CURRENT STATUS OF GREEN SOLVENT PRETREATMENTS FOR BIOMASS FRACTIONATION

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ABSTRACT

Green solvents have emerged as a promising alternative to establish the biorefinery concept in the framework in which biomass is processed. These solvents are used in strategies of the bio-based circular economy, promoting efficient and sustainable bioprocessing. This paper is a comprehensive review, overviewing technologies regarding pretreatments with green solvents and their potential for industrial applications within lignocellulosic biomass biorefineries. It is presented a discussion on the positive and negative aspects of pretreatment technologies employing four green solvent classes: deep eutectic solvents (DES), ionic liquids (IL), supercritical fluids, and biomass-derived solvents. Their performance is assessed in terms of effectiveness on modifying lignocellulose's structure.

Keywords: Circular economy. Pretreatment. Sustainable solvents. Biomass processing

1 INTRODUCTION

The biorefinery concept is the cornerstone of a framework in which biomass is processed into multiple products such as biofuels, bioactive compounds, and biomaterials. Lignocellulosic biomass is the most abundant plant resource from where monomers can be derived and transformed into value added bio-based chemicals.[1] However, their recalcitrant fibers are complex materials to process. The use of biomass as a feedstock includes several process steps, such as extraction, fractionation, conversion, and separation.[2] Since the selection of a proper solvent for processing biomass depends on the environmental impact it promotes, green solvents have emerged as an alternative to minimize the process impact.

Chemicals such as deep eutectic solvents (DES), ionic liquids (ILs), supercritical fluids, and biomass-derived solvents can be taken as green solvents.[3] As will be discussed in this review, these solvents have shown promising features to be used as substitutes for conventional solvents in biomass pretreatments. In addition to their effective performance, they present interesting characteristics such as recyclability, low toxicity, and biodegradability.

This paper presents a comprehensive review concerning the current use of green solvents in lignocellulosic biomass pretreatments. It overviews technologies and provides a discussion on their potential for industrial applications and commercial viability. Studies from the last six years (2018–2023) concerning the development of innovative pretreatments for lignocellulosic biomass using green solvents were reviewed.

2 MATERIAL & METHODS

The literature review was performed in the Web of Science and Science Direct databases, using a set of predefined keywords, and their possible combinations and Boolean operators. The keywords "deep eutectic solvents", "ionic liquids", "supercritical fluids", and "biomass-derived solvents" were followed by the operator "and", "pretreatment", and "lignocellulosic biomass" to increase the obtained results' relevance. Only peer-reviewed journal articles were included, and articles collected from the two different databases were merged to remove duplicates.

A single database consisting of 177 papers was obtained and assessed using a method[4] to compare the impact factor of the journals, year of publication, and number of citations of publications. The most relevant articles were selected based on the scope and research question of this review. Thus, they were assessed in terms of the efficiency of components removal and retention, considering the chemical structure of lignocellulosic biomass before and after pretreatments.

3 BIBLIOGRAPHIC REVIEW DATA

To gain deeper insights into the trends in publications regarding green solvents and lignocellulose pretreatment, Fig. 1 displays the bibliographic review data collected from Web of Science and Science Direct databases. Among the 177 articles collected in this bibliographic research, China is the most productive country, with 78 publications, followed by USA and India, which published 20 and 14 papers, respectively. A great deal of those studies focused on developing lignocellulosic biomass pretreatments to enhance enzymatic hydrolysis and bioethanol production.

In the following section, we assess the relevance of the techniques and innovations described in selected papers, grouping the discussion per class of green solvents.

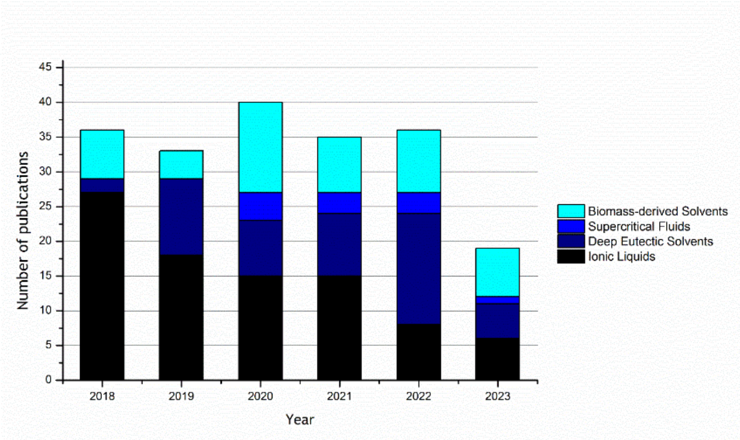

Figure 1 Trend in the number of articles published over 6 years reporting the use of green solvents in the pretreatment of lignocellulosic biomass, according to the relevance criteria and predefined keywords.

