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Research paper

Development and validation of a fast method based on infrared spectroscopy for biochar quality assessment

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ABSTRACT

New analytical tools that enable analytical laboratories to quantitatively and qualitatively analyze alternative and renewable solid biofuels are needed. Fourier transform infrared (FTIR) spectroscopy was applied in combination with a two-step multivariate modelling procedure. In the first instance, a C&RT (classification and regression trees) model was developed and validated for use in distinguishing different biomass origins and possible sources of contamination. Once the solid fuels were correctly identified, the model was used to predict the concentrations of individual components using partial least squares regression (PLSR) models. The first C&RT model differentiated between the different classes of biofuel origins. Using the absorption intensity in the wavenumber range of 1800–400 cm^{-1}, the prediction had a recovery of between 92% and 99%. The second C&RT model differentiated between the possible sources of contamination, which could be predicted with a recovery between 76% and 91% based on the FTIR results. Accuracy profiles based on the analysis results of validation samples were then calculated to prove the reliability of the developed regression models. The developed spectroscopic methods rapidly and adequately determined (qualitative analysis) the origin of the biofuels and indicated the possible source of contamination. The effects of two spectral data pre-processing methods (PQN & SNV) were also compared based on the accuracy of the developed models.

1. Introduction

Non-food biomass crops offer a sustainable source of energy and platform chemicals. Most of the energy stored in the crop biomass is in the cell wall, which constitutes the largest fraction of lignocellulosic biomass [1]. Lignocellulosic biomass has been recognized as an alternative source material for the production of chemicals and fuels because it is renewable and could reduce greenhouse gas emissions by replacing petroleum sources. The major components of lignocellulosic biomass are cellulose, hemicellulose, and lignin. The three polymers that compose the cell wall of plants (cellulose, hemicellulose and lignin) rank amongst the most abundant biopolymers on the planet, and their proportional concentrations range between 40 and 50%, 10–40% and 5–30% of the total biomass by weight, respectively. The absolute and relative concentrations of the components of the cell wall have a great influence on biomass quality, i.e., its suitability for conversion to heat, power and chemical products [1,2]. Cellulose and hemicellulose are polysaccharides, which can be hydrolyzed to molecules with a relatively low degree of polymerization for further biological/chemical utilization. The next generation of cellulosic ethanol is being developed from these polysaccharides via microbial fermentation. Lignin, a phenolic polymer, is also an important source material for industrial applications such as the production of adhesive resin. Additionally, lignin and cellulose are being developed for the synthesis of biodegradable polymers [3].

The biomass and fuels obtained using various methods of biomass conversion are valuable alternative source materials for power and heat generation and the synthesis of valuable chemical products. Biomass is currently used in power plants, but its use in power and heat generation is associated with certain technological problems. As a material (physically), biomass is radically different from hard coal or lignite and creates other problems during its preparation for combustion in existing installations compared to the use of coal. Raw biomass is characterized by a wide range of moisture contents and must be dried to obtain a homogenous moisture content prior to shredding [4,5].

These thermochemical processes demand feedstocks with low moisture contents and high energy densities, often equated with high levels of the polyaromatic polymer lignin [1,2,6]. This material has more appropriate physical characteristics and can be directly used for combustion and co-combustion with alternative fuels. Unfortunately, technological problems are not the only challenge to freely using thermally upgraded biomass; problems also exist regarding the legal

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regulations of the European Union and the regulations of the member states. An important question is how to determine what type of biomass fuel has been processed and to ensure that it does not contain additives that are not biodegradable to a greater extent than substances of natural origin (biomass). These considerations and previously conducted research [4,7–11] have motivated the development of appropriate models that can be applied as standard analytical methods in laboratory systems. The first works in this area involved proximate and ultimate analyses of the fuels and the chemical composition of their ash; therefore, in the present study, Fourier transform infrared spectroscopy (FTIR) was applied to develop and validate a fast method for biochar quality assessment.

Fourier transform infrared (FTIR) spectroscopy is a type of molecular vibrational spectroscopy that detects the absorbance of chemical functional groups in different regions between 4000 and 400 cm^{-1}. The three main cell components, i.e., lipids, proteins, and carbohydrates, have characteristic absorbance bands in different frequency regions of the mid-infrared spectrum, giving FTIR the potential to be an effective tool for monitoring biomass composition [12]. FTIR spectroscopy, in combination with multivariate analysis, enables the analysis of biomass samples without time-consuming sample preparation. Over many years, infrared spectroscopy has become a widely used method for studying the structure of coal, producing quantitative and qualitative descriptions of the structure of carbonaceous materials [13]. In recent years, the quantitative accuracy of infrared spectral peaks has increased as a result of the rapid development of peak separation processes for overlapping bands [13]. FTIR is currently one of the most powerful techniques for the characterization of coal [14] and can be used to investigate the contributions of various functional groups.

