Chapter 1

The Use of Analytical Chemistry to Understand Biomass

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Abstract Modern chemistry plays a strong economic role in industrial activities based on biomass, with an increasing trend in the importance of its application from the deployment of biorefineries and the principles of green chemistry, which make use of the potential of biomass with decreasing negative environmental impact. In this context, analytical chemistry can contribute significantly to the biomass supply chains, be they of plant or animal origin, but with the first offering the greatest challenges and the greatest opportunity for technical and scientific advances, given its diversified chemical constitution. This chapter presents a general outlook on the application of analytical chemistry to understand biomass composition and to promote its usages.

Keywords Biomass constitution • Chemical analysis • Instrumental analysis

1.1 Introduction

The use of biomass by humans goes back to the principles of humanity, where it was used as a heat source, food, fiber, and various items, such as weapons. With the development of societies, biomass was in great demand and uncontrolled use of this natural resource led to massive deforestation of native forests in almost every continent of the globe, to a greater or lesser extent. On the other hand, agriculture also developed, leading to an increase in the production and productivity of crops, especially for human and animal consumption.

From the mid-20th century, there was a "boom" of consumer society based on petroleum derivatives, which is a nonrenewable source and highly polluting raw material; this might be noticed by the large amount of produced plastic products.

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However, the same society began to notice that oil is a finite source, with serious problems observed in several producing countries, such as political and social instability, wars, and environmental disasters.

Modern chemistry plays a strong economic role in industrial activities based on biomass, with an increasing trend in the importance of its application from the deployment of biorefineries and the principles of green chemistry, which make use of the potential of biomass with decreasing negative environmental impact. In this context, analytical chemistry can contribute significantly to the biomass supply chains, be they of plant or animal origin, but the first offers the greatest challenges and the greatest opportunity for technical and scientific advances, given its diversified chemical constitution. It is worth mentioning that chemical analysis is used to examine the composition, for the characterization of physical

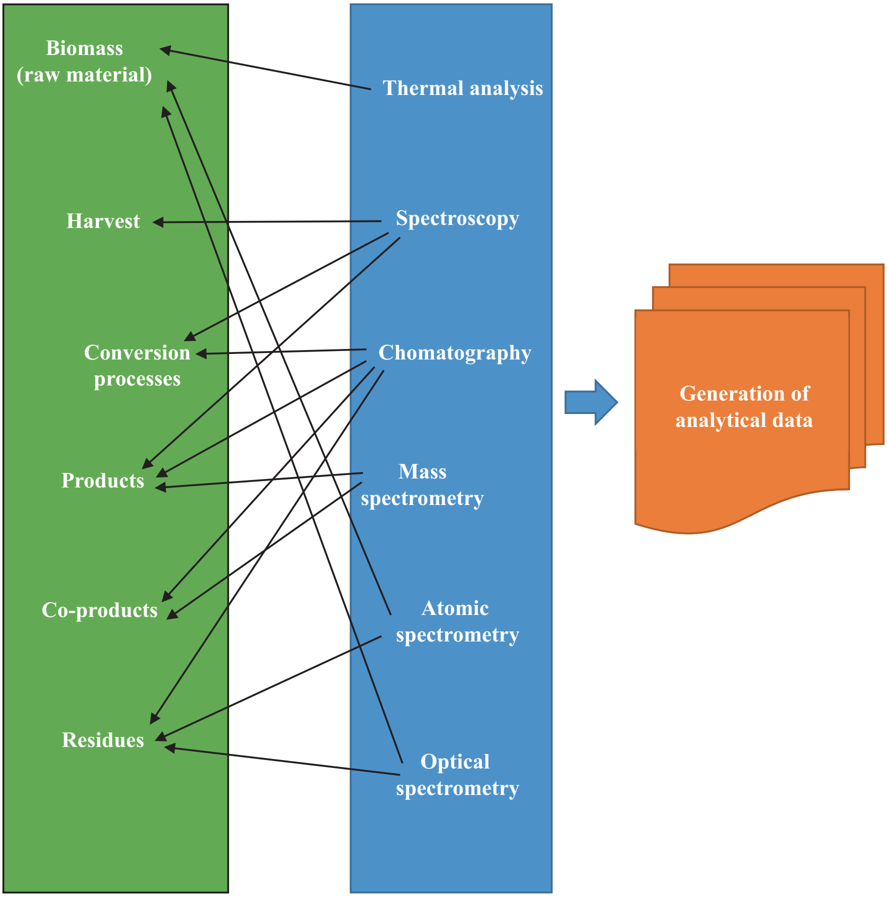


Fig. 1.1 A flowchart of the relationship between components of a biomass chain and chemical analyses to generate analytical data. This relationship is a proposal of use and other combinations can be established according to physicochemical properties, economic aspects, and equipment availability

and chemical properties, and for determining the concentration of chemical species of interest. Figure 1.1 shows, in a simplified way, components of an economic chain from biomass and the application of analytical techniques.

