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ORIGINAL PAPER

Cellulose Fiber Isolation and Characterization from Sweet Blue Lupin Hull and Canola Straw

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Abstract
In this study, cellulose fibers were removed from crop by-products using a combination of sodium hydroxide treatment followed by acidified sodium chlorite treatment. The objective was to obtain high recovery of cellulose by optimizing treatment conditions with sodium hydroxide (5–20%, 25–75 °C and 2–10 h) followed by acidified sodium chlorite (1.7%, 75 °C for 2–6 h) to remove maximum lignin and hemicellulose, as well as to investigate the effect of lignin content of the starting materials on the treatment efficiency. Samples were characterized for their chemical composition, crystallinity, thermal behavior and morphology to evaluate the effects of treatments on the fibers' structure. The optimum sodium hydroxide treatment conditions for maximum cellulose recovery was at 15% NaOH concentration, 99 °C and 6 h. Subsequent acidified sodium chlorite treatment at 75 °C was found to be effective in removing both hemicellulose and lignin, resulting in higher recovery of cellulose in lupin hull (~95%) and canola straw (~93%). The resultant cellulose fibers of both crop by-products had increased crystallinity without changing cellulose I structure (~68–73%). Improved thermal stabilities were observed with increased onset of degradation temperatures up to 307–318 °C. Morphological investigations validated the effectiveness of treatments, revealing disrupted cell wall matrix and increased surface area due to the removal of non-cellulosics. The results suggest that the optimized combination of sodium hydroxide and acidified sodium chlorite treatments could be effectively used for the isolation of cellulose fibers from sweet blue lupin hull and canola straw, which find a great number of uses in a wide range of industrial applications.

Keywords Acidified sodium chlorite · Canola straw · Cellulose · Lignocellulosic biomass · Lupin hull · Sodium hydroxide

Introduction

Agro-industrial residues represent an inexpensive, abundant and readily available source of renewable lignocellulosic biomass. Obtaining high value-added compounds from those under-utilized biomass minimizes environmental concerns and adds high economic returns to the industry. Therefore, fractionation of agro-industrial residues to isolate cellulose fibers has created a great deal of research interest and an extraordinary attention as cellulose has a great number of uses within different industries. Various applications of cellulose, its derivatives, nanofibers and nanocrystals, include its use in paper making, building materials, pharmaceuticals, cosmetics, insulation, food, animal feed and liquid fuel production [1–6].

Isolation of cellulose can be performed by different procedures which have advantages and drawbacks related to the final composition and structural features. These methods include alkaline [7], acid [8], oxidation [9], organosolv treatments [10], subcritical water treatment [11] and/or their different combinations to remove the non-cellulosic components such as lignin and hemicellulose. Among them, alkaline treatment with sodium hydroxide (NaOH) is known to be very effective to achieve complete biomass hydrolysis, avoiding the use of polluting and corrosive chemicals. This treatment effectively solubilizes the lignin fraction as well as the hemicellulose fraction while exhibiting only minor

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cellulose solubilisation [12]. This process destructs the cell wall of biomass by dissolving matrix materials like hemicelluloses and lignin, and cleaves the α-ether linkages between lignin and hemicelluloses and the ester bonds between lignin and/or hemicelluloses [13]. The NaOH treatments of lignocellulosic biomass have been reported to achieve 50% hemicellulose dissolution and 60–80% delignification at the conditions of 0.5–10% NaOH, 60–180 °C and 5–60 min treatment time [14–16]. However, only NaOH treatment cannot remove all of the non-cellulosic components. Another well-known method especially for lignin elimination is the use of acidified sodium chlorite (ASC) treatment but this method can also affect hemicelluloses, depending on the processing conditions [17]. Under acidic conditions, sodium chlorite dissociates into highly reactive chlorine and chloride anion to destroy the cell wall matrix, resulting in a white color residue upon lignin removal [18]. Efficiency of both treatments vary, depending considerably on experimental conditions such as temperature, concentration and treatment time in addition to the type of feedstock and the amount of lignin content in the starting material. Thus, optimized combinations of NaOH and ASC offer a promising alternative to remove non-cellulosic components without impacting cellulose, thereby resulting in high cellulose recovery. Successful isolation of cellulose fibers from energy cane bagasse was reported by Yue et al. [19] with the final composition of 84.1% cellulose, 2.4% hemicellulose and 6.5% lignin using NaOH treatment (20%/10 h/98 °C) followed by ASC ($NaClO_2$/fibers: 0.75/L and CH_3COOH/suspension: 1/50).

In the present study, lupin hull and canola straw were used as the feedstocks for the isolation of cellulose fibers using combined NaOH and ASC treatments. Lupin hull was chosen as a representative low lignin feedstock (< 10%) and canola straw as a high lignin feedstock (20–25%) for comparison purposes of the treatment efficiency. In addition, their high cellulose contents (35–45%) make them ideal renewable biomass sources to obtain cellulose fibers. An extensive literature search indicates that no research in the context of cellulose isolation from these biomasses using a combined NaOH treatment followed by ASC treatment has been reported to date. Therefore, the aim of this study was to optimize treatment conditions of NaOH followed by ASC treatment for maximum cellulose recovery from lupin hull and canola straw, and to investigate the effect of lignin content of the starting materials on the treatment efficiency. Effects of NaOH treatment parameters, such as concentration (5–20%, wt/wt), temperature (25–99 °C), time (2–10 h), and ASC treatment conditions (1.7% wt/wt, 75 °C and 2–6 h time) on removal of non-cellulosic components (hemicellulose and lignin) were also evaluated. Chemical composition, crystallinity, thermal behavior and morphological analysis of the raw and treated samples were performed to investigate the effects of treatments on the structural features of fibers.

