

Amaranth (*Amarantus L.*) is a potential source of raw material for biofuels production

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Abstract. In the near future, an increased demand is expected for biomass-phytomass as an inexpensive environmentally friendly raw material source for production of renewable CO₂-neutral fuel. The search for new energy crops, which have potential yields of more than 60 tonnes of dry matter (DM) per hectare annually, as a raw material base for industrial production of different biofuels, is becoming a task of strategic importance. The chosen Amaranth species hold much promise in fulfilling these demands. This contribution deals with evaluation of specific phytomass residue as potential energy raw material and biofuel, results of laboratory measurements and analysis of solid residue by its thermo-oxidizing treatment. Chemical analyses and bomb calorimetry of Amaranth phytomass have been carried out on crop samples grown at the Slovak Agricultural University (SAU) in Nitra. High heating value (HHV) is in the range of 15.48 – 16.61 MJ.kg⁻¹d.b., and ash content varies from 10.17 to 22 % d.b.; ash analysis showed that the ash residue contains 1mg.kg⁻¹ of cadmium; 5.05 of cobalt; 11.28 mg.kg⁻¹ of copper; 4.9 mg.kg⁻¹ of nickel; 34.3 mg.kg⁻¹ of zinc. Results of the analyses have proved that this plant grown on a polluted field has a high tendency to absorb heavy metals from the soil.

Keywords: *Amaranth*, biomass characteristics, energy crops, yield, ash, heavy metals, calorific values, moisture content, polluting elements.

INTRODUCTION

Biomass generally has been taken as the only indigenous renewable energy resource capable of displacing large amounts of solid, liquid, and gaseous fossil fuels. As a widely dispersed, naturally occurring carbon resource, biomass is a logical choice as a raw material for the production of a broad range of fossil fuel substitutes.

Amaranth is a plant species with the C₄ photosynthetic pathway. These plant species are distinguished by a significantly high DM yield potential and lower quality in comparison with plant species with the C₃ photosynthetic pathway.

Amaranth is distinctive. It is known for its significantly high yield as well as quality. Some of its numerous species are becoming an increasingly important resource

for healthy food (the seeds have high nutritional value); the unprocessed biomass is used primarily as fodder in many countries but especially by Central American Indians, who were the original cultivators.

The utilization of biomass as a renewable energy source for some advanced bio-energy systems indicates, however, that biomass can be an excellent and prospective biofuel. It has become clear that current knowledge of biomass physical properties, especially of new energy crops or plants cultivated in polluted fields, is not sufficient for further optimization of industrial energy plants or domestic bio-energy units. For this reason it is necessary to explore biomass, especially new energy plant species as fed into the bio-energy system. Without this, there can be no guarantee that the biofuel will perform satisfactorily under operating conditions.

It is clear that our research on Amaranth as a potential energy crop has not included a definitive taxonomic study but it could be an important key link in future environmental protection.

Objectives:

- To study physical properties including thermal behaviour of Amaranth-phytomass as fuel;
- To determine:
 - ◆ heating value of Amaranth phytomass,
 - ◆ ash content and its chemical composition.

MATERIAL AND METHODS

1. Crop material

The crop samples of Amaranth for chemical analyses and bomb calorimetry were obtained from experimental sites of the SAU in Nitra.

The actual and potential yield of Amaranth is still being investigated for Slovak climate and soil conditions. Yields of Amaranth biomass are in the range of 50-260 tonnes of green matter (GM) (or 10-60 t of DM) per hectare and growing season, depending on the chosen plant species and location of cultivation, including soil condition.

2. Methods used for the characterisation of Amaranth-phytomass

Solid fuels: Amaranth phytomass dry matter energy value (combustion heat) was determined by means of adiabatic instrument IKA C4000 (Analysentechnik Heitersheim). Gross calorific value and heat capacity of the calorimetric system were determined by a software programme C-402, according to the DIN 51900 standard.

Biofuels: Determinations of ash content and its chemical composition, and analyses of basic properties of waste-combustion residues, were made according to the Statute of Slovak Government No. 15/1996 Digest about the treatment of waste.

