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An experimental approach to the chemical properties and the ash melting behavior in agricultural biomass

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Abstract The present paper presents an experimental approach to the chemical and physical properties of the agricultural biomass from the point of view of the use of the biodegradable materials as fuel in incinerators at small and large scales. The wide variety of biomass sources implies a wide range of biomass fuel properties, both physically and chemically. Waste biomass could provide a significant part of the energy demand if appropriate conversion technologies are used. The types of agricultural biomass considered are corn, corn stalk, cereal mix, wheat, oatmeal, barley, corncob, rye, two-row barley, and corn and corncob mix. The study underlines the physical and chemical properties for analyzed materials. Using a statistical treatment to compare our set of data for different types of materials with the existing data from the literature, it can be noted that the net calorific values presented in this work are not statistically different from the mean value of the existing data in the literature. The net calorific values of the selected biomass ranged from 16,566 to 17,984 kJ kg^{-1} (dry basis). During the experiment, the flowing temperatures of the selected agricultural biomass were between 880 and 1480 °C. The flowing temperature values for the presented data are different than the mean values of data from references. So, the combustion facility allows the use of fuel from many local sources, thus making the control and minimization of the major part of the operational cost possible. The ash melting process is strongly influenced by its chemical composition, and it takes place in a wide temperature range. Therefore, the present work describes the characteristic points of the ash melting behavior. A complete proximate and ultimate laboratory analysis was conducted in order to determine the physical and chemical material characteristics [C, H, N, volatile matter, moisture, ash content, and gross and net calorific values (GCV and NCV, respectively)], the major and minor elements (Mg, Al, Si, P, S, Cl, K, Ca, Mn, Fe, Zn, Cr, Mn, Ni, Cu and Pb) and the ash melting points (SST, DT, HT and FT) for the analyzed materials that are further used in the combustion processes.

Keywords Agricultural biomass · Elemental analysis · Ash melting behavior

Introduction

In nowadays, the biomass covers a wide range of applications to combustion processes, and it is increasingly involved in energy production, as a renewable energy source.

There is a high potential of available biomass, i.e., wood, energy crops and agricultural products [1]. Bio-energy plays a vital role in the energy supply of many developing countries [2]. Still, it is the main energy source in a number of countries and regions (e.g., Bhutan 86 %, Nepal 97 %, Asia 16 % and Africa 39 %). The main use of bio-energy in these countries is firewood, which is used for cooking and heating [3].

Exploitation of biomass through modern technologies contributes to CO2 emission reduction and offers significant cost-effective opportunities with additional economic and

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social benefits. Bio-energy acts as a substitute for the use of fossil fuels.

The biomass utilization in all its forms can be considered part of a closed carbon cycle. Romania possesses a large potential of biomass and is expected to benefit from recent technologies in order to use the potential energy accumulated in the biomass [4]. In this context, the general properties of the agricultural materials are of relevance from the point of view of the biomass use as fuel material for a large variety of end users, from automotive biodiesel [5] to large combustion power plants.

The selection and design of any biomass combustion system are mainly determined by the characteristics of the fuels, by the performance of the available or necessary equipment, by the fuel availability and the local legislation.

The thermal processes, i.e., combustion, gasification and pyrolysis, appear as particularly suitable to convert the biomass into an energy source [6]. All these processes are based on pyrolysis, a process during which the biomass is converted under the effect of heat only into gas and a solid carbonaceous residue.

The biomass fuel can be securely sourced on small scales; however, on larger scales, it is currently difficult to secure. The utilization of biomass for energy generation raises several questions concerning the availability of sufficient biomass resources and the reliability of the fuel supply to meet this goal. The local availability of the biomass fuel and transportation costs will usually be a decision factor for selecting the appropriate combustion technology.

The new fuel preparation, combustion and flue gas cleaning technologies are more efficient and cleaner than the previous combustion systems and can be utilized for multi-fuel feed. The high fuel flexibility ensured by modern combustion technology allows fuel from many sources. However, research is still needed to increase fuel flexibility and reduce the operating and maintenance costs.

Co-firing 15 % of biomass with coal, SO_2, NO_x, CO, CO_2 and fly ash concentrations in the flue gases are lower than when burning only coal [7]. The characteristics of the biomass (i.e., the diversity of quality, low density and humidity) limit, however, the wide use of combustion [8].

Materials and methods

The research materials came from the local sources located near Timisoara city. The agricultural biomass samples were selected to be representative of the species that are potentially usable as feedstock in the thermal processes.

The samples of the tested materials, presented in Table 1, were prepared in order to proceed with laboratory determinations. Thus, the samples were pre-dried, homogenized and reduced in size to a value of 0.5 mm in order to decrease the samples' heterogeneity.

