

The Transition of Scientific Research from Biomass-to-Energy/Biofuels to Biomass-to-Biochemicals in a Biorefinery Systems Framework

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1. Introduction

Only through renewable carbon source valorization will it be possible to obtain a high-impact transition from a fossil-based system to a renewable-based system. In particular, biomass is the only renewable source containing carbon atoms able to replace fuels, chemicals, and materials. In recent years, scientific research has focused less on biomass valorization producing energy (thermal or electricity). This was due to the lower economic attraction of biomass as an energy source compared to other renewable sources (e.g., solar, wind, geo, etc.). On the other hand, attention has moved to biomass valorization to obtain high-added value compounds, replacing fossil-based products. This editorial collects together leading publications highlighting this scientific transition process.

2. Biomass-to-Energy/Biofuels

The first example of the integration of bioresources with fossil sources to produce energy was represented by Integrated Gasification Combined Cycle (IGCC) plants. In particular, Sofia et al. (2013) [1] studied a process simulation model to co-feed coal and solid biomass, producing electricity with the lowest CO₂ emissions. The gasification process of both feedstocks led to a 16% decrease in fossil CO₂ emissions at the price of a loss of net power lower than 6%. Ahorsu et al. [2] focused on all aspects concerning the transition to biomass valorization by biorefineries, i.e., biomass composition (cellulose, hemicellulose, lignin if lignocellulosic material; humidity degree, triglyceride/fatty acids distribution, sugars concentration if wet wastes), biorefinery classification (from 1st to 4th generation), target products obtainable (ethanol, biodiesel, methane, hydrogen), and the process technologies used for biomass transformation (biochemical, chemical, or thermochemical). Finally, the authors described the market diffusion of biofuels and biorefineries from the perspective of bio-based chemicals and derivatives substituting fossil-based fuels. In particular, Caposciutti et al. [3] studied the transition to upgraded biogas, substituting conventional biogas power plants. In this work, a biochemical process (anaerobic digestion) was analyzed using a numerical model of the existing case study. In particular, the impact on biomethane productivity was estimated considering an upgrading system based on CO₂ absorption and a cogeneration unit by the internal combustion engine valorizing a variable percentage of biogas. Importantly, excess biomethane production means that the plant is totally dependent on external energy sources. As for the environmental impact, an optimal level of biomethane production exists that minimizes the emissions of equivalent CO₂. However, high biomethane subsidies can encourage plant managers to increase biomethane production, reducing CO₂ savings.

3. Transition to Biomass-to-Biochemicals

Temporim et al. [4] and Kohli et al. [5] focused on two opposite aspects of biomass valorization: polygeneration to energy and biochemical production, respectively. In the