Materials and Methods

Materials

Sweet blue lupin hull and canola straw were provided by Ceapro Inc. (Edmonton, AB, Canada) and Dr. Barry Irving (University of Alberta), respectively. Samples were ground in a centrifugal mill (Retsch, Haan, Germany) using a 1 mm particle size sieve. The ACS reagent grade chemicals, such as sodium hydroxide, sodium chlorite, acetic acid, sulfuric acid, and sugar standards (D(+)glucose, D(+)xylose, D(+)galactose, L(+)arabinose, and D(+)mannose with purity ≥ 96%) were obtained from Fisher Scientific (Pittsburgh, PA, USA) and used as received without further purification.

Cellulose Isolation

Before NaOH/ASC treatments, samples were extracted with toluene–ethanol (2:1, v/v) for 8 h at 80 °C in a Soxhlet apparatus to minimize the influence of extractives on the chemical composition analysis. For NaOH treatments, 5 g of lupin hull or canola straw were soaked at specific NaOH concentrations of 5–20%, with 20:1 liquid to solid ratio, for different times (2–10 h) under constant mixing. After treatments, the solid residue and liquid extract were separated by vacuum filtration. The obtained solid residues were washed repeatedly with distilled water until a neutral pH was reached, and then they were dried in an oven at 40 °C for 48 h, and the extracts were stored in the freezer at − 18 °C for further analysis.

Dissolved lignin in the liquid extract at optimized NaOH treatments was removed by lowering the pH below 1.5 with the use of sulfuric acid. The precipitated lignin fraction was vacuum filtered, and washed with hot water many times until a neutral pH was reached, and freeze-dried. The obtained lignin was then analyzed by a thermogravimetric (TG) analyzer.

NaOH treated samples at optimized conditions were then ASC treated for further removal of non-cellulosic components. Samples were treated at a constant concentration of 1.7% ASC (with 50:1 suspension to CH_3COOH volume ratio) with 10:1 liquid to solid ratio and a temperature of 75 °C according to a modified method [20] for 2–6 h under constant mixing. Fresh ASC was added every 2 h, after filtering the sample and removing the old ASC solution to maintain the pH below 4. The resultant samples were subsequently washed with abundant water and oven-dried at 40 °C for 48 h.

Characterization

Chemical Composition

Untreated and treated samples were analyzed for lignin, hemicellulose and cellulose contents following the NREL standard analytical procedures [21]. Lignin contents were determined by treating samples with 72% sulfuric acid for 1 h in a water bath at 30 °C, and then diluting to 4% sulfuric acid and autoclaving at 121 °C for 1 h. Acid insoluble lignin was calculated from the weight of the residue obtained after filtration of the hydrolysate, and acid soluble lignin in the hydrolysate was measured spectrophotometrically at 320 nm. The total lignin contents of the samples were expressed as the sum of the acid insoluble lignin and acid soluble lignin. Total hemicellulose (xylose, galactose, arabinose, and mannose) and cellulose (glucose) in the hydrolysates were determined using an Agilent 1290 HPLC system (Agilent Technologies, Santa Clara, CA, USA) with an ELSD detector and a Shodex sugar SP0810 column (300 mm × 8 mm; Phenomenex, Torrance, CA, USA) operated at 80 °C. A 10% (v/v) acetonitrile solution was used as the mobile phase at a flow rate of 0.4 mL/min.

X-ray Diffraction Analysis

X-ray diffraction (XRD) analysis was performed using a PANalytical Empyrean X-ray diffractometer (Empyrean, PANalytical B.V., Almelo, Netherlands) with a PIXcel 3D detector, over the 2θ range of 5°–45°. Cu Kα source tube was used at the conditions of 40 kV and 40 mA. The scanning speed was 0.6° 2θ per minute with a 0.01 step size. The crystallinity index (CI) of samples was determined based on the empirical method described by Segal et al. [22]:

$$CI = \frac{I_{002} + I_{am}}{I_{002}} \times 100 \quad (1)$$

where I_{002} is the peak intensity of the crystalline portion of biomass (cellulose) at $2\theta = 22.5°$ and I_{am} is the peak intensity of the amorphous region at $2\theta = 18.4°$.

Thermo-gravimetric Analysis

Thermo-gravimetric analysis was performed using a TG 209 F1 Libra (TG 209 F1 Libra, NETZSCH, Selb, Germany). Approximately 10–15 mg of sample was loaded into the aluminum pan, and then heated from 30 to 600 °C at a 10 °C/min heating rate under 20 mL/min of dry nitrogen flow.

Scanning Electron Microscopy Analysis

Scanning electron microscopy (SEM) images of the untreated and treated lupin hull and canola straw were analyzed using field emission scanning electron microscopy (S4700 FE-SEM, Hitachi, Tokyo, Japan). A thin layer of the sample was applied to a sample mount using double-sided carbon tape, and sputter coated with gold prior to analysis (Desk V HP TSC, Denton Vacuum LLC, NJ, USA).

Statistical Analysis

Data were presented as mean ± standard deviation based on at least double analyses. Statistical analysis of the data was done using the SPSS (version 17.0) software package at 95% confidence interval.

Results and Discussion

Chemical Composition

Table 1 shows the chemical composition of raw and treated lupin hull and canola straw at different conditions. Untreated lupin hull consisted of 45.2 ± 2.1% cellulose, 25.4 ± 1.4% hemicellulose and 7.8 ± 0.4% lignin, while untreated canola straw consisted of 38 ± 1.5% cellulose, 24 ± 1.6% hemicellulose and 21 ± 0.9% lignin. According to the compositional analysis of lupin hull, cellulose and hemicellulose contents are similar to those reported by Bailey et al. [23], while their lignin content determined was lower (~0.4%) compared to our study, which can be related to the variety, harvesting conditions used and/or the different analytical method applied for compositional analysis. On the other hand, cellulose, hemicellulose and lignin contents of canola straw used in this study were similar to those reported by Pronky and Mazza [24]. The protein contents of the biomasses used in this study were 6.7 and 2.1% for lupin hull and canola straw, respectively, while the ash contents were below 10%, specifically 4.2% for lupin hull and 3.3% for canola straw.

