

REVIEW

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# Green chemistry, sustainable agriculture and processing systems: a Brazilian overview

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## Abstract

There is a pressing need for renewable and optimal use of resources towards sustainable primary production and processing systems worldwide. Current technologies for food and feedstock production are held accountable for several environmental problems, such as for instance soil and water contamination due to the use of hazardous substances, generation of toxic products and even excess of biomass that is considered waste. To minimize or solve these questions in order to produce an adequate quantity of reliable and healthy food, fibers and other products and energy, new paradigms focusing on sustainable agriculture, bio-based industries or biorefineries have emerged over the last decades. Biorefineries integrate sustainable and environmentally friendly concepts of Green Chemistry with intelligent and integrated farming processes, optimizing the agricultural production. Thermochemical and biochemical processes are excellent alternatives for the production of new classes of renewable biofuels and feedstock, showing relatively small impact on greenhouse gas emissions and important pathways to obtain platform chemicals. This review discusses the current and incipient technological developments for using biomass to generate bio-based chemicals over the last decade, focusing on Green Chemistry concepts towards sustainable agriculture and processing models in Brazil.

**Keywords:** Green chemistry; Sustainable agriculture; Environmental sustainability; Biorefinery; Biofuel; Platform chemical; Brazilian context

## Introduction

### Green chemistry, primary production, and processing systems in Brazil

In the face of an ever-increasing economy with competitive market policies, the demand for food, feed, fuel, and products can lead to serious problems in chemical processes due to excessive amounts of hazardous chemicals and the residues generated. To overcome these obstacles and impel the economy toward a more sustainable panorama, in 1998, Anastas and Warner [1] coined the term 'Green Chemistry' and formulated the twelve principles. These guidelines are approaches to be explored in order to promote a cleaner and more environmentally friendly way of doing chemistry, which includes using less hazardous substances and solvents and renewable feedstock, encouraging the concept of atom and energy economy by reducing unnecessary synthesis steps or designing alternative routes,

and also prevent or avoid the generation of residues and/or toxic substances [2,3]. Corrêa et al. [4] explored the evolution of Green Chemistry in Brazil, showing that there was a great deal of effort applied to a greener development in several different areas of chemistry, namely organic and inorganic synthesis and analytical chemistry. The authors stressed that the country has very favorable conditions to develop new trends in biomass conversion technologies for biofuels and bio-based products. Nevertheless, some recent studies [5] have shown that the understanding of Brazilian chemical researchers towards environmental sustainability, sustainable development, and the role of Green Chemistry has been further elaborated to improve the researchers' conceptual reasoning and more uniform understanding about the role of Green Chemistry in a new agribusiness paradigm. More recently, a transition has been observed towards an optimal and renewable use of biomass based on sustainable production systems to generate food and other bio-based products with adequate social value, low inputs, enhanced ecosystem services, zero waste, as well as minimum environmental impact and greenhouse gas emissions [6-10].

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It is estimated that globally, 140 billion tons of agricultural biomass is generated every year, and the use of green strategies to produce high value-added products could represent a reduction of roughly 50 billion tons of fossil fuels needed, enough to greatly reduce greenhouse gas (GHG) emissions and our dependence on non-renewable materials [11]. By employing adequate strategies and high-density and fast-growing crops such as sugarcane, a negative carbon footprint is also possible [12,13]. For instance, the cultivation of palm oil in northern Brazil for biodiesel production generates a GHG emission balance of approximately  $-208$  kg CO<sub>2</sub> equiv./1,000 kg crude palm oil per year [14].

Brazil is a world leader in terms of Green Chemistry in agriculture, and it was the first country to have, at a large scale, biofuels as part of its energy matrix. Due to early investments in the area with policies such as PROALCOOL in 1975, a federal program to prioritize domestic sugarcane-based ethanol distilleries in response to the 1970s oil crisis and which prevented the emission of 675 million tons of CO<sub>2</sub> from fossil fuel burning, have saved almost 50 billion US dollars in expenditures with oil and other non-renewable resources [15,16]. Similar early twenty first-century initiatives focusing on biodiesel production such as the PROBIO-DIESEL and PNPB (Brazilian Biodiesel Production Program) have placed Brazil on one of the main biodiesel production spots, with estimates that show the country is responsible for more than 11% of global biodiesel production, the second biggest producer after the USA [17]. Nevertheless, as assessed by Rathmann et al. [18], the main goals outlined by those programs were not fully achieved in its initial stage, this was mainly due to the use of the traditional production cost methods using soybean oil and methanol because of the competitive markets for soybean and high import prices for methanol, but there is considerable space for social, economic, and technological growth by developing commercially feasible biodiesel plants based on alternative triglycerides feedstock (palm, sunflower, castor bean, etc.), ethyl transesterification routes, and more economical processes which could overcome the actual problems [19-25]. The country is also a world reference in production and export of several commodities such as orange juice, sugar, and soybean products, and it is estimated that at least one fourth of all agricultural products commercialized worldwide are from Brazil [11]. Given this condition, it is crucial for Brazil to focus its development on innovative strategies and integrated management primarily based on green solutions for crops and industrial processes in order to keep the country as one of the key players in the agribusiness scenario.