Deep eutectic solvents (DES), defined as a liquid mixture of two or more solids that associated to form a liquid at a temperature lower than the melting points of its pure compounds,[5] are commonly composed of hydrogen-bond acceptor (HBA) and hydrogen-bond donor (HBD) non-toxic components. The flexible chemical properties of DES have attracted the attention of research groups that evaluated this promising class of solvents in fractionating lignocellulosic biomass. For instance, the studies by Shen et al.,[6] Lin et al.,[7] and Chen et al.[8] evaluated pretreatments based on DES solvents formulated with choline chloride (ChCl) as the HBA. The authors demonstrated that in addition to enhancing enzyme accessibility to cellulose, the proposed pretreatments maintained the structural integrity of the obtained lignin and yielded satisfactory solvent recovery rates.. Although ChCl is the most common HBA (mixed with different carboxylic acids, and combinations of carbohydrates, urea derivatives, and chloride salts), publications such as Guo et al.[9] and Chen et al.[10] have shown that benzyltriethylammonium (BTEAC) chloride and guanidine hydrochloride could also be used for that purpose. It is important to mention that current studies on DES efficiency must consider the demand for economic evaluations. Moreover, some critical issues for the fractionation efficiency are the pH of DES and the solvent's properties, such as viscosity.

Ionic liquids (ILs) are presented as suitable replacements for organic solvents due to their interesting properties such as non-flammability, thermal stability, negligible vapor pressure, and good performance.[11] ILs are classified as organic salts, consisting of cations (commonly organic) and anions of varying types and structures, such as nitrates, acetates, trifluoroacetates, tetrafluoroborate, and others. Their tunable nature and low melting point (usually lower than 100°C) make ILs a promising alternative for biomass processing studies. Publications such as Alayoubi et al.[12] and Nargotra et al.[13] evaluated aprotic ionic liquids (AILs) composed of organic molecular-cations in the pretreatment of biomass for enhancing saccharification and sequential hydrolysis. The authors showed that the AIL-based pretreatments were able to increase the process sugar and ethanol yields. However, although AILs have been the major class of ILs for most applications since the mid-90's, their synthesis is conducted through an expensive multistep process involving alkylation and anion exchange.[14] On the other hand, protic ionic liquids (PILs) can be synthesized in a single step reaction, thus, more suitable for the establishment of mass production. Gschwend et al.,[15] Chambon et al.,[16] and Pin et al.[17] investigated the use of different formulation of PILs in the pretreatment of lignocellulosic biomass. Their results showed the efficacy of the proposed pretreatments to increase the ethanol yield, and their effectiveness for biomass delignification. Moreover, the feasibility of the conversion of lignocellulose through PIL-based pretreatments have been also demonstrated by techno-economic studies.[18]

Supercritical fluids (SF), such as supercritical carbon dioxide (scCO2) can be used solo or in combination, for instance, to improve organic solvent diffusion into lignocellulosic material. SF are appreciated as green solvents, suitable for the lignocellulose pretreatment.[19] Hermsdorff and coworkers,[20] for example, reported the use of a pretreatment technique based on scCO2, aqueous ethanol, and organic acid catalysts. The authors reported that the pretreatment produced pulps with better accessibility to enzymes, demonstrated by increased enzymatic hydrolysis. SF-based pretreatments have also demonstrated to be effective for obtaining lignin with high antioxidant activity at high recovery yields in the publication by Du et al.[21] It is important to mention that the authors evaluated a ternary scCO2/ethanol/water pretreatment system, suggesting the positive perspective of using the SF combined with organic solvent and water pretreatments. Indeed, the use of combined solvents at favorable pressure and temperature conditions helped to overcome scCO2 weaknesses, such as its low efficiency for removing lignin. The advancement of research involving combined organic and supercritical fluid (SF) solvents pretreatment has the potential to capitalize on certain strengths of SF technology, such as its effectiveness in rapidly dissolving hemicellulose.

The bio-based solvents category refers to solvents obtained from a wide range of renewable sources (e.g., crops and agro-industrial residues). Innovative biomass-derived solvents suchlike tetrahydrofuran (THF) and γ-valerolactone (GVL) have risen as alternatives to solvents derived from fossil resources. For instance, studies such as Meng et al.[22] investigated the effect of pretreatment strategies based on THF to solubilize and fractionate lignin, showing that a THF-based pretreatment remove a similar amount of lignin as that removed in the EtOH-based strategy four times faster. On the other hand, GVL's relevance is demonstrated by the increasing number of publications devoted to its use in the pretreatment of biomass. The papers by Tan et al.,[23] Wu et al.,[24] and Yin et al.[25] demonstrated that GVL is an effective solvent in biomass fractionation and can produce lignin of uniform molecule weight distribution, in pretreatments catalyzed by various acids. Dimethyl isosorbide (DMI) is also a versatile chemical platform that stands out among the newly developed biomass-derived solvents. The group of Yang et al.[26] have shown that the acid catalyzed DMI/H_2O pretreatment is effective to remove > 90% of lignin and hemicellulose. It must be noted that despite being renewable, biomass-derived solvents such as 2-MeTHF often present significant environmental concerns. Hence, the production of the biomass-derived solvents must rely mostly on the use of biomass residuals from land used primarily for growing crops.

4 CONCLUSION

This work demonstrates the flexibility in using different green solvents, catalysts, and process conditions to develop fractionation processes. An increasing number of research groups have focused on different approaches to utilize the lignocellulose completely. Particularly, research on pretreatments to enhance the enzymatic hydrolysis is still the most common application.

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