This chapter presents a general outlook on the application of analytical chemistry in order to understand biomass composition and to promote its usages.

1.2 Plant Biomass Diversity and Composition

According to data from the Food and Agriculture Organization of the United Nations (UN FAO), global biomass production for agri-industrial usages has reached 1,558.5 Gtons, with a huge contribution to the bioeconomy; it comprises cereals, oil crops, roots and tubers, vegetables, fruit, and fiber (UN FAO 2013). The high heterogeneity and consequent large chemical complexity of plant biomass become the raw material for various end products, such as energy, food, chemicals, pharmaceuticals, and materials. We can highlight four types of plant biomass of great economic interest, and to which we turn our attention: oil, saccharides (or sugars), starch, and lignocellulosic. Soybean (*Glycine max*) and palm oil (*Elaeis guineensis*) are examples of oil plant species; sugarcane (*Saccharum* spp.) and sorghum (*Sorghum bicolor* (L.) Moench) are biomass saccharides; maize (*Zea mays*) is a starchy biomass; and bagasse, straw, and wood biomass are lignocellulosic biomass. Each has its structural features and its chemical characteristics, which are directly related to analytical technology and the best technical approach to be applied during chemical analysis (Vaz 2014, 2015). Figures 1.2 1.3, 1.4, 1.5, 1.6, and 1.7 show the chemical structure of components of these biomass types, and Tables 1.1, 1.2, 1.3, and 1.4 show their m/m percentages.

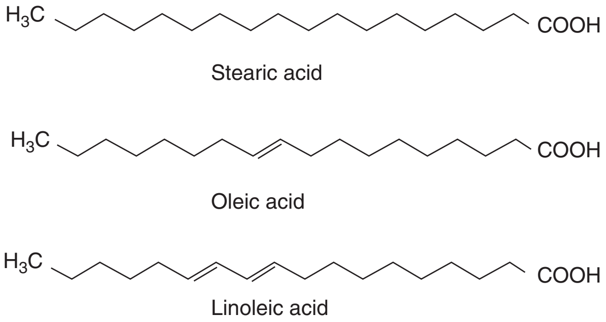


Fig. 1.2 Some chemical structures of fatty acids from oleaginous plants, such as soybean

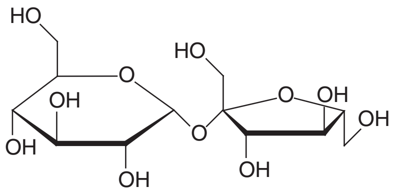
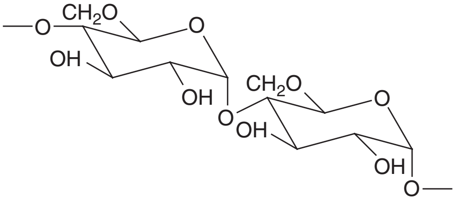


Fig. 1.3 Chemical structure of sucrose, a disaccharide present in sugarcane (author). The D-glucose moiety is on the *left* and the D-fructose moiety is on the *right*, linked by *α*–*β*–D-disaccharide bonds

Fig. 1.4 Chemical structure of starch polymer; the glucose unities (monomers) are linked by *α*–1–4–D-disaccharide bonds



