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Identification of different woody biomass for energy purpose by means of Soft Independent Modeling of Class Analogy applied to thermogravimetric analysis

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ABSTRACT

In the renewable energy production solid biomass has became one of the most important source for power and heat generation, in particular woody materials in the form of wood chips, pellet and briquette. Technical standards on solid biofuels require information about origin and source of the biomass, differentiating for example between coniferous and broadleaf. In this work different wood samples were classified employing a method based on thermogravimetric analysis followed by Principal Component Analysis and Soft Independent Modeling of Class Analogy as supervised pattern recognition method.

The best results were obtained considering the temperature range between 200 and 300 °C, corresponding to hemicellulose degradation. The method results very efficient (100% recognition) at identifying between hardwood and softwood. Nevertheless it shows a good potential to classify single species. This method can be used to assess the quality of solid biofuels with respect to the requirements defined by the specific technical standards.

1. Introduction

Renewable energy production can help countries meet their sustainable development targets. Solid biomass has became one of the most important renewable source for power and heat generation, in particular woody materials in the form of wood chips, pellet and briquette. These biofuels are currently incentivized in many European countries [1] and their quality is important because affecting the combustion behavior and related emissions [2]. Technical standards on solid biofuels (EN 14961-1 [3], recently superseded by EN ISO 17225-1 [4]) classify solid biofuels also on the basis of their origin and sources, differentiating for example between coniferous and broadleaf. Many pellet producers claim on the bag's label the type of wood used, because this can represent a choice factor for the customers. Wood typology identification in these biofuels is difficult since wood is unstructured and the evaluation cannot be made on the basis of macroscopic characteristics (e.g. color, odor, density, grain pattern). Other analytical techniques can be performed to identify the wood such as microscopy techniques and chemical analysis [5], but are time- and money-consuming and skilled operators are required. It is therefore important to define a cheaper and more quicker analysis for wood classification.

Many works on wood identification that using alternative analytical techniques can be found in literature, most of which based on image and spectrum analyses. Gurau [6], for example, has used an imaging analysis method coupled with a microscope to identify different species of wood by quantifying their anatomical structures. An automatic wood recognition method based on image processing and artificial neural network was designed by Khalid et al. [7] to recognize species of tropical Malaysian woods.

The infrared spectroscopic technique was broadly employed in wood sector, almost always in combination with multivariate analysis, also for classification purpose. Chen et al. [8] have effectively classified between hardwood and softwood woody samples by means of FTIR (Fourier Transform Infrared) spectroscopy using PCA (Principal Component Analysis) and HCA (Hierarchical Cluster Analysis). Some authors [9,10] have used a similar approach to identify species hard to be distinguished.

The thermal behavior of wood in inert atmosphere depends on degradation of its three main constituent that are: hemicellulose,

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cellulose and lignin [11]. These three compounds, as highlighted in other works [12,13], show different ranges of thermal degradations as a result of different chemical compositions and structures: hemicellulose, which has amorphous and branched structure, decomposes first at low temperatures (around 220 ÷ 315 °C [13]), while cellulose exhibits a more thermal resistance with a sharper degradation range (around 315 ÷ 400 °C [13]). Last, the decomposition of the lignin happens in a very broad range (200 ÷ 500 °C) but with a reduced volatilization with respect to the other two compounds [12–14]. The proportion among wood components as well as their chemical (lignin and hemicellulose compositions [15,16]) and structural properties affect the thermal behavior of the wood making it characteristic. In addition, the presence of extractives, non structural substances composed by low molecular weight organic compounds, i.e. lipids, phenolic compounds, terpenoids, fatty acids, resin acids and waxes [17,18], can modify the thermal behavior of the wood, mainly at low temperature as observed by other author [19].

For this reason, the TGA (Thermogravimetric Analysis) provides useful information for wood identification purpose even if at the present not many works can be found in literature. A classification of different species of wood by means of thermogravimetric curves and using nonparametric functional discriminant technique was performed by Tarrìo-Saavedra et al. [5] which have obtained good results for species classification and for the distinction of hardwood – softwood – tropical. Multivariate statistical supervised classification methods such as LDA (Linear Discriminant Analysis), *k*-NN (*k* Nearest Neighbors), NBC (Naïve Bayes), NN (Neural Networks) and SVM (Support Vector Machines), have been tested by Francisco-Fernández et al. [20] demonstrating that wood species classification is possible by applying these supervised classification techniques to the thermogravimetric curves.

According to the authors, another multivariate statistical supervised classification method suited for wood classification with TGA is the SIMCA (Soft Independent Modeling of Class Analogy) and, to our knowledge, no work can be found in literature.