3. Experimental procedures

Thermo-oxidation reactions from the given samples of Amaranth phytomass were carried out under laboratory conditions at controlled burning temperature by means of air oxygen.

The surplus that remained after oxidation samples were gravimetrically fixed and adapted for analytic fixing of the chosen elements.

The analysis consisted in the preparation of water lye with de-ionised water followed by the process of elution with solid matter in a 3% solution of nitric acid, purified for spectral analysis.

Eluates were analytically prepared and individual elements were fixed by GBC 932AB Plus AAS (AAS – ICP) methods. Mercury was fixed by mercury analyser.

The results showed that the methods are suitable for the determination of selected heavy metal contents in vegetables and grains, e.g. Amaranth.

RESULTS

Different crops are likely to have a similar calorific value per unit weight of DM [4]. In general, moisture content (MC), ash content (AC), as well as growing parameters (e.g. location, different fertilisation treatments, nutrient balance, lye, year, and others) mainly effect the calorific value of the phytomass as a potential raw material for biofuel production.

1. Calorific value of *Amaranthus cruentus* - *Giganteus*

The lower and higher heating values were determined according to DIN 51900. Data on proximate and ultimate compositions and heating values are given on a dry basis.

HH value of Amaranth DM varies from 15.5 to 17.0 MJ.kg⁻¹, low heating value (LHV) is range 13-14 MJ.kg⁻¹ at 10 % MC.

The analysis results confirm Amaranth phytomass to be a low-grade fuel in comparison with coal.

A summary of the results obtained in laboratory analyses of Amaranth phytomass as a fuel is presented in Table 1.

Thermal conversion quality is determined by many factors, including water content at harvest, and ash, alkali, Cl and N content. Limited data available shows that as a low input C₄ plant with a low water requirement, Amaranth has high ash and alkali content in comparison with a typical wood crop and a typical C₃ crop like grass species.

Table 1: Results of lab-analyses of Amaranth cruentus “Giganteus” phytomass

Fuel			Amaranth matter, 2001			Amaranth matter, 2000
Type			Inflorescence & leaves	Stems	Average	Stems
Measured value		Unit				
MC as received	Wt-r	%	11.80-19.70	12.80-20.10		14.70 - 22.40
Average MC, Ave. MC	Wt-r	%	15.75	16.45	16.10	18.60
MC in analytical sample	W-a	%	6.94	6.18	6.56	6.05
Ash content	A-d	%	15.40	10.17	12.79	13.03
Sulphur content	St-d	%	0.57	0.11	0.34	0.18
Carbon content,	C-d	%	41.00	43.50	42.25	40.00
Hydrogen content	H-d	%	5.70	6.20	5.95	5.10
Nitrogen content	N-d	%	2.50	0.80	1.65	1.20
High heating value	HHV	MJ/kg				
Analytical sample	Qs-d	MJ/kg	15.72	16.61	16.17	15.48
Low heating value	LHV	MJ/kg				
Dry matter, DM	Qi-d	MJ/kg	14.48	15.26	14.87	14.35
“as received”, Ave. MC	Qi-r	MJ/kg	11.81	12.34	12.08	11.23

Table 2: Representation of chosen elements in water lye and lye of 3 % nitric acid from solid matter after sample annealing at temperatures 800-850 °C calculation for 1 kg of solid residue - ash [mg.kg^{-1}]

No	Element	Element concentration in solid surplus		Sum [mg.kg^{-1}]	Emission limit [mg.m^{-3}]
		From water lye	From lye with 3 % NO_3		
1.	F	< 0.05	< 0.05	< 0.05	10.0
2.	Pb	< 0.10	1.25	1.25	5.0
3.	Cd	< 0.20	1.00	1.00	0.2
4.	Cr	< 0.02	2.50	2.50	5.0 (no Cr^{VI})
5.	Co	0.50	5.05	5.05	2.0
6.	Cu	< 0.30	11.28	11.28	5.0
7.	Ni	< 0.10	4.90	4.90	2.0
8.	Zn	< 0.10	34.30	34.30	5.0
9.	As	< 3.00	< 3.00	< 3.00	2.0
10.	Sb	< 0.50	< 0.50	< 0.50	5.0
11.	Sn	< 1.00	< 1.00	< 1.00	5.0
12.	Se	< 5.00	< 5.00	< 5.00	2.0
13.	Hg	0.0134	0.005	0.0184	0.2
14.	B	1.00	8.25	9.25	-
15.	Conductivity	$5.21 \mu\text{S.cm}^{-1}$	-	-	-
16.	pH	11.13	-	-	-

2. Ash analyses of Amaranth

Data regarding ash content with its chemical components is among the most important for thorough analyses and classification of potential biomass as a fuel.