This review focuses on the main green techniques and processes already in use and on those already under development to use biomass for generating bio-based

chemicals (fuels and platform molecules) described in the literature over the last decade. The focus is on the Green Chemistry principles for the primary biomass production and transformation processes, taking into account the Brazilian context.

## Review

### Use of available biomass

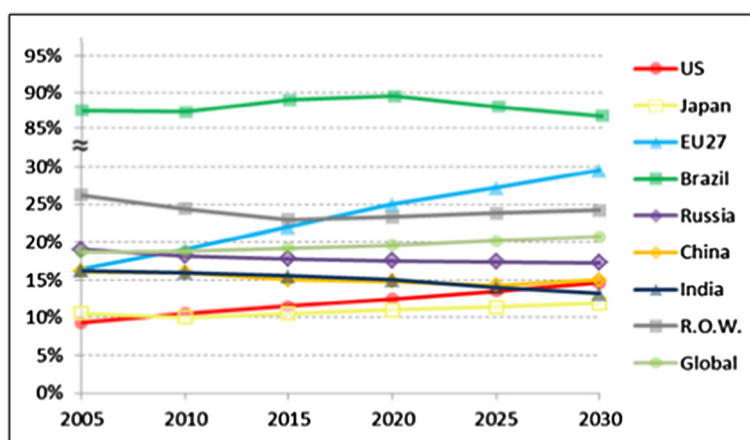
Even with the increase in the share of renewable sources in the world energy matrix, Brazil has a unique perspective regarding this scenario, as can be seen in the forecast data in Figure 1. Brazil's historic background shows its environmentally friendly technology practices for electric energy production, which generates over 80% of the country's energy requirements through such green routes, at least three times more than in any other region. While hydropower is the main driving force, and which is already responsible for 5% of the country's energy matrix, by applying new technologies and expanding to other biomass resources, it is estimated that this share can increase to almost 30% [26].

Biomass used for electricity generation is a growing industry. It started in a robust way with the installation of cogeneration heat and electric power systems by burning sugarcane bagasse to produce all energy needed in the process and sell the surplus for profit, thus presenting another green alternative to lower the dependence on hydropower. From approximately 8GW of electrical energy produced from biomass cogeneration, 80% comes from sugarcane, with the rest produced mainly by black liquor, wood chips, biogas, and rice husks [27]. Though not commercially available, several other agricultural wastes might be explored as fuel source depending on regional characteristics such as corn stalk, soybean stems, wheat straws, cotton branches, coconut shells and coffee husks, among others [28,29].

Although the burning of biomass or related products seems to be a promising alternative which is less polluting because of its nearly neutral carbon footprint, it is considered an inefficient process due to the underutilization of several complex chemical structures found as a major component of biomass, the lignocellulosic matrix, which could be transformed into commercially important feedstock in modern factories called biorefineries, which are able to combine, substitute, and even surpass conventional petrochemicals.

### The concept of biorefineries

There is a global trend impelling the transformation of energetic matrix from fossil to renewable feedstock. They generate less hazardous substance such as fine particulates, lead, and sulfur by-products, as well as noxious greenhouse gases such as CH<sub>4</sub>, CO, and CO<sub>2</sub>, among others [30]. Wyman and Goodman [31] have proposed



**Figure 1** Future renewable energy sources utilization in relative terms of total energy consumed by country/region. Adapted from [26].

an alternative way of dealing with lignocellulosic material, which would use refinery-like processing to transform them into a new set of molecules that could be used in well-established processes, as well as new building blocks to supply the production needs. They coined the term biorefinery, which can be defined as 'the sustainable processing of biomass into a spectrum of marketable products and energy' [32,33]. This concept is linked to two different objectives, the creation of a strong and economic viable bio-based niche connected to a high-ranking approach for obtaining new and renewable raw materials to outdo petroleum derivatives [34]. It is supposed that a biorefinery would be able to create, in the same physical space, environmentally friendly processes for obtaining biofuels, chemical products, electrical power, and heat [35]. There are some examples of readily available material that can be obtained by direct extraction from biomass but, in general, the matrix needs to be transformed into the desired products [36]. For example, Mariano et al. [37] evaluated the utilization of pentoses from sugarcane biomass for the production of biogas, *n*-butanol, and acetone in a simulation of an integrated first and second generation sugarcane biorefinery, with exciting results showing that the production would be profitable even without the optimization of processing technologies.

