Toward petroleum-free with plant-based chemistry

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Abstract

Depletion of fossil resources, global warming, and increasing world's population represents major Damocles' sword for humanity to ensure its future against famine, climate change and the end of the petroleum era. Solutions will come from production of plant-based chemicals which is not new, nor a historical artefact. On earth, 99% of the biomass alive is composed of plants and microorganisms. Due to this biodiversity, it could be sufficient as a comprehensive sustainable resource of reagents for industry. Against this background, what will be needed for the industry worldwide to solve the long-standing unresolved problem of how to convert plant-biomass into reagents, ingredients and products with acceptable societal, environmental, and cost levels? There is an urgent need for conceptual leap in fundamental and applied research by original "multi-scales understanding". Mitigating climate change fueled by anthropogenic activities with plant-based green chemistry to establish a circular bio-based economy while adhering to the sustainable development goals is the scope of this perspective review.

Keywords: Plant-biomass, Reagents, Plant-based green chemistry, Sustainable Development Goals

Introduction

Plant-based chemistry has been used probably since the discovery of fire. Egyptians and Phoenicians, Jews and Arabs, Indians and Chinese, Greeks and Romans, and even Mayas and Aztecs all possessed a culture of using plants as source of reagents for cosmetic, perfumery, medicine, food ingredients and products, colors and dyes, and building materials. Until the start of the petroleum era, plant-derived biomass, due to plant biodiversity, was the primary source of reagents, ingredients and products for food and non-food applications. The spectacular growth of petroleum-based processes led to a withdrawal from those based on plant biomass. Almost all major economies in the developed and developing world have mature refineries which could transform petrol, a complex liquid mixture to variety of reagents and products essential and vital for our life and modernity.

Depletion of fossil resources, global warming, and increasing world's population represents major Damocles' sword(s) for humanity to ensure its future against famine, climate change and the end of petroleum era, which are interconnected. If we consider that these fossil resources have been formed from a large number of plants, algae, and zooplankton, and also the point that on earth, 99% of the biomass alive is composed of plants and microorganisms, and it is evident that they could be sufficient as comprehensive sustainable resources for reagents in chemical and food industries for millions of years. The future of humanity could be secured by establishing a sustainable and circular economy that relies on the biodiversity with not only plants as green solution, but also macro and microalgae as blue solution, and microorganisms as white solution, and insects as brown solution.

Nowadays, based on research and innovations in the 20th century, we know that in a technical point of view, almost all petroleum based-chemicals and materials could be substituted by their plant-based counterparts. However, the cost of bio-based production in many cases exceeds the cost of petrochemical production. With a petroleum refinery, we can separate and transform petrol to huge number of alkanes and aromatic compounds as building blocks; in contrast; agri-food industries largely adhere to the "one cultivation - one product paradigm". The problem is "*the missing link*": how to convert plant-biomass into reagents, ingredients and products for industries worldwide with acceptable societal, environmental, and cost levels. Solutions require innovations that break away from the past rather than simple continuity with *"Plant-Based"* Green Chemistry.

Green Chemistry is based on principles [1] that could reduce the environmental impact of nonrenewable resources (petrol, gas and coal) on chemical and food industries: perfumery, pharma, food, fine chemicals, pesticides… Many industries and academia adhere to these principles and change the face of chemistry. The next challenge will be the use of starting chemical materials from renewable resources such as plants and microorganisms, but also to obtain these synthons and ingredients by sustainable, green extraction and separation technologies (Figure 1).