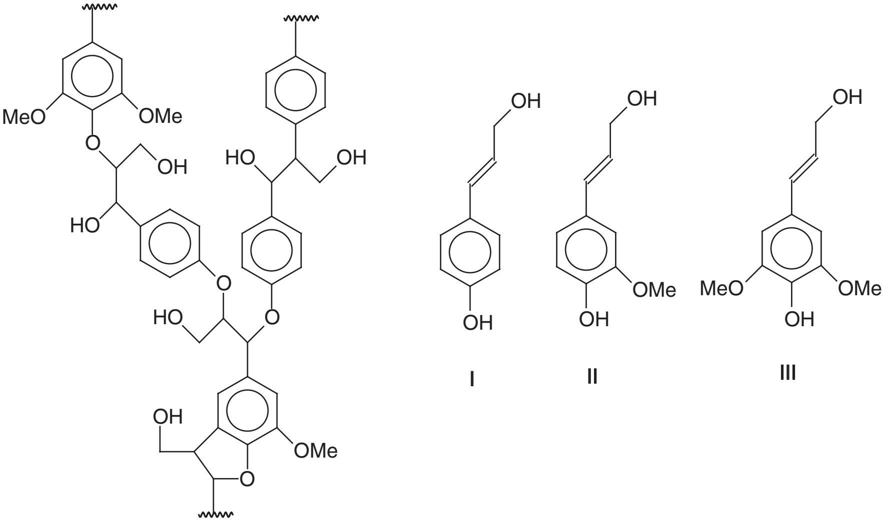
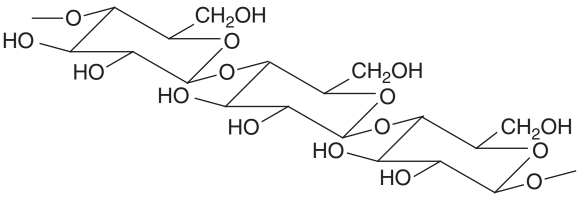


Fig. 1.5 Lignin structure (*left*) and its precursors (*right*): (*I*) *p*-coumaryl alcohol, (*II*) coniferyl alcohol, and (*III*) sinapyl alcohol

Fig. 1.6 Chemical structure of cellulose; the glucose units are linked by a 1,4–*β*–D bond



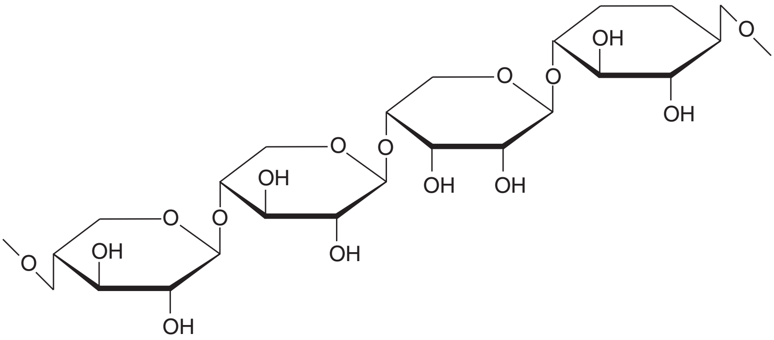


Fig. 1.7 Chemical structure of hemicellulose; the oligomeric units composed of D-glucose and pentoses (mainly D-xylose) are linked by means of a 1,4–β–D bond

Table 1.1 Chemical composition of oils extracted from oleaginous biomass (Gunstone 2004)

Plant	% m/m Palmitic acid	% m/m Stearic acid	% m/m Oleic acid	% m/m Linoleic acid	% m/m Triacylglycerols
Palm oil	44	4	39	10	3
Soybean	11	4	23	8	1

Table 1.2 Chemical composition of broth extracted from sugarcane (Faria et al. 2011) and sweet sorghum (Mamma et al. 1995)

Plant	% m/m Sucrose	% m/m Glucose	% m/m Organic acid
Sugarcane	85.3	–	24
Sweet sorghum	14.8	1.5	–

Table 1.3 Chemical composition of corn grain flour (Sandhu et al. 2007), cassava (Charles et al. 2005), and potato (Liu et al. 2007)

Plant	% m/m Starch	% m/m Protein	% m/m Fiber	% m/m Others
Corn (flour from grain)	90.1	6.5	0.52	1.99 (lipd)
Cassava (pulp)	83.8	1.5	2.5	0.2 (lipd)
Potato (pulp)	71.5	8.6	5.4	–

Table 1.4 Chemical composition of cellulosic biomasses (Vassilev et al. 2012)

Biomass	% m/m Cellulose	% m/m Hemicellulose	% m/m Lignin
Barley straw	48.6	29.7	21.7
Corn cobs	48.1	37.2	14.7
Grasses	34.2	44.7	21.1
Sugarcane bagasse	42.7	33.1	24.2
Rice husks	43.8	31.6	24.6
Wheat straw	44.5	33.2	22.3
Eucalyptus	52.7	15.4	31.9

