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Mineral composition and ash content of six major energy crops

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ABSTRACT

The chemical composition of biofuels has not received adequate attention given that it is an important aspect in the introduction of energy crops. In this study, the ash content and mineral composition (C, N, Al, Ca, Cl, Fe, K, Mg, Na, P, S, Si) of stems, leaves and reproductive organs of some promising energy crops were determined and compared with the respective recommended thresholds reported in literature. Overall, cynara exhibited the highest ash and mineral contents, which indicate high slagging, fouling and corrosion tendencies. However, cynara also showed the lowest Si content, both in leaves ($4.3\,g\,kg^{-1}$) and in stems ($0.9\,g\,kg^{-1}$).

Sweet sorghum and giant reed exhibited the highest N content (up to $16\,g\,kg^{-1}$), which greatly exceeded the recommended limits in leaves. Importantly, Cl always exceeded the recommended limits (up to $18\,mg\,kg^{-1}$ in cynara), both in stems and in leaves, thus resulting in a major stumbling block for all crops. Several significant correlations among elements were found at a single plant part; conversely these correlations were generally very weak considering different plant components, with the exception of K ($r = 0.91^{**}$), P ($r = 0.94^{**}$) and ashes ($r = 0.64^{**}$). Generally, leaves resulted in a significant deterioration of biofuel quality when compared with stems and flower heads. Therefore, agricultural strategies aimed at reducing the leaf component (e.g. by delaying the harvest) may considerably improve the suitability of biofuels for current combustion plants.

1. Introduction

The development of energy crops is a central aim of the European Commission's energy policy [1], with million hectares being expected to be allocated to dedicated energy crops in the short term. So far, much effort has been addressed to evaluate the potential yield of dedicated crops [2–5], while the quality of biofuels have not received as much attention [6,7]. Biomass quality can drastically lower the net energy output, both limiting the effectiveness of conversion plants [7] and decreasing the heating value. 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 $0.2\,MJ\,kg^{-1}$ [8]. Furthermore, ashes and inorganic elements (e.g. alkali) produced during combustion may cause a number of serious problems to power plants through slagging, corrosion and fouling. The basic mechanisms of these processes have been investigated and are now reasonably well understood [9]. Fouling is generally defined as the accumulation of unwanted materials on the surfaces of processing equipment leading to a decrease in the exchanger efficiency; slagging is related to the low melting point of deposits, which causes the formation of a glassy layer that must be removed. Finally, corrosion is caused by the interaction between deposits and metal surface of the exchanger, which involves extra costs in maintenance,

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whilst significantly decreasing the plant life-span [10]. Importantly, the degree of fouling, slagging and corrosion is strictly dependent on ashes and minerals released during combustion [7], a process that substantially depends on biomass characteristics [5,11]. Therefore, classifying crops on the basis of their mineral composition is needed to evaluate their suitability for different conversion processes and to understand which technological properties of the conversion plants should be modified for a given biofuel. For example, it is well known that during combustion, the volatile elements such as S and Cl can form sub-micron particles condensing as salts [12] that, in the presence of high temperatures and K and Si, may lead the sticky deposit to grow-up rapidly [13]. Energy crops are generally rich in K and Si, the first representing about 1% of the biomass dry weight, almost all potentially vaporizing during combustion. Because of the high melting point (1700 °C), Si would not be a problem in itself, but in the presence of K or Ca, Si easily reacts with them forming alkali silicates of much lower melting points (about 700 °C) [12]. Again, P can also increase the slagging potential of deposits [12], while other alkali elements such as Na, Mg or salts like chlorides, carbonates and sulfides, easily form eutectics, a mixture of two or more solid phases that lowers the melting point.

Because of the influence on slagging, the ratios between K, Ca and Si should be also taken into account in evaluating biofuel quality. For example, Reumerman and Van den Berg [10] showed miscanthus biomass as having high Si/K and Ca/K ratios, which contributed to a lower slagging tendency. It follows that, irrespective of yield levels, biofuels containing high Si and Ca, along with a low K, should be better suited to energy end-use. Nonetheless, raw materials are also rather rich in Cl, a major factor in deposit formation, which may react with K and form primary fouling compounds. Again, Cl has a role in transporting alkali to surfaces, thus contributing to the corrosion of tubes of power plants and heat exchangers [12,13].

