Industrial Crops and Products 94 (2016) 480–489

Contents lists available at ScienceDirect

Industrial Crops and Products

journal homepage: www.elsevier.com/locate/indcrop

Fibrous residues of palm oil as a source of green chemical building blocks

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ARTICLE INFO

Article history:
Received 13 April 2016
Received in revised form 8 August 2016
Accepted 6 September 2016
Available online 14 September 2016

Keywords:
Green chemistry
Lignin
Plant fibers
Cellulose
Agribusiness

ABSTRACT

Oil palm is an important industrial crop, and is usually harvested to obtain lipids and proteins. However, such biomass can be a source of important chemical biomacromolecules with several industrial applications. The aim of this work was to extract cellulose nanocrystals (CNC), cellulose nanofibrils (CNF), and lignin from pressed oil palm mesocarp fibers (POPMF). Initially, fibers were acetosolv pulped, resulting in two fractions: a lignin-rich black liquor and cellulose-rich pulp. Lignin was recovered from the black liquor and totally chlorine-free (TCF) bleaching was applied to purify the cellulose. Fibers and biomacromolecules were characterized using several methods including SEM, FEG/SEM, TEM, DRX, GPC, zeta potential, TGA, and FTIR. The pulping-bleaching treatment improved the amount of crystalline cellulose in the pulp, yielding CNC with good thermal stability, a length of 289 nm, diameter of 11 nm, and an aspect ratio of 26. The lignin presented a high purity, with a syringyl-rich structure and good thermal stability. Such characteristics highlight the potential use of POPMF lignin as a green building-block and POPMF nanocellulose materials as renewable biomaterials.

1. Introduction

Many agroindustrial byproducts are lignocellulosic materials and serve as vast sources of important biomacromolecules such as hemicellulose, lignin, and cellulose. Such macromolecules are interesting because of the wide range of possible industrial applications (Shinoj et al., 2011; Ghaffar and Fan, 2014). The use of such renewable materials opens a new sector in the chemical market, with potential positive impacts on mankind and the environment.

Oil palm (Elaeis guineensis) is an important industrial crop, with a world production of around 266 million tonnes of fruit in an area of around 18 million hectares, with a yield of 14.8 t/ha (FAO, 2015). Almost half of the fruit mass is considered a byproduct or waste, and is burned in mill boilers as pressed oil palm mesocarp fibers (POPMFs), or is discarded in stabilization ponds as palm oil mill effluent (POME) (Kudakasseril Kurian et al., 2013; Yunos et al., 2012).

Biorefineries try to extract useful raw materials from biomass for industrial applications with minimal loss and environmental impact (Xu et al., 2014). Many technological pathways, such as the use of ecofriendly solvents in organosolv pulping are used to fractionate the biomass and to disassemble the molecular building blocks through partial hydrolysis and solubilization of the lignin and hemicelluloses. In this process, green solvents like acetic acid (acetosolv pulping), or ethanol (ethanosolv pulping) are catalyzed with strong acids (hydrochloric acid or sulfuric). These chlorine-free reagents has been used to whiten the cellulosic pulp obtained from organosolv pulping because there is no generation of organochlorine compounds in the presence of organic matter in water bodies (Ferrer et al., 2013).

Lignin is a constituent of plant cell walls, and comprises 21% to 29% of POPMF (Souza et al., 2015; Aziz et al., 2002). For several years, lignin was treated as waste in pulp mills, and was burned

Abbreviations: POPMF, pressed oil palm mesocarp fibers; CNC, cellulose nanocrystals; CNF, cellulose nanofibrils; FOP, fruit oil palm.

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http://dx.doi.org/10.1016/j.indcrop.2016.09.012
0926-6690/

in the boilers (Stewart, 2008). Recently, several studies have highlighted the value of lignin from different plant materials, as it is an interesting renewable source of aromatic moieties instead of oil (Laurichesse and Avérous, 2014). Lignin can be used as a building block for phenols in phenol-formaldehyde resins, and as a renewable binder, lignosulfonate, antioxidant, UV stabilizer, and surfactant (Laurichesse and Avérous, 2014; Hussin et al., 2013; Panesar et al., 2013).

Cellulose is a major natural biopolymer. Plants produce around 10^{10} million tonnes of cellulose per year. The hydrogen bonds between β-D-glucose units lead to interesting chemical and mechanical properties (Juwaied et al., 2011). The presence of crystalline and amorphous domains in cellulose allows for the production of two different nanoscale building blocks: cellulose nanocrystal (CNCs) and microfibrillated cellulose (CNF) (Souza et al., 2015; Su et al., 2015). The former is a needle-like structure, primarily composed of crystalline cellulose, and the latter has a longer and more flexible network structure, formed by amorphous and crystalline cellulose (Aziz et al., 2002; Khalis et al., 2011). Both materials can be used as building blocks for different industrial applications, and to confer better properties via mechanical reinforcement and enzyme support (Brinchi et al., 2013).

In the current study, organosolv pulping with acetic acid and bleaching with totally chlorine-free reagents were carried out on POPMFs to fractionate the biomass in lignin and cellulose, and produce green building blocks. This approach adds value to agroindustrial byproducts of important plant supply chains and generates nanoscale materials for industrial applications.

