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Review

A critical review of analytical methods in pretreatment of lignocelluloses: Composition, imaging, and crystallinity

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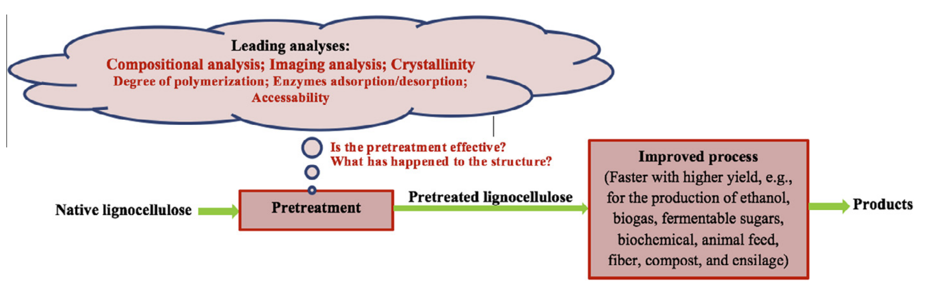
HIGHLIGHTS

- Pretreatment of lignocelluloses are among the crucial steps in a number of bioprocesses.
- Compositional, imaging, and crystallinity measurements are widely used for analysis.
- Advantages, drawbacks, approaches, practical details, and points are presented.
- The methods need special care and preparations, discussed in this paper.

GRAPHICAL ABSTRACT



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ABSTRACT

Lignocelluloses are widely investigated as renewable substrates to produce biofuels, e.g., ethanol, methane, hydrogen, and butanol, as well as chemicals such as citric acid, lactic acid, and xanthan gum. However, lignocelluloses have a recalcitrance structure to resist microbial and enzymatic attacks; therefore, many physical, thermal, chemical, and biological pretreatment methods have been developed to open up their structure. The efficiency of these pretreatments was studied using a variety of analytical methods that address their image, composition, crystallinity, degree of polymerization, enzyme adsorption/desorption, and accessibility. This paper presents a critical review of the first three categories of these methods as well as their constraints in various applications. The advantages, drawbacks, approaches, practical details, and some points that should be considered in the experimental methods to reach reliable and promising conclusions are also discussed.

1. Lignocelluloses and pretreatment

Pretreatment is a process in which the carbohydrates, particularly cellulose, get ready for an enzymatic or microbial attack (Fig. 1). This process is mainly used to improve the ethanol and biogas production; however, it can also be used to improve the production yield of all biochemicals from lignocelluloses as well as for the improvement of animal feed, fiber properties, and compositing (Ghasemi et al., 2013; Jeihanipour et al., 2010a; Karimi and Pandey, 2014; Salehian et al., 2013). This pretreatment can be a physical process such as milling; a chemical treatment by, for example, alkali, acids, or cellulose solvents; biological pretreatment, e.g., by white-rot fungi or lignin-degrading enzymes; or a combination of these processes (Karimi and Chisti, 2015; Kumar and Wyman, 2013). Several reviews and book chapters have been presented, describing different pretreatment processes (e.g., Kumar and Wyman, 2013; Shafiei et al., 2015; Taherzadeh and Karimi, 2008); however, none of them was focused on the analyses used to investigate the pretreatment effects on the lignocelluloses. This is the main purpose of this paper.

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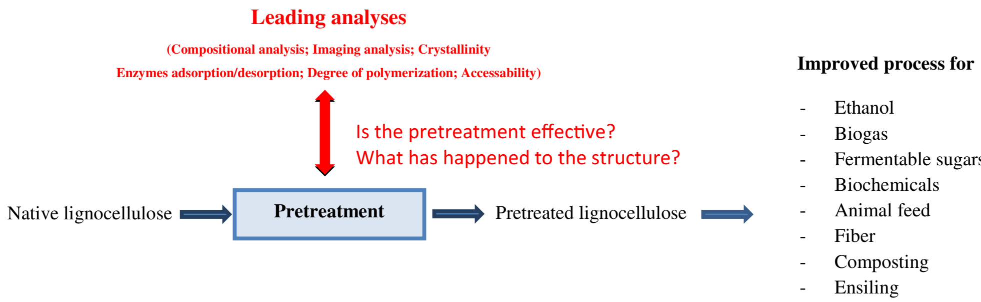

Fig. 1. Analysis of the pretreatment of the lignocelluloses for different purposes.

