

# Comparative analysis of agricultural materials influenced by anaerobic fermentation for biogas production in terms of ash melting behavior

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**Abstract** The aim of this paper is to present a comparative study in terms of determining general properties of four different agricultural residual substrates before and after the anaerobic fermentation process inside a pilot installation dedicated to this type of applications. The influence of anaerobic digestion can be observed from the modifications it brings to the general properties of the used materials. This work underlines positive and negative influences for pH correction agents relative to material further use in combustion process with impact on the characteristic temperatures on which the materials modify their physical properties. All used materials present a high energetic level making them useful even as residues after anaerobic fermentation.

**Keywords** Agricultural biomass · Anaerobic digestion · Chemical analysis · Ash melting behavior

## Introduction

Nowadays, the use of biomass represents one of the most accessible ways of recovery for renewable materials. In this context, using of residual agricultural residues has a major role relative to the fact that this type of materials can be

found in large quantities. There is a high potential of available biomass (wood, energy crops, agricultural products) [1].

The thermal processes, i.e., pyrolysis, combustion, gasification, appear as suitable to convert the biomass into an energy source [2, 3].

Two fundamental aspects related to biomass use as fuel are: first to extend and improve the basic knowledge on composition and properties; and second to apply this knowledge for the most advanced and sustainable utilization of biomass. The systematic identification, quantification and characterization of chemical and phase composition of a given solid fuel are the initial and most important steps during the investigation and application of such fuel [4]. Biomass composition and properties are fundamental, but samples specific type, location, collection as well storage, handling and processing condition are also important to know.

In Europe, biogas production from various biomass wastes is becoming more and more important. Between 2014 and 2023, the number of biogas plants fermenting municipal and industrial biodegradable waste in Europe will increase by about 650 to more than 1450, according to European Biogas Association report. This will raise total electrical capacity from 900 MW in 2014 to around 1.750 MW by 2023 without any negative influence on food and feed production [5].

Romania has quite ideal conditions for biogas as a very important pillar of the future energy supply structure of the country. Annual production potential is estimated of about 1.18 billion cubic meters of biogas. The heat generation potential from biogas in turn totals approximately 14,800 TJ per year and the power generation potential of 350,000 TOE per year. Currently, about 1700 TOE cogenerated electricity and approximately 1900 TOE heat

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are generated from biogas per year. The government targets the increased use of biogas especially in connection with CHP units [6]. Spark ignition engines can be fueled with biogas without major changes and conversion efficiency is very high when cogeneration is employed [7, 8].

Despite the high potential in terms of biogas production from agricultural sources, Romania has among the lowest biogas production in Europe [5, 9].

Anaerobic digestion (AD) is one of the ways in which the agricultural substrate can be converted in biogas, which, in its term can be used as fuel for firing processes with influence on obtaining clean energy [10].

The nature of the biomass and the operational conditions used during anaerobic digestion, determine the chemical composition of the biogas. The digestate, which contains nitrogen and phosphorus, can be used as a soil amendment. Systematic studies about trace elements in biomass and biomass ash are only at an initial stage of investigation and more work is needed [11, 12]. Regulations exist in some countries which specify the limiting and guiding values for the contents of some elements (Ca, Cd, Cl, Co, Cr, Cu, K, N, Ni, Pb, S, V, Zn) in biomass fuels and their biomass ash in respect of their unrestricted use [13, 14].

In their utilization, biogas and digestate are of equal importance in energy production, and they also make a significant contribution to systemic greenhouse gas (GHG) mitigation by recycling household and agricultural waste. Further improvement can be obtained in both energy production and emissions mitigation when the ratio of the three biogas utilization pathways (heating, illumination, and fuel) is adjusted [15].

## Materials and methods

The first step was documentation upon the used materials namely the biomass types, before and after the fermentation process for a period of 65 days for a small, used inside a pilot installation for biogas production.

The research materials came from the local sources located near Timisoara city. The types of agricultural biomass considered are corn cob, cereal mix, wheat bran and two row barley. Table 1 presents the used samples for analysis.

