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Analysis of soluble and insoluble fractions of alkali and subcritical water treated sugarcane bagasse

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ABSTRACT

A set of experimental trials were carried out to fractionate Taiwanese sugarcane bagasse as a result of alkaline and subcritical water treatments. The alkaline treatments were done at 120 °C using 0, 1, 2 and 4 M sodium hydroxide while the subcritical water treatments were performed in a reactor at 120, 140, 160 and 180 °C and 13 bar. The effects of alkali and subcritical water treatments on the solubilization of sugarcane bagasse were investigated. Soluble phenolic acids and neutral sugars contents of liquid fractions were determined and discussed. Also, the chemical compositions (moisture content and elemental analysis) and structural elucidation (FT-IR, ^{1}H NMR, and ^{13}C NMR spectral data) of solid fractions are analyzed and explained. Moreover, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and differential thermal analysis (DTG) techniques were employed for the thermal analysis of the solid fractions.

1. Introduction

Amongst various agricultural residues, sugar cane bagasse, a waste in the process of sugar extraction, is one of the most abundant low-cost lignocelullosic material (Cardona, Quintero, & Paz, 2010), in which about 54 million dry tons of bagasse is produced annually throughout the world (Rodrigues, Felipe, Sil, & Vitolo, 2003; Rodrigues et al., 2010). This renewable source represents a great morphological heterogeneity, consists of fiber bundles and other structural elements like vessels, parenchyma, and epithelial cells (Rainey, Covey, & Shore, 2006). According to data collected in the literatures (Gnansounou, 2010; Godshall, 2005; Hailing & Simms-Borre, 2008; Mirza, Ahmad & Majeed, 2008; Mohamed, Mohammadi & Darzi, 2010; Pandey, Soccol, Nigam, & Soccol, 2000; Sasaki, Adschiri, & Arai, 2003, 2004), about 40–50% of the dry residue is the glucose polymer cellulose, much of which is in a crystalline structure. Another 25–35% is hemicelluloses, an amorphous polymer usually composed of xylose, arabinose, galactose, glucose, and mannose. The remainder (10–14%) is mostly lignin plus lesser amounts of minerals, waxes, and other compounds. Because of its low ash content (2%), bagasse offers numerous advantages over other crop residues such as rice straw and wheat straw, which have 17.5% and 11.0%, respectively, ash contents, for usage in bioconversion processes using microbial cultures (Pandey et al., 2000).

The most frequent uses for sugarcane bagasse is direct combustion for energy production (Kilicaslan, Sarac, Özdemír, & Ermíş, 1999; Neureiter, Danner, Thomasser, Saidi, & Braun, 2002), production of chemical compounds such as furfural or hydroxymethyl-furfural (HMF) (Almazán, González, & Gálvez, 2001; Gong, Chen, & Chen, 1993), paper paste (Caraschi, Campana, & Curvelho, 1996; Nagieb, Abd-El-Sayed, E-I-Sakhawy, & Khalil, 2000; Shukry, Hassan, Yousef, & Fadel, 2002), phenolic compounds (Rodrigues et al., 2003; Rodrigues et al., 2010), ethanol (David, Fornasier, Greindl-Fallon, & Vanlautem, 1985; Dawson & Boopathy, 2008; Grethlein & Converse, 1991; Hailing & Simms-Borre, 2008; Laser et al., 2002; Pandey et al., 2000). After cellulose and hemicellulose, lignin is considered to be the most abundant natural polymer present on planet earth (Argyropolous and Menachem, 1988; Glasser, Barnett, Rials, & Saraf, 1984; Glasser & Leitheiser, 1984; Goheen & Henderson, 1978; Goheen & Hoyt, 1981; Saraf & Glasser, 1984; Wu & Glasser, 1984). Hence, with an apparent lack of petroleum-based materials as well as a desire to utilize green materials, there are renewed interest in the chemistry and technology of lignin (Felipe et al., 1996; Felipe et al., 1995; Felipe, Vitolo, Mancilha, & Silva, 1997; Nimz & Casten, 1986).

It was reported that, subcritical water has similar potential as supercritical water as an extraction medium with different water

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state, but is less expensive (Sasaki et al., 2003, 2004; Sealock, Elliot, Baker, & Butner, 1993), in which subcritical water requires less energy input since the temperature and pressure are lower that those of supercritical water. The applications of subcritical water can be divided into two main categories: extraction and conversion of biomass, such as extraction of antioxidant compounds from rosemary plants (Ibanez et al., 2003), extraction of whitening agents and azo dyes in paper samples (de los Santos, Batlle, Salafranca, & Nerín, 2005), extraction of anthocyanins from red grape skin (Yu & Howard, 2005), extraction of dioxins (Hashimoto, Watanabe, Nose, & Morita, 2004). Also, subcritical water can also be used for liquifying biomass into bio-oil and other liquid fuels (Sealock et al., 1993), such as liquification of corn stalks to bio-oil (Song, Hu, Zhu, Wang, & Chen, 2004). Like other supercritical fluids, adding catalysts can also enhance the subcritical water reaction (Nelson et al., 1984; Sealock et al., 1993; Song et al., 2004).

A search in literature data shows a number of studies have been done on alkaline, acidic, enzymatic treatments on sugarcane bagasse (Pandey et al., 2000; Sun & Cheng, 2002, 2004; Sun, Sun, Sun, & Su, 2004). However, only one paper was recorded about the hydrothermal treatments of bagasse (Sasaki et al., 2003, 2004). The principal drawback in any chemical process employing and agricultural materials is that it is not possible, either technically or on a laboratory scale, to separate these three components (cellulose, hemicellulose and lignin) without changing their chemical structures. In the present paper, the experimental results of the fractionation of Taiwanese sugarcane bagasse during alkaline and subcritical water treatments were presented. The effects of both alkali and subcritical water treatments on the solubilization of sugarcane bagasse were carried out and presented. Chemical analyses of liquid fractions as well as physical and chemical compositions of the solid fractions were investigated. Moreover, structural elucidation (FT-IR, ^{1}H NMR, and ^{13}C NMR spectral data) of solid fractions resulted from the alkali and subcritical treated bagasse were analyzed and explained. Finally, thermal analysis of solid fractions was investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and differential thermal analysis (DTG) techniques.