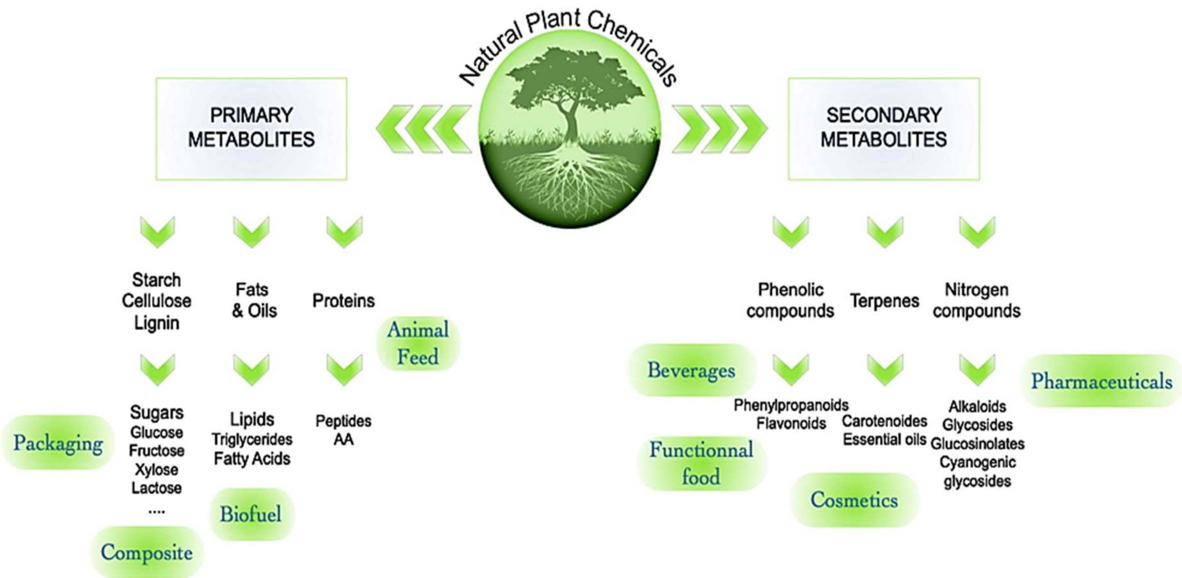

Figure 1: Classes of natural plant chemicals.

Extraction: Unlocking the gateway to plant-based green chemistry

The primary raw material for the obtention of petrochemical feedstocks is crude petroleum oil which is in turn refined and fractionated as per requirements. The key distinction between the refining of petroleum crude oil and biorefining of plant biomasses is in the apparent state of the initial material. In the case of crude oil refining, the starting material (i.e. crude oil) is in a liquid or slurry state with impurities. Whereas, in the case of plant matrices, the initial biomass predominantly exists in solid-state. Benign extraction techniques are the first and foremost step employed in order to retrieve the natural plant chemicals such as the primary and secondary metabolites. Implementation of a non-destructive extraction technique as the primary step in a biorefinery or cascading use scheme would enable further improvement in biomass valorization resulting in the obtention of several chemical constituents (Figure 2) including essential oils, waxes, sterols, triglycerides, phospholipids, fatty acids, polyphenols, pigments, proteins and carbohydrates [2,3]. Extraction process comprises several unit operations namely pretreatment of plant material (thermal or non-thermal drying, size reduction…) and post-treatment of liquid extract which includes separation, concentration, purification, etc. The principal unit operation in this dynamic is the solid-liquid extraction which is the most common in plant material based extraction systems. Optimization of the extraction parameters is crucial and failure to do so often might result in time-consuming and energy-intensive processes [4]. The growing importance of green extraction and its application for plant-based biomass refinery has been the subject of numerous research and review articles [5,6,7,8]. The utilization of bio-based synthons and ingredients undeniably offers various advantages but the transformation has to be feasible and can not come at any cost [9]. The viability of embracing bio-based products has to be reasonable in terms of economy and ecology; that way the sustainability aspect of the transformation process is preserved. The ideal scenario is not only to have bio-based ingredients but also to have bio-based ingredients extracted with green technologies.

