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Article

Hot Compressed Water Extraction of Lignin by Using a Flow-Through Reactor

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Abstract. Japanese rice straw, an agricultural by-product, was utilized for the extraction of lignin by hot compressed water at temperatures of 443–503 K and a pressure of 4.0 MPa using a flow-through system, a simple and environmentally friendly extraction method requiring no chemicals other than water. Under these conditions, thermal softening of the Japanese rice straw occurred, allowing the removal of lignin via depolymerization reactions. Lignin as an extraction product was analyzed using ultraviolet-visible (UV–vis) spectrophotometry. Lignin recovery approached 85 % when the extraction was performed at 443 and 473 K with a flow rate of 4.67 ml min⁻¹. At a constant residence time, recovery amounts increased with increasing flow rate at each temperature. The results suggested that this process may result in an advanced plant biomass components extraction technology.

Keywords: Biomass, extraction, lignin, rice straw, subcritical.

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1. Introduction

Biomass is matter derived directly or indirectly from plants which is utilized in substantial amounts as energy or material. The main constituents of wood biomass are cellulose (40~45 wt%), hemicellulose (25~35 wt%), lignin (15~30 wt%) and other compounds (up to 10 wt%) [1]. Cellulose and hemicellulose can be enzymatically hydrolyzed to monomeric sugars after pre-treatment aiming at hydrolytic cleavage of its partially crystalline structure [2]. Recently, supercritical water treatment has been found possible without the addition of chemicals or oxygen, making it a potential method for pre-treatment of large quantities of biomass. This treatment causes specific hydrolysis of cellulose and hemicellulose and physically destructs tissues [2–5]. Lignin is another primary component of plant biomass and contains many oxygen functional groups. Phenolic chemicals can also be obtained from lignin by chemical degradation processes [5–10]. Lignin or biomass can be converted to gases by a gasification process; the major products from lignin gasification include H₂, CO, CO₂ and CH₄ [11–15].

The plant biomass thermal decomposition process requires that biomass be separated into its components, conventionally under subcritical conditions. This process is crucial for the complete and most efficient conversion of the lignin, hemicellulose, and cellulose to their highest-value products. For example, the extraction of lignin from wood is needed in pulp and paper production as well as for ethanol production. Hydrolysis occurs by the addition of acids, bases or organic solvents, a process necessitating neutralization in order to reduce corrosion of the reactor [16–18]; recycling of these chemicals is also necessary so as to reduce negative impacts on the environment as well as on subsequent process. To eliminate such costs, non-catalytic hydrothermal processes have been studied [19–22]. At elevated temperatures and pressures, liquid water can be used to fractionate biomass into its constituents [23, 24]. The ionic product of water changes in tandem with temperature [25]. Therefore, hot compressed water extraction is considered suitable for the hydrolysis process because it gives the highest ionic product. Mok and Antal 1992 [26] succeeded in solubilizing most hemicellulose together with lignin in hot compressed water using a tubular percolating reactor; this was performed for the production of xylitol and furfural from hemicellulose or as a pretreatment for enzymatic hydrolysis of cellulose. Rogalinski *et al.* 2008 [27] conducted liquid hot water pretreatment of rye straw and rye silage in both a batch and a continuous flow reactor; they reported that liquid hot water provides an excellent reaction medium for the pretreatment of biomass. High degrees of biomass solubilization are possible. Chandra *et al.* 2012 [28] conducted methane fermentation study on pretreated substrates of rice straw biomass revealed that NaOH and hydrothermal pretreatments results into highly significant amount of increase in biogas and methane production yields.

This work presents hot compressed water extraction using a continuous process to isolate lignin from plant biomass. Japanese rice straw, used as a starting material, is an agricultural by-product usually left in the field after harvest and subsequently burnt or used as animal feed. Although the Japanese rice straw also has high potential for ethanol production via fermentation process, its cellulose needs proper pretreatment for complete conversion, and lignin cannot be converted by fermentation [29, 30]. Therefore, this process was anticipated to allow for the effective removal of lignin. In addition, Converti *et al.* 2010 [31] suggested that vanillin could be produced from lignin-rich wastes. They explained that vanillin recovered from the sulfite spent liquor came from guaiacyl units of lignin solubilized by alkaline oxidation during softwoods pulping.