Carbon, hydrogen and nitrogen determination

The used equipment for C, H and N determinations was a LECO TruSpec CHN model. The standard used for those determinations was EN 15104—solid biofuels—determination of total content of carbon, hydrogen and nitrogen. The samples were weighed (for a domain between 0.1 and 0.3 g/sample) and introduced inside a zinc foil and into the carousel of the equipment. Between the samples, on a regular basis, reference materials are inserted to check the system precision.

Volatile matter content determination

The volatile matter content determinations were made according to the standard EN 15148—solid biofuels—determination of the content of volatile matter. Through the mass difference, the volatile matter content was determined for the considered samples (three times of determination). The volatile matter content was corrected to a dry basis by using the moisture content.

Moisture content determination

The operations were made according to standard EN 14774—solid biofuels—determination of moisture content—oven-dry method; three determinations were made for each sample; for accuracy, the determinations were repeated once more for samples with high moisture content.

Ash content determination

The determination of the ash content for the selected materials was conducted using standard EN 14775—solid biofuels—determination of ash content. The ash content determination process has two steps: First, the crucibles with the weighed samples are introduced inside the furnace and let at least 1 h at 250 °C to allow volatile matter elimination before ignition (the temperature is raised up constantly to 250 °C over a period of 30–50 min). After this initial step, the temperature inside the furnace is raised to 550 °C, and the samples will reside for a minimum of 2 h. The ash content was corrected to a dry basis by using the moisture content.

Calorific value determination

The samples' calorific values were determined with IKA C 5000 calorimeter, which follows the standard EN 14918—

Table 1 Biomass samples used for laboratory determinations

No.	Material	Origin source and details
1.	Corn stalk	Entire plant without grains or cob, Banat region
2.	Corn	Adjacent area from Timişoara–Şag
3.	Cereal mix	Adjacent area from Timişoara–Şag Represents a mixture of wheat, corn and sunflower husks
4.	Wheat	Adjacent area from Timişoara–Şag
5.	Oatmeal	Only grains—adjacent area from Timişoara–Şag
6.	Barley	Only grains—adjacent area from Timişoara–Şag
7.	Corncob	Only cob without grains, Banat region
8.	Rye	Only grains—adjacent area from Timişoara–Şag
9.	Corn 75 % Corncob 25 %	Adjacent area from Timişoara–Şag
10.	Two-row barley	Only grains—adjacent area from Timişoara–Şag

solid biofuels—determination of calorific value. For each material, three determinations were made, in order to verify whether the calorific value between determinations is lower than 120 J g^{-1}. In order to obtain the net calorific value, inside the protocol, data regarding the nitrates and sulfates were introduced; they were determined by using ion chromatography for the collected liquid of each sample. The calorific value was corrected to a dry basis by using the moisture content.

Ion chromatography

The ion chromatography is used in general for the liquid analysis. The used apparatus is a DIONEX ICS–2100 model equipped with calibration for fluoride, chloride, nitrites, nitrates, bromides, sulfates and phosphates. For the used samples, nitrates and sulfates were determined to correct the obtained calorific value of each sample (according to the standard EN 15289).

Major and minor chemical element determination

For the major and minor elements (heavy metals), the determinations could not be made according to standards (EN 15290 and EN 15297). Each material was prepared as described: The weighed quantity (7–8 g) was introduced inside a hot mounting press (Struers Pronto Press—10 model). Each sample was prepared using a heating temperature of 140 °C with an applied force of 50 kN.

The samples prepared as described before were positioned in specified places inside the analysis equipment, which is a wave length dispersion XRF, PANalitycal MagiX Pro model. After the system check, the determinations were initiated.

Ash melting behavior

The determinations were made according to the standard CEN/TS 15370—1—solid biofuels—determination of ash melting behavior. The used equipment was a heating microscope from LECO, model EF 700, dedicated to this type of determination. For each material, two determinations were made. The process was visualized with the help of a camera positioned inside the heating microscope in order to determine the characteristic points for the ash melting behavior [shrinking starting temperature (SST), deformation temperature (DT), hemisphere temperature (HT) and flowing temperature (FT)]. The average value for the two determinations is rounded to the next round value, ascendant or descendant according to the unit value (larger or smaller than five).

Results and discussion

The previous works indicated that the combustion of biomass, without fossil fuels, led to technical problems such as corrosion and fouling on the hot surfaces [9, 10]. The biomass blended with coal during combustion is more advantageous to solve the problems encountered when it is burned alone. With careful planning, the boilers designed for multi-fuel use may accept new fuels without any problems. The fluidized bed boilers designed for coal co-firing can be converted to biomass/coal co-firing ones with a relatively small investment [11].

The combustion of the agricultural biomass is strongly affected by the physicochemical properties. Numerous studies [11–16] have investigated their impact on the boiler performances and/or emission levels.

