



Biomass: Renewable carbon resource for chemical and energy industry

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Chemistry is indispensable for the elaboration of all products used in everyday life, such as manufactured goods, materials, fuels and devices for energy, construction, transportation, foods, pharmaceutical products, personal care products, and devices for communication. Considering the broadness of this sector and its necessary growth for ensuring development and technical progress to an increasing world population, the time has come for a new chemical era in which the environmental impact of chemical products, in terms of hazards, life cycle, carbon footprint, and sustainability of resources, is minimized. Utilization of biomass to produce chemicals, energy products, and materials is an important route toward sustainable development. This perspective gives a brief overview of the use of biomass as a renewable resource, analyzing its evolution over the years in terms of motives and societal issues, highlighting the seminal contributions, and stressing how the remaining challenges will require contributions from all facets of the chemical sciences.

SIGNIFICANCE AND MOTIVES OF BIOMASS UTILIZATION: THE GREEN CHEMISTRY CONTEXT

Awareness of biomass has benefited from concepts and principles established since the 1990s, such as Sheldon's environmental factor,¹ Trost's

atom economy,² and more globally the Anastas' and Warner's Green Chemistry principles³ and the Green Carbon Science of He and coworkers.⁴ These are now the bases of modern chemistry, ultimately reaching Anastas' Hippocratic Oath for chemistry, swearing that no chemical process or product should result in any harm, in a global vision including scientific, technological, societal, cultural, and ethical issues.⁵ Among universal sustainable development goals, responsible consumption and production addresses the key issue of starting materials used for the manufacture of chemicals.

Biomass includes all molecular and macromolecular compounds arising from vegetables, agricultural products, forestry products, and anything left over. Use of renewable feedstocks, principally biomass, is an important part of green chemistry. At the same time, the principles of green chemistry also guide the whole process of biomass utilization. Using biomass for chemistry cannot be considered as an end in itself without keeping all other green chemistry principles. Efficiency of reactions, atom economy, limitation of resource consumption, prevention of waste, and safety of processes and products also apply when biomass is used, at all stages, from biomass production and conversion to biobased products up to their final utilization.

In one way, this means going back to the pre-oil era when biomass was the only carbon resource in the early ages of chemistry while aiming to meet the present