The SIMCA, first introduced by Wold [21], is a multivariate method for supervised classification based on the comparison between an unknown sample and previously defined class models, or SIMCA boxes, built on principal components for each class individually and the classification is made evaluating the interclass distance between sample and models [22]. Basically, a PCA model is constructed for each known class and then a multidimensional space, or hyper-box, is defined selecting the suitable confidence limits. Unknown samples which fall inside an hyper-box are classified, with a certain probability, in that class. With SIMCA classification a sample can be classified as a member of one or more classes as well as associated with no class [23].

This supervised pattern recognition method coupled with GC–MS or IR techniques has been successfully applied in several fields such as petroleum product quality [24,25], pharmaceutical [26], food [27,28] as well as in wood classification [29,30].

In this study, thirty samples of different wood species were analyzed by TGA. The Principal Component Analysis was applied on second derivatives of thermogram in order to identify the temperature range associated with the best separation between hardwood and softwood groups and then SIMCA was evaluated as supervised pattern recognition method on it.

2. Material and methods

2.1. Sample preparation

In this study, eighteen different hardwoods and twelve softwoods, reported in Table 1, have been collected and analyzed.

Table 1
List of wood samples analyzed.

Hardwood (n = 18)	Softwood (n = 12)
Turkey oak (*Quercus cerris*) A – Tur_A	Larch (*Larix decidua*) A – Lar_A
Turkey oak (*Quercus cerris*)B – Tur_B	Larch (*Larix decidua*) B – Lar_B
Durmast oak (*Quercus petraea*) A – Dur_A	Larch (*Larix decidua*) C – Lar_C
Durmast oak (*Quercus petraea*) B – Dur_B	Larch (*Larix decidua*) D – Lar_D
Beech (*Fagus sylvatica*) A – Be_A	Silver fir (*Abies alba*) A – Sil_A
Beech (*Fagus sylvatica*) B – Be_B	Silver fir (*Abies alba*) B – Sil_B
Beech (*Fagus sylvatica*) C – Be_C	Silver fir (*Abies alba*) C – Sil_C
Chestnut (*Castanea sativa*) A – Ch_A	Aleppo Pine (*Pinus halepensis*) – APin
Chestnut (*Castanea sativa*) B – Ch_B	Pine (*Pinus sylvestris*) A – Pin_A
Chestnut (*Castanea sativa*) C – Ch_C	Pine (*Pinus sylvestris*) B – Pin_B
Chestnut (*Castanea sativa*) D – Ch_D	Pine (*Pinus sylvestris*) C – Pin_C
Ash (*Fraxinus ornus*) A – As_A	Monterey cypress (*Cupressus macrocarpa*) – Cyp
Ash (*Fraxinus ornus*)B – As_B	
Eastern black walnut (*Juglans nigra*) – BWal	
Walnut (*Juglans regia*) – Wal	
Maple (*Acer campestre*) – Map	
Alder (*Alnus glutinosa*) – Ald	
Huckberry (*Ulmus laevis*)- Huc	

Besides the common dedicated-wood species for biofuel pellet production in Europe (e.g. Beech, Silver Fir), typical woods species from furniture sector have been selected for the data set in order to enhance the robustness of the classification method. Furthermore, joinery and sawmill residues like sawdust and wood shavings of different origin can be used to produce biofuel pellet as well. The samples were obtained from whole pieces of wood with well known origin, like beams or boards from sawmills and debarked tree log disks wood slices. All the samples were initially reduced in smaller pieces then were grinded by means of a cutting mill (mod. SM 2000, RETSCH) and the particles size between 0.25 and 0.50 mm was selected for TGA. All samples were stored in plastic container until analysis.

2.2. Thermal analysis

A thermogravimetric analyzer (mod. STA PT1600, LINSEIS) was employed to perform the thermogravimetric tests: a small amount of wood (around 10 mg) was placed in an alumina crucible and heated in inert atmosphere. During the whole test the loss weight was recorded against time or temperature (1 point per second) to return a function called thermogram (TG). According to Grønli [31] the heating program was set with an initial drying step, consisting in an heating rate of 30 °C min^{-1} up to 110 °C with an holding time of 30 min, and followed by a non-isothermal heating of 5 °C min^{-1} up to 700 °C. The initial drying step of woody samples was necessary to compare the thermal behavior of dried samples. Small sample masses and low heating rate were chosen in order to reduce mass and heat transfer limitation as reported by other authors [32]. Nitrogen was used during the analysis at a flow rate of 100 cm^3 min^{-1} to maintain an inert environment during the whole test. To eliminate the buoyancy effect from TG signal a thermogravimetric test was performed at the same conditions of the samples but without material in crucible and the signal was subtracted from all TGs.

2.3. Multivariate data analyses

All TGs collected were elaborated before performing the multivariate data analysis. As a first step, for each TG, the portion associated to water loss was excluded and the range between