A.D. Moreno, E. Tomás-Pejó, M. Ballesteros, M.J. Negro. Chapter 16 - Pretreatment Technologies for Lignocellulosic Biomass Deconstruction Within a Biorefinery Perspective. Editor(s): Ashok Pandey, Christian Larroche, Claude-Gilles Dussap, Edgard Gnansounou, Samir Kumar Khanal, Steven Ricke; In: Biomass, Biofuels, Biochemicals, Biofuels: Alternative Feedstocks and Conversion Processes for the Production of Liquid and Gaseous Biofuels (Second Edition), Academic Press, 2019, Pages 379-399, ISBN: 9780128168561, https://doi.org/10.1016/B978-0-12-816856-1.00016-6

Chapter 16 - Pretreatment technologies for lignocellulosic biomass deconstruction within a biorefinery perspective

Moreno, A.D.[1]; Tomás-Pejó, E.[2]; Ballesteros, M.[1,2]; Negro, M.J.[1*]

[1]CIEMAT, Department of Energy, Biofuels Unit, 28040 Madrid, Spain.

[2]IMDEA Energy, Biotechnological Processes Unit, 28035 Móstoles, Spain.

[*]**Correspondence to:** María José Negro, CIEMAT, Department of Energy, Biofuels Unit, Avda. Complutense 40, 28040 Madrid, Spain. **Phone:** +34 91 346 6146 **E-mail**: **mariajose.negro@ciemat.es**

ABSTRACT

Lignocellulosic biomass will definitely contribute to the implementation of a bio-based economy towards mitigating the negative environmental impacts promoted by the extensive use of oil-derived fuels. In a biorefinery context, lignocellulosic sugars constitute an interesting platform to be transformed into a wide range of products (fuels, chemicals, materials) through fermentative processes. Moreover, lignin also represents an important source for producing certain oxygen-containing aromatic compounds. Nevertheless, the highly recalcitrant structure of lignocellulose limits these conversion processes by hindering the accessibility of biomass. The development of an effective fractionation technology is therefore of utmost importance for the optimal valorization of lignocellulose components into the targeted products. In the last years, several pretreatment processes have been evaluated, some of them even at commercial scale, for

increasing the accessibility of different lignocellulosic feedstocks. This chapter includes an updated revision of the most interesting pretreatment technologies for lignocellulosic conversion in a fermentation-based biorefinery, highlighting the most recent results and the main challenges to overcome towards cost-effective industrial processes.

Keywords: lignocellulose, sugar platform, pretreatment, enzymatic hydrolysis, fermentation-based biorefineries.

1. INTRODUCTION

With a yearly production of more than 10^{10} MT, lignocellulosic biomass is considered the major renewable material on Earth[1]. This fact makes this resource an excellent raw material to develop a bio-based economy and bring to an end the current dependence on fossil fuels. In this context, future biorefineries –multiproduct industries similar to current petroleum-based refineries– will guarantee the sustainable use of lignocellulosic feedstocks. Lignocellulosic biorefineries will therefore provide the market with different industrially attractive compounds, including biofuels, chemicals and materials, while cutting back our massive greenhouse gas emissions[2].

Lignocellulosic materials are built up by three main polymers: cellulose, hemicellulose and lignin along with a lower proportion of pectins, proteins, extractives and ash[3]. These components are linked together with different covalent and non-covalent bindings to form a complex matrix very hard to disrupt. In a biorefinery from lignocellulose, the sugar platform may lead to the production of biofuels and other bioproducts through biochemical processes (Figure 1). For this purpose, carbohydrates should be first hydrolyzed using enzymatic catalysts in order to obtain the corresponding monomers. Then, the resulting sugars can be converted into the desired product(s) by fermentation processes. Furthermore, the lignin platform could give rise to a wide spectrum of oxygen-containing aromatic compounds that are very difficult to produce via petrochemical routes.

The recalcitrant structure of lignocellulose and its heterogeneous composition hampers, however, the accessibility of the sugar components to enzymes, thus limiting the hydrolysis of these materials. To overcome the physico-chemical barrier of lignocellulosic feedstocks and ease the hydrolysis process, different pretreatment methods have been designed and tested[4]. Enzyme accessibility depends on the type of pretreatment and the nature of the raw material, and is usually attained by modifying and/or breaking down the lignin structure, disrupting the crystalline structure of cellulose and/or promoting hemicelluloses solubilization[5,6]. For instance, pretreatment technologies such as organosolv, supercritical fluids and biological pretreatments are capable of lignin removal[7,8,9]. Hydrothermal (steam explosion, liquid hot water) and/or acid pretreatments promote solubilization of hemicelluloses and lignin redistribution[10]. Finally, mechanical comminution and ammonia fiber explosion have shown to be effective in reducing cellulose crystallinity[11,12].

Insert Figure 1

In addition of being an essential step for lignocellulose conversion, pretreatment has a great impact on the process economics. In fact, it is second after feedstock to contribute to the overall costs (about 1/3 of the total costs)[13]. Also, pretreatment influences the subsequent hydrolysis and fermentation steps due to the release of several biomass-degradation compounds that are inhibitory for both enzymes and fermenting microorganisms. Overall, these facts point out to the necessity of developing efficient pretreatment technologies to reduce final product prices and ensure the success in their commercial implementation[5,14]. In the last years, research has been focused on identifying, evaluating, developing and demonstrating appropriate pretreatment