Table 2 Carbon, hydrogen, nitrogen and volatile matter content

No.	Material	Carbon content/%	Hydrogen content/%	Nitrogen content/%	Volatile matter content (db)/%
1.	Corn stalk	42.8	6.0	0.51	75.7
2.	Corn	40.35	6.5	1.29	85.5
3.	Cereal mix	40.7	6.7	1.16	84.9
4.	Wheat	40.1	6.4	1.35	84.1
5.	Oatmeal	42.53	6.5	1.66	82.4
6.	Barley	40.2	6.2	1.44	82.5
7.	Corncob	45.2	5.8	0.31	80.4
8.	Rye	40.4	6.3	1.44	84.4
9.	Corn 75 %	41.3			84.9
	Corncob 25 %		6.4	1.29	
10.	Two-row barley	40.1	6.5	1.38	82.4

Table 3 Moisture, ash, GCV and NCV values

No.	Material	Moisture content (db)/%	Ash content (db)/%	Gross calorific value (db)/J g^{-1}	Net calorific value (db)/J g^{-1}
1.	Corn stalk	5.91	5.17	18,447	17,060
2.	Corn	10.2	1.58	18,460	16,887
3.	Cereal mix	10.7	1.53	18,464	16,820
4.	Wheat	9.92	1.63	18,125	16,566
5.	Oatmeal	9.03	3.19	19,547	17,984
6.	Barley	10.6	2.52	18,667	17,291
7.	Corncob	3.48	1.58	18,859	17,530
8.	Rye	10.0	1.67	18,632	17,302
9.	Corn 75 %	9.67	1.35	18,470	16,904
	Corncob 25 %				
10.	Two-row barley	10.7	2.22	18,354	16,763

Table 2 presents the elemental analysis and volatile matter content. It was found that the selected material does not show large differences from each other. Regarding the nitrogen content, the corn stalk and the corncob present a lower value than the average of the investigated materials.

From the calorific value, Table 3 indicates that the analyzed agricultural biomass is suitable for being used in combustion processes. The comparison on the net calorific value basis reveals that the samples show similarity, comparable with other published works [17, 18]. The NCV is between 16,566 kJ kg^{-1} (wheat) and 17,984 kJ kg^{-1} (oatmeal). The ash content is low for the analyzed materials except for the corn stalk. The moisture content is the key factor determining the net energy content of the biomass material. The dry biomass has a greater calorific value (or net energy potential), as it uses little of its energy to evaporate any moisture.

It was checked with a *t* test that the presented net calorific values are not statistically different from the mean value of existing data in the literature.

So, in the case of wheat, for the data from literature [15] with a mean of 17,664.0, a *P* value 0.0808 cannot reject the null hypothesis (the obtained value is 16,566) at the significance level 0.05.

A different statistical behavior results for the ash contents in the case of wheat. So, the results from this paper for ash contents were checked with a t test and compared to a lot of observations with a mean of 5.862 from literature [22]. Since the *P* value for the test is 0.0018, <0.05, the null hypothesis is rejected at the 95.0 % confidence level.

The ash percentage has lower values for the analyzed sample, meaning that the residual material does not affect the combustion chamber for long periods of usage.

The sulfur (S) and chlorine (Cl) contents in the fuel suggest the possibility of SO_2 and HCl formation and a

Table 4 Major chemical elements

A

No.	Material	Mg/mg kg^{-1}	Al/mg kg^{-1}	Si/mg kg^{-1}	P/mg kg^{-1}	S/mg kg^{-1}	Cl/mg kg^{-1}
1.	Corn stalk	700	280	6980	2410	850	610
2.	Corn	890	140	580	3510	1030	340
3.	Cereal mix	820	110	310	2610	940	470
4.	Wheat	740	70	220	2930	1010	490
5.	Oatmeal	650	80	6120	2500	1440	490
6.	Barley	600	70	3490	2600	1140	1040
7.	Corncob	320	80	2520	630	330	960
8.	Rye	640	130	300	2280	1110	750
9.	Corn 75 % Corncob 25 %	860	110	600	3180	920	360
10.	Two-row barley	540	80	3790	2360	1140	970

B

No.	Material	K/mg kg^{-1}	Ca/mg kg^{-1}	Mn/mg kg^{-1}	Fe/mg kg^{-1}	Zn/mg kg^{-1}
1.	Corn	3950	1260	10	100	20
2.	Cereal mix	4280	940	20	90	20
3.	Wheat	3400	620	40	70	20
4.	Oatmeal	3000	1010	50	180	20
5.	Wheat bran	11,300	950	140	160	70
6.	Barley	5100	680	20	100	30
7.	Corncob	6250	910	10	320	20
8.	Rye	5230	620	30	80	40
9.	Corn 75 % Corncob 25 %	4110	660	10	130	20
10.	Two-row barley	4590	1150	20	70	30

possible corrosion in the structural elements of the boilers. The practical rules for the selection of the biofuels are related to Cl/S ratio which must be lower than 0.454 [19].