1.3 Chemical Analysis and Its Application in Biomass Study

Chemical analysis, in a general way, can be considered as the use of concepts of analytical chemistry and its technical and analytical methods in the research and actual troubleshooting of varying complexity in different scientific and technological fields. Chemical analysis can generate both qualitative and quantitative information. Techniques and analytical methods provide support for the implementation of regulatory legislation and the market environment, such as the carbon credit market in order to ensure the quality of raw materials and yields of manufacturing processes, while also allowing the development of new products and materials that add value to the biomass. Chemical analyses play an important role in the exploitation of biomass and are supporting technologies for all processing stages of production chains, such as sugarcane, soybean, corn, forestry, pulp and paper, and agribusiness waste, among others.

In the study of biomass and its transformation, or conversion processes, the application of chemical analysis can take place as follows:

- Determining the chemical constitution of various biomass (raw materials), products, by-products, co-products, and wastes
- Monitoring of chemical, biochemical, and thermochemical conversion processes
- Observation of physical and chemical properties and characteristics of biomass and their molecular constituents

Nowadays, there are several possible methodological approaches, as well as a large number of analytical techniques, available and chemical analysis can be applied to all operations in a biomass chain, hence its importance for monitoring and quality control of raw materials, products, processes, and waste.

The analytical techniques used in the quantification of *analytes*—the species of interest for the analysis—are divided into two classes: classical techniques, based on mass, volume, charge, and mol measurement, which provide absolute values; and instrumental techniques, based on relative values, expressed as mg L^{-1}, mg kg^{-1}, μg m^{-3}, and so on.

Until the early 20th century, chemists employed the separation of analytes by techniques such as extraction, precipitation, and distillation. For qualitative analysis, these separated analytes were treated with appropriate reagents to produce compounds that could be identified by properties such as solubility, color, and melting and boiling points. Quantitative analysis was done using simple techniques with good accuracy, which are used to this day, volumetry (volume measurement) and gravimetry (mass measurement); these are typical examples of classical techniques.

Since then, different aspects of the observed classical techniques began to be investigated and several experiments have been carried out aiming to measure analytes from some particular physicochemical property, usually associated with phenomena such as the absorption and emission of radiation, which are the beginning of instrumental techniques, such as atomic spectrometry and molecular spectroscopy.

These findings stimulated the development of a wide variety of instruments that are used in this technical class. The techniques are generally faster than the classical ones and are used in the determination of low concentrations of analyte, such as trace concentrations of ng L^{-1} values or below it.

The following equations express the foundations of these two sets of techniques:

$$A_{S(c)} = kn_{A(c)} \tag{1.1}$$

$$A_{S(c)} = kC_{A(f)} \tag{1.2}$$

Equation 1.1 applies to classical techniques, where $A_{S(c)}$ is the measured signal—or the response—of the analyte, k is the proportionality constant to be standardized, and $n_{A(c)}$ is the number of moles, charge, or mass obtained from the measuring. On the other hand, Equation 1.2 applies to instrumental techniques, where the measured signal $A_{S(i)}$ is also the response of the analyte, k is the proportionality constant to be standardized again, and $C_{A(i)}$ is the relative concentration of the analyte measurement. However, some spectroscopic and microscopic techniques covered in this book do not necessarily obey these two concepts, but mainly report the structural characteristics of the sample.

Table 1.5 lists certain physical properties operated by analytical techniques and promoting the measured response.

The instrumental techniques measure a physical phenomenon resulting from a molecular or atomic property that is qualitatively or quantitatively related to the

Table 1.5 Physical properties used in analytical techniques most commonly used in the chemical analysis of biomass (modified from Skoog et al. 1996)

Properties	Instrumental technique
Absorption of radiation	Spectrophotometry and photometry (ultraviolet and visible) Atomic spectrometry Infrared spectroscopy (near, medium, and far) Nuclear magnetic resonance (solid and liquid states)
Electric current	Voltammetries (cyclic, square wave, anodic, cathodic, polarography)
Diffraction of radiation	X-ray diffraction
Emission of radiation	Emission spectroscopy (X-ray, ultraviolet, and visible) Optical emission spectrometry Fluorescence (X-ray, ultraviolet, and visible)
Mass	Gravimetry
Electrical potential	Potentiometry
Thermal properties	Gravimetric and volumetric Calorimetry Thermal analysis
Ratio mass/charge	Mass spectrometry
Refraction of radiation	Refractometry and interferometry
Electric resistance	Conductimetry