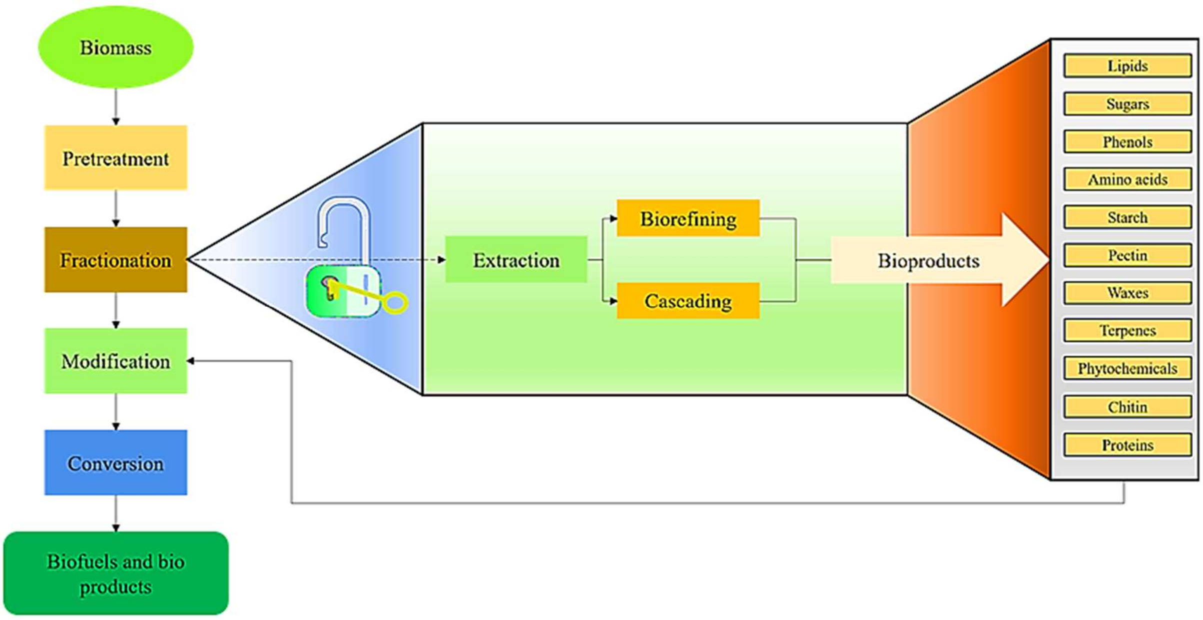

Figure 2. Extraction: a key component in plant-based green chemistry.

Future challenges: Green intensification techniques and alternative solvents

The major impediments in the transformation of biomass for the provision of chemical compounds and bioproducts are the inherent complexity and variation in their physical and chemical compositions. This necessitates the adoption of highly complex and tedious processing conditions which drives up the operational costs and the low conversion efficiency of biomass to products could jeopardize the economic viability of the operation [2,10]. The application of innovative extraction technologies and intensification techniques such as ultrasound, microwave, instant controlled pressure drop, sub or supercritical fluid, pulsed electric fields, extrusion, ohmic, ultraviolet (UV), infrared (IR), and solar-assisted as a standalone process or in synergy can be used for exhaustive recovery of bioactive compounds from plant matrices (Figure 3). Incorporation of these green extraction and intensification tools considerably enhances the efficiency, drastically reduces the time, energy and volume of the solvent when compared to the conventional setup [11].