The samples of the tested materials, presented in Table 1 were prepared in order to proceed with laboratory determinations. For this purpose, the samples undertook a pre-drying process and size reduction until a value of 0.5 mm using two different types of Retsch laboratory mills, according to the used type of material. Biomass samples before the fermentation and after fermentation was analyzed in the same manner.

The pilot installation used for obtaining biogas from biomass through anaerobic fermentation is presented in Fig. 1 [16].

## Working principle for the biogas pilot

From the biomass deposit, the used material is passed through a mill, and then it's sent to the tank where the preparation of the suspension of biomass is made (1). For the laboratory determinations there was used a quantity of about 75 kg of material inside 2 m<sup>3</sup> of water over a period of 65 days of anaerobic fermentation.

The biomass suspension is transported with the help of the pump (2) and introduced into the fermentation reactors (3). The correction agent tank for the pH assures, through the control system, the conditions for the process of anaerobic fermentation. For pH correction was used a lime based suspension, while the temperature regime inside the anaerobic fermentation reactors was 35–37 °C. The resulted biogas is passed through a filter for retaining the H<sub>2</sub>S (5) and after that, through a system used for retaining CO<sub>2</sub> (6), after which takes place the CO<sub>2</sub> desorption and the compression of the CO<sub>2</sub> in the adjacent system (7) and the purified biogas is sent for being used (8). The used material is discharged through the means of a gravimetric system (9), and the solid material is retained for being dried using the natural drying, and after that is sent to a compost deposit for being used as a soil fertilizer. A part of the resulting liquid is neutralized when the case, in the system (10) and sent to the sewerage network, or is transported by the recirculation pump (2) from the suspension preparation tank (1). The fermentation reactors are thermostat heated with the system (11). For the homogenization of the suspension is used a bubbling system (12) made by polypropylene pipes to avoid a possible corrosion. Also, for depositing small quantities of biogas of the purpose of analyzing, the installation is equipped with a small tank (13) positioned at the top of the reservoirs.

For the laboratory determinations there was used a quantity of about 75 kg of material inside 2 mc of water over a period of 65 days of anaerobic fermentation.

For pH correction was used a lime based suspension, while the temperature regime inside the anaerobic fermentation reactors was 35–37 °C.

## Moisture content determination

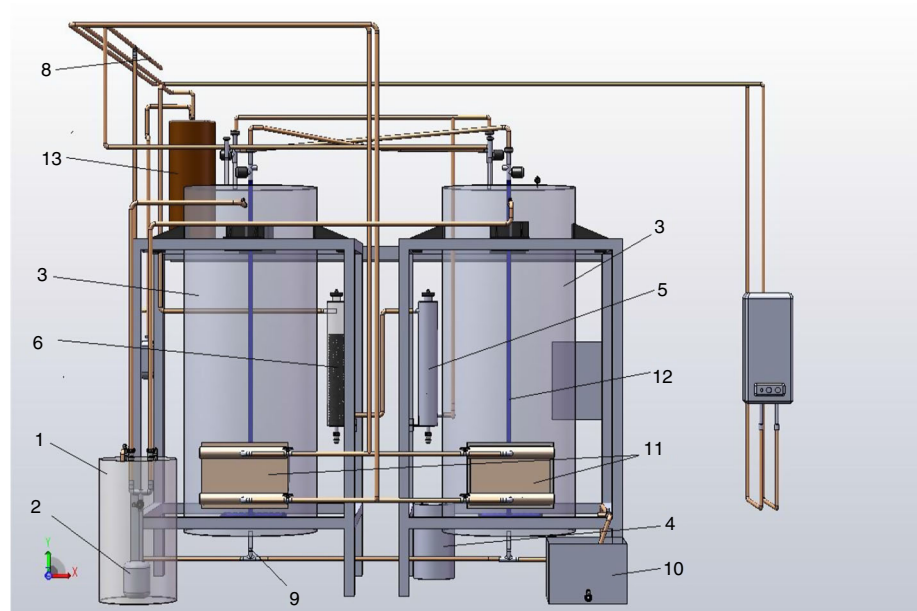
The operations were made according to standard EN 14774—solid biofuels—determination of moisture content—oven-dry method; three determinations were made for each sample.