2. Material and methods

2.1. Materials

POPMFs were kindly supplied by Embrapa Amazônia Oriental from Tailândia city in the Pará State. Reagents for pulping, bleaching (acetic acid 99.7% w/w, HCl 37% w/w, NaOH 97% w/w, H_2O_2 30% w/w), and acidic hydrolysis (H_2SO_4 98% w/w) were purchased from VETEC Química/Sigma Aldrich (Duque de Caxias, RJ, Brazil) and were used as received without further purification. POPMFs were ground in a FORTINOX cutting mill and sorted through granulometric sieves (1 mm and 0.5 mm). Fibers that were retained above the 0.5 mm screen were subjected to further treatment. Fig. 1 depicts a general flowchart for the biomacromolecule extraction.

2.2. Acetosolv pulping

The acetolsolv pulping was performed by suspending 10 g of dried POPMFs from a forced air oven into 100 mL of a mixture of 93% (w/w) acetic acid and 0.3% (w/w) HCl in a 500 mL flat bottom glass flask under atmospheric pressure, with constant stirring at 115 °C for 3 h with reflux, as determined by the experimental design of Benar and Schuchardt (1994). The mixture was filtered through a paper filter with a 28 μm pore opening, resulting in lignin-rich black liquor and partly delignified fibers. The acetosolv pulp fiber (AF) was first rinsed with 200 mL of hot (~80 °C) acetic acid (99.7% w/w) until the liquid became colorless. This black-liquor (BL) was stored for further lignin recovery. Further, the fibers were washed with 1.5 L of cold (~25 °C) distilled water until a constant pH (~6.5). The fibers were finally oven-dried at 45 °C until constant weight.

2.3. Lignin separation

Lignin-rich black liquor (BL) was concentrated in a rotary evaporator at 65 °C for separation of lignin and solvent (BUCHI R-210/215). The concentrated BL was diluted 10 times in hot (~80 °C) distilled water over 24 h. The black liquor was concentrated until 90% of the solvent was recovered, remaining around 10 g of lignin in the 100 mL of water. The separated lignin was filtered through a paper filter with a 8 μm pore opening and was oven-dried at 45 °C until a constant weight was obtained.

2.4. Cellulose separation

Acetosolv pulp fiber was bleached to remove the remaining lignin and hemicelluloses by suspending 1 g of oven dried (o.d.) pulped fiber in 32 mL of an aqueous mixture of 20 mL 4% (w/v) NaOH and 12 mL 30% (w/w) H_2O_2 under stirring for 150 min at 65 °C. The first 6 mL of peroxide was added in the beginning of the process, and the other 6 mL was added after 60 min. The bleached cellulose pulp was washed with distilled water until a constant pH (~6.5) (Pereira et al., 2014). The cellulose pulp for cellulose nanocrystal extraction was oven-dried at 45 °C until a constant weight was obtained and was stored at room temperature; the pulp for microfibrillated cellulose was not dried and was stored at ~4 °C.

2.5. Cellulose nanocrystals (CNC) extraction

CNC isolation was carried out based on a report by Cranston and Gray (2006). The hydrolysis was performed at 45 °C for 20 min using 62% (w/w) sulfuric acid. The amount of 5 g of o.d. cellulose pulp was stirred in 100 mL of the acidic solution. At the end of the process, the reaction was halted by adding 100 mL of cold (~10 °C) deionized water. The suspensions were centrifuged three times (HITACHI - CR 22GIII) at 26,400*g* (13,000 rpm) for 15 min until the supernatant became limpid between each centrifugation step, ultrasound (UNIQUE – Cell Disruptor) was applied at 90% power for 5 min to prevent particle agglomeration. Afterwards, the colloidal suspensions were dialyzed with distilled water for 48 h until they reached pH ~6.5.

2.6. Microfibrillated cellulose (CNF) production

Never-dried cellulose pulp with a dry-solid content of 10 g was suspended in 100 mL distilled water. The mixture was treated with high pressure microfluidization (MICROFLUIDICS – M110EH) at an initial pressure of 25,000 psi, with 8 passages in the 400-μm chamber and 10 passages in the 100-μm chamber.

2.7. Characterization of the fibers

Raw, acetosolv pulped fibers, and bleached fibers were characterized for moisture, ash, extractives, insoluble lignin and alpha-cellulose and determined in accordance to TAPPI T 421 om-02 (2002), TAPPI T 211 om-02 (2002), TAPPI T 204 cm-97 (1997), TAPPI T 222 om-02, (2000), TAPPI T 203 cm-99 (2009), respectively. The lignin was characterized as insoluble lignin content (TAPPI T 222 om-02, (2000)). The holocellulose content was measured using the procedure described by Yokoyama et al. (2002a,b) and the hemicellulose content was determined as the difference between holocellulose and alpha-cellulose amounts.

Yields of treated fibers (Y_F) after acetosolv pulping and bleaching were determined by the ratio of final (M_F) and initial (M_I) masses (dry basis) (Eq. (1)):

$$Y_F\,(\%) = (M_F/M_I)\,x100 \quad (1)$$

Lignin yield (Y_L) was calculated based on the real lignin content ($C_{L\%}$) in the initial mass of dry fibers (M_{DF}) and the final mass of dry lignin (M_L) (Eq. (2)):

$$Y_L\,(\%) = M_L x\ 100\ /\ (C_{L\%} x\ M_{DF}) \quad (2)$$

Cellulose nanostructures (nanocrystals or microfluidized) yields (Y_{CNS}) were calculated based on the α-cellulose content ($C_{C\%}$) in the