Chapter 1
Biomass and the Green Chemistry Principles

Sílvio Vaz Jr.

Abstract The need to develop renewable raw materials for industrial chemistry as a substitute for oil has been shown to be a strategic challenge for the twenty-first century. In this context, the use of plant biomass can be construed as both the alternative of using cheaper and less polluting raw materials and as a model of aggregation of economic value to the agro-industrial chains. Green chemistry (GC), based on 12 principles, emerged in the 1990s as a new philosophy in both academia and industry to break old paradigms of chemistry such as the generation of large amounts of waste and the intensive use of petrochemicals through a holistic view of processes in laboratories and industries. In the case of plant biomass, the seventh principle—*use of renewable raw materials*—is notable as a great strategic opportunity for segments related to several areas of GC worldwide. Thereby, biomass is a renewable source of a large variety of bioproducts, and green chemistry principles can be applied for its exploitation to promote sustainable processes and products. In this chapter, the application of GC principles, especially in conversion processes for biomass, is discussed with the aim to demonstrate their feasibility.

Keywords Plant biomass • Green processes • Biomass conversion

1.1 Introduction

The need to develop renewable raw materials for industrial chemistry as a substitute for oil has been shown to be a strategic challenge for the twenty-first century. In this context, the use of different types of plant biomass—starch, lignocellulosic, oleaginous, and saccharide—can be considered as an alternative for using cheaper, less polluting raw materials and as a model of aggregation of economic value to the agro-industrial chains, such as soybeans, sugarcane, corn, and forests. These lines of action may, above all, contribute to the sustainability of a wide range of

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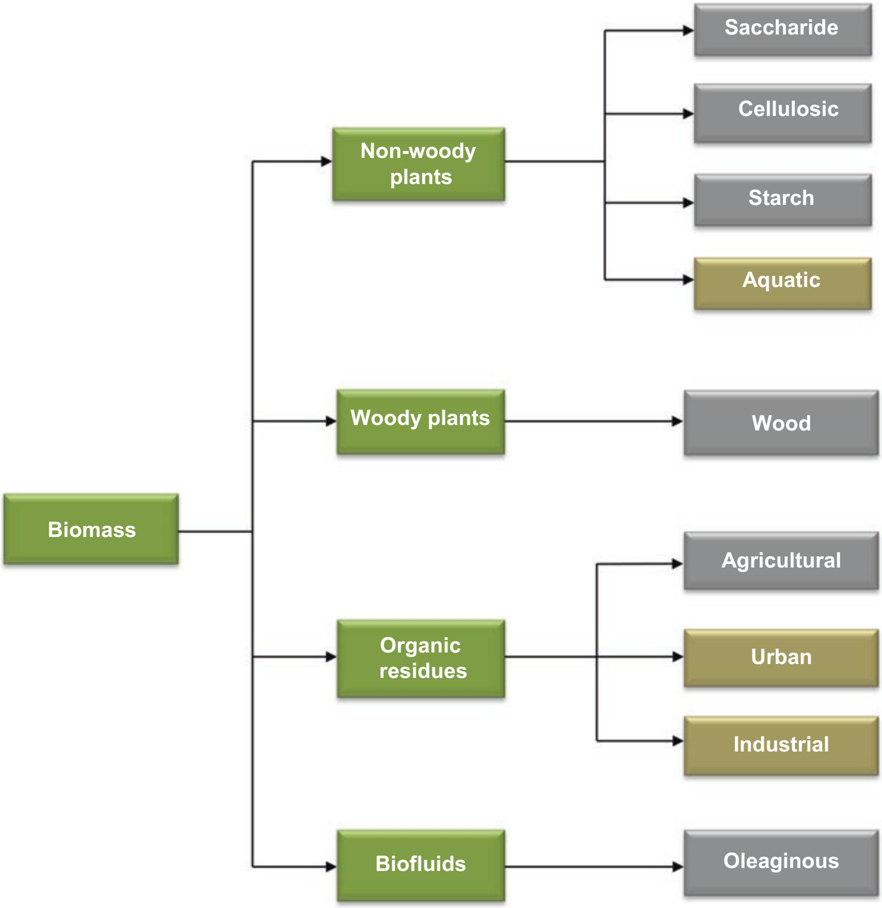

Fig. 1.1 Sources of biomass. *Gray boxes* represent the most used biomass types for industrial and research and development activities (Vaz Jr. 2014)

chemicals, especially organic chemicals (e.g., organic acids, esters, alcohols, sugars, phenolics), which are widely used in today's society.

