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BIOMASS ANALYSIS FOR COMBUSTION APPLICATIONS – CASE STUDY SCENARIOS

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ABSTRACT. Nowadays the need for renewable resources becomes more and more stringent. Biomass remains one of the most important sources of energy, being used directly or by chemical conversion processes in order to produce clean energy. Relative to this aspect, the present paper proposes the direct approach, by analyzing to biomass type materials (topinambur and Romanian hemp) in order to determine their physical and chemical characteristics and their potential use in combustion processes.

Keywords: *biomass, combustion, thermal and chemical analysis*

INTRODUCTION

The worldwide socio-economical context imposes an economical growth in the sense of obtaining heat, electricity and biofuels, but the main objective for safe energy distribution has to be overlapped with the one of sustainable development of society, which represents an essential component of the 2009/28/EC Directive regarding Renewable Energy. Energetic durability is recognized as a decisive factor in reaching a global scale sustainable development of any country [1-3].

The EU has established ambitious objectives regarding climate and energy until 2020, such as a reduction of 20% for the GHG gases (greenhouse effect) and a quota of 20% from the energetic consumption in the UE should be produced by renewable energy sources. At global level there exists an urgent demand for bioenergy and the renewable energy sources are sufficient

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for offering potential to all energetic needs worldwide necessary in the next century [4-5]. The residual materials obtained from forestry, agriculture and organic waste (for example municipal solid waste) would be enough to ensure between 50 and 150 EJ/year and the difference can be obtained from energetic crops, excessive forest growing and optimized agricultural productivity [6]. Short rotation coppice (SRC) can be a factor in reduction of energetic dependence of a country and GHG and can contribute as a lever to regional durable development, especially in rural areas, where there is need for new working places and to create a durable economy in order to attract young population [7].

Aside solar and wind energy, bioenergy represents one of the most used renewable energy technologies [8], and at global level the main concern is to obtain independence from fossil fuels while identifying potential sources and increased usage on a large scale of “fuel mix”.

The concept “bioenergy” (energy from biomass), included in the term “green energy” (renewable energy), describes an alternative solution, ecological, apart from the classical form of using carbon based sources. If biomass is directly used for heat and / or energy generation, by being just a fuel (or an energy source), the energy generated from it is called bioenergy [9,10].

“The ratio between the mass of organic substance versus a certain surface and time unit” [11], as biomass can be defined, including all the organic matter produced through metabolic processes of living organisms in chemical form, constitutes in fact the resource with the highest potential usage for man. Biomass is in essence the ensemble for non-fossil organic matter, which includes: wood, animal residues, oils and vegetable residues from forestry, agriculture and industry but also cereals and fruits from which ethanol can be produced. Biomass reserves are especially wood residues, agricultural residues, municipal waste and energetic crops [12, 13].

Biomass can also be used for the production of biochemicals or biomaterials [14-16].

It is one of the most promising sources of renewable energy because of its attractive properties like low production cost, low emissions, storage capacity and availability throughout the year from different sources [17-20].

It is the only renewable energy source which can be transformed in solid, liquid or gaseous fuels [21, 22].

The main forms of capitalizing biomass are:

- Direct combustion for thermal energy production;
- Pirolysis firing with syngas production ($CO + H_2$);
- Fermentation with biogas production (CH_4) or bioethanol (CH_3-CH_2-OH);
- Chemical conversion of vegetal oils by alcoholic treatment and obtaining esters (eg. biodiesel and glycerol);
- Enzymatic decay with ethanol or biodiesel production [12].

So it can be considered that biomass has an important role to play in the energy production [13], especially it the developing countries [24].

Presently the use of biomass produces about 5% from the total energy consumption at European level and in countries like Finland, Sweden and Austria it assures over 15-20%. In Romania, the electric energy production in 2016 was accomplished at a level of around 42.38% from renewable energy sources and the rest through fossil fuels according to existing data given by the National Authority for Energetic Regulation (ANRE) from monitoring the electric energy market.

According to the presented document, from all the renewable energy sources, the hydroelectric part assured 28.86% from the total produced electric energy, followed by wind installations (10.13%), solar (2.60%) and biomass (0.75%) [24].

Until 2020, the ENERO study recommends local heating and cogeneration through using wood biomass, straw and biogas obtained from anaerobic digestion of organic residues as being the main effective technologies for Romania and biomass (including biofuels used for transportation) will be the main contributor at RES quota (Renewable Energy Sources) with more than 65% from the total amount [25].