Table 1.6 Some examples of analytical techniques and their uses in the chemical analysis of biomass (modified from Vaz 2014)

Technique	Principle of measurement	Example of use	Advantages	Disadvantages
Differential scanning calorimetry	Enthalpy changes	Determination of combustion properties of biomass (exothermic or endothermic)	Small quantity of sample; high sensitivity; determines physicochemical changes in materials impossible to determine by other techniques	–
Capillary electrophoresis	Migration of ions or charged particles	High-efficiency separation for polar compounds from biomass degradation	High separation efficiency	Limitation for nonpolar compounds
Mass spectrometry	Molecular fragmentation	Structural identification and quantification of several organic compounds based on the m/z ratio	Identification and resolution of complex molecular structures	Necessity of separation techniques, such as chromatography, for a better resolution
X-ray fluorescence spectroscopy	Emission of characteristic X-rays	Multielemental quantification in solid and liquid samples from biomass residues	Easy to handle; nondestructive	Chemical composition and morphology of the sample can affect the result
Infrared spectroscopy (near and medium)	Vibrational energy absorption	Structural identification of organic compounds and lignocellulosic components	Easy to handle, mainly for near-infrared	Low resolution for compounds with same functional groups (sum of bands); however, the application of chemometrics can help to overcome this limitation
X-ray diffractometry	Intensity of X-rays diffracted	Determination of crystallinity and chemical composition of cellulose	Important physical information for natural fiber and polymer usages	Long acquisition time (hours or days) for process control

(continued)

Table 1.6 (continued)

Technique	Principle of measurement	Example of use	Advantages	Disadvantages
Scanning electron microscopy	Surface scanning with a primary electron beam	Surface and structural analysis of materials (e.g., catalysts)	Important physical information for natural fiber and polymer usages	Long acquisition time (hours or days) for process control
Nuclear magnetic resonance (e.g., ^{13}C in solid state)	Transition of nuclear spin inside atomic nuclei; interactions between nuclei–nuclei and nuclei–surrounding electrons	Structural identification of organic compounds from biomass processing (e.g., lignocellulosic and oleaginous)	Resolution of complex molecular structures	Long acquisition time (hours or days) for process control, except under a high concentration of the analyte (e.g., fatty acids)
Voltammetry (e.g., cyclic and square wave)	Changes in current as a function of potential	Chemical speciation and quantification of metals and nonmetals (e.g., catalysts for glycerin use), or verification of glucose or starchy oxidation processes	Rapid response	Search for the better electrolyte or voltammetric technique can expend time

analyte; that is, the physical phenomenon will produce a signal that is directly correlated to the presence or concentration of analyte in the sample. Table 1.6 shows some examples related to the use of instrumental techniques for the analysis of biomass and its products, and Table 1.7 shows analytical techniques widely used in the analyses of the chemical composition of raw materials.

In general, the application of an analytical method for biomass products must follow the steps presented in Fig. 1.8. Any failure or absence of the sequence compromises the reliability of the obtained results.

1.4 Sustainability and Economic Aspects of Analytical Chemistry

Based on the understanding that we should reduce or eliminate negative environmental impacts of processes and products, combined with a social and economic improvement—that is, ensure the *sustainability* of an entire production chain—we

Table 1.7 Examples of analytical techniques widely used in the analysis of the chemical composition of raw materials from biomass (modified from Vaz 2014)

Raw material	Parameter	Analytical technique	Advantages	Disadvantages
Sugarcane for ethanol production	Content of sugars	HPLC refractive index detector	Methods established	Long acquisition time for chromatographic run (approximately 30 min)
Vegetable oils for biodiesel production	Content of fatty acids and esters	GC flame ionization detector	Methods established	Necessity of organic solvent to extract the analyte
Bioenergy crops	Energetic characteristics	Near-infrared spectroscopy	Rapid response and easy to handle	Low band resolution, which can be improved by chemometrics application
Residues for gasification	Energy content	Differential scanning calorimetry	Rapid response and easy to handle	–