Treatments with NaOH were found to be efficient on affecting chemical composition of lupin hull and canola straw samples as shown in Table 1. Increasing temperature and concentration of NaOH facilitated greater removal of hemicellulose and lignin components due to the destruction of inter- and intra-hydrogen bonds in the lignocellulose structure. The lignin content of raw material decreased significantly from 7.8 to 5.7% in lupin hull, and from 21.4 to 16.4% in canola straw while the hemicellulose content was significantly reduced from 25.4 to 8.6% in lupin hull, and from 24.3 to 12.7% in canola straw at 15% NaOH concentration and 75 °C for 2 h treatment time. On the contrary, the cellulose content increased significantly from 45.2 to

Table 1 Chemical composition of lupin hull and canola straw before and after different treatments

Treatment conditions	Lupin hull				Canola straw			
	Total solid recovery (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Total solid recovery (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Untreated	100^{a*}	45.2 ± 2.1^{a}	25.4 ± 1.4^{a}	7.8 ± 0.4^{a}	100^{a}	38.5 ± 1.5^{a}	24.3 ± 1.6^{a}	21.4 ± 0.9^{a}
5% NaOH, 25 °C, 2 h	76.5 ± 0.9^{b}	58.3 ± 0.3^{b}	23.4 ± 0.3^{b}	7.5 ± 0.1^{a}	76.2 ± 0.7^{b}	49.7 ± 0.4^{b}	22.1 ± 0.5^{b}	20.5 ± 0.4^{b}
5% NaOH, 50 °C, 2 h	75.9 ± 0.4^{b}	59.1 ± 0.2^{b}	19.6 ± 0.2^{c}	7.1 ± 0.2^{b}	73.5 ± 0.2^{bc}	51.6 ± 0.3^{c}	20.3 ± 0.9^{c}	20.1 ± 0.3^{bc}
5% NaOH, 75 °C, 2 h	71.3 ± 0.7^{c}	62.6 ± 0.9^{c}	15.3 ± 1.4^{d}	6.9 ± 0.1^{bc}	69.1 ± 0.1^{c}	54.3 ± 0.3^{d}	18.2 ± 1.3^{d}	19.5 ± 0.3^{c}
10% NaOH, 25 °C, 2 h	70.3 ± 0.2^{c}	63.4 ± 0.6^{c}	14.1 ± 0.5^{e}	6.6 ± 0.1^{c}	66.2 ± 0.3^{cd}	56.5 ± 0.6^{e}	17.4 ± 1.1^{de}	19.1 ± 0.2^{cd}
10% NaOH, 50 °C, 2 h	68.1 ± 0.2^{cd}	65.2 ± 0.1^{d}	13.2 ± 0.3^{e}	6.3 ± 0.1^{cd}	63.4 ± 0.5^{d}	58.2 ± 0.5^{f}	16.9 ± 0.4^{e}	19.0 ± 0.3^{cd}
10% NaOH, 75 °C, 2 h	64.9 ± 0.4^{d}	68.5 ± 0.2^{e}	11.4 ± 0.3^{f}	6.1 ± 0.2^{d}	60.9 ± 0.2^{d}	61.2 ± 0.7^{g}	16.7 ± 0.2^{e}	18.4 ± 0.5^{d}
15% NaOH, 25 °C, 2 h	62.1 ± 0.5^{de}	71.7 ± 0.1^{f}	10.3 ± 0.3^{g}	6.1 ± 0.2^{d}	56.4 ± 0.1^{e}	65.4 ± 0.6^{h}	14.9 ± 0.2^{f}	18.0 ± 0.2^{d}
15% NaOH, 50 °C, 2 h	60.6 ± 0.2^{e}	73.4 ± 0.1^{g}	9.2 ± 0.2^{h}	5.8 ± 0.1^{de}	55.9 ± 0.1^{e}	66.1 ± 0.3^{hi}	14.6 ± 0.1^{f}	17.8 ± 0.1^{d}
15% NaOH, 75 °C, 2 h	57.4 ± 0.2^{e}	75.9 ± 0.1^{h}	8.6 ± 0.1^{h}	5.7 ± 0.1^{e}	54.6 ± 0.1^{e}	67.2 ± 0.9^{i}	12.7 ± 0.3^{g}	16.4 ± 0.3^{e}
20% NaOH, 25 °C, 2 h	59.1 ± 0.2^{e}	71.2 ± 0.2^{f}	11.1 ± 1.2^{f}	6.3 ± 0.2^{cd}	53.9 ± 0.3^{e}	65.7 ± 0.5^{h}	15.7 ± 0.3^{e}	17.9 ± 0.2^{d}
20% NaOH, 50 °C, 2 h	57.2 ± 0.3^{ef}	73.3 ± 0.2^{g}	9.8 ± 0.4^{h}	6.1 ± 0.3^{d}	52.3 ± 0.2^{e}	66.3 ± 0.4^{hi}	14.5 ± 0.7^{f}	17.3 ± 0.4^{d}
20% NaOH, 75 °C, 2 h	53.7 ± 0.2^{f}	77.1 ± 0.1^{h}	8.9 ± 0.2^{h}	5.9 ± 0.2^{de}	50.1 ± 0.1^{f}	67.8 ± 0.5^{i}	13.9 ± 0.4^{f}	16.9 ± 0.4^{e}
15% NaOH, 75 °C, 6 h	54.5 ± 0.5^{ef}	78.9 ± 0.2^{i}	8.2 ± 0.3^{h}	5.5 ± 0.2^{f}	49.9 ± 0.1^{f}	72.0 ± 1.1^{j}	12.6 ± 0.2^{g}	13.8 ± 0.2^{f}
15% NaOH, 75 °C, 10 h	52.7 ± 0.7^{fg}	81.3 ± 0.4^{j}	8.6 ± 0.3^{h}	5.3 ± 0.1^{f}	48.8 ± 0.2^{f}	72.6 ± 1.4^{j}	12.4 ± 0.2^{g}	13.6 ± 0.4^{f}
15% NaOH, 99 °C, 6 h	49.9 ± 0.5^{g}	85.9 ± 1.6^{k}	7.5 ± 0.2^{i}	4.7 ± 0.2^{g}	47.6 ± 0.1^{fg}	75.0 ± 0.9^{k}	11.5 ± 0.3^{h}	12.3 ± 0.2^{g}
15% NaOH, 99 °C, 10 h	48.6 ± 0.7^{g}	87.1 ± 1.1^{k}	7.2 ± 0.8^{i}	4.4 ± 0.2^{g}	47.0 ± 0.1^{fg}	75.6 ± 0.7^{k}	11.8 ± 0.2^{h}	12.0 ± 0.3^{g}
Opt** + 1.7% ASC, 75 °C, 2 h	47.1 ± 0.2^{gh}	90.5 ± 0.1^{l}	6.4 ± 0.2^{j}	2.9 ± 0.4^{h}	45.1 ± 0.6^{g}	77.7 ± 0.5^{l}	11.4 ± 0.3^{hi}	10.8 ± 0.5^{h}
Opt** + 1.7% ASC, 75 °C, 4 h	45.7 ± 0.1^{h}	93.2 ± 0.5^{m}	4.6 ± 0.1^{k}	1.7 ± 0.1^{i}	44.1 ± 0.2^{g}	79.4 ± 0.4^{m}	11.0 ± 0.4^{i}	8.5 ± 0.7^{i}
Opt** + 1.7% ASC, 75 °C, 6 h	44.3 ± 0.2^{h}	88.7 ± 0.6^{n}	Traces	0.8 ± 0.1^{j}	43.3 ± 0.3^{g}	81.4 ± 0.5^{n}	10.3 ± 0.3^{j}	7.9 ± 0.3^{i}