The great heterogeneity and consequent chemical complexity of plant biomass provides the raw material for end products such as energy, food, chemicals, pharmaceuticals, and materials. As commented, we can highlight four types of plant biomass of great economic interest, to which we now turn our attention: oil crops or oleaginous, saccharides (or sugary), starchy, 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 (Vaz Jr. 2016). Figure 1.1 shows the classification of the sources of plant biomass.

Green chemistry (GC) emerged in the 1990s in countries such as the United States and England, spreading rapidly throughout the world as a new philosophy in both academia and industry and breaking old paradigms of chemistry, such as the generation of large amounts of waste and the intensive use of petrochemicals, through a holistic view of processes in laboratories and industries (Anastas and Kirchhoff 2002). This approach, described in the 12 principles, proposes to consider, among other aspects, the reduction of waste generation, atomic and energy economy, and the use of renewable raw materials (Anastas and Warner 1998).

The use of renewable raw materials is an extremely strategic issue for large biomass producer countries, such as Brazil, the United States, Germany, and France. These raw materials, the agro-industrial biomass, are an abundant and cheap feedstock for the transformation processes of chemistry or the conversion processes applied to biomass, which are biocatalytic, chemocatalytic, fermentative, and thermochemical.

Thus, the use of biomass through chemistry opens up new possibilities of business and wealth generation for a large number of countries, as well as promoting a less negative impact on the environment and the sustainability of biomass chains.

Chemical compounds are the products with the highest potential to add value into a generic biomass chain, given the importance of the conventional chemical industry and the fine chemical industry in different sectors of the economy. It is possible to highlight compounds that can be used as building blocks, synthetic intermediates, polymers, and specialties, among others; such ideas can be greatly explored by biorefineries (Kamm et al. 2006). On the other hand, the need to develop technologies to obtain these products presents considerable bottlenecks to be overcome related to technical, scientific, and market issues.

The 12 fundamental principles of GC are as follows (ACS Green Chemistry Institute 2017):

1. **Prevention**

   It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy**

   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Syntheses**

   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals**

   Chemical products should be designed to effect their desired function while minimizing their toxicity.
5. **Safer Solvents and Auxiliaries**

   The use of auxiliary substances (e.g., solvents, separation agents) should be made unnecessary wherever possible and innocuous when used.
6. **Design for Energy Efficiency**

Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. **Use of Renewable Feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives**
   Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.
9. **Catalysis**
   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation**
    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.
11. **Real-Time Analysis for Pollution Prevention**
    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control before the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention**
    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

These concepts, which also refer to clean production and green innovations, are already relatively widespread for industrial applications, particularly in countries with a well-developed chemical industry and with strict controls over the emission of pollutants. The concepts are based on the assumption that chemical processes with potential for negative impact on the environment will be replaced by less polluting or nonpolluting processes. Clean technology, reduction of pollutants at source, environmental chemistry, and GC are denominations that have emerged and were minted during the past two decades to translate concerns for chemical sustainability (Sheldon 2014).

In the case of plant biomass, the seventh principle—the use of renewable raw materials—stands out as a great strategic opportunity for several areas of GC worldwide. Examples of market segments that may be positively impacted by GC and the use of biomass are these:

- Polymers and materials for various applications
- Chemical commodities such as monomers
- Pharmaceuticals, cosmetics, and hygiene products
- Fine chemicals (agrochemicals, catalysts, etc.) and specialties
- Fuels and energy

In this way, it is possible to observe the great range of opportunities associated with the use of plant biomass for chemistry, which is better observed in Fig. 1.2.