Both presently and also as estimation for 2020, the main biomass contribution in our country is represented by wood and agricultural residues, used for heating the traditional rural stoves, which is about 40% from the living population [25].

Using biomass in firing processes still presents technical issues because of the difficulty to model the combustion behavior due to the large number of biomass types with different chemical compositions, which can vary significantly.

Biomass has certain disadvantages as solid fuel: high water and Oxygen content, hydrophilic nature, low calorific value, high bulk density and energetic density, and also posing problems regarding transportation, storage and usage. Transportation costs are generally high, which can affect the process economical viability [26].

In order to partially overcome those problems, biomass can be pretreated and transformed ib products like pellets and briquettes. Through this type of processing it can be obtained a homogenous and solid product with high density, thus having an improvement in terms of biomass quality and reduction of the supply chain [27, 28].

Knowing the physical and chemical characteristics for the used products is very important in order to better understand the burned fuel behavior in order to better consolidate the biomass supply chain viability. The process of obtaining pellets / briquettes is improved in order to be used for capitalization of agro-industrial residues [29].

It is a known fact that the primary matter has a great influence over the qualities of pellets and briquettes. For forestry biomass, the leafs have a superior heating value than the wood fractions [30,31], but they also present a high ash content which implies more industrial problems like abrasive wear in firing boilers / ovens.

RESULTS AND DISCUSSION

There were conducted both physical and chemical analysis and thermal analysis in order to better determine the potential applications for the studied materials in combustion processes.

Next tables will underline the obtained results for the laboratory determinations.

For comparison reasons there will be added two other different materials previously used for analysis purposes in order to observe a basic comparison relative to chemical properties [32] but having in mind the fact that the main focus is made on the first two materials used for laboratory determinations (positions 1 and 2 in the next tables).

Table 1. Experimental results (part 1)

No.	**MATERIAL**	**Moisture content [%]**	**Ash content (db) [%]**	**Gross calorific value (db) [J/g]**	**Net calorific value (db) [J/g]**
1	Hemp RO	15,5	2,87	19334	17940
2	Topinambur	11,3	5,94	18277	16903
3	Wheat bran	9,7	5,54	19034	17520
4	Two row barley	10,7	2,22	18354	16763

Table 2. Experimental results (part 2)

No.	**MATERIAL**	**Carbon content (db) [%]**	**Hydrogen content (db) [%]**	**Nitrogen content (db) [%]**	**Volatile matter content (db) [%]**
1	Hemp RO	48,3	5,4	0,45	79,1
2	Topinambur	45,6	5,59	1,46	74,3
3	Wheat bran	41,3	6,2	2,06	78,4
4	Two row barley	40,1	6,5	1,38	82,4

It can be observed from table 2 that the ash content of the two studied materials is relatively low, which represents a good indicator of combustion use due to the fact that there are low quantities of residual materials after the process. By comparison with other materials it can be observed that there can be lower values (two row barley in our case) that are better suited for further use in firing processes. Also the calorific values are relatively high, which implies high energetic levels for all materials.

Table 3. Experimental results (part 3)

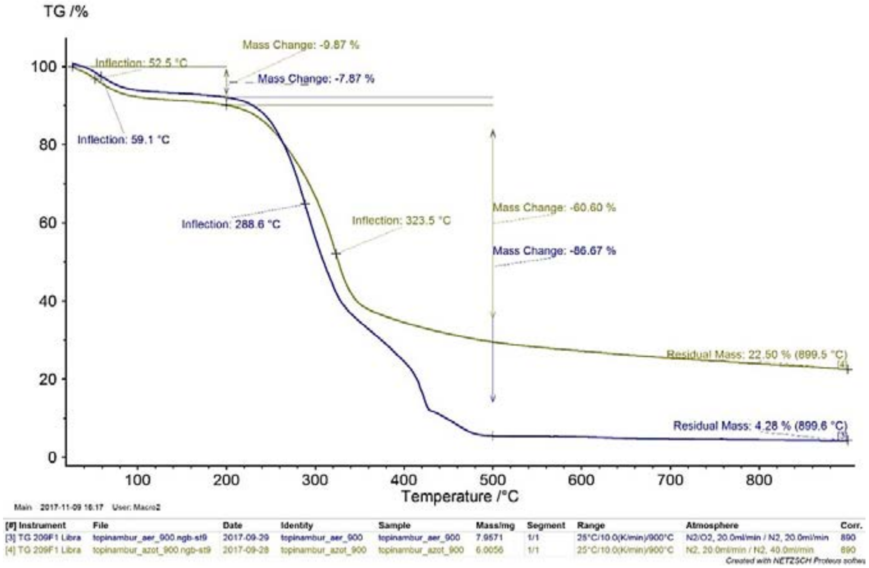
No.	**MATERIAL**	**Sulphur content (db) [%]**	**Chlorine content (db) [%]**	**Oxygen Content (db) [%]**
1	Hemp RO	0.008	0.001	43.0
2	Topinambur	0.117	0.258	41.0
3	Wheat bran	0.014	0.004	42.0
4	Two row barley	0.014	0.009	43.0

