Chapter 6
The Future of Biomaterials Engineering and Biomass Pretreatments

The energy and environmental crises that the world is facing are forcing us to reassess the efficient use of natural resources and to identify alternative uses through clean technologies. In this sense, lignocellulosic biomass has considerable potential to meet the current energy demand of the modern world. Trends drive biotechnology in search of improved products. To overcome current energy problems, lignocellulosic biomass, in addition to the circular economy, is expected to be the main focus of research in the near future.

Some technical challenges of biomass pretreatments that need to be addressed to be commercially viable in biomass processing are described below. We cover general and then specific promising techniques, with recommendations that provide directions for future research.

6.1 General Challenges

Laboratory-scale experiments of pretreatments were thoroughly discussed, including the reaction mechanisms, optimal conditions of the various processes, and the degradation kinetics. Future research should focus on optimizing the techniques reported in previous chapters, as well as on how and where they are being used. For example, in catalytic and enzymatic pretreatments, new compounds and enzymes need to be studied to increase efficacy while decreasing long-term toxicity.

Pretreatment process parameters should be studied with process optimization techniques, including experimental design, to increase production and maximize energy consumption [1]. Various response difficulties can be resolved using alternative techniques, sequentially or concomitantly. The combination of two or three pretreatment methods can be considered for commercial-scale process development. A physical pretreatment method such as extrusion can be integrated with biological and ionic pretreatment methods. An integrated method can overcome many economic, environmental, and technological problems of a single pretreatment method. An example of this may be the integration of ionic pretreatment with microwave

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or ultrasound methods instead of conventional heating, dilute acid or alkaline treatments, and steam explosion. In so doing, the advantages of each technique can be realized and the disadvantages can be minimized.

Another challenge is the establishment of scale-up rules and rheological studies. The study of hydrodynamics and kinetics of reactions occurring during pretreatments is extremely important for the development of large-scale processes. Studies involving the design and optimization of pretreatment reactors are rare in the literature. Normally, dimensional analyses are performed to establish scaling rules. Dimensional analysis is a mathematical method involving measurements of mass, length, and time to establish scaling rules. We recommend that the knowledge obtained on the laboratory and bench scales be used to establish scaling rules and to study hydrodynamics and reaction kinetics on a large scale [2].

Rheological investigation of pretreatment reactions to understand mass and heat transfer mechanisms and identify ways to improve process efficiency and solvent recovery, where appropriate, is of paramount importance. Future work should focus on the effects of shear rate, temperature, concentration, and viscosity of the employed fluids. We should leverage our understanding of Newtonian, non-Newtonian, and pseudoplastic behavior of reaction liquids under different operating conditions [2].

6.2 One-Off Challenges

Some pretreatment techniques deserve to be highlighted as promising and considered the main alternatives for the future. However, in addition to opportunities, they nevertheless present challenges that need to be overcome.

6.2.1 Microwave

Microwave can be considered an affordable and environmentally friendly technology, yielding gains over those of conventional heating reactions. Microwave pretreatments lead to high yields and reduce process times. However, there are few studies on the use of microwave reactors for lignocellulosic biomass, requiring pilot- or industrial-scale pretreatments to dedicate efforts in this area. The development of microwave reactors and systems is required to operate at high loads and high pressures to prevent the formation of hot spots that lead to the formation of inhibitor compounds; therefore, homogeneous heat transfer should be performed.

Microwave heating to decrease lignocellulosic biomass recalcitrance is a technology that is just beginning to be developed and can be considered as a technique that is not well established because of the few types of biomass that have been studied. The dielectric properties of lignocellulosic biomass should be studied to select the most suitable microwave materials and to facilitate the establishment of optimal pretreatment conditions [3].

Despite the fact that microwave irradiation has advantages and increases biofuel production, there remain some aspects of technology that require further investigation, including the formation of inhibitors. Biomass pretreatment results in better digestibility and improved biofuel production through anaerobic digestion and fermentation processes; however, pretreatments can also generate inhibitors. Studies of microwave pretreatment in lignocellulosic biomass have reported generation of inhibitors such as 5-HMF, furfural, phenolic compounds, and acetic acids [4–7]. One of the strategies to circumvent this inhibition is the use of activated charcoal for microwave-assisted hydrolysate detoxification; nevertheless, the use of activated charcoal as a detoxifying agent has also resulted in glucose losses [4, 7]. Studies involving inhibitor removal represent an area for future research. It is desirable to document effects of inhibitors managed without influence on carbon production, including the acclimatization of microorganisms to inhibitors before the production of biofuels, using recalcitrant and larger substrates to prevent formation of inhibitors.