### Second generation fuel: bioethanol

Over the last 10 years, several different groups have studied the most suitable routes for biomass biotransformation, with most of the efforts focused on the production of bioethanol from the lignocellulosic matrix [38-43]. While cellulolytic enzymes for efficient transformation of cellulose have been thoroughly described over the last decade in several different examples, the use of hemicellulose and lignin as substrate is a more incipient technology [44]. Several papers discuss the feasibility of integrating 2G ethanol into conventional

ethanol producing units [45-49], but as of yet, there are no commercial plants available. Among the reasons, the complexity of processes such as low yield, lack of effective complete hydrolysis, pentose, and phenolic acid biotransformation technologies, and also financial drawbacks result in lower capital returns [50,51].

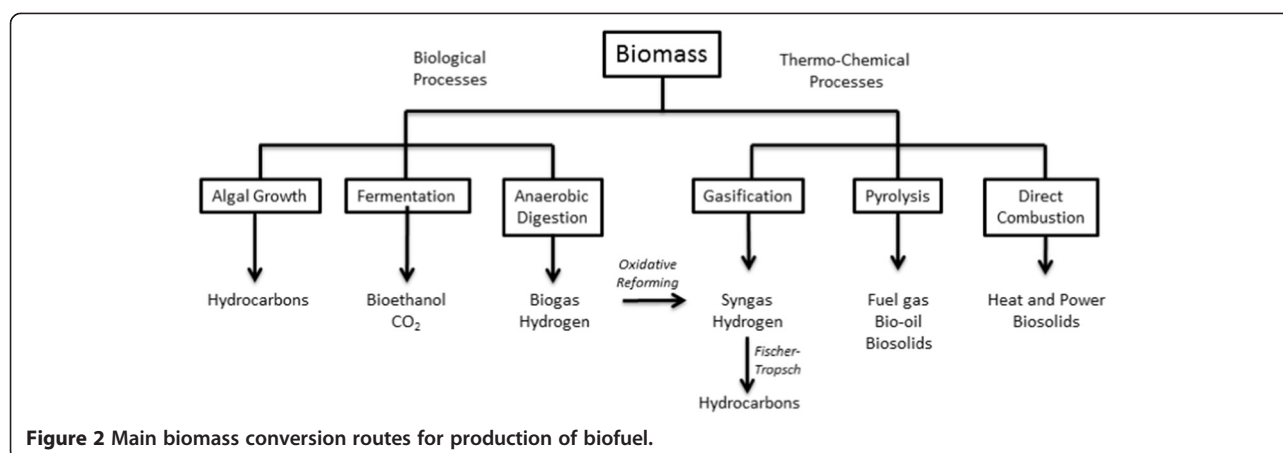
### Other alternative biofuels

Although ethanol is by far the most explored biofuel in Brazil, several other alternatives have been studied in order to improve the possibility of biomass reuse. Following global tendencies, studies on thermochemical and biological processes of biomass conversion have increased considerably over the past years [28]. The main techniques applied for biomass conversion to biofuels are described in Figure 2.

Gasification of biomass involves the conversion of organic matter in the presence of oxygen in the form of air, steam or pure O<sub>2</sub> with air/fuel ratios below the stoichiometric quantity. This low supply of oxidative agents hinders complete combustion of carbon and hydrogen into CO<sub>2</sub> and H<sub>2</sub>O, thus releasing a synthetic fuel gas (syngas) made primarily of CO and H<sub>2</sub> with smaller amounts of CH<sub>4</sub>, CO<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub>O [52,53]. Centeno et al. [54] used a mathematical model to predict the performance of a feasible biomass-to-energy conversion process, which was optimized by Brazilian researchers [55-57].

Syngas produced from biomass pyrolysis and gasification is an important intermediate for the synthesis of large numbers of industrial products [58]. For instance, Fischer-Tropsch synthesis (FTS) involves diverse complex reactions to produce low-molecular-weight hydrocarbons from syngas [59].

Hotza and Costa [60] reviewed Brazil's current developments on hydrogen production from renewable resources. The authors have identified bottlenecks in the country's development, where although several different research



**Figure 2** Main biomass conversion routes for production of biofuel.

groups have interesting approaches for hydrogen fuel cell development, little research was carried out on the reuse of biomass for the generation of hydrogen. Also, some studies are already evaluating the production of third-generation biofuels, but the application of such processes are still hindered by their capital-intensive nature [61,62].