2. Experimental

2.1. Sugarcane bagasse pretreatment

Sugarcane bagasse used in this study was collected from a local market (Taipei, Taiwan). Sugarcane bagasse was pretreated according to a variant of the methodology reported (Brányik, Vicente, Cruz, & Teixeira, 2001). The sugarcane bagasse was firstly dried under sunlight, then in oven at 105 °C. The dried sugarcane bagasse was cut into small pieces, homogenized in a single lot. It was then ground using a laboratory mill and screened to obtain 35 mesh (0.5 mm) powders. After that, the powdered sugarcane bagasse was washed with distilled water, dried at 100 °C until constant weight and stored in desiccator at room temperature.

2.2. Alkaline treatment

The mechanism of alkaline hydrolysis is similar to that occurs in the Kraft paper pulping, which includes hydrolysis of the intermolecular ester bonds cross-linking lignin to other components such as hemicellulose. Dried sugarcane bagasse sample (1.5 g) was sterilized at 121 °C, 1.5 bar for 30 min in a 250 mL-Erlenmeyer flask, mixed with 10 mL of NaOH solution (0, 1, 2 or 4 M), then incubated in a rotary shaker at 120 rpm for 2 h at room temperature, and then washed with sterilized deionized water (300 mL) and dried under the same conditions. The weight loss as a consequence of the alkaline treatment was determined with the help of controls. The resulted bagasse was delignified using several NaOH solutions (1.0, 2.0, and 4.0 M) applied at a ratio of 5 mL of solution/g of bagasse. The final concentration of NaOH was 50 mg/g of bagasse. The mixture was then autoclaved at 121 °C for 2 h. After this treatment, the mixture was ultra filtrated with 5 kD and 15 kD molecular cut-off membrane to remove high molecular particles/carbohydrates such as protein and viscous polysaccharides. The solid residue was removed as waste, and the liquid extract was micro-filtered using 0.45 μm pore filters, and then the pH was adjusted with HCl to 5.0. After this treatment, the liquid extract (soluble lignin and hemicellulose) was micro-filtered again using 0.2 μm pore filters prior to analytical analysis.

2.3. Subcritical water treatment

The equipment for subcritical water extraction used in this research was constructed by Ju-Shan Industrial Co., Ltd in Taiwan. There are three main parts in this equipment, subcritical reactor, heater, and control devices. The reactor was made from stainless steel, and the total inner volume was about 90 mL. A thermocouple and a pressure gauge were connected to the reactor. The process was run under batch mode. For subcritical water extraction, nitrogen gas (99.9% purity) purchased from Dong-Xing Company (Taiwan) was used to maintain high pressure inside the reactor.

One gram of dried sugarcane bagasse was mixed with 50 mL of deionized water. The mixture was heated in the subcritical reactor to a pre-determined temperature (120, 140, 160 or 180 °C), and nitrogen was introduced into the reactor until the initial pressure in the reactor reached 13 bar. High pressure was firstly introduced to ensure the experiment was conducted under subcritical water condition (15, 22, 24, and 31 bar at 120, 140, 160, and 180 °C). A retention time of 1 h was maintained when temperature inside the reactor reached the desired reaction temperature. The sample was then cooled down until the temperature was below 30 °C. The mixture was then filtered using filter paper, and the residue was washed by 150 mL of deionized water. The residue was dried in an oven for 2 days and stored for analyses. The volume of the liquid fraction was adjusted with deionized water until 500 mL, centrifuged and then filtered through 0.22 μm syringe filter before subjected to HPLC analyses.

2.4. Solubilization of sugarcane bagasse

The water-solubilization percentage of sugarcane bagasse (X) was calculated as the ratio of the weight of the residue (W) to the initial weight of the untreated bagasse (W_O) by the equation: $X = W_O - W/W_O \times 100$.

2.5. Liquid fraction analysis

Phenolic acids (*p*-coumaric acid, ferulic acid, vanillin, syringic acid, 5-hydroxymethyl-furfural, and *p*-hydroxybenzoic acid) derived from soluble lignin were analyzed qualitatively and quantitatively by HPLC (a chromatographic system consisting of a Waters In-Line Degasser Model ILD, a Waters HPLC Pump Model 616, a Waters 717 auto sampler and a 2487 Dual Wavelength Absorbance Detector at 320 nm, and a Waters C_{18} column), using 0.01 N H_2SO_4 with 20% methanol and 3% propanol as the eluent at a flow rate of 1 mL min^{-1} and an injection volume of 20 μL. Also, the concentrations of D-xylose, D-glucose, L-arabinose, galactose, mannose, rhamnose and uronic acids were determined with a Shimadzu (Kyoto, Japan) high-performance liquid chromatograph (HPLC), using a refractive index (RI) detector and Bio-Rad (Hercules, CA) Aminex HPX-87H column (300 mm × 7.8 mm) at 45 °C and 0.01 N H_2SO_4 as the eluent at a flow rate of 0.6 mL min^{-1} and an injection

volume of 20 μL. The concentrations of furfural and 5-HMF were determined with a Shimadzu high-performance liquid chromatograph (HPLC), using a dual absorbance detector (SPD-10^{A}Uv–vis) at 276 nm wavelength and a Hewlett-Packard RP 18 (200 mm) column at 25 °C, a 1:8 acetonitrile-to-water ratio and 1% acetic acid as the eluent at a flow rate of 0.8 mL min^{-1} and a sample volume of 20 μL. Calibrations were performed with standard solutions of *p*-coumaric acid, ferulic acid, vanillin, syringic acid, 5-hydroxymethyl-furfural, *p*-hydroxybenzoic acid, D-xylose, D-glucose, L-arabinose, galactose, mannose, rhamnose, and galacturonic acids. Each experimental variable was run three times, and the results were expressed as mean value ± standard deviation.

