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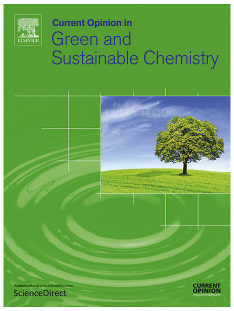

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[illegible] es for green solvents in the deconstruction and refining of biomass

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KEYWORDS: ionic liquid (IL), gamma-valerolactone (GVL), biorefinery, biomass fractionation, ionosolv pulping, organosolv pulping.

ABSTRACT

In quest of shifting to a sustainable biobased economy, lignocellulose is becoming an increasingly important feedstock. However, its valorization demands the deconstruction of the lignocellulosic matrix and selective fractionation of the single constituents. Established pulping and refining technologies are often focusing on the isolation of cellulose only or suffer from environmental shortcomings.

Herein, we discuss the most recent developments regarding two novel solvent systems for biomass refining. We summarize the latest progress made in the area of ionic liquids, with a special emphasis on the techno-economic feasibility in terms of costs and recyclability. In the second part, we highlight the global achievements in the field of gamma-valerolactone-based pulping of biomass, looking at the key contributions from various continents.

1 INTRODUCTION

With the advent of Bioeconomy, plant material is turning into feedstock of growing importance. Lignocellulosic polymers are penetrating rapidly sectors that used to be dominated by synthetic polymers, and replace them gradually. However, efficient biorefinery concepts require the separation and purification of the constituents from their pristine lignocellulosic matrix. Currently, dissolving wood pulps are produced by acid sulfite and vapor-phase prehydrolysis kraft (PHK) processes, both developed in the 1950s. The growing demand for high-purity dissolving pulps and need for energy- and chemical-saving processes require the development of novel concepts that yield both pure cellulose pulps and platform chemicals for advanced biorefinery strategies. Herein we discuss two emerging solvents that have shown great potential for biomass fractionation and refining. We highlight the most recent developments in the respective fields to provide a perspective on their future potential.

2 IONIC LIQUID-BASED BIOREFINERY

Only slightly more than 10 years ago, Fort et al. and Kilpeläinen et al. reported independently that certain ionic liquids are capable of dissolving the entire lignocellulosic matrix [1,2]. This has opened a new research field and stimulated investigations on the use of ionic liquids for the deconstruction and refining of lignocellulosic biomass.

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Essentially, two strategies have been explored:

1) Dissolution of the entire wood matrix followed by selective precipitation of single constituents. Usually a cellulose-rich fraction is isolated first before a lignin-rich fraction is obtained in a second phase-separation step. Complete dissolution is typically energy intensive and regeneration leads to cellulose II, which might not be desirable for some applications.

2) Only selected parts are solubilized upon treatment in the IL-system, usually mostly lignin and hemicellulose, with a cellulose rich fraction remaining undissolved. Due to its similarity to the organosolv process, Hallett et al. have coined the term ionoSolv process, which is increasingly adapted also by other research groups [3].

For a summary of the early development of IL-based fractionation processes the reader is referred to some selected, recently published review articles [4,5]. It should be noted that respective fractionation technologies are predominantly focusing on the production of a cellulose-rich feedstock that is accessible for enzymatic digestion. The IL-pretreatment is designed to reduce the lignin content and the crystallinity of the feedstock to accelerate and improve the enzymatic degradation. Only very few studies can be found that aim for the production of (wood)pulp with properties comparable to established pulping procedures (kraft, sulfite).

Besides, challenges associated with the scale-up of procedures developed in a laboratory environment are rarely addressed. Singh et al. have up-scaled fractionation experiments to a several-liter scale and after overcoming initial problems associated with the phase separation, the results were in line with previous laboratory experiments or even better [6]. Similar observations were made by Hallett et al., prompting them to give a positive outlook on an industrial implementation [3].

Price

A reoccurring argument against large-scale IL-based processes is the currently high price of many ionic liquids. Biomass dissolving ILs are typically in the range of 100 $/kg. Although the high cost can be mostly attributed to the small scale of global IL production, aprotic ILs often require a two-step synthesis and even at large-scale commercial production the price might not drop below 10 $/kg [7].

Several strategies are pursued to alleviate this problem. Substitution of large parts of ionic liquid by conventional molecular solvents in the pulping medium have been proposed. A recent review summarized that even small amounts of IL can show the desired catalytic effect in the deconstruction of biomass [8].

Several research groups focus on the implementation of low-cost protic ionic liquids as pulping medium [9]. Hallett and co-worker have developed the aforementioned ionoSolv process, which is based on the protic IL triethylammonium hydrogensulphate with 20 wt% water [3]. The authors estimate an IL cost of 1.24 $/kg which is already close to common organic solvents.