Contents have been expressed on dry weight basis as mean ± standard deviation of at least double determinations

*Different letters in the same column are statistically different from each other

**Opt: Optimized condition (15% NaOH, 99 °C, 6 h)

75.9% in lupin hull and from 38.5 to 67.2% in canola straw at the same treatment conditions. The chemical composition values of 15% NaOH treated samples were not significantly different from those treated with 20% NaOH at all temperatures investigated for 2 h. This behavior may be attributed to the excessive swelling of the cellulose in the presence of 15–20% alkali concentration. One of the functions of alkali is to serve as a swelling agent to cellulose, thereby allowing better extraction of hemicelluloses. Although mild alkali solutions could not be able to break the cellulose and hemicellulose complex efficiently, higher alkali concentrations might prevent the further separation of hemicelluloses from the fiber structure as it swells extensively the microfibers [25]. On the other hand, increasing 15% NaOH treatment

time to 6 h and temperature to 99 °C resulted in improved removal of hemicellulose and lignin in both samples. The hemicellulose and lignin contents after treatment with 15% NaOH, 99 °C for 6 h were further reduced to 7.5 and 4.7%, respectively, in lupin hull, and 11.5 and 12.3%, respectively, in canola straw. However, further increasing the treatment time to 10 h did not significantly affect the chemical composition values of both samples.

Figure 1 shows the effect of NaOH treatment on hemicellulose and lignin removal amounts of lupin hull and canola straw. Although the amounts of removed lignin (50–60%) were similar for all NaOH treated samples of lupin hull and canola straw, the amounts of hemicellulose removal from lupin hull (up to 80%) were higher than those from canola straw (up to 70%). The higher amounts of hemicellulose removal in lupin hull can be attributed to the low amount of lignin (< 10%), which makes hemicellulose more accessible to hydrolysis. As known, lignin surrounds cellulose and hemicellulose, forming a complex structure that makes lignocellulosic biomass highly recalcitrant to enzymes, pathogens and microorganisms [26]. Strong lignin interactions keep the hemicellulose unexposed and inaccessible. Depolymerization and removal of lignin provides improved susceptibility for the remaining hemicellulose and cellulose for further breakdown of their structures as lignin fails to act as a protective shield. Therefore, the efficient removal of hemicellulose would be expected to depend on the low amount of lignin present in the starting material and/or efficient removal of lignin with the treatment applied. It is a challenge to completely delignify the biomass since lignin is located within the deep cell wall and tends to recondensate. Lignin is physically stiff due to its strong polyring bonds of C–O–C, C–C and hydrophobic bonds [27].