2.6. Solid fractions analysis

2.6.1. Moisture content

Moisture content was determined using Lab Analytical Procedure number 001 (LAP-001) from National Renewable Energy Lab (NREL) (Ehrman, 1994). It was measured in triplicate for both shredded and 40 mesh cotton stalk samples. Samples (3 g) were placed in the convection oven overnight (or until constant weight was achieved) at 105 °C and weighed. The percent moisture was calculated with the following formula:

$$\%\ \text{Moisture} = 100\% - \left(\frac{W_2 - W}{W_1 - W}\right) \times 100$$

where W is the weight of dish; W_1 is the initial sample weight + dish weight (g); W_2 is the dried sample weight + dish weight (g)

2.6.2. Thermal analysis

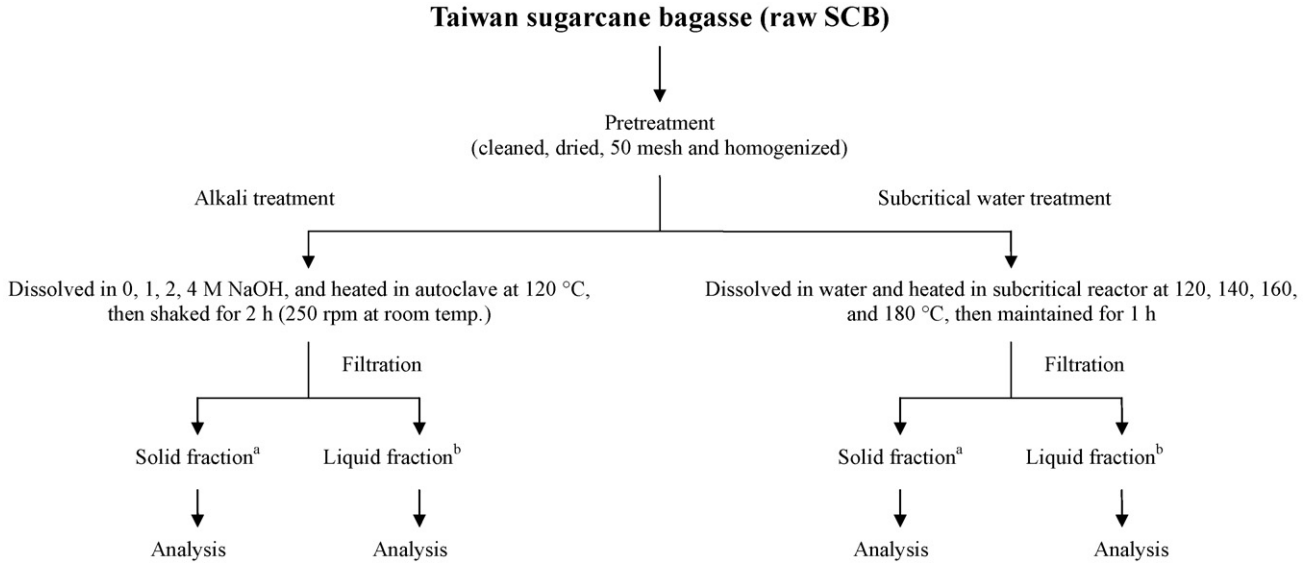
2.6.2.1. Thermogravimetry (TGA) and derived thermogravimetry (DTG). TG is a technique in which the mass of a substance is measured as a function of temperature while the substance is subjected to a controlled temperature program. A Perkin-Elmer series 7 thermogravimetric analyzer (TGA-7) was used for TG and DTG analysis (Colaço, Sen, Thangavelu, Pinder, & Roser, 1992; Sola-Penna & Meyer-Fernandes, 1998). Two to five milligrams of each sample was assayed. The carrier gas was nitrogen (99.9%) at 30 mL min^{-1} and a scan rate of 10 °C min^{-1} was employed.

2.6.2.2. Differential scanning calorimetry (DSC). DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a residual solid samples is measured as a function of temperature. For all samples, the same temperature throughout the experiment was maintained (Dean, 1995; Pungor, 1995). Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly with time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The Perkin-Elmer series seven differential scanning (DSC-7) instrument was used to characterize the thermal behavior of the solid fractions. Two to five milligrams of each powder sample was placed into an aluminum sample pan and sealed. The sample was submitted to thermal treatment using a scan rate of 10 °C min^{-1} pure nitrogen (99.9%) was used as the carrier gas at 30 mL min^{-1}.

2.6.3. Structural analyses

2.6.3.1. Elemental analysis. The elemental analyses (C, H, O, S, and N) were performed on a LECO-CHSNO-9320 type elemental analyzer. Samples were ground to fine powder and each sample (1 mg, dry basis) was weighted on tin foil and placed into the elemental furnace and subjected to complete combustion in a pure oxygen environment. For oxygen content analysis, each sample (1 mg) was placed inside a silver capsule and placed into the furnace and heated at 1000 °C. After complete combustion, samples were screened using infrared detector to determine the oxygen content.

2.6.3.2. FT-IR absorption spectroscopy analysis. For FT-IR measurements, the infrared spectra of each sample were recorded by Fourier transform infrared spectrometer (FT-IR), Model, Bio-Rad Digilab, FTS-3500.



[a]**Solid fraction**: prior to analysis, washed several times by pure water, then dried. By applying analytical analysis such as elemental analysis, FT-IR, ^{1}H-, ^{13}C- NMR, and TG/DTA were employed to determine its chemical structure and certain physical characters.

[b]**Liquid fraction**: prior to analysis, samples were subjected to 2 % H_2O_2, and neutralize to pH 7 using H_3PO_4, then filtrated by 0.45 μm pore filters. Analytical techniques, mainly HPLC, were employed for the determination to determine the phenolic contents, glucose, xylose, arabinose, furfural, etc.

Chart 1. Fractionation of sugarcane bagasse.

Table 1
Effect of alkali and subcritical water treatments on the solubilization (%) of raw Taiwanese sugarcane bagasse.

Fraction	Alkali treatment, NaOH (M)				Subcritical water treatment			
	0	1	2	4	120 °C	140 °C	160 °C	180 °C
Soluble (liquid fraction)	19.97 ± 1.48[a]	31.08 ± 0.60	65.21 ± 0.77	69.55 ± 0.91	31.16 ± 0.98	50.99 ± 1.17	60.34 ± 0.52	66.86 ± 2.62
Residue (solid fraction)	80.03 ± 1.48	68.92 ± 0.60	34.21 ± 0.77	30.45 ± 0.91	68.84 ± 0.98	49.01 ± 1.17	39.66 ± 0.52	33.14 ± 2.62

[a] Each experimental variable was run three times, and the results were expressed via mean value and standard deviation. A two-tailed p value of less than 0.05 was considered to be statistically significant.

