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Organosolv delignification of agricultural residues (date palm fronds, *Phoenix dactylifera* L.) of the United Arab Emirates

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HIGHLIGHTS

- Date palm fronds are an abundant lignocellulosic residue in the United Arab Emirates.
- The biomass is rich in lignin and was efficiently pretreated by organosolv delignification.
- Lignin was separated by precipitation, while the remaining cellulose fibers are a good substrate for bioethanol production.

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ABSTRACT

Date palm fronds (primary agricultural residue of the United Arab Emirates) were used as a feedstock in an ethanol–water organosolv delignification process to generate organosolv lignin (OSL) and enzymatically digestible cellulose-rich pulp. Conditions of the treatment (temperature, catalyst concentration and amount of ethanol in the digesting solvent mixture) were screened and preliminarily optimized for OSL recovery and digestibility of the cellulose-rich pulp as primary and secondary response variables, respectively. OSL recovery was positively influenced only by temperature (140–200 °C), while the digestibility of the cellulose pulp was positively influenced by temperature and negatively influenced by ethanol content in the digesting solvent. Maximum production of 12.93 g lignin/100 g RM (raw material) and 21.38 g glucose/100 g RM was achieved. Xylan losses reached up to 70%, increasing with temperature. Addition of the catalyst (sulfuric acid) was found to have no significant influence on any of the responses investigated.

1. Introduction

The Middle East is the top global producer of dates, possessing 70% of the world's date palm (*Phoenix dactylifera* L.) resources, estimated at 120 million trees [1]. Furthermore, the date palm serves a decorative purpose in the green landscapes of the United Arab Emirates (UAE). This results in the UAE being a producer of over 1.5 million ton of agricultural and landscaping residues, majority of which includes date palm waste [2]. As the country develops rapidly, this number can be expected to increase. Leaves and fronds represent the main residue fraction from the palm-based agriculture and landscaping [1]. Currently, the agricultural waste is not being used in any marketable way, and due to the probable waste production increase, the issue should be addressed in a sustainable manner, utilizing the entire potential of the plant. Being a typical lignocellulosic material, date palm waste can be considered a good feedstock for bioproducts and biofuels, using already available technologies, including various pretreatment and fractionation methods, followed by either biological or chemical refining to obtain final products such as fuels, chemicals or polymers. As the climate of the region is arid, the biomass does not contain large amount of moisture, limiting the need for pre-processing.

One of the most effective and optimized technologies for lignocellulosic biomass fractionation is the organosolv delignification [3]. Originating from pulp and paper industry, the process is aiming to remove the protective polymer of the plant (lignin) into the organic solvent, partially dissolving hemicellulose sugars into the aqueous phase and leaving cellulose-rich fibers as a solid [3–5]. Even though the process is considered complicated due to organic solvents use and the added recovery steps (which is often

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associated with added cost [6]), it actually has the potential for fresh water conservation. Using the highest possible content of the volatile organic ingredient and careful optimization of the recovery steps can limit the cost of recycling and reduce the use of fresh water, which is an important aspect for arid and semi-arid regions.

Lignin has been reported to be an interesting (although not yet economically feasible) substrate to produce some commodity chemicals and polymers [7–9]. A common issue in lignin processing is its purity and uniformity. In general, lignin characterization is the challenging, crucial step to find the optimal utilization method and further processing conditions. Cellulose fraction can be used in various applications, including biofuel such as bioethanol, but also cellulose acetate or glucose for further processing. Producing relatively pure streams of intermediates is an essential step to a sustainable biorefinery, as it limits the purification steps and waste streams. Organosolv lignin, especially produced at low-severity conditions, contains the least amount of contaminants (carbohydrates, ash or modifiers from the digestion medium) and is relatively low in molecular weight [10,11]. It makes lignin a good source of solid fuel (with a heating value of about 26 GJ/ton), which can alternatively be burned to provide heating required by the process [12,13].

Organosolv pretreatment has been widely used to produce delignified cellulose fibers for the bioethanol production. Delignification efficiencies were reported to reach 44% for sugar cane bagasse using a traditional ethanol-based treatment [14] and up to 75% for wheat straw using acetic acid as a solvent [15]. Focusing on producing fermentable pulp is a limited approach and can be efficiently achieved by applying more robust pretreatment methods, such as dilute acid [16]. Organosolv delignification presents an opportunity to fully utilize biomass energy potential and create a holistic biorefinery via a less common "lignin-first" approach.