To further remove the residual lignin and hemicellulose, the NaOH treated samples at optimized conditions (15% NaOH/99 °C/6 h) were then subjected to ASC treatment for 2–6 h at 75 °C with fresh ASC added every 2 h. As anticipated, the hemicellulose and lignin contents of NaOH treated samples were further reduced and cellulose content was further increased as a function of treatment time. At

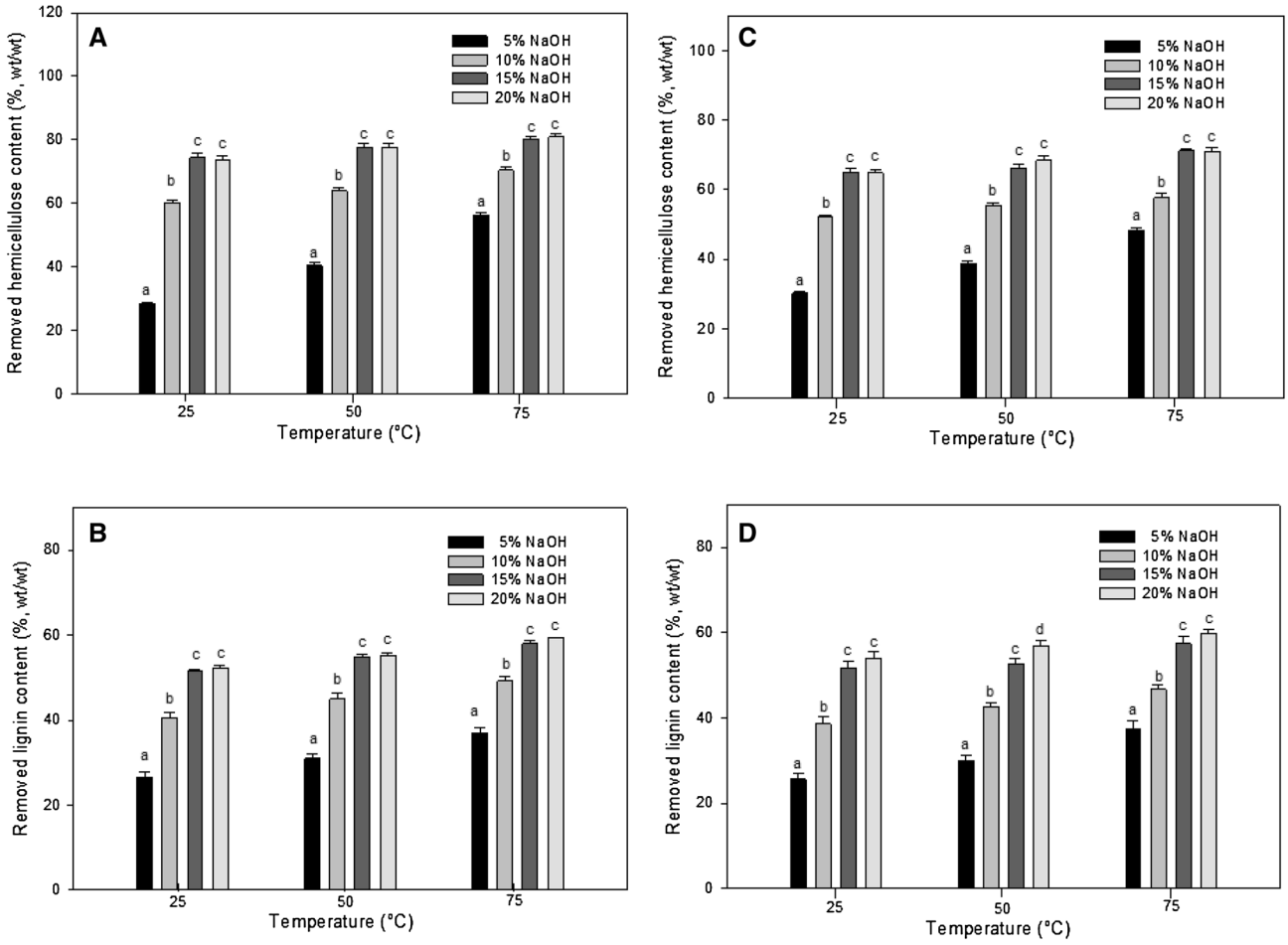

Fig. 1 Effect of NaOH concentration and time on hemicellulose and lignin removal of **a**, **b** lupin hull, and **c**, **d** canola straw. Means with different letters within each temperature are different from each other at $p < 0.05$

the end of 6 h of ASC treatment, the lignin content of lupin hull decreased to 0.8%, while the lignin content of canola straw decreased to 7.9% as reported in Table 1. The cellulose content of canola straw increased continuously up to 81.4% after 6 h ASC treatment; however, cellulose content of lupin hull first increased up to 93.2% after 4 h treatment, and then increasing the treatment time to 6 h resulted in a decrease of cellulose content to 88.7%, which was not the case for canola straw with a higher lignin content. It is hypothesized that ASC treatment of biomass containing below 1% lignin had a detrimental effect on cellulose degree of polymerization due to hydrolysis and/or oxidative cleavage of the cellulose chain [28]. Therefore, degradation of cellulose in lupin hull at this condition could be related to its lignin content of < 1%. Hubbell and Ragauskas [17] treated two types of pure cellulose, Avicel PH-101 and Whatman filter paper, with ASC in the presence of varying amounts of incorporated lignin (up to 30%). They also reported that ASC treatment caused significant damage to the cellulose component of the substrate, containing < 1% lignin.

Figure 2 demonstrates the effects on cellulose, hemicellulose and lignin recovery of lupin hull and canola straw of combined NaOH (15% NaOH/99 °C/6 h) and ASC treatments of 2, 4 and 6 h. For both samples, more than 90% of the original cellulose fibers were recovered. However, a treatment time beyond 4 h seemed to have a negative impact on the cellulose recovery of lupin hull with about 7% decrease, probably due to cellulose degradation to glucose as the lignin amount was below 1% as discussed earlier, and no hemicellulose content was detectable in lupin hull. Treatment with NaOH followed by ASC treatment of lupin hull and canola straw up to 6 h led to lignin recovery of 4.7 and 16.2%, indicating the removal of 95.2 and 83.7% of the original lignin, respectively. Similarly, the hemicellulose fraction removal for lupin hull was much higher than that of canola straw, with amounts of 91.2 and 81.4% for lupin hull and canola straw, respectively. Also, < 1% ash for both samples and only traces of proteins were obtained at the end of the NaOH–ASC treatments.