Inside each vessel it was weighed approximately 2–3 g of material (balance precision 0.0001); three

**Table 1** Biomass samples used for laboratory determinations

No.	Material	Origin source and details
1.	Cereal mix	Adiacent area from Timișoara-Șag. Represents a mixture of wheat, corn and sunflower husks
2.	Cereal mix*	Fermented material for 65 days. Predried material
3.	Wheat bran	Adiacent area from Timișoara-Șag
4.	Wheat bran*	Fermented material for 65 days. Predried material
5.	Corn 75 % Corncob 25 %	Adiacent area from Timișoara-Șag
6.	Corn 75 % Corncob 25 %*	Fermented material for 65 days. Predried material
7.	Two row barley	Only grains—Adiacent area from Timișoara-Șag
8.	Two row barley*	Only grains—Fermented material for 65 days. Predried material

\* Describes the samples after 65 days anaerobe fermentation inside the tables

**Fig. 1** Schematic configuration of pilot installation used for obtaining biogas from biomass

determinations were made for each sample. These samples were introduced inside the furnace at 105 °C for a period until mass constancy. After the drying period, the samples were let to cool down (for approximately 5–10 min) and introduced in a desiccator for 5–10 min. After this period of time the samples were weighed again and the data were introduced in the specified protocol. 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.

Before introducing the samples inside the furnace, the crucibles are let inside for about 2 h at 550 °C and after

this operation they are let to cool down for 10–15 min. After the crucibles are cooled, they are put out from the desiccator, weighed and inside each of them it will be weighed minimum 1 g of material (balance precision 0.0001). The furnace is switched off after this step in order to cool down until a temperature lower than 200 °C.

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 but for increasing the quality of the precision the materials are let over night at this temperature (about 16–17 h).

After the determination the samples are put down from the furnace and let to cool for 2–3 min outside and introduced inside a desiccator for another 3–5 min; the cooled samples are then weighed and the results are introduced inside the corresponding protocol.

For precision determinations, for samples with high ash content the determinations were repeated once more.

It is difficult to number the crucibles, hence the numbered position inside the protocols because of the high temperatures. 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—solid biofuels—determination of calorific value.

Before calorific value determination, the samples are prepared for the analysis inside the calorimetric bomb, the preparation part is related to using a hydraulic press in order to make a small pill like pellet of 0.6–0.8 g which is going to be inserted into the bomb, which in its turn will be introduced inside the calorimeter because the expected heating value is in the calibrated rank. The determination starts after the material data is introduced in the bomb protocol (weighed quantity, identification number for the sample and the user).

For each material, three determinations were made, in order to verify whether the calorific value between determinations is lower than  $120 \text{ J g}^{-1}$ .

For the same material is used the same bomb for avoiding impurities from other samples, and during the determinations there were used to bombs in parallel. After the bomb finishes the digestion process, its interior is washed with ultra-pure water and the washing liquid was filled into a flask until mark with ultra-pure water for each sample with the corresponding identification number on it.

The obtained values are then introduced inside the corresponding protocol for obtaining the calorific value.

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.

### Sample preparation for XRF analysis

For major elements and minor elements (heavy metals) the determinations could not be made according to standards, (EN 15290 and EN 15297). Each material had to be prepared as described below.

It will be weighed a quantity of about 7–8 g (balance precision 0.01), because of process validation,

The weighed quantity will be introduced inside a hot mounting press (Struers PRONTO PRESS—10 models). The material was prepared using a heating temperature of  $140 \text{ }^\circ\text{C}$  with an applied force of 50 kN.

The obtained pellet is not to be touched on the frontal part but only on lateral sides in order to avoid contamination with impurities.

### Laboratory analysis using X-ray fluorescence (XRF) for major and minor chemical elements determination

The prepared samples were introduced inside the specified places inside the analysis equipment, which is a PANalytical MagiXPro model (wave length dispersion XRF).

Using the proper software specific data were introduced there for each sample of material (identification number, description, allocated position, type of analysis: minor or major chemical elements). The determinations were initiated after system was checked.