2. Experimental Section

2.1. Materials

Japanese rice straw was obtained from a Hokkaido, Japan facility jointly developed with the New Energy and Industrial Technology Development Organization (NEDO). It was shredded by a laboratory mill to a particle size of < 2 mm and passed through 16-mesh sieves. After this process, the sample was refrigerated at < 278 K. The initial composition of the Japanese rice straw was cellulose 36.4%, hemicellulose 25.8%, lignin 12.6%, and other 25.2%. Distilled water obtained from a water distillation apparatus (Shibata Co., model PW-16, Japan) was used as a solvent. Lignin in powder form was obtained from Tokyo Kasei Kogyo Co. Ltd. (Japan). Xylan from beechwood and cellulose was purchased from Sigma-Aldrich Japan K. K., Tokyo, Japan. The analytical reagents used were 97 % H₂SO₄ and 99.7% methanol (Wako Pure Chemicals Industries Ltd., Japan, used as received).

2.2. Experimental Setup and Procedure

A schematic diagram of the apparatus is shown in Fig. 1. This apparatus consists of a high-pressure pump, heater, reactor, thermocontrollers and back-pressure regulators (BPR). The pre-heater was fabricated from 1/8 inch stainless-steel tubing (SUS316) with a volume of 50 mL and was heated using a mantel heater at temperatures of 443–503 K. The 1/16 inch stainless-steel tube was used to introduce the hot water from the pre-heater to the reactor that was placed in an oven. The reactor volume was 30 mL and was also made of stainless steel (SUS316). After the reactor inclusive of 5.0 g of the Japanese rice straw was installed in the system, distilled water at room temperature was pumped through the reactor inclusive pre-heater for a few minutes to purge air, completely wet the Japanese rice straw in the reactor, and pressurize the system to the set pressure of 4.0 MPa by controlling the back-pressure regulator (BPR) monitored by pressure gauge (P). When the system reached the desired pressure and a steady state was achieved, an electric heater was applied to heat the water. In this study, the reactor temperature was kept at 443–503 K. Both the temperature of the pre-heater, reactor and the electric heater were measured using K-type thermocouples. The time required to heat up the reactor from room temperature to the desired temperature was 5–8 min, after which the reactor temperature equaled the electric heater temperature. After the temperature at the reactor area reached a preset temperature, the pump was used to feed the water at 1.42, 2.92, and 4.67 ml min⁻¹. During experiment, temperatures of the reactor water inlet (T_1) and outlet (T_2) were monitored. A profile of temperature is plotted in Fig. 2. Next, the outlet water was passed through the double-tube-type heat exchanger to quench the reaction. The time of each experiment was 60 min; therefore, the volumes of the collected extract were 85, 175, and 280 mL. Once the temperature in the reactor decreased to about 318 K, cold water (20 mL) was pumped through the system to purge liquid remaining in the reactor. For analysis, the extracts were collected and diluted to exact volumes of 100, 200, and 300 mL. These products were identified and quantified directly using GC–MS (gas chromatography mass spectrometry) and UV–vis spectrophotometry.

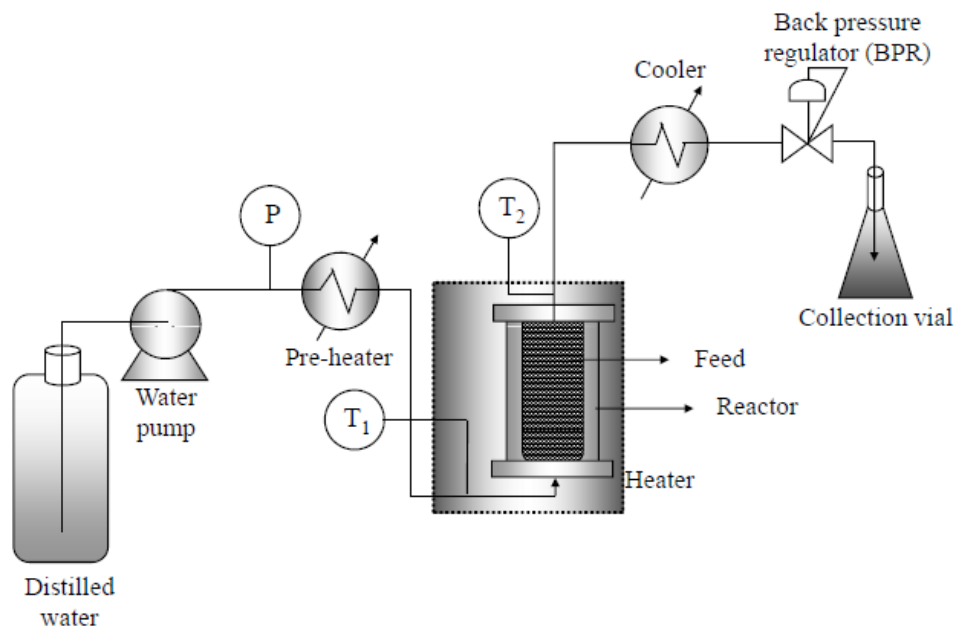


Fig. 1. Schematic diagram of hot compressed water extraction.