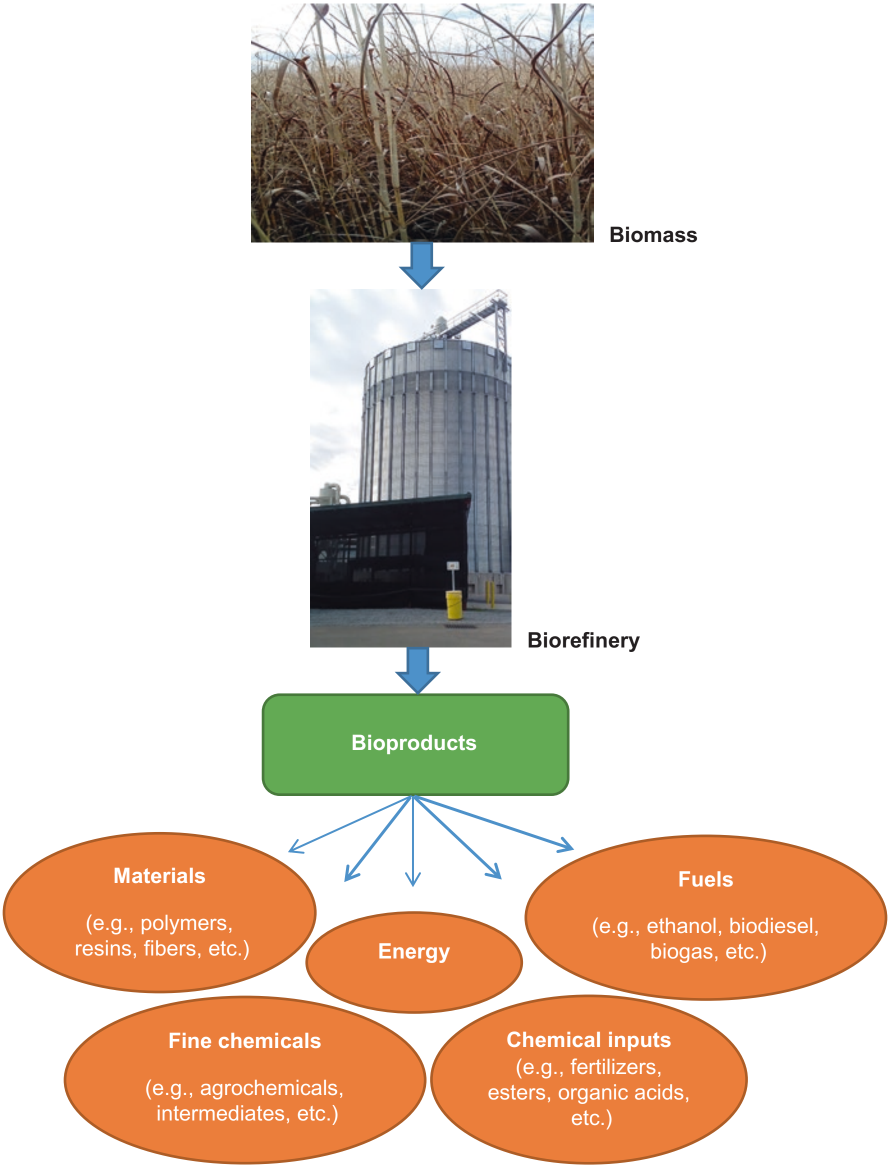

Fig. 1.2 Products that can be obtained from plant biomass by means of a biorefinery and their conversion processes

1.2 Exploring the Green Chemistry Principles in Biomass Conversion

The application of the 12 principles at the same time in a process is the ideal situation but it is not always possible. Raw materials, working conditions, budget restriction, and other factors could be limiting. On the other hand, the application of all principles could cause a process to become not feasible.

We can see that those principles were formulated and more easily applied for two main areas: analytical chemistry and industrial chemistry. Both areas include processes in which principles such as prevention (principle 1), safer solvents and auxiliaries (principle 5), and inherently safer chemistry (principle 12) are feasible for direct application, differing from R&D activities. Of course, R&D is not excluded from GC because green processes and products can be developed based mainly on the use of renewable feedstock (principle 7).

