Production of Bio-Derived Fuels and Chemicals

Thaddeus Chukwuemeka Ezeji

Department of Animal Sciences and Ohio Agricultural Research and Development Center (OARDC), The Ohio State University, 305 Gerlaugh Hall, 1680 Madison Avenue, Wooster, OH 44691, USA; ezeji.1@osu.edu

Keywords: lignocellulose; biomass; pretreatment; butanol; ethanol; butanediol; acetone; LDMIC; hydrogen

The great demand for, and impending depletion of petroleum reserves, the associated impact of fossil fuel consumption on the environment, and volatility in the energy market have elicited extensive research on alternative sources of traditional petroleum-derived products such as biofuels and bio-chemicals. Fossil oil is largely associated with gasoline, however, approximately 6000 petroleum-derived products currently exist in the market, with diverse applications. Ironically, while biofuels are more popular with the public, the other petroleum-derived products have not attracted similar attention despite the vast economic values for these products. Thus, given the finite nature of petroleum, it is timely to deploy substantial resources and research efforts to the development of renewable chemicals (similar to the efforts devoted to biofuels). Theoretically, bio-production of gasoline-like fuels and the 6000 petroleum-derived products is within the realm of possibility, because aquatic and terrestrial ecosystems harbor an abundance of diverse microorganisms, capable of catalyzing unlimited numbers of chemical reactions. Moreover, the fields of synthetic biology and metabolic engineering have evolved to the point that a wide range of microorganisms can be induced or manipulated to catalyze foreign or vastly improve indigenous biosynthetic reactions. Hence the need for this Special Issue to provide a platform for highlighting recent progress on fuel and chemical production from renewable resources such as lignocellulosic biomass.

This Special Issue, titled Biofuels and Biochemicals Production, consists of 13 articles in which eleven and two are research and review articles, respectively. The Special Issue covers themes on the development of different methodologies for efficient conversion of lignocellulosic biomass, agricultural wastes, carbon dioxide, and carbon monoxide to fuels (ethanol, butanol, hydrogen), chemicals (2,3-butanediol, acetone, acetic acid), and enzymes (cellulase). Some of the articles in this Special Issue provide recent advancements on pretreatment and hydrolysis of lignocellulosic biomass (LB) to lignocellulosic biomass hydrolysates (LBH), challenges associated with LBH utilization, and recommended mitigation strategies.

Consistent with the Biofuels and Biochemicals Production theme, the research groups of Moreno [1] and Rosentrater [2] evaluated different pre-treatment technologies for efficient disruption and separation of lignin from the hemicellulose component of the LB to facilitate enzymatic hydrolysis of the carbohydrate fraction to fermentable sugars. By combining acid-catalyzed steam explosion and alkali-based extrusion process, the protective lignin structure of barley straw was disrupted, which resulted in hydrolysates with significant amounts of glucan and hemicellulose sugars, minimal concentrations of lignocellulose derived microbial inhibitory compounds (LDMICs), and a solid residue with significant amounts of lignin [1]. In addition, the Low-Moisture Anhydrous Ammonia (LMAA) pre-treatment method enhanced enzymatic hydrolysis of the cellulose component of the LB to glucose, thus, the potential is great for LMAA for LB pre-treatment [2]. Consistent with enzymatic hydrolysis of the cellulose component of LB, Bajaj’s group contributes an article that highlights the capacity of Bacillus subtilis SV1 to use agroindustrial residues (LB) as carbon and nitrogen sources for...
growth and ionic liquid (IL) stable cellulase production followed by the hydrolysis of IL-pretreated LB to fermentable sugars [3]. Unfortunately, pre-treatment and hydrolysis of LB can result in the formation of a complex mixture of LDMICs that are toxic to fermenting microbes. Examples of LDMICs are furfural, hydroxymethylfurfural (HMF), benzaldehyde, syringaldehyde, and acetic, ferulic, glucuronic, p-coumaric, syringic, levulinic acids, and so on [4]. Overcoming the barriers imposed by LDMICs motivated the study conducted by Marinova’s group in which LDMICs of phenol origin in LBH were detoxified using nanofiltration, flocculation, laccase, and combinations thereof [5]. Detoxification of LBH by a combination of flocculation and laccase enzymes before fermentation drastically reduced the concentration of LDMICs in LBH, and significantly improved the fermentation of LBH to butanol [5].