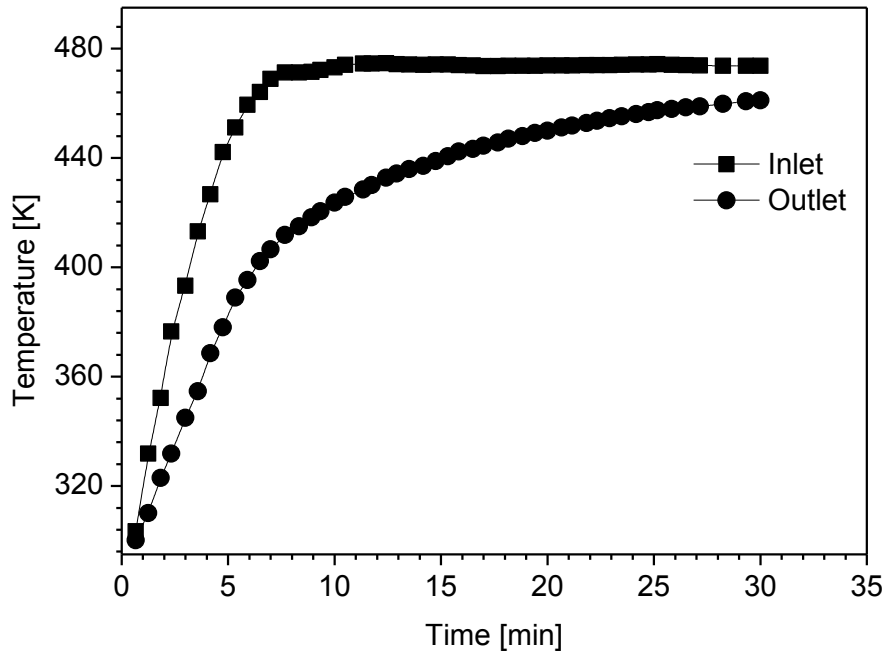


Fig. 2. Typical temperature profile for hot compressed water extraction at pressure of 4 MPa and 2.92 ml min⁻¹ water flowrate.

2.3. Analytical Methods

Analysis of lignin content in an extracts was conducted using UV-vis spectrophotometry V-550 (Jasco Corporation, Japan). UV-vis spectra were recorded with a PC-driven scanning spectrophotometer, operating in the fast scan mode, allowing spectra of between 190 and 800 nm with 10 nm min⁻¹ of bands. The liquid products were analyzed in a quartz cuvette with a 1 cm path length. The acid soluble lignin content was determined on the hydrolysate by measuring UV-vis absorption at 205 nm in 1 cm quartz cells. It was evaluated according to Beer's law:

$$A = \varepsilon d C \quad (1)$$

where A = absorbance; ε = absorptivity (L g⁻¹ cm⁻¹); d = path length (1 cm), and C = concentration of lignin (g L⁻¹). Based on the calculation, the value of extinction coefficient (ε) was 110 L g⁻¹ cm⁻¹ as adopted from Dence data [32, 33]. Hence,

$$C = \frac{A}{110} D \quad (2)$$

where $D = V_D / V_0$; V_D = volume of diluted extract, and V_0 = volume of original extract taken. The acid soluble lignin content in the extract sample was calculated as follows:

$$\text{Lignin [wt \%]} = \frac{C \times V \times 100}{1000 \times W} \quad (3)$$

where V = total volume of the extract [L] and W = dry weight of sample [g].