Another aspect that remains to be improved regarding microwave irradiation is energy efficiency. Pretreatment was successfully applied to various biomasses improving biofuel production in most studies. However, energy efficiencies were negative in most studies, suggesting that increased biofuel production would not compensate for energy input from microwave systems. Biodiesel production, on the other hand, is an example where it was found that the microwave-assisted was more energy efficient than conventional process [8–12]. The energy efficiency and energy consumption of microwave-assisted pretreatment techniques should be the focus of future research, as this will determine the economic viability and even scalability of this technology.

Technical aspects such as the addition of microwave absorbers should also be studied. Only dielectric compounds are able to absorb microwaves for subsequent heating. Biomass in general has poor dielectric properties; therefore, a microwave absorber becomes indispensable in processes that need to reach high temperatures [13, 14]. Heterogeneous materials can produce non-uniform heating, creating additional problems [15]. Another major challenge of large-scale application is that microwaves cannot penetrate through a large amount of raw material [16, 17]. This imposes a severe restriction on the amount of materials that can be heated. If the amount of raw material that can be processed is very low, this severely affects the viability of pretreatment technology and the process of producing biofuel on a large scale.

Process parameters involving microwave heating for biomass pretreatment will need optimization and should consider the raw material that will be pretreated to minimize inhibitor formation and maximize biofuel production, energy efficiency, and process economics. Mathematical modeling of such processes prior to large-scale implementation will be an important tool in determining the feasibility of technology [18].

6.2.2 Biological

Pretreatments involving microorganisms and enzymatic cocktails have great potential; however, some challenges have yet to be overcome. These challenges include long pretreatment times, non-selective lignin breakdown, and relatively low yields compared to other thermochemical methods. Biological pretreatment results may vary depending on biomass composition and degree of recalcitrance, strains, and variations in the metabolic efficiency of microorganisms, and even the high selectivity of enzymes precludes successful performance for various types of biomass.

On the other hand, some studies reported a higher efficiency of biological pretreatments compared to conventional techniques. Fungal pretreatment is the best approach among biological pretreatments; however, the long incubation time restricts its application on a large scale. By contrast, bacterial growth is faster, resulting in shorter pretreatment times; however, the yields are lower [19–21].

Non-selective lignin removal or loss of cellulose and hemicellulose strongly depends on the fungal strains, the pretreated biomass, and the operating conditions. Although holocellulose loss, especially hemicellulose, was also observed in conventional methods with the formation of several inhibitors, carbohydrate loss appeared to be greater with fungal pretreatments, because microorganisms end up using these fractions as substrates for their growth [22–24].

To overcome such challenges, biological pretreatments must be combined with other techniques to reduce overall pretreatment time and increase efficiency. For example, the combined pretreatment of fungus and milling resulted in a significant improvement in delignification of rice straw from 92% (fungus) to 165% (fungus + milling) [25, 26].

Another interesting strategy is the use of microbial consortia, knowing that such associations are able to reduce pretreatment times. Isolation and use of microbial strains with high selective power have been suggested to minimize carbohydrate loss. Such losses can be further reduced by optimizing the pretreatment conditions and genetic modification of genes encoding ligninolytic enzymes [27, 28].

One of the research trends involving biological pretreatments is the selection of microorganisms residing in the alimentary canal of ruminant animals. These microorganisms hydrolyze various recalcitrant components present in the plant cell wall by producing various extracellular hydrolytic enzymes [29–33].

Additional efforts should be focused on achieving the best efficiency, specificity, and tolerance by applying metabolic engineering, mutagenesis, and genomic mutation. Several techniques are available for gene editing that can also be applied to ligninolytic microorganisms to increase pretreatment efficiency [34–36]. The development and application of genetically modified organisms are intended to overcome the challenges encountered from naturally occurring strains.

In many cases, we are still in the process of developing tools to manipulate particular species; nevertheless, advances are being made on the laboratory and pilot scales [37]. Genetically modified organisms have a unique potential not only to produce more enzymes but also to generate those that can tolerate extreme operating/environmental conditions [37, 38]. Recent research has focused on the direct application of genetic engineering to enzyme production as well as to microorganisms, significantly improving the ability of enzymes to break down lignocellulosic biomass. This technique led to the fusion of enzymes from two species of bacteria to solubilize lignin [39, 40].

