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A biorefinery concept for simultaneous recovery of cellulosic ethanol and phenolic compounds from oil palm fronds: Process optimization

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ABSTRACT

In this study, process optimization of an ultrasonic-assisted organosolv/liquid oxidative pretreatment (SOP) of oil palm fronds (OPFs) for the simultaneous recovery of cellulose, bioethanol and biochemicals (i.e. phenolic compounds) in a biorefinery concept was carried out. The effects of time (30–60 min.), temperature (40–80 °C), NaOH concentration (1–5%) and sample:solvent ratio (1:10–1:50 g/ml) on cellulose content, bioethanol yield and total phenolics contents (TPC) after SOP were investigated. At optimum conditions of pretreatment (i.e. 60 °C, 40 min, 3% w/v aq. NaOH and 1:20 g/ml sample to solvent ratio), the recovered cellulose (55.30%) which served as substrate for enzymatic hydrolysis and subsequent fermentation yielded about 20.1 g/l glucose, 11.3 g/l xylose and 9.3 g/l bioethanol (yield of 0.769 g/g). The pretreatment liquor (mostly regarded as wastes) obtained at the optimum pretreatment conditions contained about 4.691 mg gallic acid equivalent (GAE)/g OPFs of TPC, 0.297 mg vanillic acid (VA)/g OPFs, 1.591 mg gallic acid (GA)/g OPFs and 0.331 mg quercetin (QU)/g OPFs. The pretreatment liquor was again analyzed to possess high antiradical scavenging activity (about 97.2%) compared to the synthetic antioxidant, 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) (80.7%) at 100 ppm. Thus one sustainable way of managing wastes in biorefinery is the recovery of multi-bioproducts (e.g. bioethanol and biochemicals) during the pretreatment process.

1. Introduction

Lignocellulosic materials like oil palm fronds (OPFs) are potential sources of sustainable bioethanol because they are regarded as wastes with limited commercial utilization. Cellulosic ethanol has not reached commercial advancement like corn or sugarcane ethanol due to the sophisticated technology that is involved [1,2]. In view of this, there are numerous on-going pilot and laboratory scale studies to optimize cellulosic ethanol production. Due to the recalcitrant nature of lignin in lignocellulosic biomass, pretreatment becomes very necessary as a major step in the biorefining processes in order to facilitate enzymatic or chemical hydrolysis for enhanced bioethanol production [3]. The pretreatment processes of biomass generate huge amounts of wastewater, which are not utilized sustainably for value-added products. In a cellulosic ethanol refinery for instance, the recovery of biochemicals like phenolic compounds from the pretreatment liquor can be integrated into the biorefinery concept for sustainable bioethanol production [4,5]. In this study, apart from utilizing the cellulose for bioethanol production, the potential of upgrading the pretreatment liquor (mostly discarded as wastewater in biorefineries) into value-added bio-products (i.e. phenolic compounds) was assessed.

Cellulose, the most dominant renewable polymer can be isolated from lignocellulosic biomass using various pretreatment methods like solid–liquid extraction with organic solvents, acid/alkaline hydrolysis [6], ultrasonic-assisted extraction [7], microwave assisted extraction [8], pressurized liquid extraction [9], hydrothermal extraction [10,11] etc. Ofori-Boateng and Lee [12] have assessed organosolv pretreatment of OPFs to be the most thermodynamically sustainable pretreatment method among steam explosion and microbial pretreatment methods. Ultrasonication is the process of applying sound energy at frequencies greater than 20 kHz in order to dissociate the particles in a sample's matrix to improve mass transfer [13]. Thus, during lignocellulosic pretreatment, ultrasound energy coupled with organosolvation at low temperature would enhance mass transfer by improving the penetrative effect of the solvent into the cell structure of the biomass to cause cell disruption resulting from the collapse of cavitation bubbles

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produced by sonication [13]. During ultrasonication, there is evolution of powerful hydromechanical shear forces through the reaction medium which helps to easily dissociate the cells of the materials present in the cavitation area. Ultrasound is again employed in pretreatment techniques in order to achieve high extraction efficiencies at low temperatures, short times and high sample amounts (or low quantity of solvents) compared to the other pretreatment methods. This study reports the effects of ultrasonic-assisted organosolv pretreatment (SOP) of OPFs on the recovery of phenolic compounds, cellulose and bioethanol using NaOH as catalyst.

Plant materials such as OPFs are endowed with bioactive phytochemicals such as vitamins, terpenoids, phenolic compounds and other secondary metabolites, which are rich sources of antioxidants [14,15]. The tremendous rise in chronic diseases such as hypertension, diabetes and obesity. are mostly due to the parlous effects of free radicals in foods which have strong capabilities of destroying lipids and lipid-soluble substances hence generating unwanted chemicals which are dangerous to human body cells [16]. As a result, many health-conscious people are resorting to food supplements packed with phytochemicals like phenolic compounds which have beneficial antioxidant, anti-mutagenic, anti-inflammatory and anticancer activities to the body [17,18]. However, the present food supplements and phytochemicals are obtained from synthetic sources which are costly hence the need to seek for alternative sources of natural phytomedicines. Plant-based phenolic compounds and polyphenols are the groups of secondary metabolites that have aromatic rings with one or more hydroxyl substitutes and they can be synthesized through the shikimate pathway or phenylpropanoid metabolism [19]. Generally, phenolic compounds include simple phenols, phenolic acids, tannins, flavonoids and coumarins which are often found in plants in the form of glycosides or esters [20]. Hemicellulose and lignin form particular group of phenolic compounds [21] which could be recovered in biomass pretreatment liquor for sustainable bioethanol production.