2.6.3.3. NMR analysis. The ^{1}H, and ^{13}C NMR spectra were recorded on Bruker AV-400 or AV-500 spectrometers, using TMS as the internal standard. The chemical shifts are given in δ (ppm).

2.7. Statistical analysis

Data obtained were expressed as the mean standard deviation (SD). The statistical significance of differences was assessed using analysis of variance. Non-linear regression analyses of experimental data were performed. A two-tailed p value of less than 0.05 was considered to be statistically significant.

3. Results and discussion

Chart 1 summarizes the fractionation of sugarcane bagasse upon alkali and subcritical water treatments and the analysis procedures of soluble and insoluble fractions resulted from both treatments. The yields of the insoluble extraction residue are close to the cellu-

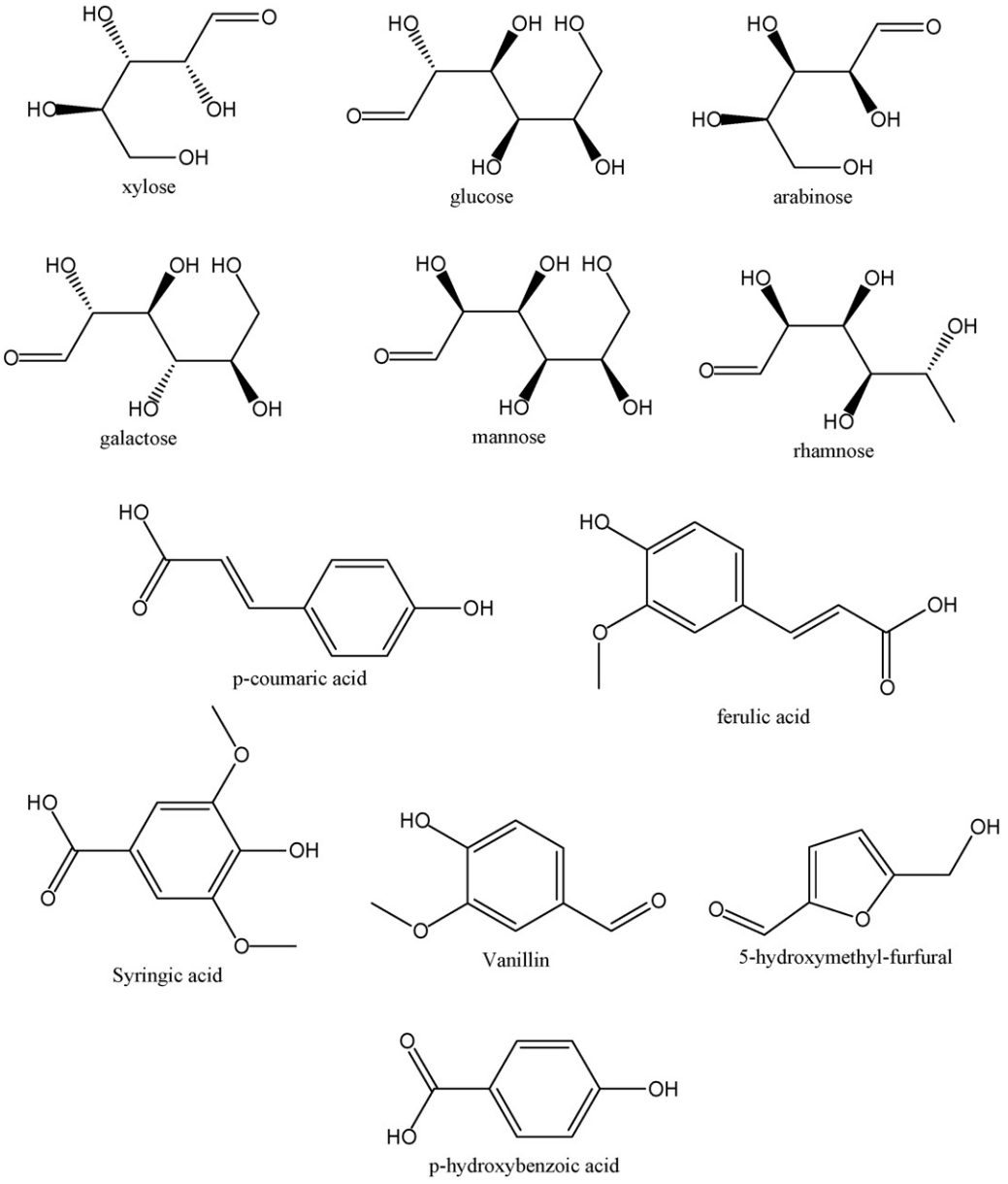


Chart 2. Chemical structures of isolated phenolates and neutral sugars.

Table 2
Liquid fraction analysis.