### 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.

The obtained values are presented in form of peaks on a chromatogram from which are selected the retention times according to the used standard (reference standard solutions inside the carousel), measured and compared with the existing etalon (for the used samples there were determined just the nitrates and sulphates for correcting the obtained calorific value).

The carousel has 50 positions, the first position is the “blank” sample, positions 2–3 are standard reference solutions and positions 45–50 are filled with rinsing solutions of the used needle used for sampling. Between positions 4 and 44 are introduced samples (vessels with a volume of approximately 5 mL) and after this step there are made system check-ups for all the components.

If the diagnosis succeeds, the analysis is started; after finalizing the determination, the automatic marking of the system inside of the obtained chromatogram is deleted and replaced with a new one corresponding to the new values, surfaces are determined and the values for each analyzed element are obtained.

For the used samples, nitrates and sulfates were determined to correct the obtained calorific value of each sample (according to the standard EN 15289).

### Carbon, hydrogen and nitrogen determination

The used equipment for Carbon, Hydrogen and Nitrogen 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.

Before the analysis, a general system check takes place using “blank” tests and reference materials for equipment calibration. Those results are used also for recalculating the results using the new calculated value which is made after obtaining constant values for the three presented elements.

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 in parallel with introducing the sample data inside the protocol. For analysis are used Oxygen of high purity, for a complete combustion of the resulting combustion gas and Helium for Nitrogen content determination. Also for putting in motion different components, pressurized air is used on a continuous basis.

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.

The empty crucibles are introduced inside the furnace at  $900 \pm 10$  °C for about 60 min and after this period are put out and let to cool down for 10 min and introduced inside a desiccator. After the crucibles are cooled down it is weighed a quantity of minimum  $1 \pm 0.1$  g of material.

The crucibles are then inserted into the furnace for exactly 7 min and after this time period are let out to cool to room temperature and inserted into a desiccator. After the crucibles are cooled down, are weighed again and the results are inserted into the corresponding protocol.

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.

### Major and minor chemical elements 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 wave length dispersion XRF, PANalytical MagiX Pro model. After the system check, the determinations were initiated.

### Ash melting behaviour

For this purpose, for each material it was calculated the necessary quantity for obtaining 2 g of ash using the same method as for ash content determination (Standard EN 14775). For the laboratory determinations it was needed 1–2 g of ash for each material.

The determinations were made according to the standard CEN/TS 15370-1—Solid biofuels—Determination of ash melting behaviour. 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. In the first phase, the ash is mixed with 1–2 drops of ultra-pure water so it would create a semi-dry paste. After a small quantity of the paste is inserted inside a pressing device having as a main result a cone of small size, which will be placed on a ceramic plate used for the determinations. On each ceramic plate it can be positioned a maximum of 5 cylinders for the laboratory analysis. The ceramic plate together with the cylinders is inserted inside the apparatus.

Before the determinations a system check is recommended. Using the corresponding software are introduced the data for each sample (identification number, position), after which are made the determinations.

After the determinations are finished, the ceramic plate is put out from the device, let to cool down and the results are interpreted according to the standard specifications.

In this stage the process is visualized due to a camera positioned inside the heating microscope in order to determine the characteristic points for ash melting behaviour (shrinking starting temperature (SST), deformation temperature (DT), hemisphere temperature (HT) and flowing temperature (FT)).

The average value for the two determinations is determined and it is rounded to the next round value, ascendant or descendant according to the unit value (larger or smaller than five).

## Results and discussion

The overall analysis was performed both in terms of chemical and physical characteristics, while the ash melting behavior was monitored and conclusions were traced relative to influence factors (temperature, residence time, pH correction) which can modify the general material properties.

Next tables underline the obtained results for the laboratory determinations. Table 2 indicates that, from the calorific value point of view, the analyzed agricultural biomass is suitable for being used in combustion processes. The comparison on the net calorific value basis between four different agricultural residual substrates before and after the anaerobic fermentation process reveals that the samples show major differences as the gross or net calorific values for samples decrease with about 50 % after the anaerobic fermentation process. The ash content is low for the analyzed materials before anaerobic fermentation process and it increases after. 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 has been demonstrated that heating values are negatively related to ash content, with every 1 % increase in ash concentration decreasing the heating value by 0.2 MJ kg<sup>-1</sup> [17].