To go beyond conversion of LB to fermentable sugars and produce usable products with lesser carbon footprints, Rorke and Kana [6] evaluated the feasibility of using Monod and modified Gompertz models to study the kinetic behaviour of a bioethanol fermentation process using sorghum leaves and *Saccharomyces cerevisiae* as a substrate and fermentation microorganism, respectively. Interestingly, obtained Monod and modified Gompertz coefficients indicated that waste sorghum leaves can serve as an efficient substrate for bioethanol production. Similarly, Bardi and Cutzu [7] evaluated production of ethanol from agricultural wastes (apple, kiwifruit, peach wastes, and corn threshing residue) using residual thermal energy from ethanol distillation column. Their article recapitulates different concentrations of ethanol obtained from these wastes during ethanolic fermentation with *S. cerevisiae*. With the exception of peach wastes, all the waste substrates assessed had promise for industrial ethanol fermentation, a finding that bodes well with use of non-food crops for biofuel production. Additionally, Krömer’s group contributes a technical note that describes simultaneous quantitation of sugars, carboxylates, alcohols and aldehydes in fermentation broth by High Performance Liquid Chromatography (HPLC) [8]. The developed method allows quantitation of 21 compounds in a single process, and could be used in LB pretreatment, hydrolysis, and fermentation of LBH to fuels and chemicals’ research.

The two articles from Atiyeh’s and Sekoai’s groups focus on production of ethanol and acetic acid from synthesis gas by *Clostridium ragsdalei* [9] and optimization of fermentative production of hydrogen using Box–Behnken design [10]. Notably, Atiyeh’s article is the first study on continuous operation of syngas fermentations in a trickle-bed reactor (TBR) for ethanol and acetic acid production, and the report highlights operational constraints and challenges of continuous syngas fermentation in TBR, and how the bioreactor operation can be restarted after major accidents such as flooding and power shutdown [9]. Sekoai’s study indicates that there can be an improved biohydrogen production yield of 603.5 mL H$_2$/g total volatile solid (TVS) or more which is achievable at optimized operational set point variables of 39.56 g/L, 82.58 h, 5.56, and 37.9 °C for substrate concentration, fermentation time, pH, and temperature, respectively; a finding that could facilitate the use of large-scale biohydrogen production processes [10].

Fermentative production of chiral compounds is currently receiving remarkable attention because of the numerous industrial applications in the biofuel, synthetic rubber, bioplastics, cosmetics, and flavor industries, and high cost of production from chemical synthetic routes. Recognizing the importance of chiral compounds in the biotechnology industry, our group [11] contributed an article in which process development for enhanced 2,3-butanediol (2,3-BD) production by non-pathogenic bacterium, *Paenibacillus polymyxa* DSM 365, was emphasized. Indeed, while our group was able to increase the concentration of 2-3-BD from 47 g/L (un-optimized) to 68.5 g/L (optimized) under fed-batch fermentation condition, the results underscore an interaction between medium components and fermentation conditions, which tends to influence 2,3-BD and undesirable exopolysaccharides (EPS) production [11]. Although butanol is an achiral compound, it is an important chemical with many applications in the production of solvents, butyl acetates, butylamines, plasticizers, amino resins, etc. [12]. These facts were echoed by Li’s group whose article focused on the feasibility of using acidified fibrous immobilization materials (cotton balls, modal fiber and charcoal fiber) to improve production [13]. By pre-treating modal fiber materials with 3.5% HCl for 12 h, the structure of modal
fibers was etched to decrease mass transfer resistance, increased adsorption of C. acetobutylicum to the material, and ultimately, enhanced the kinetics of acetone butanol ethanol (ABE) fermentation [13].

The review articles in this Special Issue provide insights into syngas fermentation [14] and the significance of laccases in the development of LB as an important substrate for the production of renewable fuels and chemicals [15]. The review article contributed by Phillips et al. [14] indicates that integration of thermochemical gasification of LB and wastes to syngas (CO, CO$_2$ and H$_2$) and syngas fermentation by autotrophic bacteria is a robust and potentially economical process for the production of fuels and chemicals. Important concepts such as Wood–Ljungdahl biochemical pathway reactions and applications, gas solubility, mass transfer, thermodynamics of enzyme-catalyzed reactions, electrochemistry and cellular electron carriers and fermentation kinetics, were highlighted [14]. The review article contributed by Fillat et al. [15] provides important studies and perspectives on the use of laccases as a delignification and detoxification tool for efficient conversion of LB into value-added products, with emphasis on lignocellulosic ethanol production; highlighting major challenges and opportunities, and plausible ways to integrate the enzymes in the future lignocellulose-allied industries.

In conclusion, it is my hope that this Special Issue will serve as a useful resource for students, teachers, professors, engineers, government personnel, and anyone actively or passively involved in renewable fuels and chemical production and research. In summary, I wish to thank our article contributors, Editorial Board members, Ad Hoc reviewers, and Assistant Editors of this journal, whose contributions made the publication of this Special Issue possible.

Conflicts of Interest: The author declares no conflict of interest.

References
1. Oliva, J.M.; Negro, M.J.; Manzanares, P.; Ballesteros, I.; Chamorro, M.A.; Sáez, F.; Ballesteros, M.; Moreno, A.D. A Sequential Steam Explosion and Reactive Extrusion Pretreatment for Lignocellulosic Biomass Conversion within a Fermentation-Based Biorefinery Perspective. Fermentation 2017, 3, 15. [CrossRef]


© 2017 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).