With the ASC treatment, non-cellulosics were removed, and the solid residue turned into white color, suggesting successful isolation of cellulose-rich fraction. In the case of lupin hull, the solid residue appeared white after the first 2 h of treatment. However, the solid residue of canola straw still appeared yellow after the first 2 h of treatment, which was a visual evidence of certain amounts of hemicellulose and lignin present. Then, the white color of canola straw residue was obtained at the end of 4 h treatment time.

Overall, more than 90% of the cellulose fibers were isolated from both samples as a result of combined NaOH and ASC treatments. However, higher amounts of non-cellulosic components removal (~ 95% of lignin and > 92% of hemicellulose) was observed for lupin hull compared to those of canola straw (~ 84% of lignin and ~ 81% of hemicellulose), which can be related with the much lower lignin content of lupin hull in the starting material.

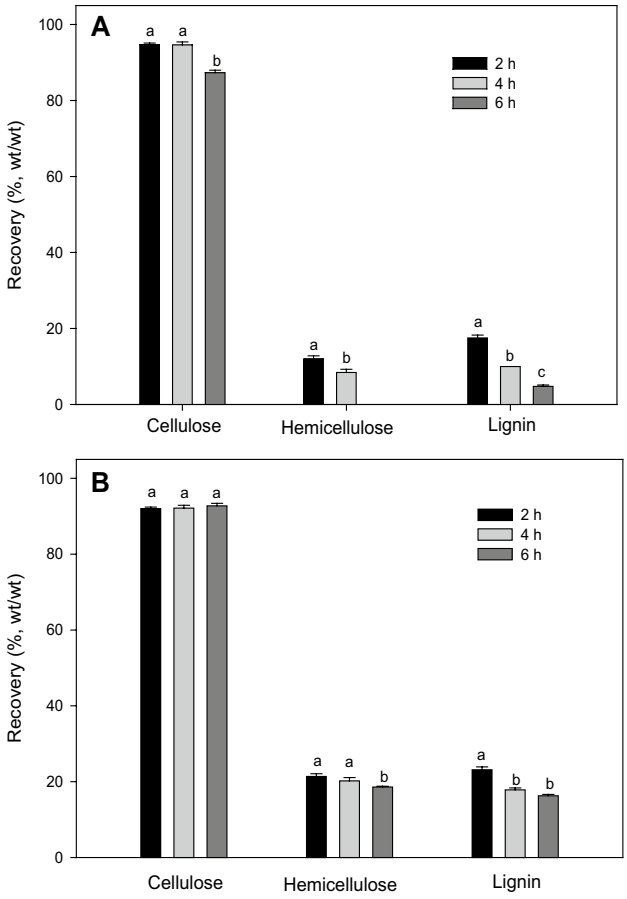

Fig. 2 Effect of ASC treatment (1.7%/75 °C) time (2, 4 and 6 h) on cellulose, hemicellulose, and lignin recovery of **a** lupin hull and **b** canola straw treated at optimum NaOH conditions (15% NaOH/99 °C/6 h). Means with different letters within each biomass fraction are different from each other at $p < 0.05$

Crystallinity

Figure 3 shows the XRD patterns of untreated, NaOH and ASC treated lupin hull and canola straw and their corresponding CI values. The results clearly demonstrated the increase in the crystallinity of both samples after NaOH and ASC treatments. Moreover, the crystalline structure of cellulose in both samples was maintained after both treatments as all XRD diffractograms showed two peaks at around $2\theta = 16.5°$ and 22.5°, which are associated with the typical crystalline structure of cellulose I [29]. Separation of the molecular chains of cellulose in the presence of NaOH usually lead to destruction of cellulose I structure, which is then transformed into cellulose II [30]. In this study, 15% NaOH concentration did not affect the cellulose structure. Yue et al.

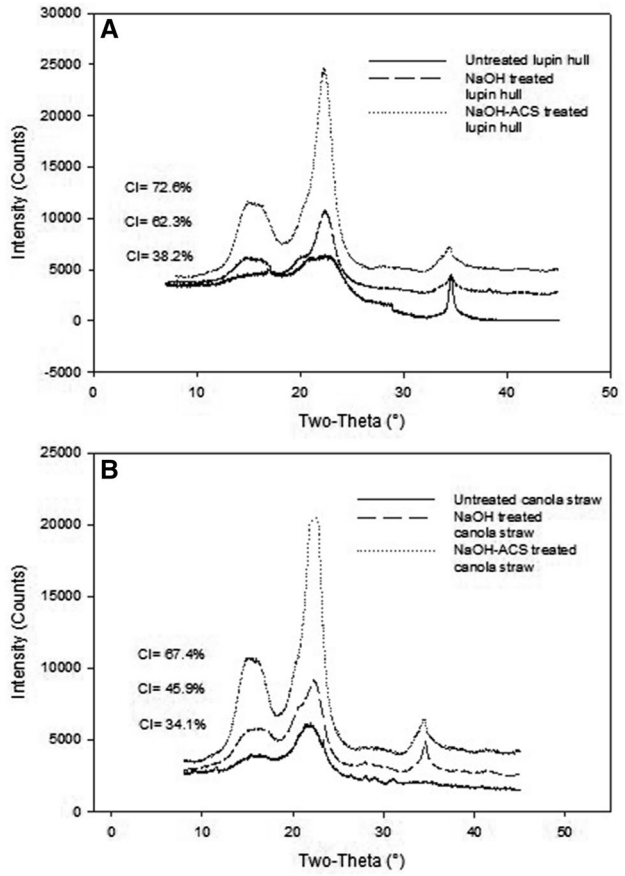

Fig. 3 XRD patterns of untreated, NaOH (15%/99 °C/6 h) and NaOH–ASC (ASC: 1.7%/75 °C/6 h) treated lupin hull (**a**) and canola straw (**b**) and their crystallinity index (CI) values

