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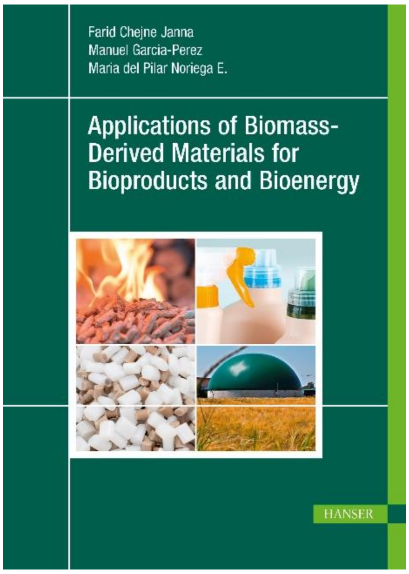

Sample Pages

Applications of Biomass-Derived Materials for Bioproducts and Bioenergy

Farid Chejne Janna, Manuel Garcia-Perez and María del Pilar Noriega E.

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Manuel Garcia-Perez is a professor and chair of Biological Systems Engineering at Washington State University. He has spent two decades researching lignocellulosic material thermochemical conversion for biofuel and chemical production. His work includes studying and understanding cellulose, hemicellulose, and lignin thermochemical reactions and exploring crude bio-oils. He focuses on improving pyrolysis and carbonization reactors for selectivity and refining pyrolysis oils. Dr. Garcia-Perez is also very active in developing and characterizing engineered carbonaceous materials.

Maria del Pilar Noriega Escobar graduated as a chemical engineer at the Universidad Pontificia Bolivariana (UPB), Colombia, and holds a doctorate degree (Ph. D.) in Mechanical Engineering from the University of Wisconsin-Madison, USA. She undertook graduate studies in polymer chemistry of the Technical University of Dresden, Germany, and in polymer extrusion at the institute IKT, University of Stuttgart, Germany. She is a fellow of the Extrusion Division Board of Directors of the Society of Plastics Engineers (SPE) USA. She is co-author of six technical books and many papers in international journals, as well as co-inventor of four patents granted in Colombia, three granted patents in the U.S., and six international patent applications. She is a member of the Mission of Wise Men of Colombia, 2019, and was Technical Director and Director General of the ICIPC (Plastic and Rubber Research Institute) in Colombia. She is the R&D and Innovation Director of Daabon Group on the field of green chemistry and biorefineries.

Preface

Climate change is an issue that concerns the entire world and presents a significant challenge for the global energy sector. The challenge lies in eliminating greenhouse gas emissions that contribute to a climate catastrophe, protecting the energy supply against increasingly intense and frequent weather disruptions, and meeting the growing demand for electricity.

Therefore, there is an urgent need for a transition towards an energy matrix that replaces the use of fossil fuels in all productive sectors. One alternative is the utilization of biomass, such as agricultural waste, as a source of high-value products and energy. This poses a significant challenge for the development of green chemistry within a circular economy.

While the growing need for renewable energy can be satisfied from other renewables, biomass is our only significant source of renewable carbon-based chemicals and fuels. The use of biomass resources is thus receiving increasing attention. Ever more companies and industries are becoming aware of the importance of this new trend and realize that investment in modern technology based on renewable resources will be important to develop their businesses in a sustainable way, i. e., as part of a sustainable circular economy.

Despite this, few scientists and engineers have been appropriately trained to work in the interdisciplinary field of biomass economy. Traditional academic disciplines are not well organized to train engineers and scientists to develop new biorefinery concepts and bio-based products (including bio-based polymers) in industry. Professionals and graduate students must acquire knowledge outside traditional academic disciplines to gain an appreciation of the system. These new concepts tailored to local conditions as well as centralized biorefineries are essential to increase biomass use.

The integration of old and new pathways to satisfy global and local markets is the basic skill required to create new biomass processing alternatives. Few universities offer training to develop and integrate pathways to convert biomass into other forms of energy and useful products.

