as every material received S ration above 1.9 and in most cases Cl ratio above 1.9, both pistachio and hazelnut shells combustion can lead to ash slagging despite the examined biomass pyrolysis pre-treatment. Although high slagging potential for both biomass, hazelnut shells have lower slagging risk. Alkali index confirms however that in both cases presence of slagging during the process is certain. On the other hand receiving BSEI value lower than 7 hazelnut seems to have ash softening temperature (AST) set below 1000 ^{o}C setting some combustion technologies for hazelnut on much more strict level, than in case of pistachio that according to BSEI have AST between 1000 and 1200 ^{o}C. Hazelnuts have base-to-acid ratio much lower that pistachio which suggest lower presence of fouling with use of this material. Additionally fouling seems to decrease with increase of pre-treatment pyrolysis temperature in both cases.

4 Conclusions

Hazelnut and pistachio shells were pyrolyzed in three different temperatures and resulting chars were evaluated in respect for their corrosion potential in combustion processes. Elemental and spectrophotometric analysis has shown very low sulphur concentrations of under 100 ppm and minimal chlorine concentrations.

Despite relatively low char yield for both nutshells, sulphur and chlorine concentration haven't increased dramatically due to their partial release during pyrolysis. Sulphur and chlorine ratio analysis shown that both pistachio and hazelnut shells have considerable potential for alkali chlorine/sulphite corrosion with pistachio shells possibly weaker intensity in case of hazelnut due to relatively lower Cl/S values.

Further analysis aimed at ash composition revealed typical potassium, calcium and aluminium rich ashes in case of hazelnut and additionally large presence of sodium and iron and phosphorous in case of pistachio shells. Estimation of ash properties with several ash quality evaluation indices like BSEI, Cl and S ratio, Alkali index and base-to-acid ratio pointed that both materials are highly susceptible to cause slagging during combustion with higher fouling potential for pistachio shells but lower ash softening temperature for hazelnut (<1000 in comparison with 1000-1200 for pistachio). As a result both processed pistachio and hazelnut shells chars and their raw counterparts nevertheless of pyrolysis temperature are unsuitable for a fuel because of potential equipment maintenance need. It is generally beneficial properties like high lower heating value and low moisture content suggest however that they could be suitable as additive to other solid fuels. In case of untreated nutshells reported by literature the corrosive influence would noticeable weaker and would possibly allow for its use as standalone fuel material.

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