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Editorial

Special Issue on "Bioethanol Production Processes"

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The transportation sector is facing a profound challenge to utilize a greater proportion of sustainable substitutes in relation to oil-derived products. Bioethanol is leading this transition worldwide as it can be easily obtained via the fermentation of starch- and sugar-based feedstocks. As an alternative to the traditional production processes, also known as first-generation (1G) technologies, the use of lignocellulosic biomass is expected to play a key role as a carbohydrate-rich feedstock in the production of ethanol fuel and will definitely contribute to the resolution of the food vs. fuel debate. According to Duque et al. [1], the efficient use of lignocellulose requires: (1) an effective fractionation process to increase the accessibility of hydrolytic enzymes to carbohydrates; (2) the use of key activities to reach complete biomass saccharification; and (3) the use of robust microbial strains capable of converting sugar mixtures and coping with the inhibitory compounds present during fermentation processes. In addition, several strategies such as working at high-gravity conditions, using relatively high temperatures during fermentation, and designing specific process configurations have been also investigated in order to maximize advanced ethanol production from lignocellulosic materials.

Advanced bioethanol can also be obtained from marine resources. The use of seawater, seaweed and/or microalgae biomass are some examples of these uses. In this context, Zaky [2] underlines the development of coastal integrated marine biorefinery (CIMB) systems as important methods for the production of biofuels (including bioethanol) and bio-based products. These CIMB systems help to reduce the use of arable land and freshwater, increasing the economic and environmental value of these systems. The implementation of CIMB systems therefore contribute towards achieving a negative water footprint (WF) and a negative carbon footprint (CF) for the targeted biorefinery products.

Despite the great efforts made by the industry and the research community in recent decades, advanced bioethanol production processes still require further developments if we are to fully implement the technology. With the aim of achieving a cost-effective modality of advanced bioethanol production, Susmozas et al. [3] consider the co-production of biofuels and value-added products, as well as the retrofitting of 1G ethanol facilities with state-of-the-art equipment from advanced processes, as attractive alternative biorefinery strategies. In the case of retrofitting approaches, these methods often result in lower capital expenditure (CAPEX), shorter lead times, faster implementation, fewer production time losses, and lower risks than would be implied by building a completely new advanced ethanol facility. As such, they should be taken into account in order to promote the transition from 1G technologies to advanced ethanol production.

This Special Issue of *Processes*, entitled "Bioethanol Production Processes", showcases novel advances in the development and implementation of cost-effective conversion technologies for use in bioethanol production. The Special Issue concerned is available online at https://www.mdpi.com/journal/processes/special_issues/Bioethanol_Production_Processes.

1. Biomass Processing and Integrated Biorefineries

Biomass fractionation is key to making an effective and complete use of this resource. Targeting the disruption of the complex and recalcitrant carbohydrate–lignin matrix, different pretreatment technologies have been designed and tested towards facilitating access to, and recovery of, the corresponding sugars and valuable compounds. Chopda et al. [4] study the use of an acid-catalyzed ethanol organosolv pretreatment of oat husks, without the need for a previous milling step, promoting the delignification of this feedstock and allowing the recovery of three different streams (i.e., glucan-rich, hemicellulosic compound-rich and lignin-rich streams). The resulting glucan fraction shows very high digestibility potential (up to 90%), while the collected high-purity lignin offers the possibility for higher-value applications of this component. On the other hand, Bedő et al. [5] and Buruiană et al. [6] investigate the use of dilute–acid pretreatment for the valorization of brewer's spent grain and sweet sorghum, respectively, within a biorefinery approach. This pretreatment allows the conversion of these substrates for the co-production of ethanol and hemicellulosic sugars in the form of both mono- and oligo- saccharides.

The use of novel microorganisms also benefits the further development of biorefineries, as they provide novel enzyme activities and fermenting strains. As highlighted by Zuliani et al. [7], thermophiles therefore represent valuable tools as sources of thermostable enzymes which can withstand harsh industrial conditions (i.e., extreme pH, high temperature, long process time, presence of organic solvents, etc.) while ensuring the required standards of reproducibility. In addition, the use of thermophiles as fermentative microorganisms for bioethanol production also enables the performance of a one-pot/one-phase simultaneous saccharification and fermentation (SSF). This may contribute to lowering the required enzyme doses together with providing the benefit of integrating these two stages.

Another important aspect in the implementation of biorefineries is the search for cheap sugar-rich raw materials that do not compete with the food sector. In this context, the identification and estimation of all the biomass available in a specific region is crucial to evaluating the viability of the related biorefinery. Basaglia et al. [8] investigate the availability of residual inexpensive agro-food biomasses in the Northeastern Italy that feed an advanced bioethanol plant located in this area, with the wheat straw and vine shoots being the most promising substrates. These authors claim the possibility of sustaining bioethanol production within this specific district by using the identified agro-food residues. Algal biomass also represents another promising feedstock. Cioroiu Tirpan et al. [9] investigate the potential of the brown algae *Cystoseira barbata* to produce bioethanol and added-value bioactive compounds with antimicrobial, antifungal, antiviral, and antitumor properties. In total, 19 active compounds are identified in the resulting fermenting broth. This alga therefore offers the possibility of producing energy as well as representing a dietary supplement, although it must be cultivated in abundance to provide enough biomass.

