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Wheat straw lignin extraction with bio-based solvents using enabling technologies

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ABSTRACT

Two bio-based solvents, natural deep eutectic solvents (NaDESs) and γ-valerolactone (GVL), have been used under microwave (MW), and ultrasound (US) irradiation to design an efficient and sustainable process for wheat straw delignification and have been compared with the traditional alkali procedure. Best delignification (45%) was achieved with a three-component NaDES (lactic acid/glycerol/choline chloride) under MW irradiation (at 120 °C in 30 min), with solid/liquid ratio of 1:50. A GVL/water mixture (8:2) also gave an efficient delignification (27%) under US irradiation (40 kHz, 200 W) at 50 °C for 60 min. Analytical pyrolysis (Py) coupled with GC/MS/FID, provides valuable information on the extracts' chemical profile. DPPH and Folin–Ciocalteu tests highlighted the efficiency of MW- and US-assisted extraction as well as the extracts quality. The highest antioxidant activity for the NaDES extracts was obtained under US irradiation.

1. Introduction

One of the hottest topics in the current scientific literature is the design of sustainable procedures for the valorization of lignocellulosic biomass from agricultural, industrial, and forest residues [1,2] via extractions using bio-based solvents [3–6], and microwave (MW) and ultrasound (US) irradiations [7–10]. The major challenge in efficient biomass exploitation is still the reduction of lignin and hemicellulose within their complex lignocellulosic structure to facilitate subsequent cellulose conversion to value-added chemicals via either enzymatic hydrolysis or catalytic procedures [11]. Lignin is widely treated as a waste product in bioethanol production, it is mainly recycled as fuel for energy balance [12], but further valorization is worthy of investigation [13,14], as it is the second most abundant natural polymer after cellulose [15]. Lignin is a three-dimensional highly cross-linked macromolecule made up of three main phenyl propane units (monolignols), namely, coniferyl alcohol (G), sinapyl alcohol (S), and minor amounts of *p*-coumaryl alcohol (H), which are interwoven by a series of characteristic linkages, such as CeOeC and CeC bonds [16,17].

In particular, the destruction of the majority of lignin ether bonds during the biomass delignification process

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generally results in an increased phenolic hydroxyl group content in the lignin structure. These compounds are essential for the product's radical scavenging activity [18]; they can trap radicals and become phenoxyl radicals themselves. Furthermore, the methoxyl groups located in the *ortho* position play an important role in phenoxyl radical stabilization [19], which is also a step toward the capture of radicals and the subsequent antioxidant effect of lignin [20–22]. Lignin has two main advantages as an antioxidant: it is of natural origin and is a polymeric structure. Antioxidant polymers have been a topic of great interest for researchers in many industrial fields [23], meaning that lignin and lignin-related polymers have been started to be used as additives in biodegradable packaging materials [24], as food additives [25], and in cosmetics products [26]. However, the high chemical heterogeneity of lignin also makes it necessary to consider how antioxidant activity can be influenced by biomass processing conditions [27,28]. Delignification processes may affect the functional groups and molecular weight of recovered lignins, conditioning their antioxidant properties. For this reason, finding an effective and sustainable means of recovering lignin from lignocellulosic biomass may be the first step toward its valorization as an antioxidant. It has recently been demonstrated that the extraction of lignin from wheat straw (WS), using organic solvents of different polarity and alkaline solutions, results in the isolation of products with good antioxidant activity [27], whereas a plethora of biological, chemical, and physical methods have been reported for lignin extraction from a variety of biomass sources [29]. However, these methods are all arduous, time-consuming, and entail high solvent and chemical consumption. Besides the complete redesign of all existing processes, the use of alternative solvents, together with the so-called enabling technologies, may also be a means to increase the efficiency of lignin extraction protocols [30]. Focusing on green extraction and mass transport enhancing methods, such as microwave-assisted extraction (MAE) and ultrasound-assisted extraction (UAE), may provide the necessary potential to accomplish faster and more gentle processes that consume less solvent than conventional methods [31]. In fact, the last few decades have seen enabling technologies being widely exploited as efficient and sustainable alternatives to traditional lignocellulose pretreatment methods [32,33]. In particular, the sonomechanical effect of US has been shown to enhance solvent penetration into cellular materials, thus improving the mass transfer of the extractive processes behind biomass pretreatment [34]. On the other hand, the MW-assisted technique has been postulated as an alternative heating technology and one that is able to reduce reaction times and improve extract efficiency and quality, compared with conventional extraction protocols [35,36]. MWs interact with polar molecules leading to the rapid and volumetric heating of irradiated mixtures and mass transfer optimization. With this efficient and selective heating, MWs can also be considered a promising approach to the thermal treatment of biowaste, especially lignocellulose [37]. However, of these numerous studies, only a few focus on MW-assisted lignin isolation and the majority of these work under acidic conditions [38,39]. Nevertheless, they do highlight the advantages that MW-assisted lignin isolation can offer, especially in terms of lignin purity and processing time. The present study reports the MW-assisted delignification of WS (one of the most abundant agricultural residues) and demonstrates the synergism that can exist between the so-called enabling technologies and bio-based solvents.

The concept of green solvents is strongly related to the principles of green chemistry, and natural deep eutectic solvents (NaDESs) have received much more recent attention than the others available [40]. A deep eutectic solvent (DES) is a fluid generally composed of two or three inexpensive and safe components that are capable of self-association, often through hydrogen-bond interactions, to form a eutectic mixture with a melting point lower than that of each individual component. DESs, similarly to the more traditionally used ionic liquids (ILs), are generally liquid at temperatures less than 100 °C. Their synthesis is 100% atom-economic and their purity is high. However, unlike ILs, they are nontoxic and biodegradable. A wide range of NaDESs have been applied across a number of chemistry fields. Particularly, noteworthy is the choline chloride series that are coupled with monosaccharides (mainly glucose and fructose), glycerol, and organic acids, which act as hydrogen bond donors [41,42]. Moreover, NaDESs have recently been used as extraction solvents for phenolic compounds [43].

The nonvolatility of NaDESs is considered to be the most challenging issue in the design of separation processes, as solvents can no longer be separated by simple distillation. For this reason, other green solvents have been tested in lignin extraction experiments, including those that arise from the conversion of biomass itself. γ-Valerolactone (GVL) is a polar aprotic solvent conventionally produced from biomass-derived levulinic acid [44] and its esters via (catalytic) hydrogenation [45]. GVL shows a number of interesting features [46]; its polarity is similar to those of the most common polar solvents (GVL's dielectric constant is 36.47, whereas those of CH_3CN, DMF, NMP, and DMA are 37.5, 36.7, 32.0, and 37.8, respectively). Furthermore, it has low melting and high boiling points (−31 and 207 °C respectively) and a flash point 96 °C, which is generally higher than that of conventional dipolar aprotic solvents. It is also quite stable under neutral conditions. GVL has recently been used as a solvent in the extraction of lignin from biomass in a cascade MW-assisted integrated process [45].

In this study, the delignification power of NaDES and GVL on WS has been maximized using US and MW irradiations. Moreover, the antioxidant property of extracts was used to assess the best extraction procedure in terms of product quality [47]. The extracts showed good antioxidant properties, thus paving the way for the application of lignin as an added value product, as an alternative to its combustion, according to the biorefinery approach. We herein demonstrate that nonconventional extraction techniques using bio-based solvents, GVL and NaDES, may be considered a valid alternative to classical methods, which use organic solvents coupled with alkali or acid treatments.

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