This book addresses the connectivity between the different biomass-related knowledge areas such as materials science, engineering disciplines, processing technology, product development, and final uses. Additionally, it includes industrial case studies, illustrated with photographs, flow diagrams, or schemes, used to provide approaches to efficient applications.

The chapters show the potential to contribute to the area of biomass-derived materials in science and technology, and aim to fill an educational gap in the biomass economy. In addition, the book outlines a strategy for understanding some intrinsic aspects of lignocellulosic biomass to serve as a starting point for any study taking advantage of it.

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Author Manuel Garcia-Perez thanks his wife, Daniela; his two best teachers, Maria and Mani; his parents, Martha and Manuel; his two sisters, Martha and Tsai; brothers-in-law Raul and Jorge and his nephews (Raul, Fernando, and Danny) because they are the rock-solid ground on which he has built his life. He is grateful to Washington State University for all the opportunities it has provided for his personal and professional development. He also wants to thank his professors, Viera, Pao, Rosabal, Falcon, Roy, and Kretschmer, and his students (Brennan, Matt, Filip, Jesus, Zhouhong, Evan, Lina, Iva, Sohrab, Kalidas, Anamaria, Tanzil, Yinglei, Michael, Jorge, Waled, Shi-Chen, Shuai, and Raiza) for their enormous generosity.

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Finally, the authors show their appreciation to Diana Maria Angel for the figures of this edition.

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1 Applications of Biomass-Derived Materials for Bioproducts and Bioenergy

1.1 Introduction

Biomass, as a natural renewable material, offers plenty of opportunities for various industrial applications in biomaterials, bioenergy, and bioproducts. However, the number of biomass resources available is so large that those interested in its utilization must consider several competing uses and conversion technologies. This book is written for undergraduate students, graduate students, and practitioners interested in understanding how to use underutilized biomass resources to produce construction materials, fuels, chemicals, fibers, and other coproducts.

The book covers thermochemical, biological, chemical, and mechanical biomass conversion approaches and explores potential integration schemes to develop new biorefineries. We aim to go beyond the segmented study of biomass conversion technologies. This book presents a single strategy focused on the main reactions/modifications that cellulose, hemicellulose, and lignin undergo to obtain targeted products. Some of the technologies studied are complementary, so analyzing the strengths and weaknesses of each processing approach is critical to identify synergisms and to propose new biorefinery concepts.

1.2 Biomass Definition

According to the US Environmental Protection Agency, biomass is a “non-fossilized and biodegradable organic material originating from plants, animals and/or micro-organisms, including products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal wastes, including gases and liquids recovered from the decomposition of non-fossilized and biodegradable organic material”[1]. According to regional, national, and international legislations, there are other definitions that provide a financial frame to develop innovative technologies that use and benefit from biomass. The main goal of a biomass engineer is “the production of renewable biological resources and the conversion of these resources and waste streams into value-added products, such as food, feed, bio-based products and bioenergy”[2].

The main biomass sources, considering a broad-base definition of any organic material that comes from plants, animals, or human activities, are described in Figure 1.1. The underlying biomass concept is visualized in the cloud of Figure 1.2.

Figure 1.1 Main sources of biomass

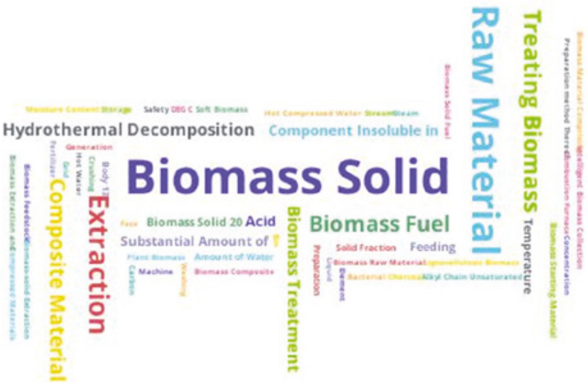

Figure 1.2 Biomass concept cloud, author’s elaboration with information of Acclaim IP