From tables 2 and 3 an overall idea is that there are low levels of sulphur and chlorine, which for combustion processes indicate low potential of degrading the furnace which uses as fuel one of the studied materials.

Table 4. Experimental results (part 4)

No.	**MATERIAL**	**Shrinking temperature [° C]**	**Deformation temperature [° C]**	**Hemisphere temperature [° C]**	**Flow temperature [° C]**
1	Hemp RO	960	1240	1300	1320
2	Topinambur	610	1280	1490	>1540
3	Wheat bran	640	670	730	740
4	Two row barley	830	1120	1300	1350

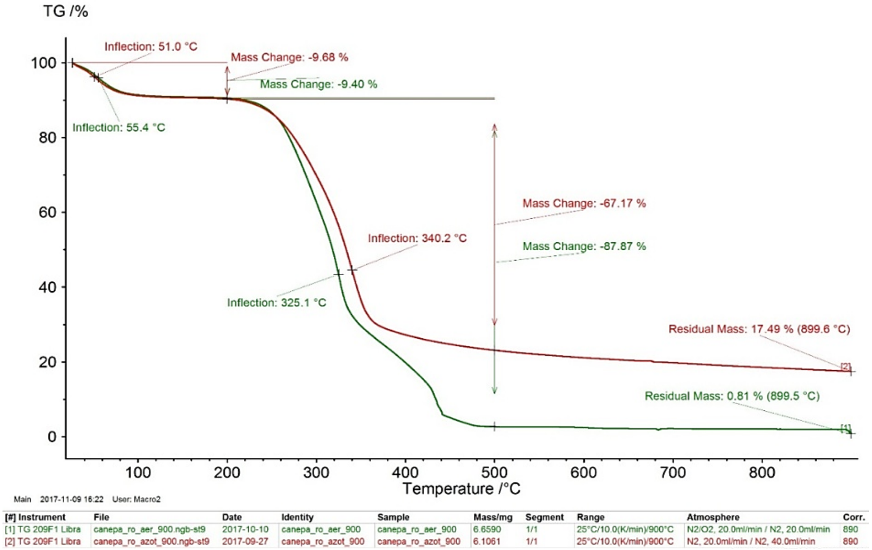
From table 4 one can determine that topinambur has a higher flow temperature than hemp, making the first material much more suitable in terms of behavior during the combustion process. By comparison with the other two materials, it can be observed that its flow temperature is in the same range as two row barley.



[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[3] TG 209F1 Libra	topinambur_aer_900.ngb-st9	2017-09-29	topinambur_aer_900	topinambur_aer_900	7.9571	1/1	25°C/10.0(K/min)/900°C	N2/O2, 20.0ml/min / N2, 20.0ml/min	890
[4] TG 209F1 Libra	topinambur_azot_900.ngb-st9	2017-09-28	topinambur_azot_900	topinambur_azot_900	6.0056	1/1	25°C/10.0(K/min)/900°C	N2, 20.0ml/min / N2, 40.0ml/min	890

Figure 1. TG curves for topinambur under air and nitrogen

The TG curves present two degradation steps, the first from 25 to 200°C, associated with water loss, and the second from 200 to 500 °C associated to thermal decomposition of the samples.