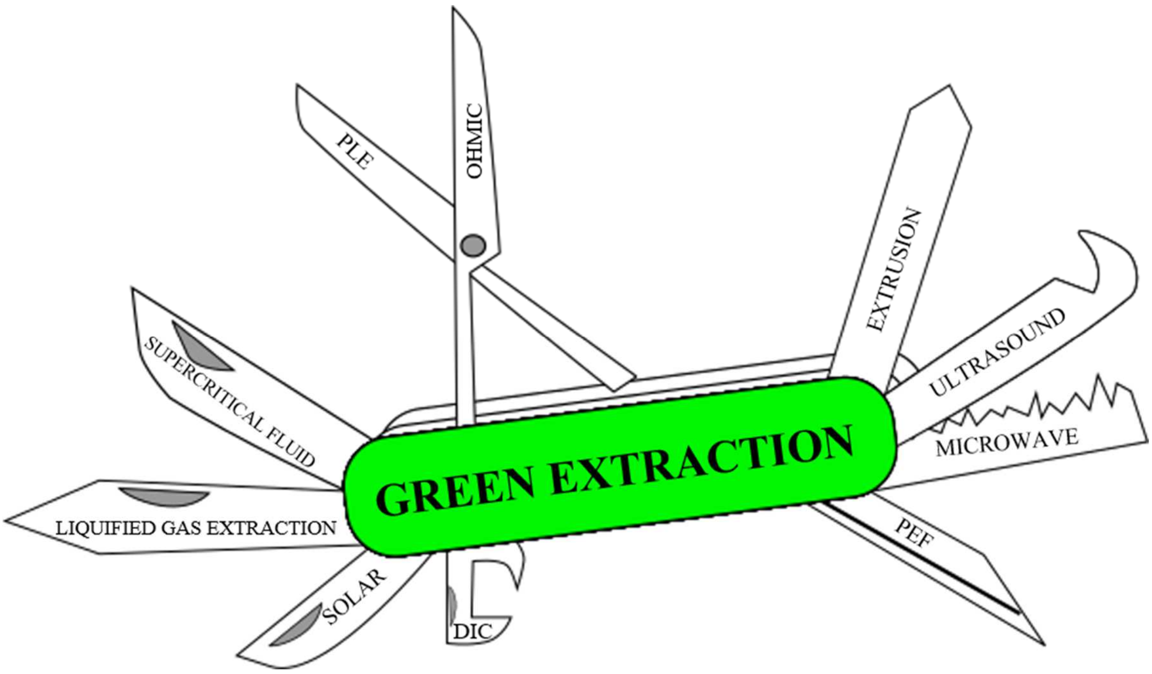

Figure 3. Overview of green extraction and intensification techniques.

Finding a suitable alternative to replace petroleum-based solvent for the green extraction of natural products is an intricate task. The ideal alternative solvent should possess the following traits: high solvency; high flash points; low toxicity; lower environmental impact; easily biodegradable; origin from renewable resources, reasonable priced, and easily recyclable without any deleterious effect to the environment. Several studies focusing on alternative solvents (Figure 4) for the green extraction of natural compounds have been communicated and are summarized in [12].