Biomass is a heterogeneous raw material, whose physicochemical composition is variable due to its diverse types and origins. The characteristics and properties of

[1] *https://www3.epa.gov/carbon-footprint-calculator/tool/definitions/biomass.html*

[2] *https://op.europa.eu/en/publication-detail/-/publication/c8b2f69f-4314-11ea-b81b-01aa75ed71a1/language-en*

the biomass determine to a significant extent the proper design of equipment, the plant layout, and the behavior of the unit operations, such as solids handling, solids conveying, drying, grinding, pelletizing, storage, and transformation to usable heat, fuels, and power. Some of the most important properties are the bulk density, particle density, particle size and distribution, compressibility, angle of repose, color, moisture and oil contents, volatiles and ash contents, calorific value, and flowability.

■ 1.3 The Role of Biomass in the Natural Carbon Cycle

The primary atmosphere of Earth, close to 4.54 billion years ago, composed of hydrogen, helium, ammonia, and methane, was dissipated by solar winds. Intense volcanic activity and the impact of asteroids and comets rich in nitrogen, ammonia, carbon dioxide, and water were responsible for the formation of the second atmosphere of our planet. The unique role of biomass and photosynthesis in the natural carbon cycle is responsible for the formation of the third atmosphere of our planet. About three billion years ago, cyanobacteria began obtaining energy from photosynthesis, releasing oxygen into the atmosphere of Earth. This allowed the reduction of atmospheric carbon dioxide (CO_2) from about 4000 ppm five hundred million years ago (Ordovician period) and close to 200 ppm three hundred million years ago (Carboniferous period). CO_2 levels today are close to 420 ppm, much higher than the preindustrial value of 280 ppm. The oxygen content on Earth’s atmosphere increased thanks to the action of photosynthetic microorganisms reaching close to 14 vol% five hundred million years ago and 35 vol% three hundred million years ago. Cyanobacteria and algae store an important fraction of the CO_2 removed from the atmosphere in the form of lipids. The accumulation of these lipids on the bottom of old seas resulted in the formation of the oil deposits we currently use to produce most of our energy, fuels, chemicals, and materials. Photosynthesis remains our only mechanism for CO_2 removal from the atmosphere; however, in today’s world, an important fraction of the biomass produced by photosynthesis is degraded by aerobic microbes back into the atmosphere in the form of CO_2, and a fraction accumulates in soils as a more recalcitrant material through complex humus formation processes.

Although fossil fuels originate from ancient biomass, this carbon (C) is not considered renewable because it has been out of the carbon cycle for millions of years. The concept of biomass is limited to material that is part of the carbon cycle happening in a short timescale. The combustion of fossil C disturbs the CO_2 content in the atmosphere.

1.4 Biomass as Our Only Renewable Source of Carbon-Based Fuels and Chemicals

While green electricity can be produced from other renewable resources (solar energy, wind, and falling water, among others), biomass is the only renewable carbon source to produce materials, fuels, and chemicals (including biopolymers and bioplastics). This fact must be understood when identifying uses for this resource in a C-constrained world. Although there are petroleum deposits to fuel our industry for many more years, the atmosphere of our planet cannot continue assimilating the quantities of CO_2 released from the combustion of fossil resources. Thus, biomass has a unique role to play to remove and sequester C from the atmosphere.

The petroleum industry is already facing great challenges to satisfy the increase in energy demand, driven by population growth and current living standards. The reserves of easy-to-extract oils are becoming scarcer, forcing the petroleum industry to exploit nonconventional oils, which are more expensive and have a higher carbon footprint. In this context, biomass resources are receiving increasing attention. More companies are becoming aware of the importance of developing products with the green C contained in this resource. Investors and policymakers agree that investing in modern technology based on renewable resources is critical to develop their businesses and society in a sustainable direction.