The elemental analysis of used materials is shown in Table 3 in terms of carbon, hydrogen, nitrogen content and volatile matter. Regarding the nitrogen content, the corn cob after anaerobic fermentation presents a lower value than the average of the investigated materials.

Compared with several references, carbon, hydrogen and volatile matter content of selected biomass show similarity with values found in the literature [18]. From the results summarized in Table 3, there is an approx. 30 % reduction of carbon content, 50 % for hydrogen and 28 % lower volatile matter in fermented residues.

Interpreting the data from Table 4, it can be noticed that the analyzed materials are suitable for combustion in power plants due to the decreases of chlorine content after anaerobic fermentation process [19]. The Cl/S ratios, is for 75 % corn with 25 % corn cob 0.391 before the anaerobic fermentation process, and becomes 0.151 after fermentation process.

Overall, two row barley present the highest Cl content before anaerobic fermentation and the lowest value after the process, by almost 89 %. Phosphorus varied considerably among selected materials, resulting in the lowest in cereal mix and two row barley, and the highest in wheat bran before and after anaerobic fermentation.

The major and minor elements together with S and Cl are relevant for the ash melting behavior, the deposit and aerosol formation, the fly ash as well as for the corrosion and the ash utilization. Magnesium (Mg) normally increase the melting temperature of the ash, while potassium (K) and chlorine (Cl) decrease it. Silica (Si) in combination

**Table 2** Moisture, ash, GCV and NCV values

No.	Material	Moisture content (db)/%	Ash content (db)/%	Gross calorific value (db)/J g <sup>-1</sup>	Net calorific value (db)/J g <sup>-1</sup>
1.	Cereal mix	10.7	1.53	18,464	16,820
2.	Cereal mix*	0.93	49.8	11,502	10,676
3.	Wheat bran	9.72	5.54	19,034	17,520
4.	Wheat bran*	3.20	54.3	9241	8506
5.	Corn 75 % Corncob 25 %	9.67	1.35	18,470	16,904
6.	Corn 75 % Corncob 25 %*	3.33	56.5	8637	7973
7.	Two row barley	10.7	2.22	18,354	16,763
8.	Two row barley*	0.75	56.9	9003	8338

**Table 3** Carbon, hydrogen, nitrogen and volatile matter content

No.	Material	Carbon content/%	Hydrogen content/%	Nitrogen content/%	Volatile matter content (db)/%
1.	Cereal mix	40.7	6.7	1.16	84.9
2.	Cereal mix*	31.5	3.7	1.22-a	61.2
3.	Wheat bran	41.3	6.2	2.06	78.4
4.	Wheat bran*	27.6	3.2	1.67	58.4
5.	Corn 75 % Corncob 25 %	41.3	6.4	1.29	84.9
6.	Corn 75 % Corncob 25 %*	26.5	2.9	0.99	58.7
7.	Two row barley	40.1	6.5	1.38	82.4
8.	Two row barley*	27.4	3.0	1.09	59.1

**Table 4** Major chemical elements (I)

No.	Material	Mg/mg kg <sup>-1</sup>	Al/mg kg <sup>-1</sup>	Si/mg kg <sup>-1</sup>	P/mg kg <sup>-1</sup>	S/mg kg <sup>-1</sup>	Cl/mg kg <sup>-1</sup>
1.	Cereal mix	820	110	310	2610	940	470
2.	Cereal mix*	790	780	1370	8970	1610	280
3.	Wheat bran	1750	60	120	7700	1490	420
4.	Wheat bran*	1190	900	1400	14,580	1870	380
5.	Corn 75 % Corncob 25 %	860	110	600	3180	920	360
6.	Corn 75 % Corncob 25 %*	610	1040	1880	5740	1190	180
7.	Two row barley	540	80	3790	2360	1140	970
8.	Two row barley*	640	1000	4210	6980	1310	110