Solvent recycling

Even if IL costs can be lowered to be on par with commercial molecular solvents, the IL-medium has to be recycled efficiently. Closed-loop operations and near-quantitative reuse of the solvent are not only of economic concern, but are also imperative from an environmental point of view. Evidently, regaining the original IL-pulping medium requires the removal of excess anti-solvent, water or alcohol in most cases. Capitalizing on the intrinsic low vapor pressure of ILs, evaporation of the anti-solvent is commonly proposed. This is an energy-intense step and the overall-economy of the IL-based refining process might suffer from it. Thus, some alternatives have been proposed. Liang et al. reported electrodialysis to recover ILs from the aqueous spent liquor [10]. However, they noticed a rapid flux decay due to membrane fouling. Solubilized low-MW lignin and related degradation products affect the performance of the anion exchange membranes. The authors added an ultrafiltration step to remove pollutants and prolong the lifetime of the membranes. In a techno-economic analysis, Singh and coworkers identified pervaporation as promising solvent removal technology. A 20 wt% IL-solution could be concentrated to >99 wt% at 100 °C and 12 kPa pressure in 4 h [11]. The authors also noted that ultrafiltration is required to maintain the integrity of the pervaporation membrane. Wang et al. investigated nanofiltration to separate water and various ILs using polyamide membranes with an effective pore size of 0.55 and 0.71 nm, respectively [12]. Retention values of up to 96% could be achieved. However, the authors used pure IL-water mixtures without any biopolymer solutes, which would likely enhance membrane fouling.

Independent of the chosen fractionation approach, the treatment of lignocellulose leads to a large number of various degradation products that remain in the spent ionic liquid liquor. Attempts to recycle the ionic liquid and re-use it for biomass treatment showed a rapid performance decay often already in the 4th cycle [13,14]. In particular the gradual accumulation of lignin in the recycled IL-solvent system deteriorated both pulping efficiency and enzymatic digestibility [15]. It is evident that purification procedures have to be implemented into respective recycling strategies to allow for a long-term use of the ionic liquid and minimize the make-up amount. This is still an idle research field. To date, only (nano-)filtration has been studied to a greater extent [11,16].

Recycling of the IL-solvent system appears less demanding when using a less complex feedstock. ILs have been utilized successfully to upgrade paper-grade wood pulp by extracting hemicelluloses [17]. Similar to the concept of the ionoSolv process, hemicelluloses are dissolved selectively in an aqueous IL-medium, yielding high-grade dissolving pulp. Near-quantitative precipitation of the dissolved hemicellulose fraction gives access to the two constituents in high purity. The selective dissolution is mostly based on differences in the molecular weight of the constituents and independent of their chemical nature. Thus, this approach proved also suitable to fractionate pure cellulose according to their molecular weight [18,19]. Only minor carbohydrate-derived degradation products can be found in the spent IL-water system, which can be reused after partial removal of water to a final water content of ca. 20 wt%.

3 GVL-BASED BIOREFINERY

Unlike synthetic ionic liquids, the cyclic ester gamma-valerolactone (GVL) is a natural substance, occurring as volatile flavor constituents in many products such as barley, coffee, cocoa, mango, honey, peach, mushrooms. GVL has been widely applied as food flavor enhancer, perfume composition or solvent for lacquer, insecticides and adhesives. In the previous decade, the adoption of GVL as a sustainable platform chemical and as green solvent for chemical conversion was revisited by Horváth and co-workers. The application portfolio of GVL was subsequently extended to biomass-related conversion technologies through pioneering research of Dumesic and coworkers. The past few years have experienced a significant rise in the use-cases of GVL in the deconstruction and refining of biomass. In the following, we would like to give a geographical overview of the most influential activities.

North America

Dumesic and co-workers from the University of Wisconsin-Madison, USA, are still the leading group with a versatile GVL-research portfolio aiming at the production of biofuels and biochemicals. They performed the biomass fractionation in concentrated GVL solution (>70 wt%) at moderate temperature (<140 °C) in the presence of sulfuric acid. In 2016, Dumesic *et al.* filed a patent describing the production of concentrated sugar for ethanol production from biomass (maple, pine and corn stover) facilitated by the pre-treatment in GVL/water/H_2SO_4 solution [20]. The patent also described the separation of the aqueous phase from the spent liquor for GVL recovery by liquid-CO_2 extraction and NaCl addition. In 2017, another biorefinery concept was introduced, enabling the production of dissolving pulp, furfural and lignin-derived carbon foam and battery anodes from white birch wood [21]. In this concept, GVL was recovered by evaporation and an advanced techno-economic model was provided. Beside the two aforementioned biorefinery concept, the Dumesic group also introduced other novel options to valorize biomass in GVL/water/H_2SO_4 medium, such as:

- Production of monomeric carbohydrates by corn stover fractionation in a ternary mixture of GVL, water and another organic solvent, (benzene, toluene, phenol, etc.) [22].
- Production of maleic acid by oxidation of furfural obtained from corncobs fractionation in aqueous GVL solution [23].
- High-yield production of furfural by dehydration of xylose obtained from maple wood fractionation in aqueous GVL solution [24].