Although the products obtained from biomass have the potential to be CO_2 neutral, the carbon footprint of a biomass-derived product will depend on whether the overall process disturbs the natural C equilibrium. When biomass is used to produce biofuels, it will still release C back into the atmosphere, but the C contained in the biomass is already part of the atmospheric C cycle. During its growth, biomass adsorbs CO_2 from the atmosphere, so the C released during the combustion of the biofuel is renewable C. However, if fossil fuels are used during the collection, transportation, or processing of biomass to obtain biofuels, the C contained in the fossil fuel is a C that was stored for millions of years underground. Releasing excessive quantities of this “dirty C” into the atmosphere could eventually compromise the environmental credentials of the biomass conversion process and even result in C-positive systems.

Ethical and moral questions arise when using edible biomass products (lipids, proteins, starch) to obtain biofuels or chemicals. Most industrialized countries produce more than enough food for domestic consumption. Farmers typically grow crops aiming to maximize their income. Therefore, to the extent that biofuels, biochemicals, and biomaterials can be produced economically and dependably, they can provide farmers with another market and ensure the viability of their food production businesses. Considering the fuels vs. food dilemma as a zero-sum game is a mistake—the growth of a robust bioeconomy could also help improve the resilience and viability of our farmers and in this way support the production and supply of food. The ethical challenge facing our generation is to fight hunger worldwide first and to grow the bioenergy industry whenever possible.

1.5 Overview of Biomass Conversion Technologies

The conversion of biomass to liquid biofuels and chemicals is highly desirable. However, there are major challenges in developing a viable bioeconomy. Biomass is a low-energy-density material that is difficult and costly to transport. Handling solids is much more difficult than handling liquid and gases. Biomass degrades during storage.

The limiting factor for biofuel and biochemical production from lignocellulosic materials is the lack of techno-economically viable technologies. Biomass-based processes involve challenging tasks in pre-treatment, unit operations, and utilization, requiring a good understanding of the process design, methods, and techniques, and the feedstock properties. Biomass transformation enters in the frame of the biorefinery conceptualization: sustainable production of food and feed materials, heat, fuels and power, and green chemicals.

Biomass conversion technologies can be classified according to the driving force responsible for the transformation of the biomass-forming biomolecules (cellulose, hemicellulose, lignin, proteins) into intermediates or the final product; see Figure 1.3.

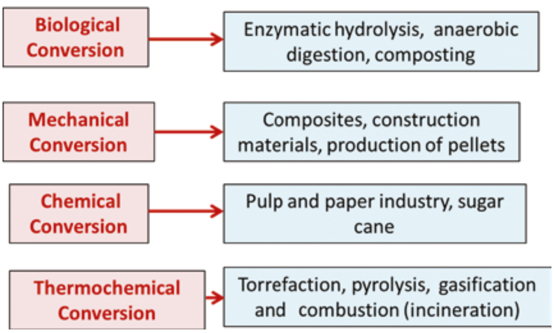

Figure 1.3 Main biomass conversion technologies

The selection of the conversion technology will depend on the advantages and disadvantages of each of them. For example, biological conversion is preferred to convert wet biomass, when the targets are specific single products. Although biochemical conversion is very selective, it tends to be slow. Thermochemical conversion, on the other hand, is typically preferred when processing dry biomass. However, it is not very selective and results often in the production of complex intermediates that are difficult to refine. Biochemical conversion into biofuels has been primarily used to produce alcohols. Thermochemical conversion is typically employed to produce mixtures of hydrocarbons (products from Fischer–Tropsch syngas or bio-oil hydrotreatment). While the biochemical conversion is conducted typically at atmospheric pressure and temperatures below 70 °C, with a reaction time of several days, the thermochemical conversion is conducted typically between 250 °C and 1200 °C, with pressures between 1 atm and 250 atm and residence times that range from seconds to hours. The price of enzymatic catalysts in biochemical conversion can be remarkably high ($0.50/gallon ethanol). Much lower catalyst prices ($0.01/gallon gasoline) are reported for thermochemical pathways. Figure 1.4 shows several technologies used for the processing of wet and dry biomass.