**Table 5** Major chemical elements (II)

No.	Material	K/mg kg <sup>-1</sup>	Mn/mg kg <sup>-1</sup>	Fe/mg kg <sup>-1</sup>	Zn/mg kg <sup>-1</sup>
1.	Cereal mix	4280	20	90	20
2.	Cereal mix*	810	80	600	90
3.	Wheat bran	11,300	140	160	70
4.	Wheat bran*	1530	10	1140	130
5.	Corn 75 % Corncob 25 %	4110	10	130	20
6.	Corn 75 % Corncob 25 %*	320	60	840	70
7.	Two row barley	4590	20	70	30
8.	Two row barley*	430	70	700	70

**Table 6** Heavy metals analysis

No.	Material	Cr/ppm	Mn/ppm	Ni/ppm	Cu/ppm	Pb/ppm
1.	Cereal mix	<5	30.0	<5	<5	450
2.	Cereal mix*	10.0	150	10.0	10.0	260
3.	Wheat bran	<5	230	<5	10.0	440
4.	Wheat bran*	10.0	250	10.0	20.0	240
5.	Corn 75 % Corncob 25 %	11.0	10.0	10.0	<5	440
6.	Corn 75 % Corncob 25 %*	20.0	110	10.0	10.0	220
7.	Two row barley	<5	30.0	<5	<5	450
8.	Two row barley*	30.0	130	10.0	10.0	230

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, each element cannot always be evaluated individually [20].

Once again, wheat bran exhibited the highest K content (Table 5), followed by two row barley and cereal mix. The other crops did not significantly differ in Mn and Zn, which ranged between 10 and 30 mg kg<sup>-1</sup> (dry matter basis).

The lowest Cr, Ni and Cu were found in two row barley and cereal mix, while wheat bran presents the highest Mn

concentration as it can see from Table 6. Pb values showed similarity in selected materials, 440 and 450 ppm before anaerobic fermentation and 220–260 ppm after anaerobic fermentation. The heavy-metal concentrations in biomass, presented in Table 6, are of considerable importance for sustainable ash utilization. However the ash from the agricultural biomass combustion contains 3–20 times lower concentrations of heavy metals than the ashes from the woody biomass [21].

The characteristic points for ash melting behavior are presented in Table 7.

**Table 7** 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.	Cereal mix	730	760	1090	1210
2.	Cereal mix*	1220	1380	1450	1460
3.	Wheat bran	640	670	730	740
4.	Wheat bran*	1150	1340	>1500	>1500
5.	Corn 75 % Corncob 25 %	760	790	960	1000
6.	Corn 75 % Corncob 25 %*	1180	1260	1445	1470
7.	Two row barley	830	1120	1300	1350
8.	Two row barley*	1120	1360	1450	1475

The melting process of the ash is strongly influenced by its chemical composition and it takes place in a wide temperature range. From the analyzed materials after 65 days anaerobe fermentation results that they have the highest flowing temperature, making them difficult to be used inside incinerators as individual substrates.

## Conclusions

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

Using a lime based suspension for pH correction together with the anaerobic fermentation process proved to have a negative influence over the ash content of the studied materials. This aspect can prove to be not suitable in terms of using the materials in cofiring processes, this aspect being a good indicator that the pH correction should be made with other materials.

Also this part influenced the points for ash melting behavior, rising the initial temperatures. This aspect is negative because of the increased quantity of residual material after firing process, which can be a problem relative to finding solutions for large scale applications in terms of depositing the remaining ash.

The anaerobic fermentation process had a good impact over the energetic consumption of the materials, the calorific value being with about 50 % lower for the material after the process, but still high enough for it to be further used for cofiring processes.

The heavy metals concentration is low, almost zero, which represents a good indicator that all the remaining materials after process could be used as fertilizers in agriculture. The only exception is lead, with high values of

concentrations and this fact could be as a result of contaminated soil.

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.

This work underlines the necessity to have complete datasets upon material properties with direct impact on further usage for cofiring processes at small and large scale for possible development of proper technologies which can use this kind of materials, or to further use the resulted residue as fertilizer for agriculture. The obtained analysis for the material after the process will give a potential solution relative to using the residue in this sense.