Compounds	Alkali treatment, NaOH (M)				Subcritical water treatment			
	0	1	2	4	120 °C	140 °C	160 °C	180 °C
Hemicelluloses contents (μg/mL)								
Xylose	0.374 ± 0.07[a]	0.393 ± 0.02	0.396 ± 0.04	0.42 ± 0.09	0.38 ± 0.06	0.4 ± 0.05	0.415 ± 0.07	0.437 ± 0.08
Glucose	0.312 ± 0.04	0.324 ± 0.06	0.337 ± 0.03	0.34 ± 0.06	0.31 ± 0.04	0.328 ± 0.09	0.382 ± 0.07	0.453 ± 0.13
Arabinose	ND[b]	0.125 ± 0.04	0.167 ± 0.09	0.191 ± 0.07	ND	ND	ND	0.184 ± 0.04
Galactose	0.064 ± 0.04	0.124 ± 0.07	0.134 ± 0.06	0.181 ± 0.04	0.048 ± 0.07	0.140 ± 0.07	0.167 ± 0.07	0.183 ± 0.03
Mannose	0.086 ± 0.08	0.082 ± 0.05	0.123 ± 0.02	0.147 ± 0.07	0.068 ± 0.06	0.094 ± 0.06	0.101 ± 0.07	0.125 ± 0.04
Rhamnose	ND	ND	0.022 ± 0.02	0.043 ± 0.04	ND	ND	ND	0.021 ± 0.01
Uronic acids	0.053 ± 0.05	0.057 ± 0.07	0.064 ± 0.01	0.084 ± 0.06	ND	0.034 ± 0.03	0.042 ± 0.02	0.063 ± 0.02
Lignins contents (μg/mL)								
p-Coumaric acid	32.13 ± 0.13	38.65 ± 0.87	143.43 ± 7.65	197.30 ± 5.9	33.43 ± 0.17	40.75 ± 0.73	133.36 ± 8.31	164.42 ± 2.63
Ferulic acid	6.34 ± 0.34	17.64 ± 0.47	21.64 ± 0.86	27.64 ± 0.64	6.14 ± 0.38	18.84 ± 0.50	21.64 ± 0.86	27.64 ± 0.35
Vanilline	0.734 ± 0.08	0.894 ± 0.10	0.94 ± 0.13	0.978 ± 0.31	0.814 ± 0.09	1.01 ± 0.32	0.974 ± 0.22	1.221 ± 0.14
Syringic acid	ND	0.003 ± 0.001	0.004 ± 0.001	0.007 ± 0.001	ND	ND	0.01 ± 0.008	0.016 ± 0.004
5-Hydroxymethyl-furfural	0.023 ± 0.04	0.036 ± 0.08	0.083 ± 0.03	0.143 ± 0.08	0.034 ± 0.01	0.042 ± 0.01	0.0471 ± 0.02	0.063 ± 0.03
p-Hydroxybenzoic acid	0.624 ± 0.04	0.837 ± 0.05	1.034 ± 0.08	1.867 ± 0.15	0.768 ± 0.05	0.774 ± 0.06	0.831 ± 0.07	0.934 ± 0.08
Klason lignin	0.734 ± 0.05	0.938 ± 0.08	1.238 ± 0.07	2.134 ± 0.17	0.984 ± 0.12	0.994 ± 0.14	1.031 ± 0.09	1.087 ± 0.07

[a] Each experimental variable was run three times, and the results were expressed via mean value and standard deviation. A two-tailed *p* value of less than 0.05 was considered to be statistically significant.
[b] ND: non-determined.

lose content of bagasse (Table 1), indicating a substantial removal of hemicelluloses and lignin during alkali and subcritical water extractions of sugarcane bagasse. Evidently, the extractability of hemicelluloses in sugarcane bagasse was increased by alkali and subcritical water treatments which are thought to be due to the chemical and thermal degradation of cell walls resulting in cell wall disruption. Such effects of alkaline delignification, acidic, and subcritical water treatments were shown (Sun & Cheng, 2002, 2004) to improve the isolation of lignin, hemicelluloses, and celluloses extractives from various plant materials (Aguilar, Ramírez, Garrote, & Vázquez, 2002; Aiello, Ferrer & Ledesma, 1996; Kondo, Ohshita, & Kyuma, 1992).

Alkaline delignification involves the addition of a base, such as sodium hydroxide, to a biomass to break down lignin and hemicellulose. The success of this method depends on the amount of lignin in the biomass. This method has had considerable success with corncobs and switch grass (Sun & Cheng, 2002, 2004). It is widely known that, phenolates and neutral sugars in plant exist in various forms, ranging from simple molecules to highly polymerized compounds. Most of these compounds have relatively low molecular weights and are soluble in water depending on their polarity and chemical structure, degree of hydroxylation, glycosylation or acylation. As well as in alkali treatments, it was noted that, the major reaction pathways for bagasse in subcritical water are hydrolysis, retro-aldol condensation, keto-enol tautomerism and dehydration (Sasaki et al., 2003, 2004). The hydrolysis reaction is important in the production of monomeric sugars as the cellulose and hemicellulose are hydrolyzed into glucose and xylose monomers, respectively. The main products of the subcritical reaction are hydrolysis products, aqueous degradation products of glucose and organic acids (Sasaki et al., 2003, 2004). The subcritical liquification of pure cellulose produces phenols, cyclopentanones and hydroquinones (Nelson et al., 1984).

It was observed that, the effect of NaOH concentration (0, 1, 2 and 4 M) on the extraction of phenolates (*p*-coumaric acid, ferulic acid, vanillin, syringic acid, 5-hydroxymethyl-furfural, and *p*-hydroxybenzoic acid) from soluble lignin extracted from sugarcane bagasse was investigated (Chart 2). As shown in Table 2, the amount of phenolic acids extracted increases with increasing NaOH concentration. (Table 2) also illustrates the effects of NaOH concentrations on the amount of phenolic acids released. It can be seen that the amount of phenolic acids released during alkaline hydrolysis of sugarcane bagasse is in the following order: *p*-coumaric acid > ferulic acid > vanillic acid > syringic acid. From the results discussed above we can concluded that some phenolic compounds are linked to cell wall components (polysaccharides, lignin). Owing to the nature of ester linkages, these compounds can be solubilized in alkaline conditions or are otherwise retained in the fiber matrix. The phenolic acids investigated are linked to lignin by ester and ether bonds and are mainly esterified to hemicellulose and lignin in sugarcane bagasse (Sun & Cheng, 2002, 2004; Xu et al., 2005). Thus alkaline treatment can be used to free them into the hydrolysates as an anion state. The alkaline hydrolysis of this material produced solution of hydroxy-cinnamic acids resulting from the breaking of α-ester bonds present in lignin–polysaccharide complexes (Fry, 1982). The major products obtained from alkaline and subcritical water treatments of sugarcane bagasse were found to be vanillin and syringaldehyde, suggesting that the bound lignin in the hemicellulosic fraction contained almost equal amounts of noncondensed guaiacyl and syringyl units. A noticeable amount of *p*-hydroxybenzoic acid and *p*-hydroxybenzaldehyde, and traces of vanillic acid, syringic acid, acetovanillone, acetosyringone, *p*-coumaric acid, and ferulic acid were also detected (Chart 2). Further evidence of the cell wall disruption by alkaline and subcritical water treatments was derived from the chemical composition of the isolated hemicellulosic fractions and their physico-chemical

Table 3
Solid fraction analysis.