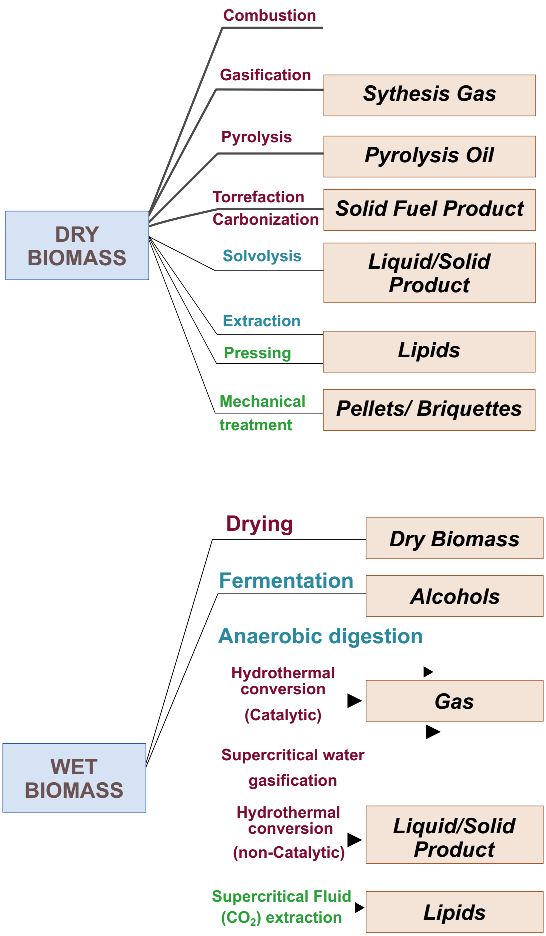

Figure 1.4 Technologies used for the processing or dry and wet biomass [Knežević et al., 2009]

In this book we will study thermochemical, biochemical, chemical, and mechanical conversion technologies. Among the thermochemical conversion technologies discussed for processing dry lignocellulosic materials are torrefaction, carbonization, pyrolysis, gasification, and combustion. Thermochemical conversion technologies are well suited for processing wet biomass, including hydrothermal liquefaction, supercritical water gasification, and wet oxidation. The biochemical conversion technologies are typically divided into aerobic and anaerobic. Ethanol production and composting are examples of aerobic technologies commonly used in industry. Biogas production via anaerobic digestion is an example of a biochemical process occurring without oxygen. Some of the most common chemical processes used for biomass processing include furfural production, production of biodiesel, pulping, and sugarcane production. Pelletization, chipping, grinding, and production of composites are examples of mechanical conversion processes in which mechanical forces are used to shape the final biomass product.

■ 1.6 Bioeconomy

According to the US Congressional Research Service, the term bioeconomy refers to “the share of economy based on products, services and processes derived from biological resources” [Gallo, 2021]. It is a fast-growing section of the economy at the crossroads of multiple sectors (pharmaceuticals, agriculture, textiles, chemicals, energy, waste management, biofuels, and biomaterials).

The definition of bioeconomy used by different countries varies slightly. For example, in Brazil, bioeconomy refers to “the generation of innovative products and services based on the country’s natural resources and ecosystem services.” In the European Union, the definition covers “all sectors and systems that rely on biological resources (animals, plants, micro-organisms, biomass, and organic wastes).” The EU also includes the interlinks between land, marine ecosystems, and the services they provide. It also includes all primary production sectors that produce biological resources (agriculture, forestry, fisheries, aquaculture) and all the industrial sectors associated. The federal government of Germany defines bioeconomy as “the production, exploitation, and use of biological resources, processes, and systems to provide products and services across all economic sectors.” Japan’s concept focuses on “a sustainable and renewable circular economy and society by using biotechnology and renewable biological resources.” The United Nations Food and Agriculture Organization (FAO) defined bioeconomy in terms of “the production, utilization, and conservation of biological resources” [NASEM, 2020].