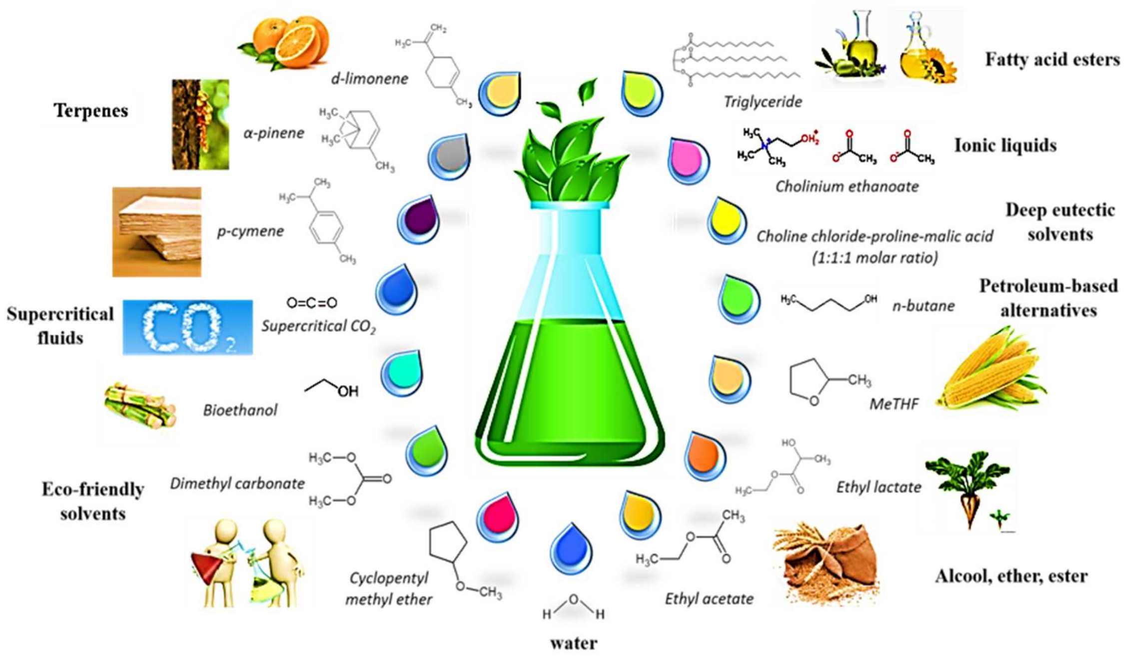

Figure 4. Alternative solvents for green extraction

"One cultivation – multi-product": A biorefinery paradigm

Alerts over the last few decades firmly pushed two critical aspects of plant biomass from agriculture and food industries largely adhering to the one cultivation-one product paradigm. The diminished use of the byproducts because they are dilute resources, and the high cost of recovery associated with it are the current obstacles in biomass valorization. The final objective is not to provide solutions for a type of biomass, but rather general models applicable to every kind of potential biomass substrates. To facilitate the transition of fossil centric global economy to a sustainability-based bioeconomy, a forward-looking approach with a stepwise adaptation of global refining schemes for the production of bioenergy, biofuels and biobased products should be considered. Authors Champagne and Matharu consolidated the processes involved in the refinement of biomass to biofuels and bioproducts along the entire supply chain into pretreatment, fractionation, modification and conversion routes [13]. Pretreatment processes have ubiquitous applications in the conversion of lignocellulosic biomass [14] and can be employed optionally for other plant-based biomasses as well. Within this framework, the fractionation process for biomass valorization can be categorized into dry and wet processing modes. Fractionation of biomass can be accomplished with different strategies: a) Biorefining: The ideal goal of any biorefining scheme is to completely valorize the biomass into a spectrum of bio-based products (food, feed and platform chemicals) of economic value and exhaust the potential functionalities offered by the matrix. This is usually achieved in a single step or multiple steps by employing various unit operations sequentially. b) Cascading use: systematic effort to exploit the biomass for higher-added-value products before utilizing it as a source for energy [15]. The deconstruction and cracking approach are other plausible alternative strategies for biomass valorization [9].

Biorefinerie(s) as success stories for Plant-Based Chemistry

The objective of biorefining is to valorize all the plant's components into products of economic significance [16]. At present, there are several types of biorefinery schemes that can be employed depending on the different inputs and outputs emerging from the transformation process of plant biomass. Almost 80% of the grapes harvested (77.8 million tons in 2018) is used for viticulture. The complete valorization of the sheer amount of by-products emerging from winemaking by means of an integrated biorefinery approach is an excellent example (Figure 5).