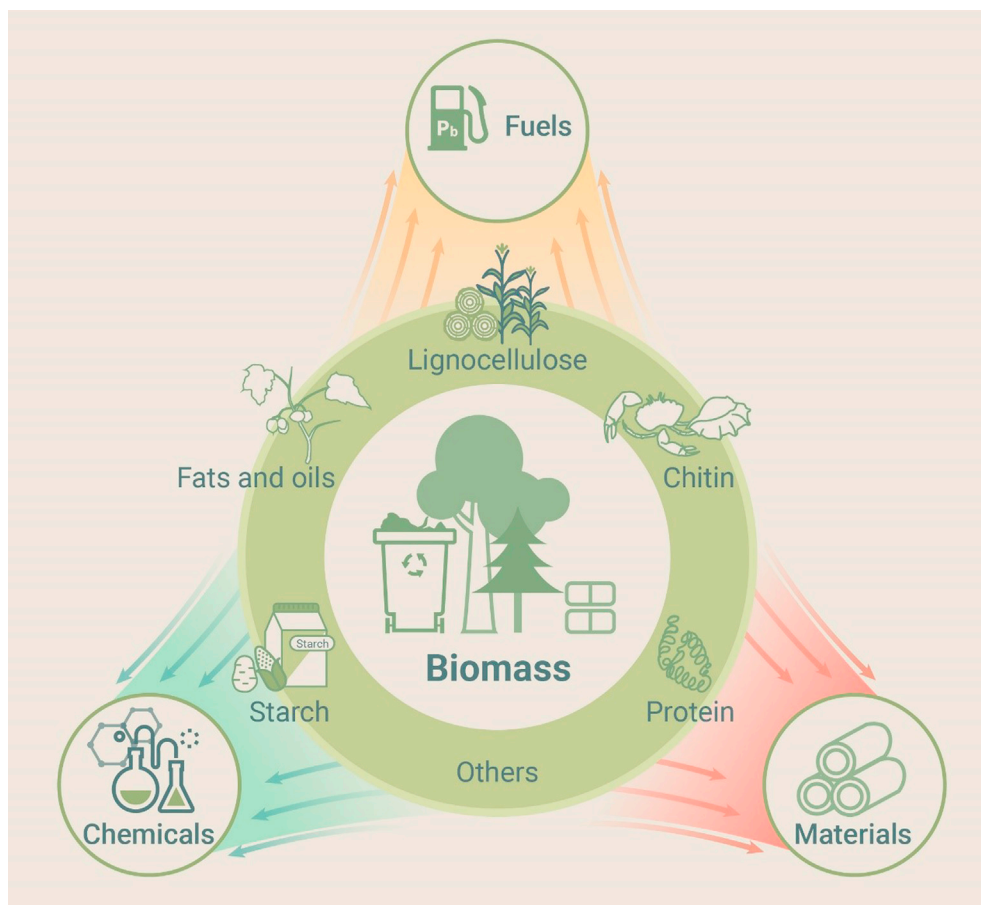


Figure 1. Opportunities for switching from fossil fuel to renewable resources for chemicals, fuels, and materials

needs of chemical products for a much more numerous and technologically advanced population.

Nature continuously produces biomass using essentially water, CO₂, and solar energy. In the times of low crop prices and expensive oil, the use of biomass in chemistry aimed essentially at providing better value for unused crops and leftovers. The momentum is nowadays supported by a more global awareness of the necessity for chemical manufacturers to renew their product portfolio with compounds incorporating more renewable carbon, following universally accepted sustainable goals, increasingly constraining regulations and consumers' practices. This must also address the issues of food versus non-food resources, cultivable land availability, soil impoverishment, water demand, and sustainability of agricultural practices.

Biomass can also provide renewable energy, similar to wind, waterfalls, or sunlight. Furthermore, most chemical products cannot be created without a carbonaceous resource. Therefore, biomass can be used as a feedstock for the manufacture of energy products and higher-added-value chemicals and materials (Figure 1). The huge quantity of non-food biomass and waste produced each year, especially lignocellulosic resources, justifies that the use of biomass has become a genuine research issue.⁶⁻¹⁰

The benefits of the use of biomass for chemistry in terms of carbon footprint should not be overstated. The carbon footprint of a chemical product is a sum of elementary impacts, including the harvesting, extraction, and transformation steps, the chemical process with synthetic sequence, separation, and purification, the use of the final product itself, and its end of life. Moving from oil to biomass accounts, therefore, only for the consumption of CO₂ during the plant growth and not more.

Preferring the use of renewable resources over fossil resources must be seen first as an opportunity for innovation and for added value, and as a way to limit dependence of the economy on oil. In the longer term this will be recognized as the pioneering steps for the chemistry of the post-oil era whenever it occurs.

CHALLENGES OF SELECTIVE BIOMASS CONVERSION

Biomass structural complexity and higher sensitivity to heat and harsh chemical conditions leads to more complex chemical reaction outcomes and, consequently, more difficult separation and isolation steps. Each family of biomolecules, including, for example, lignin, carbohydrates, and fats, exhibits specific challenges in terms of chemical reactivity and stability. Compared with hydrocarbons, their chemical structures differ significantly. For each of these families, these features define the natural trends of their chemical reactivity and, therefore, the scope of possible transformations and molecular design of new derivatives.

Additional challenges are associated with the physical status of biomolecules, either as biopolymers or as small molecules, the way they are imprisoned in the raw plant, and the way they are associated together in networks via non-covalent though strong interactions, which require specific pre-treatment and/or extraction steps.

One option is the high-temperature combustion/cracking of crude biomass. Ultimately, a mixture of carbon oxides and hydrogen can be obtained (the syngas approach), thus solving selectivity issues as compared with processes leading to complex mixtures of partially broken-down biomass. Catalyzed carbon-carbon bond formation from syngas can then readily provide already existing industrially relevant chemicals, albeit for low-value-added products.

An alternative is to target more elaborate products or intermediates (platform molecules), when sufficiently pure and well-characterized biomolecules are available, with limited or no pre-treatment.