Table 1.1 shows the application of the 12 principles in biomass exploitation. We can see how to apply each principle and what is the expected result from this application to promote green processes for biomass conversion.

Figure 1.3 shows a process that uses lignocellulosic biomass as feedstock (e.g., wood residues). Some principles are suggested to make the process more "green."

We can state these highlights from Fig. 1.3:

- Fractionation step: better for principles 1, 5, 6, 7, 11, and 12.
- Depolymerization step: better for principles 1, 5, 6, 7, 11, and 12.
- Synthesis step: better for principles 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, and 12.

1.3 Aspects of Industrial Ecology Related to Biomass Processing

Industrial ecology explores, by means of a holistic vision, a certain industrial process according to its relationship with the environment (extraction, processing, fabrication, use, disposal, etc.). It is very useful to understand the biomass transformation and have a direct synergy with GC. Figure 1.4 shows a good example of a generic conversion process from the aspects of industrial ecology. Certainly, the most important point to keep in mind is the residue generation and how to recycle it; energy consumption is also an important aspect as it can improve the sustainability of the process, mainly because of the environmental component.

Table 1.1 Use of green chemistry (GC) principles in biomass exploitation to promote green processes

GC principle	How to apply to biomass and their processes and products	Expected results
Prevention	Agro-industry can generate much waste, mainly lignocellulosic residues (e.g., sugarcane bagasse); waste reuse to reclaim chemicals, materials, and energy should be considered to explore biomass chains	Reduction of environmental issues and increase of profits
Atom economy	Optimize the use of reagents during synthesis, for example, to produce biodiesel, furfural, etc.	Waste and cost reduction
Less hazardous chemical syntheses	Change toxic solvents (e.g., hexane, benzene) to oxygenated solvents	Decrease in negative impacts on health and environment
Designing safer chemicals	Develop molecules that are environmentally and health friendly as petrochemical substitutes, which is one of the advantages of biomass as the renewable raw material	
Safer solvents and auxiliaries	The use of water as solvent should be prioritized. However, as biomass has a high chemical heterogeneity, separation is needed; membranes are good alternatives	
Design for energy efficiency	Conversion processes based on enzymes can work in mild conditions	Cost and environmental impact reduction
Use of renewable feedstocks	Intrinsic	Intrinsic
Reduce derivatives	Change a certain analytical technique (e.g., gas chromatography) based on derivative formation to another without this need (e.g., liquid chromatography) or decrease the number of steps in a synthetic route	Cost and environmental impact reduction
Catalysis	Use enzymes and heterogeneous catalysts in synthetic routes	
Design for degradation	Increase the “degradability” of products; e.g., change petrochemical plastics to biobased plastics such as starch-derived or polylactic acid	Decrease in negative impacts on health and environment
Real-time analysis for pollution prevention	Use spectroscopic probes (e.g., Raman and Fourier-transform infrared spectroscopy (FTIR)) in field and industry instead of laboratory techniques	Cost and environmental impact reduction
Inherently safer chemistry for accident prevention	Pay attention to the physicochemical properties of substances to be handled; these can be accessed in the safety data sheet (SDS). Good laboratory practices (GLP) and good production practices (GPP) should be implemented in laboratory and industry	Decrease in negative impacts on health and environment Cost reduction