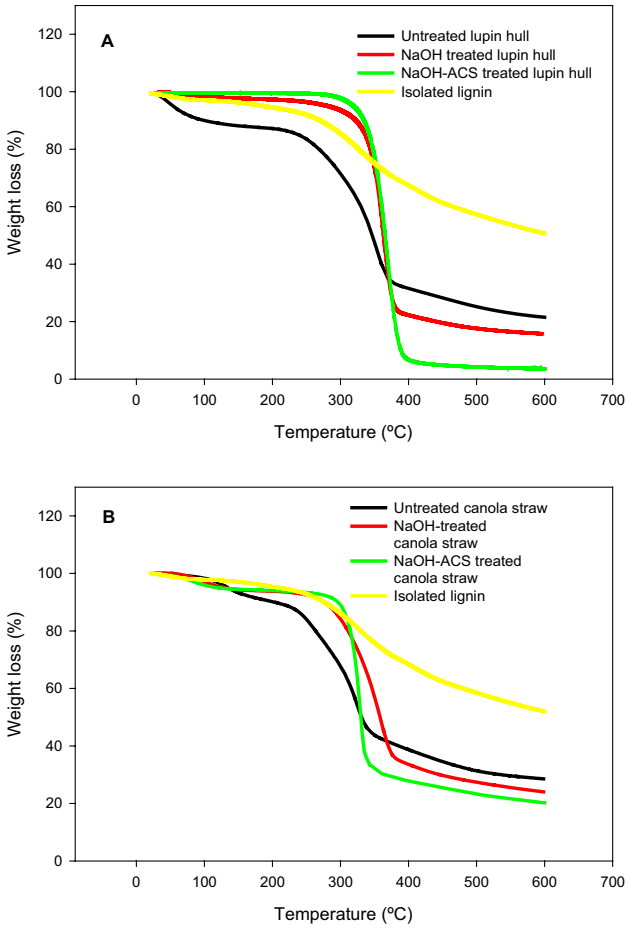

Fig. 4 Thermo-gravimetric curves of untreated, NaOH (15%/99 °C/6 h) and NaOH–ASC (ASC: 1.7%/75 °C/6 h) treated lupin hulls (**a**) and canola straw (**b**)

[19] reported that the cane bagasse conversion from cellulose I to cellulose II could not be obtained with NaOH concentrations of ≤ 10 wt%. They evaluated treatments with 10 and 20% NaOH for 1.5–10 h at 98 °C and obtained a mixture of cellulose I and II structures in the 20% NaOH treated samples for 1.5 h, indicating the presence of peaks at $2\theta = 15.16°$ and 16.60°, and a small peak at $2\theta = 12.22°$.

The CI value of untreated lupin hull (38.2%) was slightly higher than that of canola straw (34.1%). The CI values for the lupin hull treated by NaOH and NaOH–ASC were 62.3 and 72.6%, respectively. Similarly, the increased crystallinity was observed for canola straw samples, where the CI values for the NaOH treated and NaOH–ASC treated samples were found to be 45.9 and 67.4%, respectively. Such an increase in crystallinity was attributed to the removal of amorphous lignin and hemicellulose as cellulose is crystalline in nature. Therefore, the CI values of canola straw samples were less than those of lupin hull, which might be due to the fact that canola straw contains comparatively more amorphous components than that of untreated lupin hull and the treated lupin hull at the conditions investigated. These results also implied that obtained cellulose fibers have improved mechanical properties since higher crystallinity leads to higher tensile strength [31].

Thermal Behavior

Thermogravimetric analysis was carried out to investigate the degradation characteristics and thermal stability of both samples at various stages of the isolation processes. Figure 4 presents the effect of NaOH and ASC treatments on the thermal behavior of lupin hull and canola straw samples. Thermal behavior of both samples changed significantly after treatments. NaOH and ASC treated samples showed improved thermal stability with increased onset temperature of degradation, which ascribed to the removal of amorphous hemicelluloses and lignin. Because these components can form free radicals, initiating the degradation at lower temperatures than the crystalline fractions. The onset of degradation of untreated lupin hull and canola straw started at temperatures of 238 and 232 °C, respectively. After NaOH