3. Ash content

Another aspect of biofuel quality is mineral content. Silicon and other mineral contents are important in that they affect quantity and quality of ash, therefore these values should be clearly defined.

This parameter connected with Amaranth is not common in literature and the published values are considerably different (from 5 - 22 %). The difference is expressive and, if true, it is necessary to explore it by conducting further experiments.

Experimental findings of ash content in Amaranth phytomass:

The fixed state of Amaranth ash was carried out on five weighed air-dried samples, with material weighing from 1–5 grams, annealing at 520°C, for 48 hours. The solid matter remaining after annealing – ash was determined by gravimetric method; the gained value was 19.09 % ($S_x = 0.18$).

4. Chemical composition of ash

Ash from our experiments was used for fixing the state of individual elements, while particular attention was paid to ascertaining the presence of heavy metal, and was aimed at the following groups of elements:

1. mercury, thallium, cadmium
2. arsenic, nickel, chromium, cobalt
3. lead, copper, manganese.

These data are important in view of the proposal, respectively recommended working parameters of the technological equipment, which should use Amaranth phytomass as biofuel.

Results of the analyses were numbered according to their original solid surplus matter, which remained after the thermo-oxidation reaction and are listed in Table 2 as well as plotted by a column graph in Figure 1.

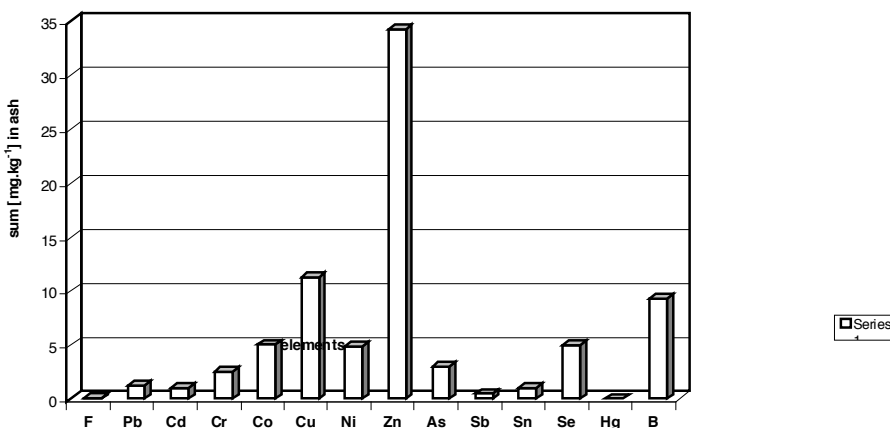


Fig. 1: Representation of chosen elements in water lye and lye of 3 % nitric acid from solid matter after sample annealing at temperatures 800-850°C calculation for 1 kg of solid residues – ash [mg.kg⁻¹].

DISCUSSION

The analyses of Amaranth samples were directed to products which arise during annealing and remain in the experimental system as solid material. The experiment itself was carried out under laboratory conditions and should be the basis for realization of larger experiments in the quarter-operating capacity. At this planned experiment, a full-fledged analysis should take place, which would be directed also to the study of gas production, which occurs during the process of thermal oxidation.

Analyses of solid matter after thermo-oxidation were made. In the case of the utilisation of parts of Amaranth for technical purposes in production of heat energy, occurrence of solid parts can be expected. These, from the point of view of evaluation of technological processes affecting environmental protection, are part of solid emissions and also solid waste, which belong within the category of dangerous waste [1, 2, 3] in waste management.