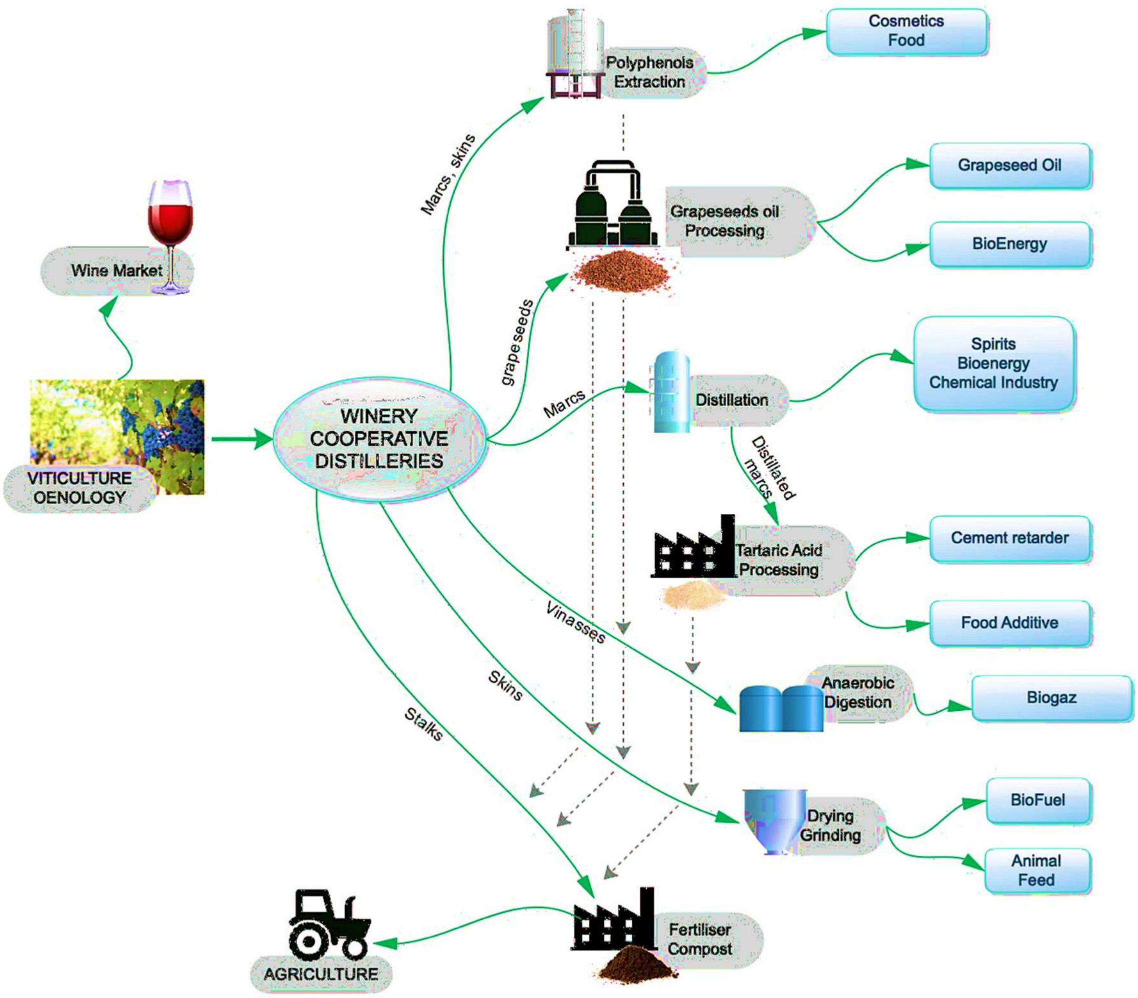

Figure 5. Scheme of wine biorefinery.

An innovative approach, which seems surprising, is the utilization of insect larvae for the bioconversion of different biomasses. Insect-based products for food and feed applications has already garnered significant attention [17]. They are considered as an alternative to conventional protein sources like fishmeal and soybean meal. The black soldier fly (BSF) in particular can be reared on a diverse range of substrates including agricultural wastes and food industry by-products. Insect bioconversion is exceptionally advantageous in terms of overcoming the physical and chemical variation challenges in the biomass. Their ability to thrive in a wide array of substrate with varying nutritional composition can be exploited and used to fabricate a structured bioconversion system which ensures thorough utilization of the biomass and obtain a standardized nutritional composition in the larvae. For instance, 1000 kg of fruit and vegetable wastes through larvae mediated bioconversion yields 125 kg of fresh larvae and almost 250 kg of frass [18]. Though the proximate composition of larvae may vary, the bioconversion ensures assimilation of high-value components (protein, lipids, minerals and other nutrients) in the larval biomass which can be retrieved by traditional biorefining or fractionation techniques. The lipid fraction of the insect finds applications in feed, food, biodiesel, and cosmetic formulations. The protein meal is widely considered as replacements for conventional protein sources. Chitin has multifarious applications and frass from insects can be used as fertilizers and soil amendments. Even the conversion of complex lignocellulosic biomass (corn stover, rice straw) can be effectuated with insects along with co-conversion agents (microbes, enzymes) [19,20,21]. The conversion efficiency of lignocellulosic biomass to platform chemical or intermediary products along with techno-economic analysis and life cycle assessment of the process could be compared with insect bioconversion for similar biomasses. Such comparisons could shed light on the economic aspects, environmental impact, technical feasibility, and overall implications of the individual systems and in turn aid in the industrial-scale adaptation of the process for guaranteed profitability and sustainability.