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was first applied to coal investigation in 1978 by Fuller and Griffiths [15]. Currently, this technique is commonly applied to characterize coal blends [16], coal macerals [17,18] and the oxidation of coal and carbon materials [19–21].

DRIFT spectroscopy can provide both chemical and structural information for all types of solid surfaces. When infrared radiation reaches a sample surface, one or several processes can occur: light can be absorbed, reflected from the surface, or penetrate the sample before being scattered. If scattering centers are randomly oriented, the phenomenon is isotropic and generates a diffuse reflectance. The scattered light is then collected and relayed to the IR detector, where the absorption by chemical groups is revealed. DRIFT spectrometry has many advantages over the conventional transmission (or reflection) FTIR method: DRIFT is fast and non-destructive and is better suited to the analysis of strongly absorbing materials [22].

The increasing use of chemometrics in environmental studies over the last two decades reflects the intensive research devoted to testing and proving the power of data processing techniques in this field [1]:

- quantitative chemical analysis,
- monitoring for environmental quality assessment, and
- modelling and prediction of toxicological effects.

Chemometric methods can be used to analyze different groups of materials, such as microalgae (lipid content determination) [12,23], slugs [28,34,45], woods [24–31], biomass chars [7–11], foods [32,33], pharmaceutical materials [35] and organic pollutants [36,44].

Partial least squares regression (PLSR) is a very versatile method for multivariate data analysis and a number of applications, including chemometrics. PLSR is a supervised method that specifically addresses multivariate problems [37] and has many applications [43,46] for the quantitative analysis of complex mixtures. PLSR is commonly used to extract orthogonal factors (latent variables), which are linear combinations of the spectral variables (FT-IR in this case) that account for as much of the manifest factor variation as possible while adequately modelling the response analytes [38]. The number of latent variables determines the polynomial model. This method is used in various applications, including the determination of biomass and polypropylene in wood plastic composites [39,40], the prediction and modelling of lignin and energy contents in biomass [41], and other biomass building blocks [42].

Some researchers have focused on describing material characteristics using a mathematical algorithm. This algorithm can then be applied to quantitatively describe the phenomenon or deterministic models (classification), whose task is to determine the nature or origin of the phenomenon (e.g., compounds of anthropogenic or natural origin in the tested materials).

Several chemometric methods can be used to develop a classification model:

- LDA – linear discriminant analysis,
- QDA – quadratic discriminant analysis,
- PLS-DA – least squares discriminant analysis,
- SIMCA – soft independent modelling by class analogy, and
- C&RT – classification and regression tree method.

The choice of classification method depends on several factors, i.e., the data quantity, data dimensionality and data class. Many frequent classification problems are difficult to solve using linear methods. An increasing variety of environmental science fields, including environmental protection and medicine, utilize analysis based on classification trees to gain more recognition. C&RTs are used in the

- determination of the origin of food products [41,48],
- classification of biomass relative to the directions of its use [10],
- determination of the specific origin of a disease entity [47], and
- classification of the quality and origin of agricultural products [49–55].

Due to practical considerations, the C&RT method, which is based on the rules of classical logic, was chosen as the research classifier. This method allows for the building and use of an intuitive classifier, which is relatively simple to implement in computer software.

Multivariate calibration methods focus on the establishment and application of mathematical models that relate multivariate instrumental signals with sample properties. In univariate calibration, a single numerical value per sample is recorded and analyzed, whereas multivariate calibration works with increasingly complex data arrays per sample and allows analytical quantitative estimations in multicomponent systems that lack selectivity [1].

The main goal of this article is to introduce a multivariate model based on FT-IR that was developed to recognize the biomass origin of biochar. The tested biochar was produced in 100% from biomass without unbiodegradable contaminants. This biofuel, which was obtained under a thermal conversion process, was similar between various samples. It is difficult to predict the polymer concentration in this material because the polymer may degrade under the processing temperature and leave no trace in the product. To address this challenge, two models were developed in addition to the models described above. The first model was used to determine the temperature of thermal conversion at which the biochar was prepared. The second model was used to determine the percentage of contaminants in the tested biochar (if any). These models provide new, urgently needed tools for confirming biochar quality.

2. Materials and methods

2.1. Materials

Three lignin-rich materials (wood biomass, straw biomass, and waste furniture - Fig. 1) were used to prepare the biochar samples. All materials were subjected to a drying process in a laboratory dryer at 105 °C until a moisture content (W_t^r) of 2–3% was obtained. Next, the