The realised measurements and analyses showed that, in solid matter after thermo-oxidation, compound elements are found which have unfavourable physiological effects in relationship to the health of human organisms. From among the elements with cancerous characteristics, cadmium (Cd) was found in solid matter (in ash) in concentration 1 mg.kg^{-1} , further chromium (Cr^{VI}), cobalt (Co) and nickel (Ni) under the laws regarding atmosphere [1] and its exacting in G SR No. 92/96 [2, 3] belong to Group 1 - polluted materials with cancerous activity; as with Cd, their content is limited by burning at 0.2 mg.m^{-3} which is also true for Cr, Co and Ni at 2 mg.m^{-3} .

Another noticeable and dangerous element was ascertainment of mercury (Hg); its concentration was found to be at the value of $13.4 \text{ }\mu\text{g.kg}^{-1}$ which is unfavourable; additionally, Cobalt and Mercury were found in parts and in water soluble form. Further observed elements protected by law in the atmosphere and waste materials are copper, lead, zinc and chromium (Cr^{III}). These elements like emissions belong to Group 3; under Group 2 polluted materials, their emission limit is fixed at 5 mg.m^{-3} in relief gas. The common concentration reaches up to 50 mg.m^{-3} in ash in the given Amaranth samples, which were cultivated in soil with a higher contamination content.

The result of the analyses, aimed at fixing concentration of chosen heavy metals in solid matter after thermo-oxidation of Amaranth phytomass, proved that this plant has a tendency to absorb some heavy metals from the surrounding soil. Due to their physiological activity heavy metals are dangerous for living organisms.

These results were confirmed by independent measuring carried out at the Department of Gardening AF - SAU in Nitra. The content of heavy metals was observed under two pedological conditions: in garden earth and in contaminated soil from the region of Rudnan [5]. Cultivation was compared also with green lettuce for eating. These experiments and results showed that Amaranth can be listed among plants which have a greater ability to accumulate up to 103 times more Pb, 240 times more Cd and 5.9 times more Hg. However, the presence of contamination in seeds was low and was within the norm in all tests. This is important especially when considering the use of Amaranth seeds in the food industry. The ability of Amaranth to accumulate heavy metal has not been evaluated in other Slovak and foreign literature.

Equal success can be evaluated for growing Amaranth in regions with burnt fuel containing oxides of sulphur. Tests with Amaranth were carried out on land near a chemical factory, where ammonium sulphate is produced. Their results showed that the growing of Amaranth is suitable under these conditions [6].

CONCLUSIONS

- Amaranth could prove to be a very attractive biomass-phytomass source because of its high yield under marginal conditions.
- The Amaranth agro-environmental system is a key link in the sustainable production of agriculture. It will play an important role as a raw material source for industrial biofuel production as well as for environmental protection in this century.
- Energy generated from Amaranth-based biofuel has a potential to reduce greenhouse gas (CO₂) emissions and to decrease dependence on diminishing supplies of fossil fuels.
- Thermal conversion quality is determined by many factors, including water content at harvest, and ash, alkali, Cl and N content.
- HH value of Amaranth DM varies from 15.5 - 17.0 MJ.kg⁻¹, LH value is range 13 – 14 MJ.kg⁻¹ at 10 % MC.
- Limited data available shows that as a low input C₄ plant with a low water requirement, Amaranth has high ash and alkali content in comparison with a typical wood crop and a typical C₃ crop such as grass species.
- Ash content of the investigated Amaranth species varies from 12-22%; in reality it is influenced by the soil in which the plant was growing or cultivated.
- At present the economic viability is still uncertain, as is the case for all biomass crops.
- It will be necessary to exploit the multifunctional uses of Amaranth crop species to increase the value per area of land and/or per tonne of biomass-phytomass.
- Many successful applications in food production, in industrial as well as the energy sector of Amaranth show promise, though research still remains to be carried out.

These are the main reasons for increasing interest in exploring phytomass quality of different Amaranth species, especially giant Amaranth, and to receive their definitive taxonomic studies. Giant Amaranth species e.g. *Amaranthus Australis L.* or *Amaranthus Cruentus L.* is one of the main crops being considered as a source of raw material for solid biomass-based production processes to acquire one of its main products – high quality biofuel.

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