The high variability in ash and mineral content among dedicated crops can be considerable as it depends on genetic and environmental factors [14] as well as physiological and morphological differences among crops [2,15]. There is an urgent need to understand how biomass quality changes with crop and biomass partition. For example, leaves are generally much richer in ash than reproductive organs and stems, in the order [15,16]. Since biomass partitioning in a standing drying crop may drastically change depending on crops, phenological stage and agricultural strategies [2], understanding ash and mineral compositions of different organs may be very helpful in assessing the best harvest time. Therefore, in this research six major energy crops (two annuals and four perennials) were characterized in terms of mineral composition and ash content at different plant organs, and compared with the recommended thresholds of mineral concentration for current boilers.

2. Materials and methods

2.1. Plant material

Four perennial (*Miscanthus sinensis X Giganteus* Greef & Deuter, *Arundo donax* L., *Cynara cardunculus* L. and *Panicum virgatum* L.) and two annual (sweet and fibre sorghum, *Sorghum bicolor* Moench) crops were characterized in terms of mineral composition and ash content, at different plant organs: leaves, stems and reproductive organs (capitula for cynara and panicula for sorghum). In addition, two row-distances (20 and 80 cm) were compared for switchgrass (*Panicum v.*). The biomass samples of perennial crops refer to a 4-year-old plant, as biomass composition was found to significantly change from young (1 or 2 years old) to mature plants (unpublished data).

The six crops were arranged according to completely randomized blocks with four replications (about 400 m^2 each), in a flat field at the experimental farm of Bologna University (44°33′N, 33 m a.s.l.). The main soil physical and chemical characteristics are presented in Table 1.

The most conventional agricultural practice was adopted for each crop. During seedbed preparation, plots were fertilized with 31 kg ha^{-1} of P, while K was not supplied, soil being rich in this element. A dose of 100 kg ha^{-1} of N (urea) was applied about 20 days after emergence/re-growth to all crops. Plots were kept free of weeds until sown or planting. From the second year onwards, weed control was no longer needed for perennial crops.

Switchgrass and sorghum were sown in late April using a mechanical drill-machine (Vignoli s.r.l.); cynara was sown manually, and giant reed (*Arundo d.*) and miscanthus were hand-planted in early May by placing rhizomes into 150 cm row-spaced furrows. The average plant density was 13 plants m^{-2} for sweet and fibre sorghum, 2 plants m^{-2} for miscanthus, 1 plants m^{-2} for giant reed, 168 (20 cm row distance) and 62 (80 cm row distance) plants m^{-2} for switchgrass, and 4 plants m^{-2} for cynara.

For all the crops, irrigation and chemical products against pests and disease were never necessary. All crops were hand-harvested in a sampling area of 9 m^2. The annual crops and cynara were harvested in September, while the others after the winter frost. After the harvest, a sub-sample of each replication (about 500 g each) was divided into leaves, stems and reproductive organs (capitula and panicula for cynara

Table 1 – Main physical and chemical characteristics of the soil

Parameters	Units	Methods	Values
Sand	g kg^{-1}	Bojoucos	270
Silt	g kg^{-1}	Bojoucos	390
Clay	g kg^{-1}	Bojoucos	340
pH		H_2O	7.2
SEC		meq 100 g^{-1}	48.2
Organic matter	g kg^{-1}	Walkey–Black	18
Total N	μg g^{-1}	Kjeldahl	1196
P-avail.	μg g^{-1}	Olsen	20
K-exch.	μg g^{-1}	$BaCl_2$+tea	265
Ca-exch.	μg g^{-1}	$BaCl_2$+tea	4592
S	μg g^{-1}	Sulphate	125
Mg-exch.	μg g^{-1}	$BaCl_2$+tea	368
Na	μg g^{-1}	$BaCl_2$+tea	48