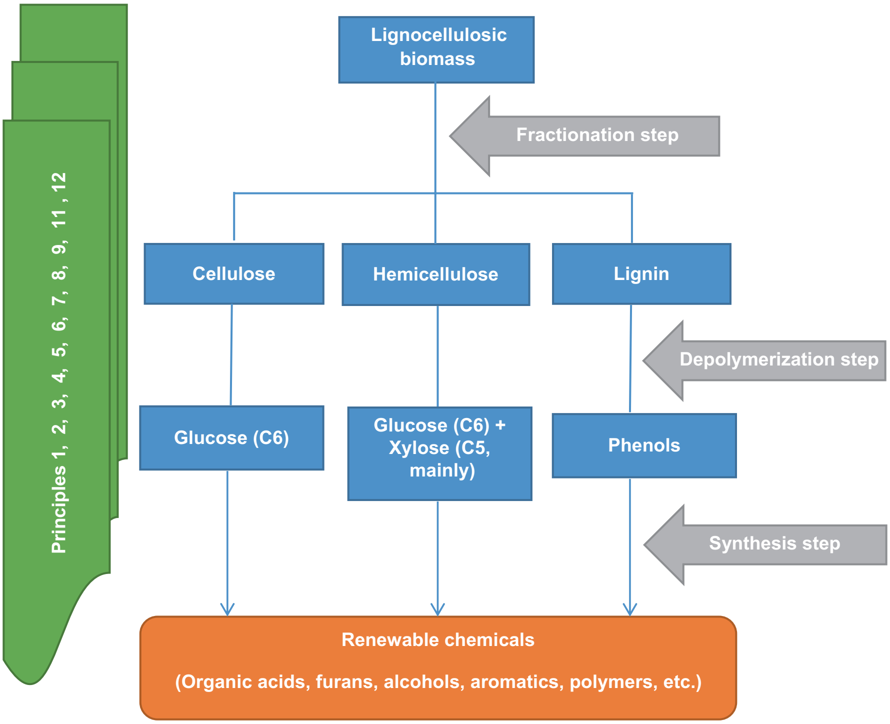

Fig. 1.3 Application of 11 GC principles (*left*) in a process of three steps (*gray arrows*) to obtain renewable chemicals

1.4 Conclusions

Biomass is a renewable source of a large variety of bioproducts, and green chemistry principles can be applied for its exploitation to promote sustainable processes and products. It is fostered by the fact that the use of biomass as feedstock for the chemical industry is one of the most representative principles.

Unfortunately, it is not easy to apply all 12 principles, and we need to choose those appropriate on the basis of biomass type, process characteristics, and products. Principles 1 (prevention), 5 (safer solvents and auxiliaries), and 12 (inherently safer chemistry) can be considered the most feasible for direct application in processes for biomass conversion.

Furthermore, industrial ecology and GC for biomass are closely related to improving environmental aspects of the conversion processes and promoting their sustainability.

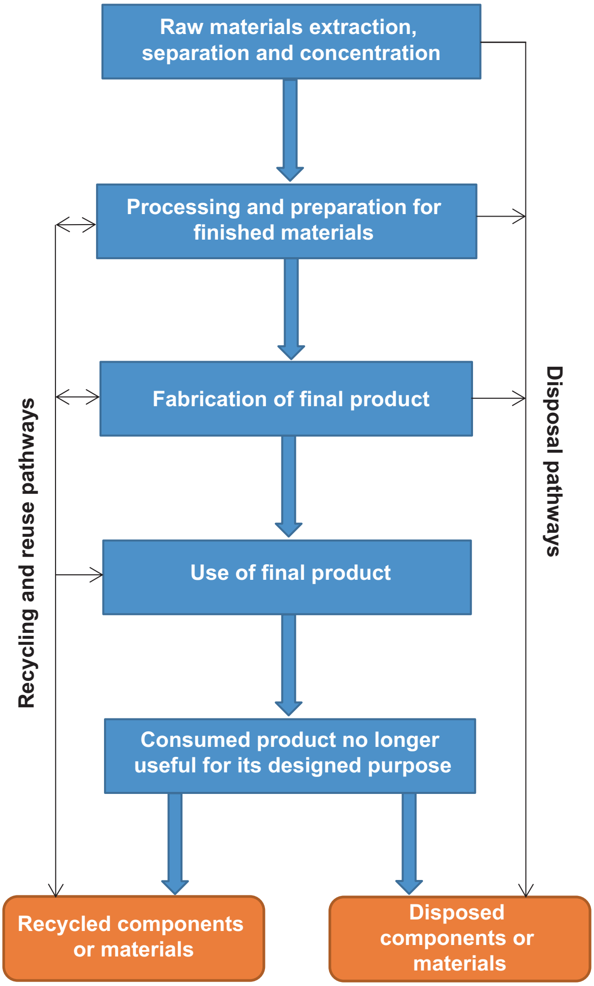

Fig. 1.4 Flowchart of a complete industrial ecosystem (*Source:* Adapted from Manahan (2000))

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