To our knowledge, date palm *P. dactylifera* L. has not been characterized or evaluated as a feedstock for biofuel and bioproducts to date. However, numerous trials have been performed using oil palm (*Elaeis guineensis* Jacq.) residues as a lignocellulosic feedstock in processes such as organosolv delignification. For instance, Malaysian empty palm fruit bunch (containing 32% of Klason lignin and 42% glucan) has been successfully processed using ethanol-aqueous organosolv treatment catalyzed by sulfuric acid, resulting in up to 52% lignin recovery [17]. Same biomass pretreated using hydrogen peroxide-aided ethanol organosolv process produced highly fermentable pulp delignified by 35% [18,19]. KOH-aided steam explosion of the oil palm fronds, much less lignified than the fruit bunch (containing about half of the lignin), was found to be very effective in lignin removal (which is a common trend [20]), achieving over 70% delignification efficiency [21]. However, steam explosion does not produce recoverable, high quality lignin as opposed to the organosolv delignification. Oil palm trunk was also investigated as a source of fermentable pulp, using alkali delignification as the pretreatment method, but with lower delignification efficiencies (22%) and without producing recoverable lignin [22]. The reported efficiency of lignin extraction from the palm tree residues are relatively low when compared to other lignocellulosic materials (e.g. poplar wood chips, corn stover, prairie grasses) processed using organosolv pretreatment (usually between 50% and 90%) [23,24]. However, the overall yields are still higher due to high lignin content in the feedstock. Furthermore, attempts of modifying the organosolv lignin structure to enhance its properties have also been made (using 1,8-dihydroxyanthraquinone or 2-naphtol as an additive in the organosolv process), which resulted in a higher delignification yield (by limiting the condensation reactions), better solubility and antioxidant properties of the recovered product [25,26].

Date palm (*P. dactylifera* L.) fronds, representing the most commonly generated agricultural and landscaping waste in the UAE, have been investigated in this study as a source of lignin and digestible cellulosic pulp for bioethanol production. Ethanol-aqueous organosolv delignification was chosen as the pretreatment and fractionation method to process the biomass, and the crucial conditions (composition of the digestion medium and temperature) were optimized to find the ranges for further detail optimization.

2. Materials and methods

2.1. Materials

Date palm (*P. dactylifera* L.) fronds were collected from date palm trees planted in Abu Dhabi in 2013. The samples were air-dried and the dried material was milled using a knife mill (IKA, 10 MF Basic) to pass through a 1 mm screen.

2.2. Biomass characterization

The dried and milled samples of palm fronds were analyzed following the standard lignocellulosic biomass characterization protocols including analysis of extractives (both water- and ethanol-soluble fractions) [27], structural carbohydrates, lignin [28] and ash [29].

2.2.1. Determination of dry mass and ash

Dry mass (DM) in raw and pretreated samples was determined gravimetrically, by weighing a biomass sample (0.5–2 g) into a ceramic crucible and drying in the oven at 105 °C to a constant weight [30]. Total ash in the raw plants was measured per dry mass basis by ashing the dried biomass in a muffle furnace at 575 °C [29].

2.2.2. Determination of extractives

Procedure for determining the extractives content was comprised of three steps – measuring the weight loss of the extracted solid and analyzing solids in the water extract and ethanol extract [27]. Dried and finely ground samples were subjected to water extraction followed by ethanol extraction using a Soxhlet apparatus. The biomass (5 g) was loaded into a cellulose thimble and subjected to 10 h of extraction with 200 g of water (with 3–4 siphon cycles per hour) and subsequent 10 h extraction with 200 g of ethanol (5–6 siphon cycles per hour). After the extraction, the solid was removed from the thimble, dried in the drying oven (at 105 °C) overnight and weighed to determine the total extractives amount (including volatile and non-volatile extractives) (Eq. (1)).

$$\mathrm{NE}\left(\frac{\mathrm{g}}{100\ \mathrm{g\ DM}}\right) = \frac{W_{\mathrm{dw/etex}}}{\mathrm{DM}} * 100 \tag{1}$$

where

NE = non-volatile extractives [g/100 g DM].
$W_{\mathrm{dw/etex}}$ = weight of the dried water or ethanol extract (evaporated to dryness) [g].
DM = dry matter of the raw sample [g].

$$\mathrm{TE}\left(\frac{\mathrm{g}}{100\ \mathrm{g\ DM}}\right) = \frac{\mathrm{DM} - \mathrm{DM_{ef}}}{\mathrm{DM}} * 100 \tag{2}$$

where

TE = total extractives [g/100 g DM].
$\mathrm{DM_{ef}}$ = extractives-free dry matter [g].

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