2. Fermentation of Sugar-Rich Hydrolysates

During advanced biomass conversion processes, the efficient use of all the sugars that are contained in the raw material is crucial in order for the procedure to have maximum cost-effectiveness. Valorization of the hemicellulosic sugar stream is therefore an essential step towards the integral use of biomass. This fraction is usually rich in pentose sugars (e.g., xylose, arabinose), which are not fermented by native *Saccharomyces cerevisiae* strains (the fermentative yeast commonly used by the ethanol industry). In addition, the presence of biomass-derived inhibitors generated during pretreatment (e.g., acetic acid, formic acid, furfural, 5-hydroxymethylfurfural, and certain phenolic compounds) makes the conversion processes even more challenging. Lopez-Linares et al. [10] investigate the combination of detoxification by overliming and activating charcoal treatment and using the recombinant *Escherichia coli* SL100, capable of utilizing both hexoses and pentoses, to convert the hemicellulosic-rich stream, obtained from dilute–acid-pretreated exhausted olive pomace, into ethanol. The proposed process allows the conversion of almost all the sugars contained in the hemicellulosic-rich hydrolysate, showing ethanol yields higher than 90% of the theoretical value. Domínguez et al. [11] follow a similar strategy for converting the resulting hydrolysates obtained from *Paulownia elongata x fortune* wood after autohydrolysis pretreatment. In this work, they show recombinant xylose-fermenting *S. cerevisiae* MEC1133 to be capable of fermenting the non-detoxified hemicellulosic stream in comparison to a native *Scheffersomyces stipitis* strain that is completely inhibited after several hours of inoculation. This result highlights cell robustness as being a key parameter in boosting fermentation performance and reducing operational costs.

The fermentation strategy is another important aspect during advanced ethanol production. Portero Barahona et al. [12] evaluate ethanol production from alkali-pretreated sugarcane bagasse, coupling a semi-continuous fermentation system with a SSF strategy. The process reaches ethanol concentrations as high as 10% (v/v) and shows itself to be stable over 30 days. On the other hand, Alqahtani et al. [13] model a continuously stirred bioreactor with recycling with the aim of providing useful results for bioreactor–settler stability and assessing the effect of key parameters on the dynamic behavior of the system, which can be useful for future optimization studies. The model identifies the feed substrate concentration, purge fraction and the recycle ratio as key parameters affecting the critical residence time, which occurs when there is a stability exchange between washout and non-trivial solution. This proposed model is based on experimental values, thus providing extra support to the resulting data derived from the study.

Reducing the operational costs during ethanol production directly impacts the biorefinery viability. Certain fermentation processes, such as the acetone–butanol–ethanol (ABE) fermentation with the *Clostridium* species, require anaerobic conditions for optimal biomass conversion. Usually, anaerobic conditions are created by using oxygen-free nitrogen gas, thus increasing cost in large-scale fermentations. Daengbussadee et al. [14] investigate the use of the aerobic bacteria *Arthrobacter* sp. to consume residual oxygen and avoid nitrogen gas fluxing into the system. A mixed culture of *Clostridium beijerinckii* and *Arthrobacter* sp. BCC 72131 shows similar product yields and productivities when compared to the monoculture system subjected to nitrogen gassing. This mixed culture may definitely contribute towards reducing final process costs, although actual values must be properly assessed.

3. Downstream Processing and In Silico Assessments

After the fermentation of the corresponding sugar-rich hydrolysate, distillation is needed to purify ethanol from the resulting broth. In addition, to reach the state of fuel-grade product, ethanol must be also dehydrated to remove excess water from the distilled ethanol–water mixture. Dehydration can be performed by using zeolites (natural and synthetic) and/or salts. Rumbo Morales et al. [15] analyze different absorbents (e.g., Clinoptilolite—S.L. Potosi, Clinoptilolite—Puebla, and Heulandite—Sonora, and Zeolite Type 3A) to separate ethanol-water mixtures, Zeolite Type 3A and Heulandite—Sonora being the materials with higher adsorption capacity. In addition, the simulation of the capacity of a a pressure swing adsorption process to dehydrate ethanol with the Zeolite Type 3A shows increased water removal when working at high pressures and constant temperature (100–120 °C). This process may also benefit from increasing the length of the column by promoting energy savings and removing other impurities. In contrast, Torres Cantero et al. [16] use the salt $CaCl_2$ as a separating agent and model the distillation process using the software Aspen Dynamics® to evaluate the control of the process. Among the different control structures investigated, the L structure is the one with the best performance, reporting a lower error rate and a lower power consumption.

The use of in silico modeling is also crucial in assessing biorefinery performance from the techno-economic, environmental and social points of view prior to scaling up the process. Sanchis-Sebastiá et al. [17] use the software known as BioSTEAM to simulate a wheat straw biorefinery and an animal bedding biorefinery and compare their economic performances. This study highlights water recycling as a critical step towards reducing the ethanol price when using animal bedding as raw material. Under these conditions, the minimum ethanol selling price per liter is estimated to be USD 0.38, which is 40% lower than the corresponding wheat straw biorefinery. In addition to evaluating the economic viability of a certain biorefinery, the life cycle assessment is required to evaluate the environmental impact of the system. Zaky et al. [18] investigate the environmental impact of implementing a coastal marine biorefinery (CMB) system for bioethanol production by evaluating the corresponding life cycle assessment. Their CMB system is based on using seawater instead of freshwater and the use of coastal regions instead of inland locations to place the biorefinery. Compared to the conventional scenario, the coastal seawater scenario significantly improves all the evaluated parameters, highlighting the effect on water depletion, natural land transformation, climate change and fossil depletion. This result clearly shows the positive impact of using seawater and coastal locations for bioethanol production and plant construction, respectively, issues which must be further explored.

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