Plant-based green chemistry: Sustainable Development Goals perspective

The Sustainable Development Goals (SDGs) put forth by the United Nations (UN) is a culmination of criteria and strategies that serve as the blueprint to achieve a better and more sustainable future for all. The 17 goals are all interconnected and achieving even one of this ambitious goal by the year 2030 will have a positive ripple effect on the rest. Adapting green extraction and refining processes for the production of platform chemicals, energy, biofuels, active pharmaceutical ingredients and other chemical intermediates will significantly accelerate the progress towards a sustainable bio-economy. Authors Anastas and Zimmerman addressed the challenges of sustainable chemistry relevant to SDGs [22]. We postulate that the plant-based green chemistry approach can have an overall impact on the 17 SDGs and it certainly influences 9 of them directly namely (Figure 6), (i) Good health and well-being: replacing petroleum solvents with alternative bio-based solvents for example, n-hexane with 2-methyloxolane can change the way edible oil refining functions; (ii) Clean water and sanitation: sourcing of biomolecules like chitin and chitosan which acts as a flocculant in water treatments, larvae-mediated waste management in animal agriculture could drastically reduce the industrial run-offs in animal agriculture; (iii) Affordable and clean energy: plant lipids for biodiesel production, biogas generation from plant biomass as a last resort in the biorefining scheme or cascading use; (iv) Industry, innovation and infrastructure: plant-based green chemistry has already paved the way for the implementation of several innovative extraction and processing techniques in industrial-scale. Further push by incentivizing the companies that gravitate towards green processes will spur more innovation for clean label products; (v) Sustainable cities and communities: self-sufficient communities and smart cities with urban vertical farms is a possibility in the near future; (vi) Responsible consumption and production: biodegradable plastics from plant-based constituents like starch and biopolymers along with regulatory push can boost responsible consumption (vii) climate action; (viii) Life below water; and (ix) Life on land: lower greenhouse emissions as a result of transformation to plant-based biomass, reduced carbon footprint and sustainable plant and animal agriculture practices are few of the aspects that can contribute to the achievement of the goals outlaid.

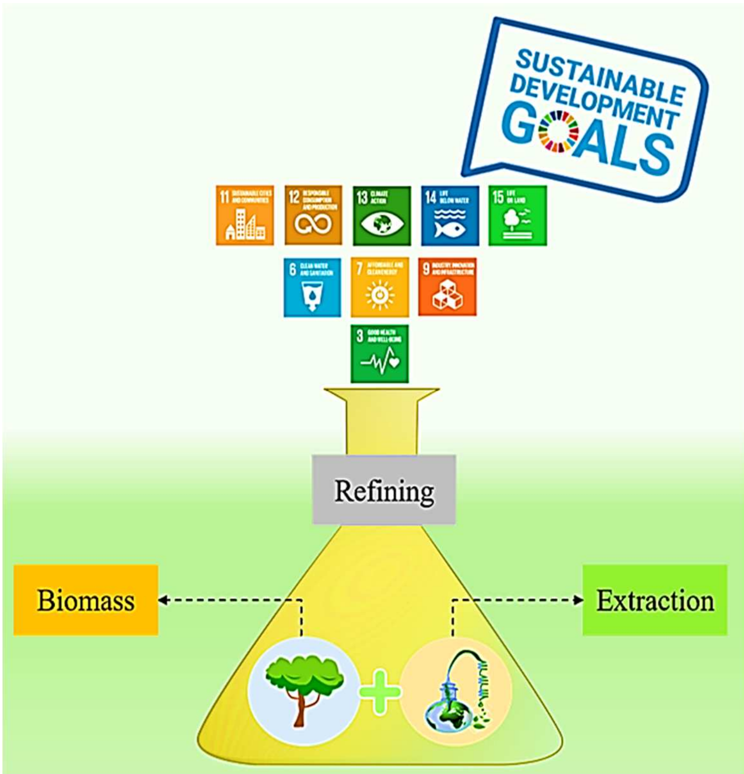

Figure 6. Plant-based green chemistry and SDGs

Conclusions and future prospects

Plant-based green chemistry could be one of the solutions from the past to the future of humanity focusing on ecologic and economic chemistry, and as a success story of the evolution of green chemistry in the 21st century towards a petroleum-free world. The most critical aspect is not only to have 100% bio-based product but to obtain 100% “sustainable” bio-based products with net positive carbon impacts and limiting the use of petroleum solvents and nonrenewable energy. There are many key challenges and barriers at different levels from microscale (petroleum-free), mesoscale (detexturation), to macroscale (biorefinery) to achieve a conceptual leap in fundamental and even in applied research for conversion of plant-biomass to reagents and ingredients with societal, environmental, and cost impacts to levels acceptable to secure humanity against the inevitable end of the petroleum era.

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