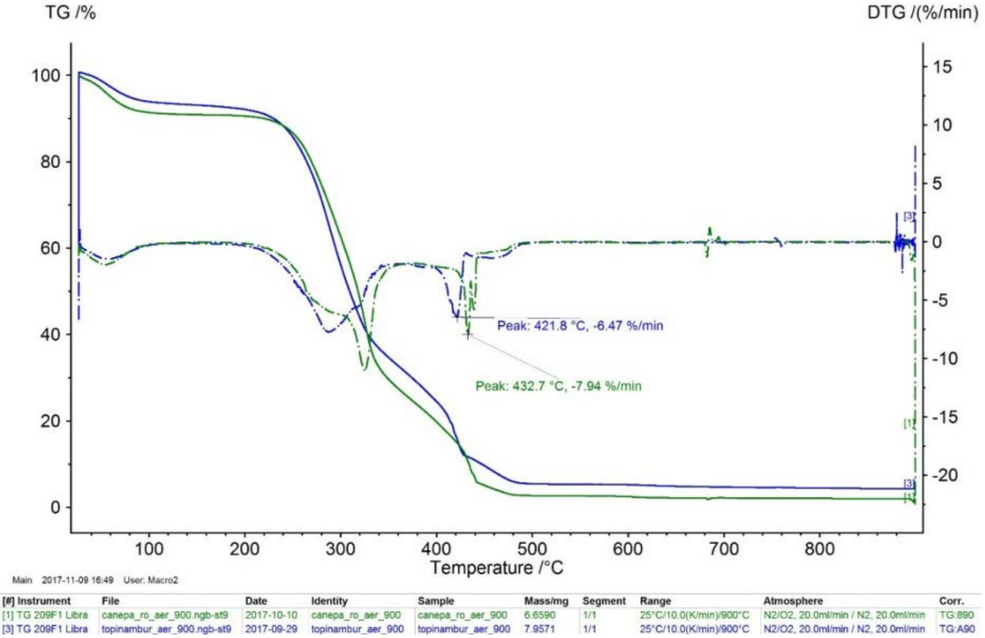


[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] TG 209F1 Libra	canepa_ro_aer_900.ngb-st9	2017-10-10	canepa_ro_aer_900	canepa_ro_aer_900	6.6590	1/1	25°C/10.0(K/min)/900°C	N2/O2, 20.0ml/min / N2, 20.0ml/min	890
[2] TG 209F1 Libra	canepa_ro_azot_900.ngb-st9	2017-09-27	canepa_ro_azot_900	canepa_ro_azot_900	6.1061	1/1	25°C/10.0(K/min)/900°C	N2, 20.0ml/min / N2, 40.0ml/min	890

Figure 2. TG curves for hemp under air and nitrogen

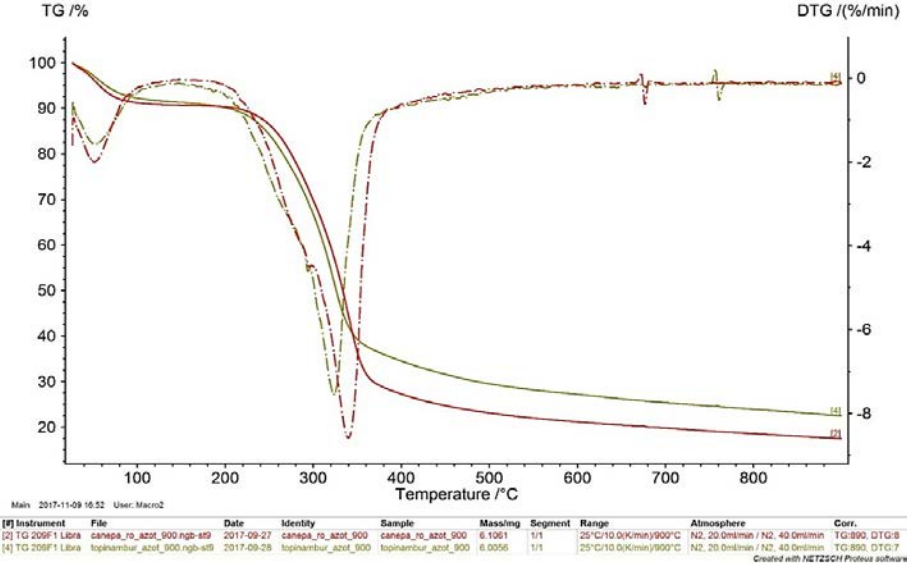
The mass loss for the first degradation step is under 10% (air or nitrogen) and for the second degradation step is under 90% for the samples under air and around 60% for the samples under nitrogen. The residual mass is under 5% for the sample in air and around 20% for the samples under nitrogen.