A definition of bioeconomy should include individual elements such as the biological resource, the conversion technology, the resulting products as well as the analysis of the supply chain and system in which these elements interact [Gallo, 2021]. Depending on how broad the definition of bioeconomy is, it may include traditional mature economic activities (such as the pulp and paper industry, the sugarcane) and large economic sectors such as agriculture, forestry, and wood manufacturing, already contributing to the global economy. Some of them are not growing sectors–their general impact on economy is, in fact, decreasing. This may explain why some prefer narrower definitions focusing on modern technologies and innovations that show a much more dynamic performance of the bioeconomy than that of the traditional biomass industry. The US National Academies of Sciences, Engineering, and Medicine (NASEM) proposed some criteria to include a sector in the bioeconomy. For example, in the case of agricultural sectors, they recommend: (1) genetic engineering when creating strain or seed, (2) advanced molecular biology techniques for marker-assisted breeding programs, (3) large informatics databases and computational techniques for either breeding applications or enhanced land use capabilities, and (4) taking advantage of biomass in a downstream bioprocessing and/or fermentation process utilizing recombinant DNA technology. Some of the industries included are precision agriculture and genetically modified crops and animals. In the case of the bio-industrial sector, they include products or chemicals produced by means of a biosynthetic route using recombinant DNA technology. Industries included are, for instance, biobased chemicals, biofuels, and biobased plastics. Table 1.1 shows some of the industries included and excluded by the US NASEM as bioeconomy. In this book we will employ a broad definition of bioeconomy because many of the technologies used in the mature industries will find applications in the emerging sections of the bioeconomy.

Table 1.1 Industries Included or Excluded from US Bioeconomy Definitions (Taken from [Gallo, 2021])

Wholly Included Industries	Partially Included Industries	Industries with Emerging Activities that May Be Included in the Future	Excluded Industries
▪ Pharmaceuticals ▪ Biotechnology research and development ▪ Medical diagnostics	▪ Crop production ▪ Electricity generation ▪ Processed food ▪ Chemicals ▪ Plastics and rubber ▪ Other physical, engineering, and life sciences research and development	▪ Livestock production ▪ Fisheries/aquaculture ▪ Forestry ▪ Mining (bioleaching) ▪ Textiles	▪ Beverages, tobacco, and leather products ▪ Wood manufacturing ▪ Paper products ▪ Furniture manufacturing ▪ Apparel ▪ Health care ▪ Druggist's goods ▪ Agriculture supplies ▪ Construction ▪ Water treatment and supply ▪ Nature tourism, hunting, and fishing

The growth in the use of biomass as a source of high-value-added products, such as cellulose, nanocellulose, hemicellulose, lignin, acids, alcohols, glycerin, sugars, furfural, aldehydes, resins, bioactive molecules, biopolymers, among others, is evident in the last decade in a vast number of intellectual property (IP) filings as shown in Figure 1.5 and Figure 1.6.