wt%	Alkali treatment, NaOH (M)				Subcritical water treatment			
	0	1	2	4	120 °C	140 °C	160 °C	180 °C
Moisture content	4.35	4.42	4.31	4.34	4.25	4.67	4.37	4.12
Elemental analysis								
Carbon	45.9	45.2	45.23	45.63	45.9	46.04	45.7	46.07
Hydrogen	6.3	6.74	7.21	7.01	6.3	6.81	6.43	6.83
Sulfur	0.36	0.34	0.3.6	0.39	0.36	0.31	0.34	0.30
Nitrogen	0.34	0.32	0.39	0.33	0.34	0.30	0.32	0.30
Oxygen	47.1	47.4	46.81	46.64	47.10	46.54	47.21	46.40
Hydrogen/carbon	0.14	0.15	0.16	0.15	0.14	0.15	0.14	0.15

properties. Table 2 gives their content of phenolates, neutral sugars and uronic acids. Obviously, in addition to xylose and arabinose, the water-extractable fraction obtained from subcritical treated bagasse was rich in glucose (28.9%), galactose, and mannose (Chart 2). However, significant differences (p-value > 0.05) in the neutral sugar composition were observed for the alkali-soluble hemicelluloses in comparison with the subcritical water extracted ones, but there are no substantial differences between the sugar composition of the hemicellulosic fractions (p-value < 0.05) obtained by extractions with alkali. Xylose is the predominant sugar component, suggesting the presence of a higher proportion of xylan, particularly in the three alkali extracts. Arabinose is the second major sugar constituent. Perceptible amounts of glucose and uronic acids (mainly glucuronic acid or 4-*O*-methyl-D-glucuronic acid (MeGlcA)) and minor quantities of galactose, rhamnose, and mannose were also detected. These results implied that the seven alkali- and subcritical water extracted soluble hemicellulosic fractions were composed mainly of glucuronoarabinoxylans or l-arabino-(4-*O*-methyl-D-glucurono)-D-xylans. The higher arabinose content indicated a higher degree of branching of the xylan chains and the higher solubility of the polymers. This phenomenon provides evidence that in bagasse cell walls arabinose, probably as a side chain in hemicelluloses, was easily solubilized during the initial extraction process, whereas this side chain was partially cleaved or degraded in the sequential alkali or subcritical water treatments. Similar results were observed in previous study on wheat straw hemicelluloses (Sun, Lawther & Banks, 1996; Sun, Xiao & Lawther, 1997). A typical composition (moisture content and elements) analysis of bagasse is given in Table 3. From this table, it is clear that there are insignificant differences in moisture content as well as the percentages of carbon, hydrogen, oxygen, nitrogen, and hydrogen/carbon ratio, between samples treated by alkali and treated by subcritical water.

Representative thermograms of insoluble solid hemicellulosic and cellulosic fractions, isolated with 0, 1, 2 and 4 M NaOH at 120 °C as well as isolated with subcritical water at 120, 140, 160, and 180 °C are shown in Figs. 1 and 2. As observed, the hemicellulosic solid fractions isolated from the alkaline hydrolysis of sugarcane bagasse are stable up to 250 °C, while the one isolated from the subcritical water treatment are stable up to 320 °C. Therefore, beyond 250

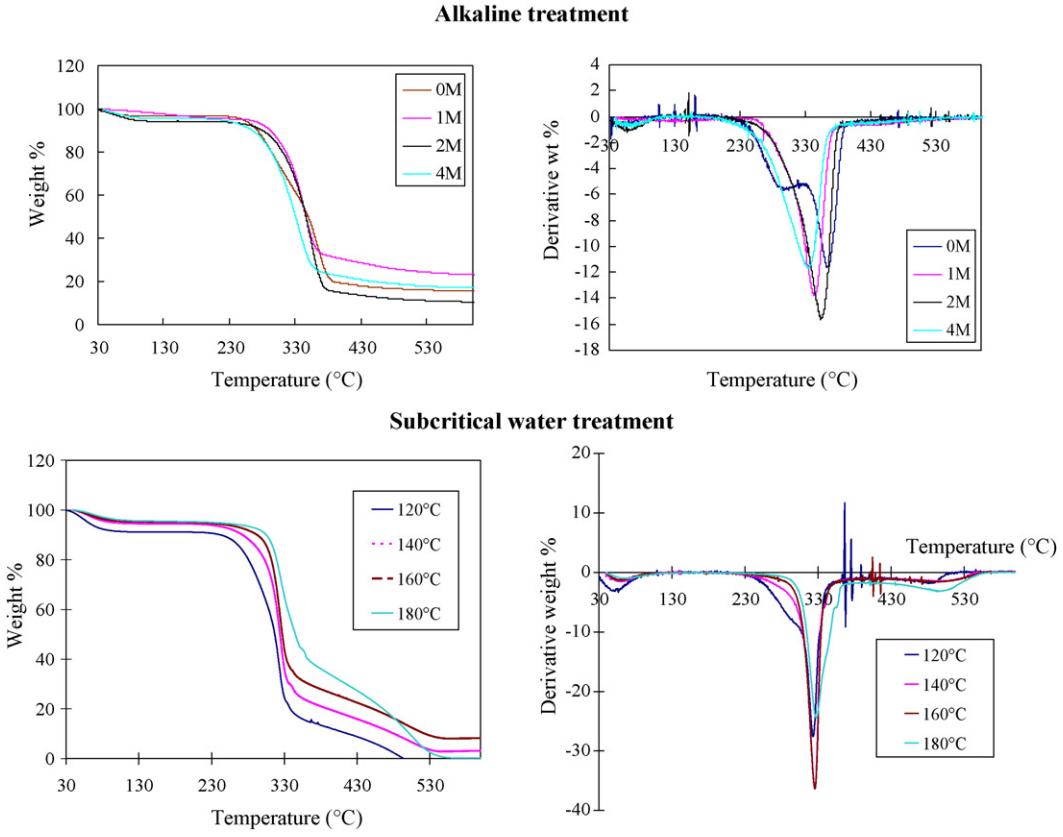


Fig. 1. TGA/DTG thermograms of solid fractions isolated by alkali and subcritical water treatments of sugarcane bagasse.