A number of analyses have been developed to investigate the effects of the pretreatment on the lignocelluloses and mainly to describe the improvements on the enzymatic or microbial hydrolysis. These analyses indicate alterations in composition, crystallinity (e.g., by FTIR and X-ray), pore size (e.g., by Simon staining), surface properties (e.g., by SEM, TEM, and AFM), enzymes adsorption/desorption, and degree of polymerization. This paper presents the details of half of these methods and makes a critical review on their applications and constraints.

In these analyses, different terms and expressions are used to describe the untreated lignocelluloses properties, including "compact structure", "inaccessible carbohydrates", "high crystalline cellulose", "cellulose crystallinity", "total crystallinity", "cellulose type I", and hemicellulose and lignin barriers. On the other hand, the terms such as "open up structure", "modified structure", "porous structure", "accessible structure", "sponge like structure", "cellulose type II", "amorphous celluloses", "amorphous carbohydrates", and "lower cellulose degree of polymerization" are used to indicate the pretreated lignocelluloses. However, not all of these terms have a scientific and well-defined meaning. Some of these terms that have scientific meanings are defined and described herein.

2. Compositional analysis of untreated and pretreated biomass

Compositional analysis of lignocellulose, before and after pretreatment, is used in almost all second-generation biofuel production studies, except in some investigations on biogas production that use volatile solids (VS) instead. Accurate and reliable analysis is important to evaluate the biofuel production. The product yield, recoveries, techno-economical evaluations, and feasibility studies are typically based on the carbohydrate content. It is also very crucial when considering running a plant on an industrial-scale (Sluiter et al., 2010; Templeton et al., 2010). Historically, the analytical methods are used for the analysis of the cellulose and lignin content, rather than the details of molecular entity. Therefore, it is difficult to compare the compositional results of one type of plant to another (Barton, 1988). Even for one type of biomass, besides complexity and variability of the lignocelluloses by themselves, a wide compositional variation reported in the literature may indicate the presence of errors in the analytical methods. It might be less problematic to evaluate the effectiveness of one type of pretreatment, as the compositional data can be compared even though the absolute values are not accurate enough. Some of the challenges in the compositional analysis are indicated in Fig. 2.

Different methods were developed for the analysis of lignocelluloses for specific applications and industries. The analysis of woody biomass using the Technical Association of Pulp and Paper Institute's (TAPPI) standards is optimized for the pulp and paper industries, in which cellulose is the most desired fraction. The Association of Official and Analytical Chemists International (AOAC) standards are suitable for herbaceous and foods analysis in the forage and feed industries, which are interested in measuring the digestibility of food and feed, in which digestible fiber is the most desired fraction (Agblevor and Pereira, 2013; Theander et al., 1995).

Most of the biomass analytical methods are not suitable for the material balance and for quantifying the individual carbohydrates required for the biofuel evaluation and to investigate the pretreatments suitability (Burkhardt et al., 2013). A general procedure on the determination of carbohydrates, acetate, lignin, and ash in biomass, presented by Sluiter et al. (2008b), provided by the National Renewable Energy Laboratory (NREL), is extensively used and cited in the literature for application in the second generation biofuels

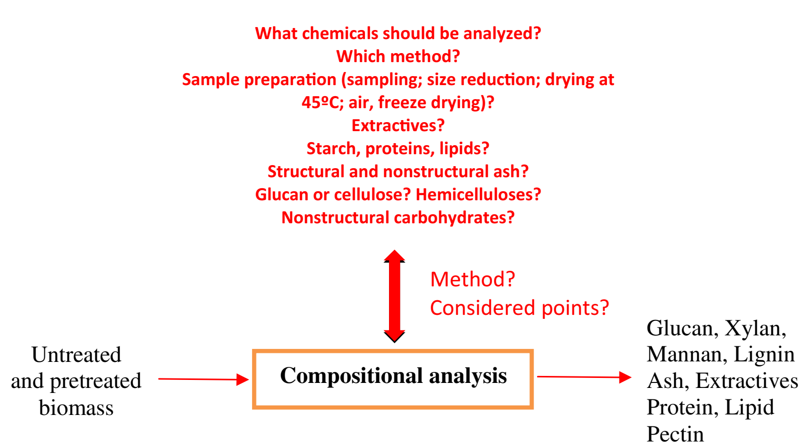

Fig. 2. Compositional analysis and challenges.