The thermal decomposition behavior under air and under nitrogen is similar for the studied samples. Due to the complex reaction, that take place under air, both samples presents around 425 °C another degradation step (figure 3), step that is missing in the analysis recorded under nitrogen (figure 4).



[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[1] TG 209F1 Libra	canepa_ro_aer_900.ngb-st9	2017-10-10	canepa_ro_aer_900	canepa_ro_aer_900	6.6590	1/1	25°C/10.0(K/min)/900°C	N2/O2, 20.0ml/min / N2, 20.0ml/min	TG:890
[3] TG 209F1 Libra	topinambur_aer_900.ngb-st9	2017-09-29	topinambur_aer_900	topinambur_aer_900	7.9571	1/1	25°C/10.0(K/min)/900°C	N2/O2, 20.0ml/min / N2, 20.0ml/min	TG:A90

Figure 3. TG curves of topinambur and hemp under air



[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[2] TG 209F1 Libra	canepa_ro_azot_900.ngb-st9	2017-09-27	canepa_ro_azot_900	canepa_ro_azot_900	6.1061	1/1	25°C/10.0(K/min)/900°C	N2, 20.0ml/min / N2, 40.0ml/min	TG:890, DTG:8
[4] TG 209F1 Libra	topinambur_azot_900.ngb-st9	2017-09-28	topinambur_azot_900	topinambur_azot_900	6.0056	1/1	25°C/10.0(K/min)/900°C	N2, 20.0ml/min / N2, 40.0ml/min	TG:890, DTG:7

Figure 4. TG curves of topinambur and hemp under nitrogen

Table 5 presents the overall characteristics determined during the thermogravimetric analysis.

Table 5. Thermogravimetric analysis

Sample	Inflexion		Mass loss (%)		Residual mass (%)
	First step	Second step	25-200◦C	200-500◦C	
Topinambur air	59.1	288.6	7.87	86.67	4.28%
Topinambur N_2	52.5	323.5	9.87	60.60	22.50
Hemp air	55.4	325.1	9.40	87.87	0.81
Hemp N_2	51.0	340.2	9.68	67.17	17.49

The first mass loss is not influenced by the medium in which the analysis is carried out (nitrogen or air) thus the temperatures values are between 50 and 60 °C, this being physical process (dehydration).

The second step is the chemical decomposition of the samples and in this case the temperatures are lower in air medium as compared in nitrogen. There is a 20 °C difference in the inflexion temperatures of the decomposing processes. Also, the mass loss is with 20% higher for the second decomposing step in air as compared in nitrogen medium.

The residual mass has lower value for the analysis that was carried out in air, fewer than 5%. Under nitrogen atmosphere the residual mass is around 20%; the difference is that in nitrogen atmosphere the carbon is decomposed as carbon black which is not oxidized to CO^2.

CONCLUSIONS

From the chemical analysis made on the two studied material, it can be considered that both of them have a relatively high energetic potential and can further be used in firing processes.

The potentially corrosive elements inside the studied materials are in low quantities and pose no risks for the burning chamber in terms of deterioration on the long run.

Topinambur presents a higher flowing temperature which makes it more difficult to liquefy and from this point of view, hemp is easier to be evaluated and approached relative to its heating properties.

Topinambur and hemp are valuable raw materials that can be used in combustion processes. These materials were summited for physical, chemical and thermal analysis in order to determine the potential applications in combustion processes.

From the thermogravimetric analysis can be concluded that the chemical decomposition take place between 200 and 500◦C. Under air, the decomposition processes have complex reactions, which take place in two steps. The residual mass was found to be under 5% under air and around 20% under nitrogen atmosphere.

EXPERIMENTAL SECTION

In the present paper there are studied 2 materials in terms of physical, chemical and thermo analytical properties relative to their potential use in combustion processes, namely topinambur and Romanian hemp.

The used standards for laboratory determinations were:

- EN ISO 18134 – Solid biofuels – Determination of moisture content – Oven dry method (3);
- EN ISO 18122- Solid biofuels - Determination of ash content;
- EN 14918 - Solid biofuels –Determination of calorific value;

- EN ISO 16948 – Solid biofuels – Determination of total content of carbon, hydrogen and nitrogen
- EN ISO 16994 - Solid biofuels — Determination of total content of sulfur and chlorine
- EN ISO 18123 – Solid biofuels – Determination of the content of volatile matter.
- CEN/TS 15370 - Determination of ash melting behavior.

Determination of moisture content.