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## References

1. Scarlat N, Martinov M, Dallemand JF. Assessment of the availability of agricultural crop residues in the European Union: potential and limitations for bioenergy use. *Waste Manag.* 2010;30(10):1889–97.
2. Dupont C, Rougé S, Berthelot A, Da Silva Perez D, Graffin A, Labalette F, Laboubee C, Mithouard JC, Pitocchi S. Suitability of wood chips and different biomass types for use in plant of BtL production by gasification. *Int J Chem React Eng.* 2010;8:A74.
3. Arvelakis S, Gehrman H, Beckmann M, Koukios EG. Studying the ash behaviour of agricultural residues using thermal analysis. *J Therm Anal Calorim.* 2003;72:1019–30.
4. Vassilev VS, Baxter D, Andersen KL, Vassileva GC, Morgan JT. An overview of the organic and inorganic phase composition of biomass. *Fuel.* 2012;94:1–33.
5. European Biogas Association. <http://european-biogas.eu/2015/03/24/100s-of-new-biogas-plants-in-the-pipeline>. Accessed 2015.



6. Renewable Energy Exhibition and Conference Group. <http://www.reeco.eu/index.php?id=3&L=4>. Accessed 2015.
7. Irimescu A, Vasiiu G, Trif-Tordai G. Performance and emissions of a small scale generator powered by a spark ignition engine with adaptive fuel injection control. *Appl Energ.* 2014;121:196–206.
8. Hosseini SE, Wahid MA. Development of biogas combustion in combined heat and power generation. *Renew Sustain Energy Rev.* 2014;40:868–75.
9. Vintila T, Neo S. Biogas in Romanian agriculture, present and perspectives. *Anim Sci Biotechnol.* 2011;44(1):465–9.
10. Quan C, Xu S, An S, Liu X. Co-pyrolysis of biomass and coal blend by TG and in a free fall reactor. *J Therm Anal Calorim.* 2014;117:817–23.
11. Mao C, Feng Y, Wang X, Ren G. Review on research achievements of biogas from anaerobic digestion. *Renew Sustain Energy Rev.* 2015;45:540–55.
12. Magdziarz A, Wilk M. Thermal characteristics of the combustion process of biomass and sewage sludge. *J Therm Anal Calorim.* 2013;114(2):519–29.
13. Vassilev VS, Baxter D, Andersen KL, Vassileva GC. An overview of the composition and application of biomass ash. Part 1. Phase—mineral and chemical composition and classification. *Fuel.* 2013;105:19–39.
14. Cioabla AE, Pop N, Calinoiu DG, Trif-Tordai G. An experimental approach to the chemical properties and the ash melting behavior in agricultural biomass. *J Therm Anal Calorim.* 2015;121:421–7.
15. Chen S, Chen B, Song D. Life-cycle energy production and emissions mitigation by comprehensive biogas-digestate utilization. *Bioresour Technol.* 2012;114:357–64.
16. Cioabla AE, Trif Tordai G, Rotaru P, Socaciu M, Ionel I. Experimental approach of co-firing and anaerobic fermentation of biomass and coal, and their thermochemical properties. *J Therm Anal Calorim.* 2012;110:395–403.
17. Energy research Centre of the Netherlands, Phyllis2 database for biomass and waste, [www.ecn.nl/phyllis2](http://www.ecn.nl/phyllis2). Accessed 2015.
18. Monti A, Di Virgilio N, Venturia G. Mineral composition and ash content of six major energy crops. *Biomass Bioenergy.* 2008;32(3):216–23.
19. Ren Q. NO<sub>x</sub> and N<sub>2</sub>O precursors from biomass pyrolysis. *Therm Anal Calorim.* 2014;115:881–5.
20. van Loo S, Koppejan J. *The handbook of biomass combustion & co-firing.* London: Earthscan Publishing House; 2007.
21. Delcarte J, Delcarte E, Maesen P, Schenkel Y. Heavy metals, PAH and PCB emissions from short rotation crop combustion. *Proceedings of the International Conference Science in Thermal and Chemical Biomass Conversion.* Victoria, Canada: CPL Press; 2006; 967–974.

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