Enzyme recycling is another approach to reduce the amount of enzyme consumed during the pretreatment process, consequently minimizing operating costs [41]. Recycling the insoluble biomass fraction after enzymatic pretreatment to the start of the process recovered cellulase activity, and as a result, enzyme consumption was reduced by 30% without significant change in final glucose yield [42]. It is noteworthy that for an industrial plant, the cost of recycling facilities (dewatering, pumping, etc.) will increase the plant's capital cost; therefore, further studies are needed to investigate whether cost savings from enzyme recycling can offset the additional capital investment of extra processing equipment [40, 43].

Again, the implementation of large-scale biological pretreatments remains hampered by various techno-economic issues. Consequently, further studies are needed to develop biological pretreatments. Key issues to be addressed in these scale-up studies should include reactor designs, biomass supply chain, decontamination and cooling of raw materials, inoculum preparation or enzymatic cocktails, microbial growth and metabolism monitoring, temperature control and ventilation, and finally, evaluation of economic factors for cost estimation [26, 28, 40, 44].

Compared to conventional thermochemical pretreatment techniques, biological and enzymatic pretreatments have lower energy consumption, requiring milder operating conditions and less by-product formation. Biological and enzymatic pretreatments are gaining increased attention and will be the main forms of pretreatments in the future.

6.2.3 Ionic Liquids

Some challenges for the use of ionic liquids in pretreatments have yet to be overcome, even with their demonstrated effectiveness.

Generally, ionic liquids tolerate high temperatures; however, there are exceptions, and such solvents have varying tolerance ranges. Biomass pretreatments usually occur at high temperatures (100 °C); therefore, the ionic liquids used should be stable at these temperatures; however, most studies are not concerned with this. The cation of the ionic liquid easily decomposes at elevated temperatures, and such dissociation is favored by the associated anion. Currently, thermogravimetric analysis is the best analysis to determine the stability of the obtained compounds, calculating the weight loss of the sample in relation to the temperature [45, 46].

Another central problem with ionic liquid pretreatments is moisture sensitivity. These substances should not contain water, and even the water content of lignocellulosic biomass should be removed prior to treatment with ionic liquids. The presence of water above 0.15% in ionic liquids causes cellulose precipitation, thereby substantially affecting the dissolution process [47]. The presence of water also affects regeneration and recycling. To avoid such problems, the biomass must be kiln-dried prior to processing, a process that entails an operation prior to the pretreatment itself. New pretreatment techniques that are moisture-tolerant should be sought [48].

Ionic liquid research should recognize the possible dangers that these substances may cause to the environment and to humans. Fortunately, ionic liquids are considered to have low environmental impacts; nevertheless, some of their toxic effects have been observed during ecotoxicological and biodegradation studies, suggesting that these chemicals should be handled with care. Because of their nonvolatile nature, ionic liquids do not enter the environment through the air; however, they are highly miscible in water and can cause damage upon entering receptor bodies [49–54]. The biocompatibility of ionic liquids with enzymes used for fermentation has yet to be improved to allow enzymatic hydrolysis in a combined reactor process [46].

As with all state-of-the-art technologies, ionic liquids are costly because the reagents used for their production are expensive. Therefore, a challenge is precisely in the production of cheap ionic liquids. Alternative methods and resources are being discovered to reduce the cost of synthesis. One alternative is recycling, which can contribute considerably to reducing the effective cost of ionic liquids for biomass pretreatment; this should be done quickly and cheaply [55]. As an example of cost reduction in manufacturing, one study reported synthesis based on various alkyl ammonium cations and hydrogen sulfate anions and their use in pretreatment. In another study, ionic liquid was recovered from the mixture after pretreatment at high percentages. The calculation of the cost of this technique was presented using a technical–economic model [56]. Several authors claimed that ionic liquid is priced relatively low at $1000 per ton [57–59]. Preparation of ionic liquids from natural sources should be sought as this will generate more economical solvents.

Ionic liquids have been studied for some years for the pretreatment of lignocellulosic biomass, because of their high efficiency, reasonable economic viability, eco-friendly, and non-toxic physicochemical characteristics. With high capacity for pretreatment of biomass components, however, it is necessary to develop economical, high-yield, ecologically correct, and viable ionic liquids for process scaling at the industrial level. Doing so will make biomass available and so abundant it can be used properly, applying all the circular economy concepts that should guide future bioprocesses.

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