#### Platform chemicals and green chemistry

Considering the need to achieve optimization both on the use of agricultural by-products and generation of high value-added products, there is a growing interest on the concept of platform chemicals, closely associated with the main pillars of Green Chemistry [63,64]. Platform molecules derived from biomass processing are not exactly the same as those obtained by crude oil. A remarkable characteristic of shifting from petroleum-derived hydrocarbon products to bio-based feedstock is that the latter presents a high oxygen content such as alcohol, ketones, aldehydes, ester, acids, phenols, furans, and others. Those molecules are responsible for the different properties of the liquid obtained from biomass, such as immiscibility with hydrocarbons, thermal, and chemical corrosiveness, low heating value and high density, such as low thermal stability [65]. Nevertheless, properties like high solubility in water and reactivity can be used as an advantage because it allows their manipulation in aqueous phase catalytic reactions under mild temperatures [66]. An initial evaluation conducted by the USDOE [67] and later improved by Bozell and Petersen [68] shows a wide range of molecules which can be listed as an important platform chemical due to their synthesis possibility and potential applications, and this includes organic acids, sugars, hydrocarbons, furans, and other aromatic molecules (Table 1).

Ethanol can also be considered a platform molecule due to its versatility as a building block. Several bio-based products can be tailored through the ethanol chemistry route, with ethylene as the only one that has been explored at a commercial scale. Companies such as Dow,

Braskem, and Solvay-Indupa are already producing green plastics in Brazil, with polyethylene (PE) plants for the former two and polyvinylchloride (PVC) for the latter [69]. Several other products can be obtained from ethanol, such as synthetic rubber made from butadiene, acetaldehyde, which is a key intermediate in several different processes, and diethyl ether, a solvent for producing cellulose plastics. Rossi et al. [70] theoretically assessed the thermodynamics of steam reforming ethanol and glycerol for hydrogen production, showing the feasibility of the process and encouraging further research in the area.

Glycerol is a by-product of biodiesel generated in quantities of up to 10% of total weight. However, glycerol obtained directly from this process has low purity, which is an undesired product for chemical and pharmaceutical applications without pretreatment [71]. As pointed out by Coronado et al. [72], molecular properties as well as impurities in crude glycerol hinder its use as fuel for generating heat and power for the biodiesel production process, as it uses by-products of other biofuels such as ethanol. Glycerol is also a very suitable substrate for bacterial growth, with several different organisms being able to use it as sole carbon source to produce several different commodities. Similarly, several microorganisms can also build a wide range of building blocks by biomass and glycerol biotransformation [73-78] (Figure 3).

Also, bio-oil can be produced by heating biomass under controlled conditions using specific equipment, obtaining a mixture of several different molecules of high-added value [80,81]. Crude bio-oil is dark brown, with a composition that varies according to the biomass used. Although coined as oil, the pyrolysis liquid does not mix with other liquid hydrocarbons due to its high oxygen content. In order to upgrade bio-oil to usual fuel such as gasoline and diesel, the samples need to be deoxygenated [51,65]. Several different biomasses have been tested for bio-oil production. There is an uncomplicated commercial process for bio-oil

**Table 1 Platform molecules**

Original platform molecules		Revised platform molecules	
[67]		[68]	
Succinic, fumaric and malic acids	Glycerol	Ethanol	Furans (furfural, HMF and 2,5-furandicarboxylic acid)
3-Hydroxypropanoic acid	Aspartic acid	Glycerol	Bio-hydrocarbons
Glucaric acid	Glutamic acid	Lactic acid	Succinic acid
Itaconic acid	Levulinic acid	3-Hydroxypropanoic acid	
3-Hydroxybutyrolactone	2,5-Furandicarboxylic acid	Levulinic acid	
Sugars (sorbitol, xylitol, arabinitol)		Sugars (sorbitol, xylitol)	

Adapted from [66].

production through fast pyrolysis operating in Brazil, named Bioware, and which has the support of the University of Campinas. The operating pilot facility has a nominal capacity of 300 kg h<sup>-1</sup>, and was built to produce bio-oil from elephant grass and sugarcane for industrial applications [51].