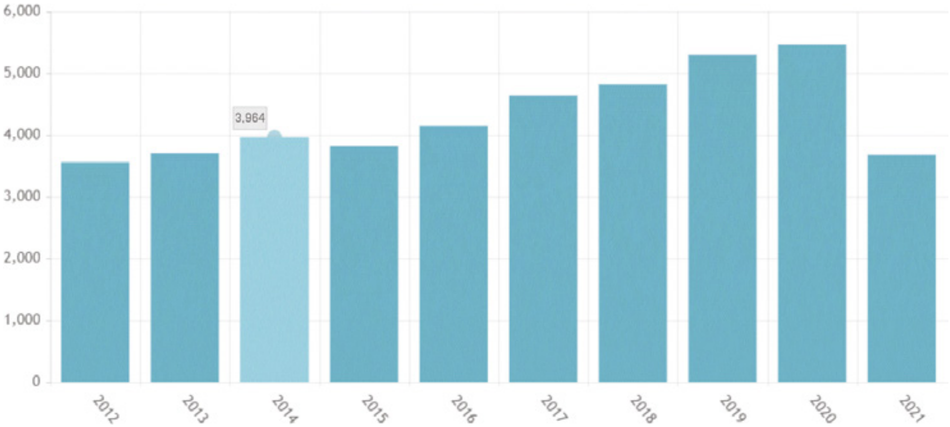

Figure 1.5 IP filings on biomass-derived materials in the last decade (*Patentscope-WIPO*)

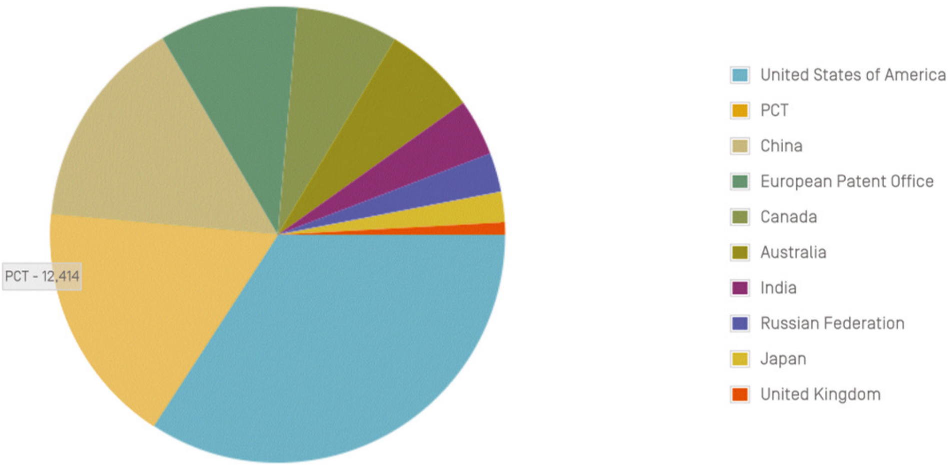

Figure 1.6 IP filings on biomass-derived materials by country (*Patentscope-WIPO*)

Bioenergy produced from biomass has shown in the last decade an important number of IP filings, as presented in Figure 1.7 and Figure 1.8.

Bioeconomy is based on biomass, and more than fifty nations worldwide are pursuing their own bioeconomy policies for supporting economic growth, environmental protection, and sustainable development [Financial Tribune, 2018]. Most nations view the development of a sustainable bioeconomy as a tool to address some of the grand challenges facing the world today (climate change, food security, energy independence, environmental sustainability) [Gallo, 2021]. Likewise, the growth of the bioeconomy is considered a fantastic opportunity to create new jobs, improve human health, and contribute to rural development. It is estimated that over the next ten years globally, the direct impact of biobased products, services, and processes could be up to $4 trillion. According to the McKinsey Global Institute (MGI), biological methods have the capacity to produce "as much as 60% of the physical inputs to global economy" [Gallo, 2021].