OPFs are the most abundant oil palm wastes generated by the oil palm industry in most Asian and African countries. In 2011 for instance, Indonesia and Malaysia together generated about 55 million tonnes of OPFs and only about 5% was utilized in the palm plantation as mulch [22] though they may serve as important dietary sources of phenolic compounds when transformned into edible materials such as high fiber bread. Almost all the parts of the oil palm tree contain many nutritional and pharmaceutical properties which have been justified through their numerous traditional uses in curing diseases such as diabetes, typhoid fever, boils and wounds [23–25]. Ofori-Boateng and Lee [26] have reviewed the benefits of the major bioactive substances found in oil palm biomass with the finding that oil palm phytochemicals have significantly high pharmacological activities. For instance, OPFs are found to contain carotenoids in the range of 245–340 μg/g DW [15] which are comparatively higher (15–40 times as many retinol equivalent) than those found in tomatoes and other leafy vegetables [27]. This article presents the first report of OPFs' phenolic compounds and their antioxidant activities. The production of value-added bio-products like phytochemicals from OPFs and other oil palm wastes in a bioethanol refinery may not only save the environment but also add economic value to the oil palm hence the progress towards sustainable development for the oil palm industry. This study examines the potential of recovering both cellulose and phenolic compounds from OPFs during the pretreatment processes in a cellulosic ethanol biorefinery. The study further investigates into the antioxidant activities of the phenolic compounds (vanillic acid, quercetin and gallic acid) in the pretreatment liquor as well as the conversion of the cellulose into ethanol using separate enzymatic hydrolysis and fermentation (SHF).

2. Experimental

2.1. Chemicals and microorganisms

Analytical grade ethanol, acetic acid, methanol and HPLC grade acetonitrile were purchased from Fisher Scientific, UK. 2,2-Diphenyl-1-picrylhydrazyl (DPPH), 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT), sodium hydroxide (NaOH) and ACS grade sodium chlorite ($NaClO_2$) were also purchased from Sigma–Aldrich (St. Louis, MO, USA). The external standards (vanillic acid, gallic acid and quercetin) were purchased from Sigma–Aldrich (St. Louis, MO, USA). Folin–Ciocalteu reagent (FCR), sodium carbonate (Na_3CO_3), aluminum chloride ($AlCl_3$), potassium bromide (KBr), sodium nitrite ($NaNO_2$), enzymes [Celluclast 1.5L (ATCC 26921) and Novozym 188 (C6105)] and baker's yeast 51471 (*Saccharomyces cerevisiae*) were purchased from Sigma–Aldrich (St. Louis, MO, USA). The activities of the enzymes were calculated following the method of Ghose [28].

2.2. Preparation of plant materials

The fresh fronds of the oil palm, *Elaeis guineensis Jacq.* were obtained from the oil palm plantation at the Engineering campus of Universiti Sains Malaysia. The petioles of the OPFs were cut into smaller pieces (about 10–20 mm long) and washed with tap water followed by deionized water. The washed samples were oven dried (Memmert Beschicking-Loading Modell 100–800) at 40 °C for 16 h. The moisture content was determined on the same day. The dried plant materials were homogenized using analytical mill (IKA(R) A11, Retsch, Germany) and then passed through a 500 μm AS 200 sieve shaker (Retsch, Germany). The samples were packed in zipped poly bags and kept at 4 °C until further pretreatment.

2.3. Simultaneous recovery of free phenolic compounds and cellulose for ethanol production

Fig. 1 shows the simplified process flow diagram of the biorefinery concept under consideration in this study. Non-cellulosic components (i.e. hemicellulose and lignin) of OPFs were removed in order to isolate the cellulose by employing NaOH-catalyzed organosolv pretreatment methods with ultrasonic assistance using ethanol (80%) as the organic solvent. The extractives of the raw OPFs were removed by soxhlet extraction prior to the organosolv/H_2O_2 pretreatment in order to obtain extractive-free OPFs as described in our previous work [29].

Sonication was carried out in a rectangular S 180/(H) Elmasonic tank (Elma Hans Schmidbauer GmbH & Co., KG, Germany) with internal dimensions of 327 × 300 × 200 mm and a maximum capacity of 18 L. The sonicator was equipped with a high-performance 37 kHz sandwich transducer system with 200 W ultrasonic power, 800 W heating power, sweep function for optimized sound field distribution in the cleaning tank, degas function for efficient degassing of the cleaning liquid, a digital timer and a temperature controller. Briefly, 5 g of the dried extractive-free samples was added to 10 ml of 5% aqueous NaOH and 40 ml of 80% ethanol in a 500 ml capacity Erlenmeyer flask. The mixture in the flask was placed in the ultrasonic cleaning bath at 50 °C for 40 min. Due to the cavitation developed during ultrasonication which leads to heat generation, the temperature in the ultrasonic bath was maintained by the recirculation of cold water in the ultrasonic cleaning bath throughout the experiment. The reaction was stopped by placing the flask and its contents in ice bath; the mixture was filtered (Whatman filter paper No. 1), and the residue (pretreated OPFs) was further delignified with 3% hydrogen peroxide (H_2O_2) at 30 °C for 3 h (pH 11) before characterization. The pretreated OPFs after