Interpreting the data from Table 4, it can be noticed that the analyzed materials are not fully suitable for combustion in power plants due to the chlorine content. The lower Cl/S ratios, under the limit, are for corn 0.330, for oatmeal 0.340 and for 75 % corn with 25 % corncob 0.391. The rest of the investigated agricultural biomass can be processed in pyrolysis or gasification.

The major and minor elements together with S and Cl are relevant for the ash melting behavior, the deposit and aerosol formation and the fly ash, as well as for the corrosion and the ash utilization. Calcium (Ca) and magnesium (Mg) normally increase the melting temperature of the ash, while potassium (K) and chlorine (Cl) decrease it. Silica (Si) in combination with potassium (K) can lead to the formation of low-melting silicates in the fly ash particles. However, due to the complex interactions between K, Cl, S, Si and Ca, each element cannot always be evaluated individually [17].

The heavy metal concentrations in biomass, presented in Table 5, are of considerable importance for sustainable ash utilization. In this regard, the ash from the agricultural biomass combustion contains 3–20 times lower concentrations of heavy metals than the ashes from the woody biomass [20].

The melting process of the ash is strongly influenced by its chemical composition, and it takes place in a wide temperature range, as depicted in Table 6.

The formation of the ash deposits on the heat exchanger surfaces occurs at a flue gas temperatures lower than 1000 °C, and generally it is a much slower process than that of slag formation. The modern fluidized bed furnaces with low bed temperatures of 650–850 °C can burn fuels with a low ash melting temperature without any sintering problems in the bed [21].

On the other hand, in case of flowing temperature, the value for wheat, which is 880 °C is less than the mean value, 1212 °C from references, while for the barley sample, the value of 1480 °C is higher than the mean value 1185 °C presented in Ref. [22]. Since the *P* value for the

Table 5 Heavy metals analysis

No.	Material	Cr/ppm	Mn/ppm	Ni/ppm	Cu/ppm	Pb/ppm
1.	Corn stalk	13.0	60.0	10.0	<5	420
2.	Corn	<5	10.0	<5	<5	450
3.	Cereal mix	<5	30.0	<5	<5	450
4.	Wheat	<5	70.0	<5	<5	450
5.	Oatmeal	11.0	80.0	10.0	<5	450
6.	Barley	<5	30.0	<5	<5	440
7.	Corncob	50.0	20.0	20.0	<5	440
8.	Rye	<5	50.0	<5	<5	444
9.	Corn 75 % Corncob 25 %	11.0	10.0	10.0	<5	440
10.	Two-row barley	<5	30.0	<5	<5	450

Table 6 Characteristic points for ash melting behavior

No.	Material	SST/°C Shrinking starting temperature	DT/°C Deformation temperature	HT/°C Hemisphere temperature	FT/°C Flowing temperature
1.	Corn stalk	1110	1150	1420	1480
2.	Corn	670	720	1240	1080
3.	Cereal mix	730	760	1090	1210
4.	Wheat	700	710	770	880
5.	Oatmeal	1150	1200	1410	1440
6.	Barley	1060	1170	1420	1480
7.	Corncob	680	1030	1270	1290
8.	Rye	580	740	1000	1310
9.	Corn 75 % Corncob 25 %	760	790	960	1000
10.	Two-row barley	830	1120	1300	1350

test is <0.05, the null hypothesis is rejected at the 95.0 % confidence level in this case.

Conclusions

The chemical properties of the agricultural biomass and the residual ash can affect the combustion and the general composition of the flue gas. The presented study has underlined the fact that in terms of the physical and chemical properties, the analyzed materials do not present significant differences.

Potassium with chlorine and sulfur in biomass fuels are the most problematic elements during the biomass combustion, which could result in issues regarding the ash deposition and high-temperature corrosion. One can observe that lead (Pb) concentrations are high for the analyzed material with impact on aerosol emissions, due to the high volatility.

From the analyzed materials, corn stalk, oatmeal and barley have the highest flowing temperature, making them difficult to be used inside incinerators as individual substrates.

The net calorific value for characterized materials makes them suitable for being used in firing or co-firing processes. The ash percentage has low values, meaning that the residual material does not affect the combustion chamber for long periods of usage. The heavy metals and sulfur content are low which has insignificant impact on the structural integrity of the furnace.

A statistical treatment has been performed, and our set of data for different type of materials was compared with the existing data from the literature.

The modern biomass technologies lead to efficient biomass conversion, being one possible direction for biomass use in developing countries like Romania.

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