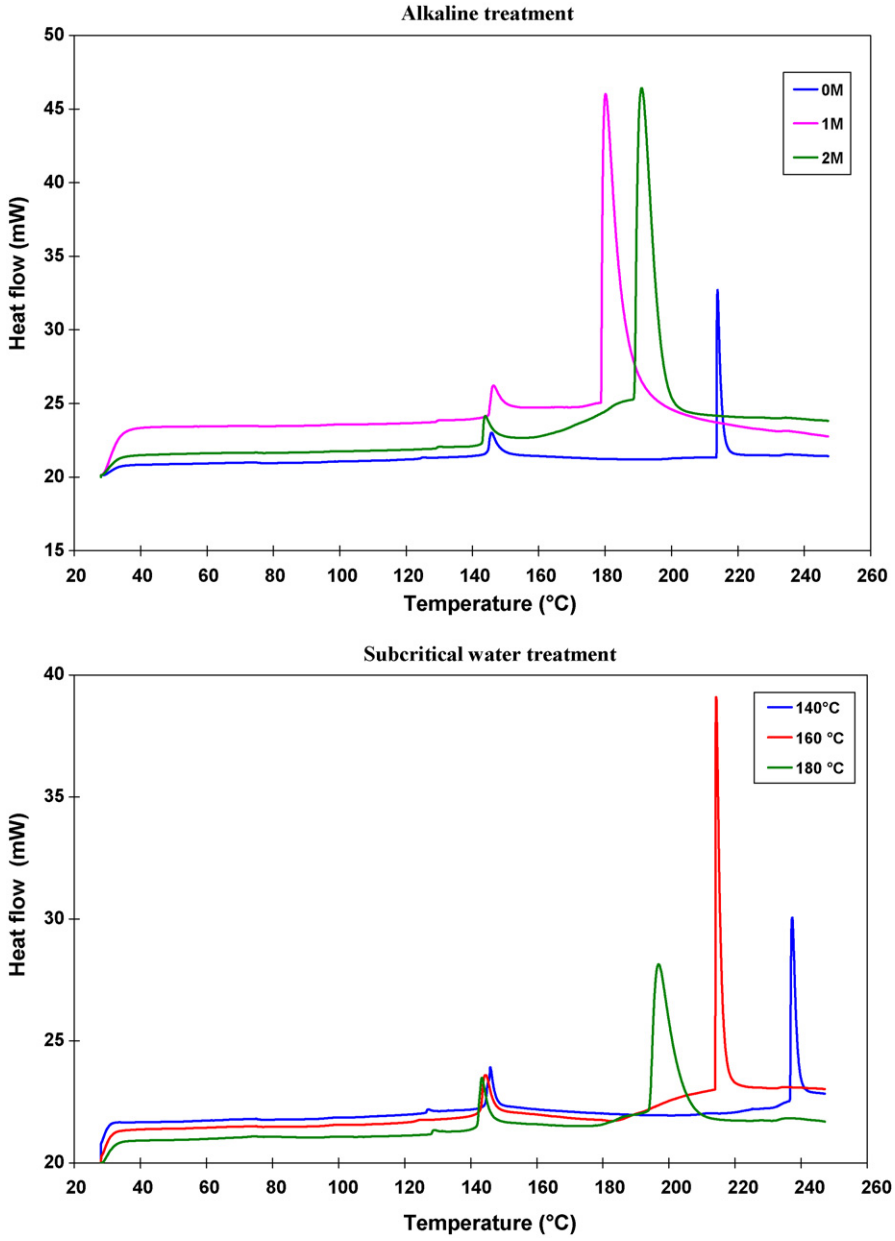


Fig. 2. DSC thermograms of solid fractions isolated by alkali and subcritical water treatments of sugarcane bagasse.

and 320 °C temperatures, thermal degradation takes place in alkaline and subcritical water treatments, respectively. At 50.0% weight loss, the decomposition temperatures of the two samples occurred at 250 and 320 °C, respectively. These data imply that the insoluble hemicellulosic and cellulosic fraction, isolated by subcritical water treatment of sugarcane bagasse, appeared to be more stable than the corresponding fraction extracted with NaOH. At 10% weight loss, the decomposition temperature of the insoluble celluloses and hemicelluloses solid fractions isolated from the alkaline hydrolysis of sugarcane bagasse occurred around 250 °C. While, the 10% weight loss decomposition temperature of the insoluble celluloses and hemicelluloses solid fractions isolated by subcritical water treatment of sugarcane bagasse at 140–200 °C occurred around 300 °C. The initial weight loss was probably due to the generation of noncombustible gases such as CO, CO_2, formic acid, and acetic acid, whereas the significant (maximum) weight loss was presumably due to the onset of pyrolysis and generation of combustible gases (Sun & Tomkinson, 2002; Sun, Tomkinson & Ye, 2003). The maximum rate of weight loss was observed between 280 and 400 °C for the insoluble celluloses and hemicelluloses solid fractions isolated from the alkaline hydrolysis of sugarcane bagasse and between 330 and 540 °C for the insoluble celluloses and hemicelluloses solid fractions isolated by subcritical water treatment of sugarcane bagasse at 140–200 °C. The DSC thermograms of the cellulosic and hemicellulosic solid fractions (Fig. 2) give one similar exothermic peak around 142 °C for the ones isolated from the alkaline hydrolysis, and subcritical treatments of sugarcane bagasse, at different conditions. Another sharp exothermic curves was showed around 180, 195, 218 °C for isolates of alkaline hydrolysis at 1, 0, 2 M NaOH, respectively, and around 195, 218, 240 °C for isolates of sub critical water hydrolysis at 180, 160, 140 °C conditions, respectively. This is due to the exothermic reactions, the disintegration of intra-molecular interaction and the decomposition of the polymer. These slight differences in DSC curves were probably due to the variations in organization of the cellulosic and hemicellulosic molecules in different fractions. In short, the thermal stability of