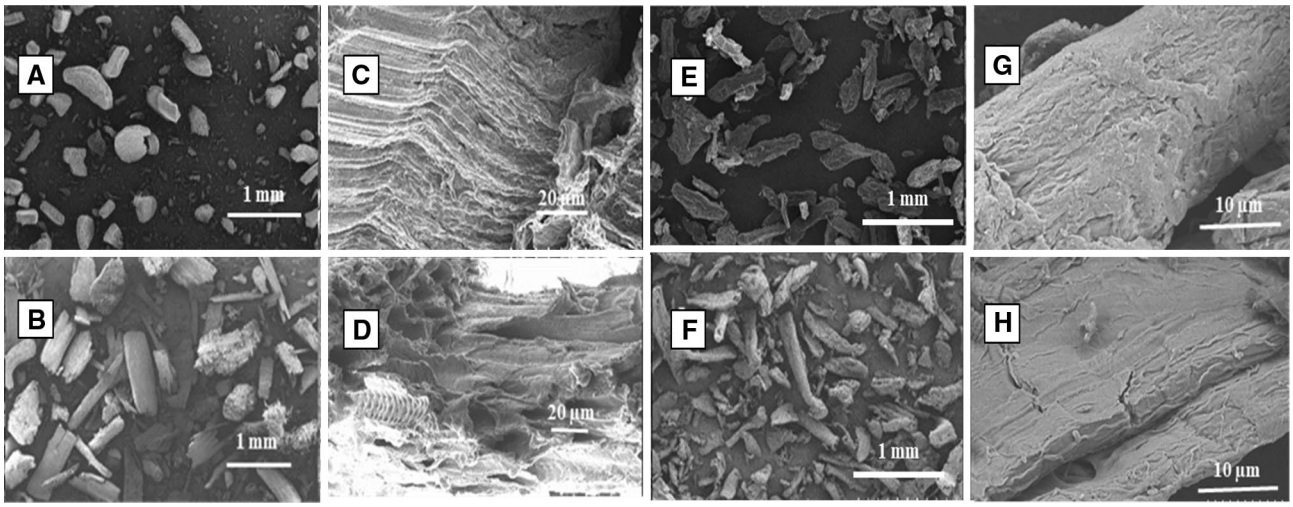

Fig. 5 Scanning electron microscopy images of untreated lupin hull (**a**), untreated canola straw (**b**), NaOH treated lupin hull (**c**), NaOH treated canola straw (**d**), NaOH–ASC treated lupin hull (**e**, **g**), NaOH–ASC treated canola straw (**f**, **h**) at the optimized conditions (NaOH: 15%/99 °C/6 h, and ASC: 1.7%/75 °C/6 h)

treatment, the onset temperature increased to 301 °C for lupin hull, and 298 °C for canola straw due to the increased crystallinity of cellulose (Fig. 3). The onset of degradation further rised in the case of NaOH–ACS treated lupin hull (318 °C) and that of the canola straw (307 °C) since majority of the amorphous components were removed.

The thermal degradation curves of lignocellulosic biomass are composed of multi-stages due to the existence of lignin, hemicellulose, and other non-cellulosic constituents with different decomposition temperatures. The first stage of the degradation begins at around 120 °C, which is regarded as the evaporation of loosely bound moisture on the surface and/or intermolecular hydrogen bonded water [32]. As shown in Fig. 4, NaOH treated and NaOH–ASC treated samples have relatively lower moisture contents of 4–6 and 1–2% than untreated lupin hull and canola straw (10–12%). This is because untreated samples are composed of more hydrophilic components like hemicellulose, which can entrap greater amount of water [33], and also depends on initial moisture content of the sample. The second stage of the degradation between 220 and 315 °C is attributed to the thermal decomposition of mainly hemicellulose and the breakdown of glycosidic linkages of cellulose [34]. The weight loss of untreated samples between 220 and 315 °C (~20% for lupin hull and ~28% for canola straw) is higher than that of NaOH treated samples (~7% for lupin hull and ~15% for canola straw) since NaOH treated samples contain less hemicelluloses due to the effective removal during treatment. The third stage of degradation between 315 and 400 °C is associated with predominantly cellulose and lignin decomposition [35]. Weight losses of the samples (~70% for lupin hull and ~45% for canola straw) in that region increased due to an increased cellulose content. The final stage of degradation above 400 °C is related to mainly lignin decomposition. However, lignin decomposition takes place in a broader temperature range than cellulose and hemicelluloses as observed in Fig. 4. More than 50% of the isolated lignin from lupin hull and canola straw were maintained at a temperature of 600 °C as they require higher temperature to reach complete degradation (800–1000 °C). The presence of various oxygen functional groups in lignin with different thermal stabilities leads to a broader decomposition temperature range [36].

Morphology

The morphology of raw and NaOH/ASC treated samples were examined to elucidate the physical changes that occurred in lupin hull and canola straw samples after each treatment. Figure 5 shows the SEM images of untreated, NaOH and ASC treated lupin hull and canola straw samples. Untreated samples were intact, displaying more compact and smooth surface structures with non-uniform shapes and low porosity (Fig. 5a, b). The significant change in fibers' morphologies was clear with disruption of the cell walls as a consequence of amounts of lignin and hemicellulose removal with 15% NaOH treatments at 99 °C for 6 h. It was observed that NaOH treated fibers of lupin hull and canola straw had increased porosity (Fig. 5c, d). The holes observed in the NaOH treated samples made the fibers more accessible for subsequent ASC treatments for an effective removal of hemicellulose and lignin. Thus, more remarkable changes were observed due to the further deconstruction of the cell walls after ASC treatments of both samples at 75 °C for 6 h,

which are visualized in Fig. 5e, f. The NaOH–ASC treated samples composed of 80–90% cellulose exhibits smoother, uniform and homogeneous fiber surface, creating a larger surface area and indicating the extensive removal of non-cellulosic components from lupin hull and canola straw (Fig. 5g, h).

Conclusions

Cellulose fibers of lupin hull and canola straw were successfully produced using combined chemical treatments with NaOH followed by ASC. The maximum cellulose obtained was 94.7% for lupin hull after treatment with 15% NaOH at 99 °C for 6 h followed by 4 h ASC treatment. For canola straw, 92.7% cellulose was obtained after treatment with 15% NaOH at 99 °C for 6 h followed by 6 h ASC treatment. The amount of non-cellulosic components removal was higher for lupin hull than that of canola straw. Lupin hull and canola straw lignin contents were reduced by about 90 and 82%, respectively. The maximum removed hemicellulose contents were 92 and 81% for lupin hull and canola straw, respectively. The treated samples increased crystallinity up to 72.6% CI for lupin hull and 67.4% CI for canola straw and improved thermal stabilities, with onset degradation up to 318 °C for lupin hull and 307 °C for canola straw. The SEM images revealed that the isolated cellulose fibers from lupin hull and canola straw obtained after NaOH/ASC treatments had more homogeneity and uniformity with increased surface area.

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