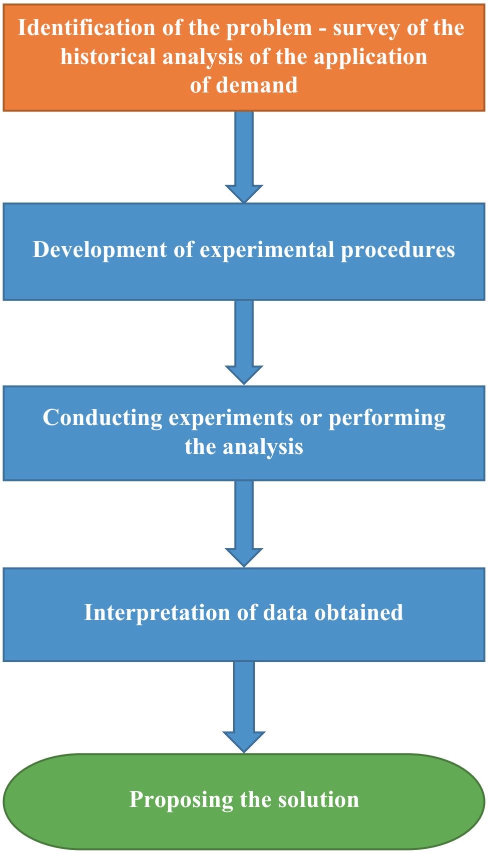


Fig. 1.8 A flowchart describing the steps for the application of an analytical method for biomass

began to consider biomass as a potential source of raw material for energy, chemicals, food, pharmaceuticals, and materials, among others. On the other hand, analytical chemistry has the commitment also to become sustainable in its application, for instance, by means of the use of green chemistry principles and strategies (de la Guardia and Garrigues 2011).

To establish a sustainable method with positive impacts to the environment, society, and economy, we can apply some of the 12 principles of green chemistry (Anastas and Warner 1998):

- Prevent the generation of waste instead of treating it.
- All reagents should be consumed for the formation of product; there should be an atom economy.
- The use of solvents, separation agents, and the like should be unnecessary if possible and innocuous when done.
- Reduce or avoid the formation of derivatives, because this involves the use of additional reagents, which can generate more waste.
- Develop analytical methodologies that can be used for real-time monitoring and control prior to the formation of toxic compounds, in order to contribute to the prevention of pollution.

Furthermore, the analysis of biomass should be, per se, based on the principles of green chemistry, inasmuch as the first use of context is reflected in the sustainability of raw materials.

Finally, the choice of an analytical technique or an analytical method should take into account the following technical and economic aspects:

- The analyte of interest and its physicochemical characteristics (solubility, pKa, speciation, etc.): a technical factor that can reduce or increase costs and the final price.
- The analytical matrix to which the analyte is sorbed (water, air, soil, sludge, biological fluid, plant, industrial waste, etc.) and physical state (solid, liquid, or gaseous): a technical factor that can reduce or increase costs and the final price.
- The need to obtain results in the short, medium, or long period of time: a market factor that can reduce or increase the final price.
- Existence of an analytical method developed and/or validated that meets the limits of detection or quantification required by law for the analyte: less effort, faster, and cost reduction.
- Impact generated by the analytical result (e.g., release of a batch of product or monitoring of effluent): as a market factor, reduces or increases the final price.
- The technique robustness, low standard deviation of the results, regardless of condition: parameters of quality control to be taken into account.
- Destructive or nondestructive technique: reduces costs.
- Satisfactory analytical response: of course, without the correct response, will not be viable.
- Cost per analysis: limiting, but not fundamental.

More detailed information about the choice of the technique and/or method can be obtained in the *Handbook of Instrumental Techniques for Analytical Chemistry* (Settle 1997).

It is always important to consider the toxicological and occupational aspects when applying analytical procedures, because chemicals usually offer a potential risk to those who handle them. Therefore, the laboratory team must be aware of implementing safety procedures and, above all, take care to follow them.

1.5 Conclusions

The chemical analysis of biomass is an important branch of analytical chemistry because it can provide information about the constitution of raw materials, products, by-products and co-products, residues, and so on. Analytical techniques can be applied to a whole biomass chain to solve many technical and scientific problems related, but not limited, to the best uses for a biomass, improvement of conversion processes, increase in the quality of products, and control of residues.

Plant biomass is a very complex analytical matrix and it needs cutting-edge techniques to understand its composition and properties, which can be replicated for its products obtained from conversion processes. Furthermore, to explore all the possibilities offered by techniques and methods is desirable for the procedure of sustainable and economic evaluation.

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