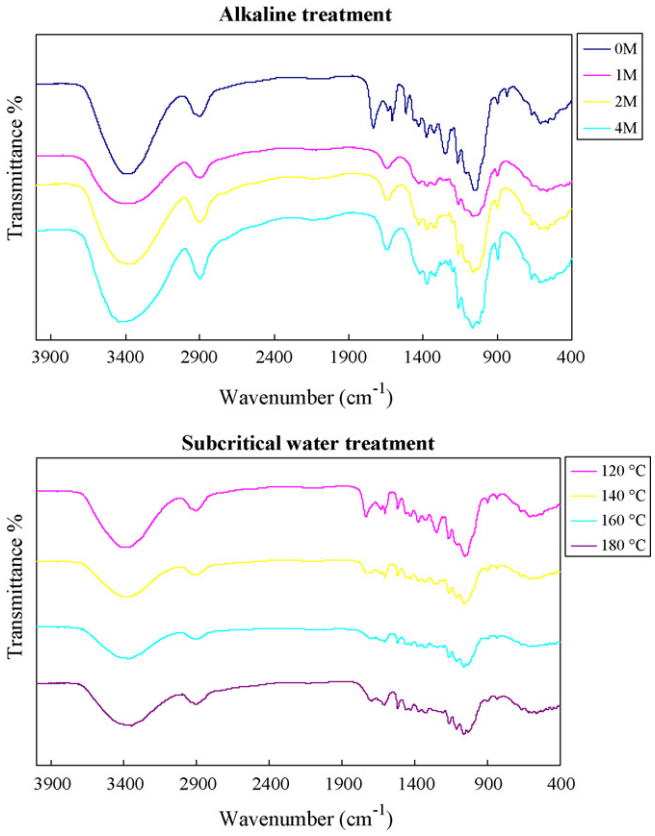


Fig. 3. FT-IR spectrums of solid fractions isolated by alkali and subcritical water treated sugarcane bagasse.

solid celluolses and hemicelluloses increased with an increase in their molecular weight.

Fig. 3 illustrates the FT-IR spectra of bagasse cellulose and hemicellulosic solid fractions isolated from alkaline hydrolysis and subcritical treatments of sugarcane bagasse. As can be seen from the diagrams, all spectra show typical signal patterns with different strengths of absorption bands in the region 700–1700 cm^{-1} which confirms that the "core" of the celluloses and hemicelluloses structures did not change significantly during alkali and subcritical water treatment processes. The FT-IR spectral data display strong, broad absorption band around 3400 cm^{-1} which arises from the stretching of –OH groups, the weak absorption band at 2920 cm^{-1} arises from C–H stretching, absorption band at 1680 cm^{-1} is indicative of the bending mode of the absorbed water, intensive and sharp band at 1050 cm^{-1} is attributed to the C–O–C stretching that is typical of xylans. Each spectrum presents a peak at 1430 cm^{-1}, which is due to the CH_2 bending and that in 1380 cm^{-1} due to the O–H bending. The absorbance at 1330 cm^{-1} arises from the C–C and C–O skeletal vibrations. The peak at, 12,560 cm^{-1} relates to the OH in-plane bending (Nieduszynski & Marchessault, 1972). In general, the absorption spectral bands at 3424, 2914, 1423, 1386, 1245, 1166, 1118, 1075, 1039, 985, and 894 cm^{-1} are associated with cellulose and hemicelluloses core structures. Obviously, bands between 1170 and 1000 cm^{-1} are typical of arabinoxylans, and the presence of the arabinosyl side chains is detected by the low intensity shoulder at 1170 cm^{-1}, corresponding to the C–O–C vibrations in hemicelluloses (Sun & Tomkinson, 2002; Sun et al., 2004; Sun, Fang, Tomkinson, & Hill, 1999). Also, β-glycosidic linkages between glucose in cellulose were detected at 950–700 cm^{-1} by a small sharp band and a shoulder at 890 cm^{-1} (Gupta, Madan & Bansal, 1987). This demonstrates the presence of predominant β-glycosidic linkages between sugar units in the cellulosic and hemicellulosic fractions extracted with alkali or subcritical treatments. The occurrence of a very weak band at 1520 cm^{-1} is due to the associated lignin in the hemicellulosic and cellulosic fractions indicating the presence of only a small amount of bound lignin in the hemicellulosic and cellulosic fraction, isolated either by alkali or subcritical water treatments.

The cellulosic and hemicellulosic fractions isolated by alkali and subcritical water treatments of sugarcane bagasse showed very similar spectra features at all conditions, indicating a similar structure of celluloses and hemicelluloses residues. The weak signals at chemical shifts of 2.0 and 1.3–1.1 ppm are indicative of the presence of methyl protons of small amounts of acetyl group and 4-*O*-methyl-D-glucuronic acid, respectively. The chemical shifts of 3.2–5.2 ppm are caused by the protons of arabinose and xylose residue of celluloses and hemicelluloses except for the strong signal at a chemical shift of 4.8 ppm (Bengtsson & Aman, 1990) which is indicative of the residual solvent (HDO). Signals at chemical shifts of 4.3/4.4 are due to the anomeric protons of β-D-xylose monosubstituted residues (Kawagishi et al., 1990). Anomeric protons of terminal α-D-arabinofuranosyl residues occur at a chemical shifts at 5.2 ppm, indicating a significant amount of substitution at C-3 and C-2 (di-substituted) of the xylose backbone (Sun et al., 1999). Resonance signals originating from phenolic compounds (5.3 ppm) are undoubtedly due to the presence of small amounts of associated lignin in the celluloses and hemicelluloses.

To achieve and confirm a complete elucidation of the structures in the cellulosic and hemicellulosic solid fractions isolated by alkali and subcritical water treatments of sugarcane bagasse, a qualitative ^{13}C NMR spectroscopy was carried out and analyzed. The ^{13}C NMR spectra of the isolated cellulosic and hemicellulosic solid fractions show five main signals at chemical shifts of (104.6, 77.3, 76.7, 75.9, and 64.2 ppm in case of alkali treatment; 108.6, 82.4, 79,8, 78.6, 77.3 ppm in case of subcritical water treatment), corresponding to main (1 → 4)-linked β-D-xylose residues. Signals at (102.3, 84.6, 81.4, 63.1, and 57.3 ppm in case of alkali treatment; 103.2, 84.2, 77.3, 73.0, and 66.2 ppm in case of subcritical water treatment) originate from α-l-arabinofuranosyl residues linked to β-D-xylans. Two signals at chemical shifts of 72.4 and 74.5 ppm indicate a galactose residue in xylan. Weak signals at a chemical shift of 59.8 ppm originated from the *O*-methoxyl group of the glucuronic acid residue in xylan. The signal at a chemical shift of 16.8 ppm indicates a small amount of associated lignin. This data reveal that both alkaline and subcritical water sugarcane bagasse treatment under the conditions used in this study did not affect the overall macromolecular structure of the resulted solid celluloses and hemicelluloses fractions.

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