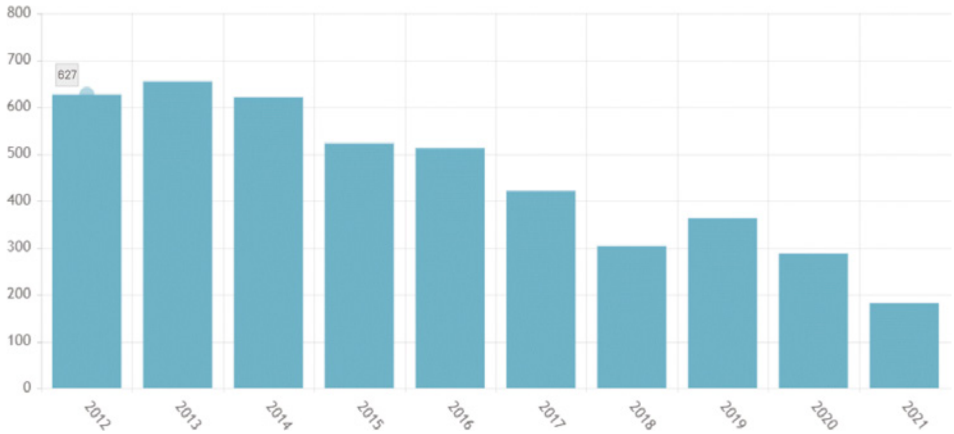

Figure 1.7 IP filings on bioenergy from biomass in the last decade (*Patentscope-WIPO*)

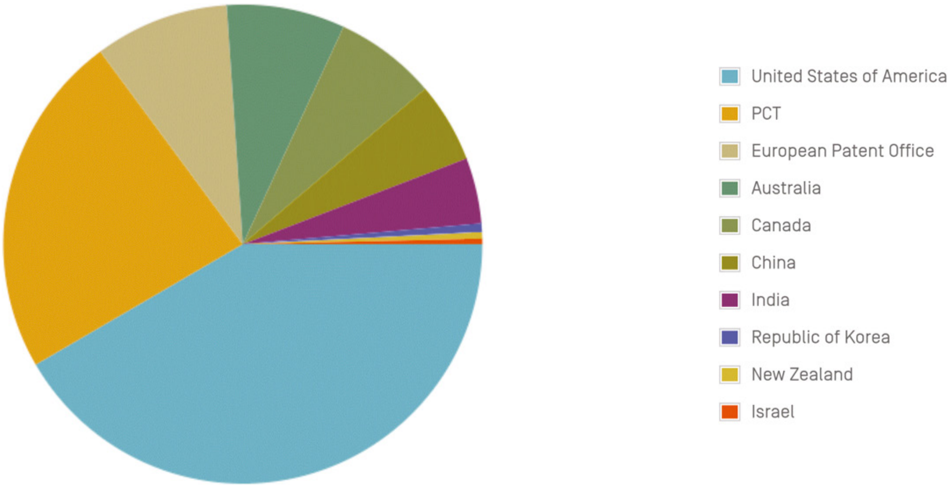

Figure 1.8 IP filings on bioenergy from biomass by country (*Patentscope-WIPO*)

Despite this, few scientists and engineers have been appropriately trained to work in the interdisciplinary field of biomass processing and economy. Traditional academic disciplines are not well organized to train engineers and scientists to develop new biorefinery concepts and a biobased products industry. The Organisation for Economic Co-operation and Development (OECD) is, however, concerned that without active support from governments and the public at large, the potential of the bioeconomy may not be realized [Gallo, 2021].

References

[Financial Tribune, 2018] *https://financialtribune.com/articles/world-economy/85.120/50-nations-pursuing-own-bioeconomy-policies* (accessed: May 12, 2023).

[Gallo, 2021] Gallo, M. (2021). The Bioeconomy: A Primer. Congressional Research Service, August 19, 2021. *https://crsreports.congress.gov//product/pdf/R/R46.881*

[Knežević et al., 2009] Knežević, D., van Swaaij, W. P.M., Kersten, S. R.A. (2009). Hydrothermal Conversion of Biomass: I, Glucose Conversion in Hot Compressed Water. *Industrial & Engineering Chemistry Research*, 48(10), 4731–4743. *https://doi.org/10.1021/ie801387v*

[NASEM, 2020] National Academies of Sciences, Engineering, and Medicine (2020). Safeguarding the Bioeconomy. Washington, DC: The National Academies Press. *https://doi.org/10.17.226/25.525*

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