An Analytical Chemist's View of Lignocellulosic Biomass

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Lignocellulosic biomass comprises wood and agricultural residues, which are sources of cellulose, hemicellulose, and lignin (the lignocellulosic fractions), and represents the major biomass source. Each of these types of lignocellulosic fractions has its own particular structural characteristics and chemistry, which can be exploited in chemical analyses. For a general approach, the quality of the biomass used determines the product quality. Therefore, reliable information is required about the chemical composition of the biomass to establish the best use (*e.g.*, most suitable conversion process and its conditions), which will influence harvest and preparation steps. Then, analytical chemistry is required to understand and control these processes, their raw materials, products, and residues.

Keywords: Lignocellulosic biomass; Analytical chemistry; Analytical techniques; Renewable chemistry

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Lignocellulosic Biomass and Its Usages

The estimated worldwide production of renewable biomass for use in biofuels, fibers, and agriculture is currently 210.7 x 10^6 tons per year. An exact value is difficult to obtain because there is a large variation in production between countries. However, the importance of biomass to the modern economy is clear. Lignocellulosic biomass comprises wood and agricultural residues, which are sources of cellulose, hemicellulose, and lignin (the lignocellulosic fractions), and represents the major biomass source; since plants can contain high amounts of lignin (18% to 35% w/w), cellulose (40% to 50% w/w), and hemicellulose (10% to 35% w/w), lignocellulosic biomass are considered as one of the most promising sources of industrial raw material. Each of these types of lignocellulosic fractions has its own particular structural characteristics and chemistry, which can be exploited in chemical analyses.

The biorefinery concept is an important strategy in the development of biomass usage and is based on the concept of a productive biomass chain similar to the petrochemical chain: fuels, energy, materials, bulk chemicals, and fine chemicals. Biorefineries use a large number of conversion processes (chemical, biochemical, and thermochemical) as a result of the chemical diversity of biomass and the high content of oxygen and water; analytical chemistry is required to understand and control these processes, their raw materials, products, and residues. The increase in the demand for bio-derived chemicals not only offers a great number of opportunities for green technologies and processes which use lignocellulosic biomass in biorefineries, based on the green chemistry principles, but it also presents several challenges related to market prices and replacement of non-renewable products (*e.g.*, petrochemicals) for a renewable chemistry.

Analytical Techniques and their Application

For a general approach, the quality of the biomass used determines the product quality. Therefore, reliable information is required about the chemical composition of the biomass to establish the best use (*e.g*., most suitable conversion process and its conditions), which will influence harvest and preparation steps. Conversion processes should be monitored for their yield, integrity, safety, and environmental impact. Effluent or residues should be monitored and analyzed for environmental control. Co-products need to be monitored to avoid interference with the product yield and product purity; however, co-products are also a good opportunity to add value to the biomass chain. Finally, products need to be monitored and analyzed to determine their yields and purity and to ensure their quality. A recent review summarizes the main techniques and their application for the analysis of biomass and its products (Vaz Jr. 2014).

The most widely used analytical techniques for lignocellulosic biomass and products are briefly described below:

- *Gravimetry* - determination of water content, by means of drying and weighing the material. Gravimetry can be applied for feedstock and product quality control;
- *Thermal analysis* - determining the water content and ash, loss of mass for constituents *versus* temperature, thermal stability, among other parameters associated with temperature effects on the material: thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) can be applied for processes, feedstock, and products;
- *Chromatography (liquid and gas)* - identification and quantification of organic compounds (volatile, semi-volatile, and nonvolatile) and inorganic, polar, and nonpolar, such as sugars from cellulose and hemicellulose, and their products of conversion processes: high performance liquid chromatography (HPLC) or ultra-high performance liquid chromatography (UPLC) with refractive index, ultraviolet–visible, diode array, fluorescence, mass spectrometry, and light scattering detectors; gas chromatography (CG) with flame ionization, thermal conductivity, electron conductivity, and mass spectrometry detectors can be applied for feedstock, processes monitoring, and quality control of products;
- *Spectroscopy and spectrometry* - identification and quantification of organic and inorganic compounds or materials, polar and nonpolar, such as metals and by-products, by means of radiation interaction or radiation production: nuclear magnetic resonance, Fourier transform infrared, X-ray diffractometry and fluorescence, ultraviolet and visible spectrophotometry, atomic absorption spectrometry (AAS), optical emission spectrometry can be applied for feedstock, process monitoring, and quality control of products;
- *Mass spectrometry* - identification and quantification of organic compounds, by means of molecular fragmentation - can be applied for process monitoring, to verify the product purity, and for metabolic engineering approaches of plants to improve fractions content (e.g., cellulose);
- *Microscopy* (e.g., scanning electron microscopy, transmission electron microscopy, and atomic force microscopy) - observation of surface atomic

composition and disposition of biomass components (morphology) - are frequently used for lignocellulosic polymers (*e.g.*, cellulose).

Conclusion

From the viewpoint of an analytical chemist, chemical analyses of lignocellulosic biomass can provide information about its constitution for feedstock usage in conversion processes, and information about its products, by-products (or co-products), and residues. Then, analytical chemistry as part of chemical sciences can contribute to a bioeconomy based on biomass use instead of non-renewable raw sources, as the oil, and an advance in biomass knowledge to develop the best uses of each source material.

Reference Cited

Vaz Jr., S. (2014) "Analytical techniques for the chemical analysis of plant biomass and biomass products," *Analytical Methods* 6, 8094-8105.

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