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first, the cardoon biomass was considered entirely burned to produce three kinds of energy: electricity by steam turbines with an energy efficiency of about 19%, heat by high-pressure steam ($\approx 51\%$), and cold by an absorption chiller ($\approx 27\%$). The second, on the other hand, demonstrated the feasibility of the production of 5-hydroxymethylfurfural (5-HMF), levulinic acid, furfurals, sugar alcohols, succinic acid, and lactic acid from sugar feedstocks and aromatics from lignin. The authors determined the need to increase the yields of the multistep synthesis processes, improve the purification steps, decrease capital costs, and develop new catalysts with longer deactivation times. Regarding thermochemical processes, Glushkov et al. [6] worked on biomass pyrolysis and gasification. In particular, the results highlighted that the composition of lignocellulosic biomass is a more important process parameter to determine the yields of gas and liquid products. The higher the cellulose content, the higher the yield of the liquid pyrolysis product. The hemicellulose content can increase the pyrolysis gas yields, and the lignin content increases the yield of the solid product (char). Another important parameter is biomass particle size; the smaller size leads to higher hydrogen concentration in the gases. These conclusions can be the basis for building conversion strategies for different kinds of biomass if dedicated to an energy conversion or a chemical application for the further chemical synthesis of fuels and chemicals. Thermochemical processes for biofuels represent an opportunity to convert heterogeneous materials that are difficult to pretreat or process directly. Marcon et al. [7] performed a techno-economic and environmental analysis to assess the integration of biomass gasification/Fischer–Tropsch synthesis into a conventional sugarcane distillery, to produce advanced liquid biofuels. Additionally, Dimethyl Ether (DME) is considered a promising bio-based liquid fuel. Giuliano et al. (2021) [8] studied its production by the synthesis of syngas derived from the gasification of the digestate. Thermodynamic analysis assessed the effect of the process conditions of both water gas shift and CO_2 absorption by Selexol[®] on the syngas composition. The environmental impact was found to be equal to $-113 \text{ kgCO}_2/\text{GJ}$, demonstrating that DME synthesis from digestate may be considered a suitable strategy for carbon dioxide recycling. On the other hand, Moran et al. [9] explored the sustainability of new biomass pretreatment processes using Deep Eutectic Solvents (DES). The utilization of choline chloride [ChCl]:glycerol and [ChCl]:urea was studied from an experimental point of view. The main results highlighted that using [ChCl]:glycerol reduced about 80% and 15% acid-soluble lignin and Klason lignin, respectively. The saccharification efficiency increases to 60, 80, and 100% for conversions of glucan, xylan, and arabinan, respectively. The authors confirmed the effectiveness and facility of DES pretreatment as a suitable method to improve biorefinery processes. Focusing again on lignocellulose conversion by pretreatment and hydrolysis, Castellini et al. [10] assessed a techno-economic analysis for the transformation of cardoon residual material to biodiesel using a 2nd generation sugars platform. In particular, a novel sugar fermentation technology was considered, using oleaginous yeasts to store triglycerides, which were converted to biodiesel as the conventional processes (i.e., transesterification). The best biodiesel production cost found was 3.63 USD/kg, making the product competitive in the current biofuel market by microbial oil. Biofuel production through biochemical processes was studied by Skiba et al. (2022) [11], converting *Miscanthus sacchariflorus* using HNO_3 -pretreatment, hydrolysis, simultaneous saccharification, and fermentation to bioethanol. A bioethanol concentration of 40 g/L was found. The impurity concentration was evaluated after the HNO_3 pretreatment, with an impurity content lower than 6.5 g/L.

4. Focus on the Biomass-to-Biochemicals Scientific Research

The 2nd-generation sugar platform is the most frequent one. De Bari et al. (2020) [12] considered the assessment of an integrated biorefinery processing 60 kton/y of lignocellulosic biomass derived from cardoon residues, producing 1,4-butanediol (bio-BDO). A cradle-to-gate simplified environmental assessment was conducted in order to evaluate the environmental impact of the process in terms of carbon footprint. The carbon footprint value calculated for the entire production process of BDO was $2.82 \text{ kgCO}_{2\text{eq}}/\text{kgBDO}$. An-

other prolific author, Clauser et al. (2018) [13], studied the optimal sizing of these kinds of biorefinery. The proposed scheme involved the production of levulinic acid, formic acid, acetic acid, and furfural. The energy used for levulinic acid production was one of the main production costs. On the front of high-added value compounds combined with microbial fermentations, Kerssemakers et al. [14] assessed the feasibility of itaconic acid production using the fungus *Aspergillus terreus*. The feasibility of using cellulose pulp was demonstrated through assays that revealed the preference of the strain in using glucose as a carbon source instead of xylose, mannose, sucrose, or glycerol. Additionally, the cellulose pulp was easily digested by enzymes without requiring a previous step of pretreatment, producing a glucose-rich hydrolysate with a very low level of inhibitor compounds, suitable for use as a fermentation medium. The production of itaconic acid was maximized, resulting in a yield of 0.62 g/g glucose consumed and productivity of 0.52 g/Lh. When no thermochemical processes are used, each lignocellulosic biomass valorization process leads to a carbonaceous residual material, a correspondingly high percentage of the initial feedstock (20–30%): lignin. Davis et al. [15] found an alternative to conventional lignin combustion, producing energy. The work aimed to review the historical background and current technology of lignin depolymerization. In particular, novel microbial routes to lignin degradation, some applications of these microbial enzymes and pathways, and the current chemical and biological technologies to upgrade lignin-derived monomers.

In conclusion, the perspective concerning the transition of biomass valorization from renewable energy production to chemical production is off the table. A possible way consists of integrating conventional energy-producing processes of biorefinery wastes with novel and or commercial-scale technologies to valorize biomass to biofuels or biochemicals. This allows for the convenience of the transformation processes of a single fraction of biomass, such as lignin, which needs further studies to reach techno-economic-environmental sustainability.

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