Other notable works from North America include the production of solubilized carbohydrates from cellulose in GVL under supercritical conditions and short reaction time [25], and the fundamental computational work on the molecular dynamics analysis of the physical deconstruction of cellulose in GVL/water medium [26].

Europe

GVL research in Europe is centered in Finland (Sixta, Aalto University) and Switzerland (Luterbacher, Ecole polytechnique fédérale de Lausanne). Being the co-inventor of the aforementioned seminal patent [20], Luterbacher adopted the H_2SO_4-catalyzed GVL fractionation process in the pretreatment of beech wood [27]. GVL proved significantly more effective in the preparation of a substrate that facilitated the high-consistency enzymatic hydrolysis. The process could generate a sugar solution with a concentration as high as 182 g/L, and GVL could be quantitatively recovered by liquid-CO_2 extraction. Further, Luterbacher *et al.* proposed wood fractionation in GVL solution in the presence of formaldehyde in order to produce a less-condensed lignin that facilitated the subsequent hydrogenolysis reactions for the production of monoaromatic compounds [28]. Meanwhile, Sixta and coworkers introduced an uncatalyzed approach for the fractionation of hardwood in a 50 wt% GVL solution at elevated temperature (>170 °C) to produce a pulp fraction readily convertible to textile fibers with properties comparable to other commercial fibers [29,30]. The pulp obtained from the uncatalyzed GVL process could also be converted to residual-lignin-containing nanofibrillated cellulose with interesting morphological, rheological and water-retention properties [31]. In order to complete their GVL biorefinery concept, Sixta *et al.* proposed preliminary solvent recycling schemes based on the combination of vacuum distillation and liquid-CO_2 extraction in which more than 90% of the lignin and GVL in the spent liquor could be recovered [32]. In Italy, Gelosia and coworkers reported the GVL pulping of steam-exploded reed (*Phragmites australis)* residues from local handicrafts workshops [33]. The resulting pulp was a potential substrate for the production of high quality dissolving pulp.

Asia

Research on biomass fractionation and conversion in GVL is concentrated in China. With a strongly developed agriculture sector in the background, wastes from annual crops have been adopted as raw materials. Some noteworthy researchers in this area are Ma (CAS Key Laboratory of Renewable Energy, Guangzhou) and Qing (Changzhou University, Jiangsu). Corn stover was utilized as substrate for the production of 5-hydroxymethylfurfural and furfural in the presence of diluted H_2SO_4 [34], different solid acids [35-39], or the bi-phasic catalyst SO_4^{2-} /SnO_2^- montmorillonite [40]. GVL was also used in the pretreatment of cotton stalk [41], bamboo shoot shell [42], and sugarcane bagasse [43], generating pre-hydrolysates with low level of inhibitors suitable for subsequent enzymatic treatments for the production of sugars or bio-butanol. The combination of GVL and ionic liquids was also reported to have positive effects on the conversion of biomass [44,45].

Outside of China, Han (Chonbuk National University, South Korea) proposed a novel pathway for the production of jet-fuel range alkenes from biomass in GVL medium [46].

Oceania

Wu and coworkers presented a fundamental study on hydrothermal decomposition of cellobiose in GVL solution [47] and work describing the production of glucose from cellulose and biomass through treatment in hot-compressed (250 °C and 100 bar) GVL solution [48]. Another notable work was the production of bio-ethanol from eucalyptus sawdust via GVL pretreatment [49].

4 CONCLUSION

In the light of these observations, both solvents seem to have realistic potential to be up-scaled to a commercially feasible level. First initiatives to build pilot plants based on the ionoSolv process have been launched. However, both technologies require an efficient solvent recovery and purification strategy. In this aspect, the GVL-development seems slightly ahead of the IL-based methods. Solvent recycling will consume considerable amounts of energy. Therefore, it is not possible to predict the overall efficiency and economy of either technology before a viable recycling concept is established. In terms of recycling, the major deficiencies are currently in the purification of the spent liquor. The removal of degradation products that accumulate upon solvent reuse is key to establish a truly closed-loop operation.

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