#### Agriculture as an alternative for reutilization of by-products

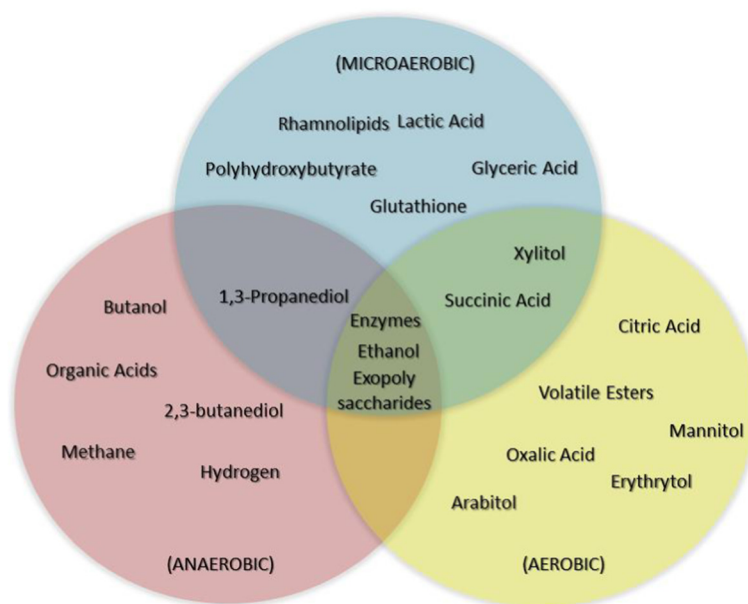
Though it has been applied worldwide for a long time, the reutilization of residues originating from other sources, such as industries and cities, is somewhat incipient in Brazil. Recently, public institutions and universities have shown interest in using one of the most efficient means of by-product disposals [82].

Herpin et al. [83] utilized secondary treated wastewater (STW) from an anaerobic/facultative pond system to irrigate coffee plantation for 43 months. They observed that although the use of STW did not negatively affect the soil-plant system, its use alone would not be

able to supply the plant with all the necessary elements and would cause some unbalance to soil composition, suggesting that new methodologies for the integrated use of fertilizers and wastewater are needed to enable the full potential of water recycling. Barros et al. [84] evaluated several treatments for the correct application of bio-solids from sewage sludge, obtaining interesting results when applied to maize crops. With the same objective, Lúcio et al. [85] studied the application of a product known as potato bio-product, a by-product from alcoholic potato fermentation, with organomineral composition similar to sugarcane vinasse.

#### More examples of using green chemistry in agriculture

Additionally, (Additional file 1: Table S1) summarizes most of the studies that have been carried out over the last decade to improve the research of green techniques for biomass transformation into fuels and platform chemicals,



**Figure 3** Example of chemicals produced by biotransformation of biomass and platform chemicals. Adapted from [79].

as well as establishing and using alternatives towards sustainable agriculture in Brazil. As can be noted, the majority of the papers focus on biofuels and platform chemicals (82%), but the development and application of biopesticides have also gained momentum in Brazil over the last years. Among the current trends in the development of biopesticides is the control of release rate and targeting of compounds by nanoencapsulation, as this technique can increase the stability and solubility of natural products and, consequently, increase their efficacy. These proposals, taking into account the plagues and crops found in Brazil, could change the manner in which natural products are used for controlling agricultural pest and insects considering an optimal and renewable use of biological resources [86-135].

## Conclusions

Simultaneously raising the awareness in government and the general population about environmental issues, the pressure by the public and non-government organizations for the production of an adequate quantity and quality of food and other primary materials, the reduction of waste emissions and the increase in prices of non-renewable fuel and feedstock have led to a significant increase in the research and development of sustainable processes for biomass generation and conversion in Brazil. These processes are strictly aligned with concepts of Green Chemistry already in use for chemical processes.

First-generation biofuels such as ethanol and biodiesel have already achieved a significant role in agribusiness through accepted and widely applied technologies. As for second generation, intense research is still needed for a fully functional industry at a suitable time. Concerning bio-based products derived from platform chemicals, the absence of well-established processes and the lack of a specific market hinder a more ostensive application of such compounds. With the development and application of reliable biomass transformation technologies, both in the academic environment as well as in the industrial sector, there will surely be a tendency to focus on the use of available biomass sources in scenarios with more value-added products. Nevertheless, the costs of such processes will continue to be the driving force for the consolidation of biomass-derived feedstock, in spite of its attractiveness from the environmental, social, and sustainable point of view.

There is a bright future for Brazil with regards to the development and application of biorefineries. The large amount of feedstock readily available and presumably close to the production sites can propel the country to a prominent position for producing renewable biofuels and high value-added products, as long as regulation policies and an effective distribution of goods through efficient production flow also follows the steps of technological expansion.

## Additional file

**Additional file 1: Table S1.** The following additional data are available with the online version of this paper. Additional data file 1 is a table listing the research related to the transformation of biomass-derived feedstock into high value-added products.

## Competing interests

The author declares they have no competing interests.

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