Indeed, important and very diverse challenges are still limiting the scope of biobased chemicals having reached the market, with satisfactory ratings in terms of both economy and sustainability. Here, we highlight which facets of chemical sciences can address the main challenges and propose future directions to solve them.

Catalysis

Reaction efficiency and selectivity requires the design of specific catalysts, with appropriate stability and activity in highly oxygenated media, able to address the multifunctional nature of biomolecular substrates while anticipating the target product stability for the avoidance of undesired over-transformed products. Selectivity issues between regioisomers or different levels of transformation (substitution, reduction, oxidation, carbon-carbon

bond cleavage) or degree of polymerization must also be addressed, as should the depletion of some metallic species, by turning to more available ones or non-metallic catalytic methods.

Solvent design

Appropriate media, benefiting from the development of the field of ionic liquids and smart mixtures with catalysts, as well as deep eutectic solvents, are able to dissolve highly bound and polar solids, and thus provide alternatives to previously employed organic solvents.

Engineering

As biomass chemistry involves solids and liquids as starting materials, often very polar, and (rarely) end products in the gas phase, processes able to manage (often very viscous) liquid and solid-liquid phase processes must be elaborated, with possible concomitant separation of target molecules to prevent over-reactions.

Theoretical chemistry and spectroscopy

Despite the size and complexity of the substrates, understanding the intrinsic relative reactivity of multifunctional biomolecules and the reactivity of immediately converted products, in addition to identifying the intermediate reactive species while taking into consideration the contributions of the solvent and the catalyst architecture, will inform us about the reaction mechanisms and the most promising pathways.

Organic synthesis

The renewal of biobased chemistry requires the development of novel efficient, atom-economical, and clean transformations of biomolecules and platform molecules. This will widen the scope of available building blocks and lead to the discovery of innovative chemicals based on original molecular design.

Analytical and environmental chemistry

Analytical methods and devices must address the high structural complexity of biomass, first for characterizing the starting resource and then for monitoring of the conversion, efficiency, and selectivity of the reaction. In combination with environmental chemistry, analytical sciences are essential for establishing the fate of the molecules once released by end users.

Materials science

The polymeric nature of lignocellulosic matter, which accounts for the major part of biomass, and the scope of possible macromolecular targets, either by modification of natural biopolymers or by polymerization of biobased monomers, induce specific issues in terms of reactivity, process, and applications.

Physical chemistry

Physical chemistry and interface sciences take their role in understanding the structure-properties relationships of new constructs based on biomolecules, with respect to both their desired applicative properties and environmental impact.

Biological science, biotechnology, and agricultural science

These are indispensable to the development of biorefineries, at all levels from pre-treatment to molecular transformations as well as biodegradation. Looking ahead, they address environmentally respectful production of biomass and aim toward crops and products yielding resources with easier downstream transformation steps. Biomass biosynthetic and metabolic pathways, with bioinspired functional properties, can also contribute to innovation and enrich the scope of methods and targets.

Economy and social sciences

Together with environmental science, these fields contribute their key viewpoints for measuring the benefits of the processes for all players, from the farmers who grow the biomass to the end users of the chemical products.

CONCLUSIONS

Preferring renewable resources for chemistry certainly must be encouraged. A carbon source is required for the synthesis of organic products. Therefore the

depletion of fossil carbon resources, either oil or coal, will herald a new era of chemistry that relies only on biomass. This will happen within the same end-of-century timescale as is considered for other essential environmental issues, and must thus be addressed now with intense research. In addition, it should be mentioned that policy incentives toward a biobased economy are also important in promoting the development of this field.

Biomass must be recognized globally not only in plants, as CO₂, algae, yeasts, and insects are sensible alternatives. In the longer term, developing reactions and processes using biomass and CO₂ for the synthesis of chemicals will be recognized as the pioneering steps of the post-oil era of chemistry. Meanwhile, this affords us opportunities to design novel chemical products and contribute to the innovation that will lead to a cleaner, sustainable, and safer chemistry.

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DECLARATION OF INTERESTS

The authors declare no competing interests.