- inside each vessel it was weighed approximately 1 g of material (balance precision 0.0001),
- there were made 3 time determinations for each sample,
- the samples were introduced inside the furnace at 105 ºC for a period until constant mass,
- after the drying period, the samples were weighed again and the data were introduced in the specified protocol,
- for precision determinations, for samples with a high moisture content the determinations were repeated once more.

Ash content determination.

- before introducing the samples inside the furnace, the crucibles are let inside for about 2 hours at 550 °C and after this operation they are let to cool down for 10 – 15 minutes,
- after the crucibles are cooled, 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 100 °C,
- the process of ash content determination has 2 steps: first, the crucibles with the weighed samples are introduced inside the furnace and let at least 1 hour 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 minutes),
- after this initial step, the temperature inside the furnace will be raised to 550 °C and thee samples will reside for a minimum of two hours
- after the determination the samples are put down from the furnace and let to cool for 2 -3 -5 minutes outside, and the cooled samples are then weighed and the results are introduced inside the corresponding protocol,
- for precision determinations, for samples with a high ash content the determinations were repeated once more
- because of the high temperatures it is difficult to number the crucibles, hence the numbered position inside the protocols,
- the ash content was corrected to dry basis by using the moisture content.

Calorific value determination.

- 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 0.3 – 0.5 g which is going to be inserted into the bomb, which in its turn will be introduced inside a calorimeter (Model IKA C 6000), because the expected heating value is in the calibrated range,
- after the material data is introduced in the bomb protocol (weighed quantity, identification number for the sample and the user) the determination starts,
- for each material there were made at least 2 determinations, in order to verify if the difference in calorific value between both determinations is lower than 120 J /g,
- after the bomb finishes the digestion process, its interior is washed with ultra pure water and the washing liquid was filled into a 100 ml 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.

Ion chromatography

- this type of chromatography is used in general for liquid analysis. the used apparatus is a Metrohm 930 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),
- inside the carrousel are introduced samples (vessels with a volume of approximately 10 ml) and after this step there are made system check-ups for all the components

Carbon, Hydrogen and Nitrogen determinations

- 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,
- between the samples are put standard materials in order to keep the equipment calibrated and the measurement precise

- the sample is weighed (at the maximum possible amount of material for a domain between 0.1 and 0.3 g / sample, because of the volume of the material) and is introduced inside a Zinc foil and into the carousel of the equipment in parallel with introducing the sample data inside the protocol,
- for analysis is used Oxygen of high purity, for a complete combustion of the resulting combustion gas and Helium for Nitrogen content determination.

Determination of the volatile matter content

- the empty crucibles are introduced inside the furnace at 900 ºC ± 10 ºC for about 60 minutes and after this period are put out and let to cool down for 20 minutes
- after the crucibles are cooled down it is weighed a quantity of minimum 1g ± 0.1 g of material,
- the crucibles are then inserted into the furnace for exactly 7 minutes and after this time period are let out to cool to room temperature
- after the crucibles are cooled down, are weighed again and the results are inserted into the corresponding protocol,
- through mass difference the volatile matter content is determined for the considered samples (three times determination),
- the volatile matter was corrected to dry basis by using the moisture content.

Determination of ash melting behavior - CEN/TS 15370 - Determination of ash melting behavior

For this type of determination there is used a thermal microscope – model IRF 1600 F

First, the materials have to be prepared: the ash is obtained using a combination of temperatures starting at 200 ºC in order to degas the sample, for about 20 hours, after which the temperature is increased slowly for about 1 hour to 250 ºC and another hour from 250 ºC to 300 ºC, after this step, the temperature is risen from 300 ºC to 550 ºC during a period of 6 hours and in the last period the material is let to preash at 550 ºC for about 2 hours.

After the ash is obtained, the next step is to prepare the sample.

A part of the ash is mixed with ethanol and introduced in a special device in order to obtain a small pellet which will be introduced inside the thermal microscope.

The pellet is introduced and kept inside the thermal microscope for three hours.

During this time, there can be observed the material modifications because of temperature influence. The main points of interest are: shrinking point, deformation point, hemisphere point and flow point.

At the end of the process, the materials are put out of the thermal equipment and readings are made with the help of specific software in order to determine the correct temperature values.

Thermogravimetric analysis (TGA) were performed on TG 209 F1 Libra equipment (Netzsch) under nitrogen and air atmosphere and under dynamic conditions 10 K/min from 20 to 900 °C.

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