The normal wavelength of 280 nm was not used because of the potential interference from furfural and hydroxymethylfurfural; these aldehydes give a sharp absorption maximum at about 280 nm, but relatively low absorbance at shorter wavelengths. Therefore, the wavelength in the region of 200–210 nm provides a reasonable measure of soluble lignin in wood [34]. In addition, the liquid product was also identified by GC-MS after extraction with methanol using a GC-MS Hewlett Packard model 6890 series GC system and 5973 mass selective detector with a DB-5 MS capillary column (J&W Scientific, length 30 m, i.d. 0.25 mm, film 0.25 μ m). The GC-MS carrier gas was He at a flow rate of 2 mL min⁻¹. The column operating conditions were as follows: injector temperature 523 K, 1 μ L of a solution in methanol injected with a split ratio of 20:1. The chromatographic exit to mass spectrometer interface temperature was 573 K. The GC oven temperature was held at 313 K for 0 min then programmed to increase at 5 K min⁻¹ to 573 K. The mass spectrometer was scanned from m/z 50 to 500 at 0.5 s decade⁻¹ of mass with an interscan interval of 0.5 s, with the results stored as a total ion chromatogram. Electron ionization and positive ion mode were used. The NIST (National Institute of Standards and Technology) library of mass spectroscopy was used to identify the compounds.

The solid product in water soluble extracted at each operating temperature were analyzed by a Spectrum One Fourier Transform Infrared Spectroscopy (FT-IR) spectrophotometer (Perkin-Elmer, Ltd., Bucks, England). Prior to this, vacuum evaporation at 333 K was used to remove water content; the products were then dried in a desiccator for 1 day at room temperature. This analysis was performed to determine the structure of the solid product after the hot compressed water extraction treatment. The samples were placed directly in the diffuse reflectance attachment sample holder between two KBr salt plates in a microcompression cell. Preflattening of the sample in a diamond cell was necessary prior to mounting. The spectra were measured in ATR (attenuated total reflectance) mode (golden single reflection ATR system, P/N 10500 series, Specac) at 4 cm⁻¹ resolution. The scanning wavenumber ranged from 650 to 4000 cm⁻¹. In addition, the ultimate analysis of solid residues remaining in the reactor was conducted using a CHN analyzer (Yanaco, CORDER MT-6). This analysis was carried out to determine the amount, typically a weight percent of an element in a compound. The most common type of elemental analysis is for carbon, hydrogen, and nitrogen (CHN analysis). This type of analysis is especially useful for organic compounds; i.e., those compounds containing carbon-carbon bonds.

3. Results and Discussion

The determination of lignin, though apparently a simple matter, is one of the least satisfactory of the analyses commonly performed on plants biomass. The methods generally used involve the solution and hydrolysis of all other plant constituents and the simple assumption that the residue after such treatment is lignin. To improve on this method, this study utilized UV-vis spectrophotometry as an analysis method to capitalize on the fact that lignin absorbs UV-visible regions more strongly than cellulose or hemicellulose. UV-vis spectra of acid soluble lignin from Japanese rice straw after hot compressed water treatment at 2.79 ml min⁻¹ are shown in Fig. 3. Absorption measurements were taken at wavelengths from 200 to 800 nm. Lignin recovery was defined as the lignin concentration obtained as calculated from the division of the absorbance derived from the absorptivity as per equation (1) with the initial concentration of lignin fed into the reactor. Essentially, this method relies on determining UV absorption of the final diluted acid solution of the Klason lignin procedure. According to Hatfield *et al.* 2005 [32] indicated that a considerable portion of the total lignin is soluble after the acid treatment and that the amount of insoluble residue is relatively insignificant in the measure of lignin content; therefore, the total lignin content was determined as insoluble Klason lignin plus the ultraviolet-estimated acid-soluble lignin. This figure shows two predominant peaks in this wavelength region, the first at 200–210 nm and the second at 270–290 nm; UV absorption between 270 and 290 nm is an indicator of aldehyde groups such as furfural and hydroxymethylfurfural, which form from carbohydrates during the acid hydrolysis. Consequently, as explained before, the UV absorption of the acid soluble lignin was measured at wavelength 200–210 nm. Wegener *et al.* 1983 [35] reported that the UV absorption maximum of acid soluble lignin samples near 200 nm can be recorded exactly and evaluated quantitatively. At around 200 nm, the UV transmittance properties was high without interference from the degradation products of polysaccharides. Maekawa *et al.* 1989 [36] concluded that the UV absorption between 200–210 nm is the preferred wavelength for measuring the absorbance of acid soluble lignin from hardwoods, softwoods, and bamboo. Jahan & Mun 2007 [37] also explained that due to the lignin molecule contains no large portion of unsaturated aliphatic units in addition to its aromatic structure, it is concluded that there are the two characteristic bands in the lignin spectrum at 200–230 and 260–280 nm. However, due to common acidic degradation products of carbohydrates which have absorbance maximums at around 280 nm, the measurement wavelength at around 205 nm is the better choice. They also explained that the absorbance of UV spectra at around 205 nm was directly proportional to the purity level of lignin.

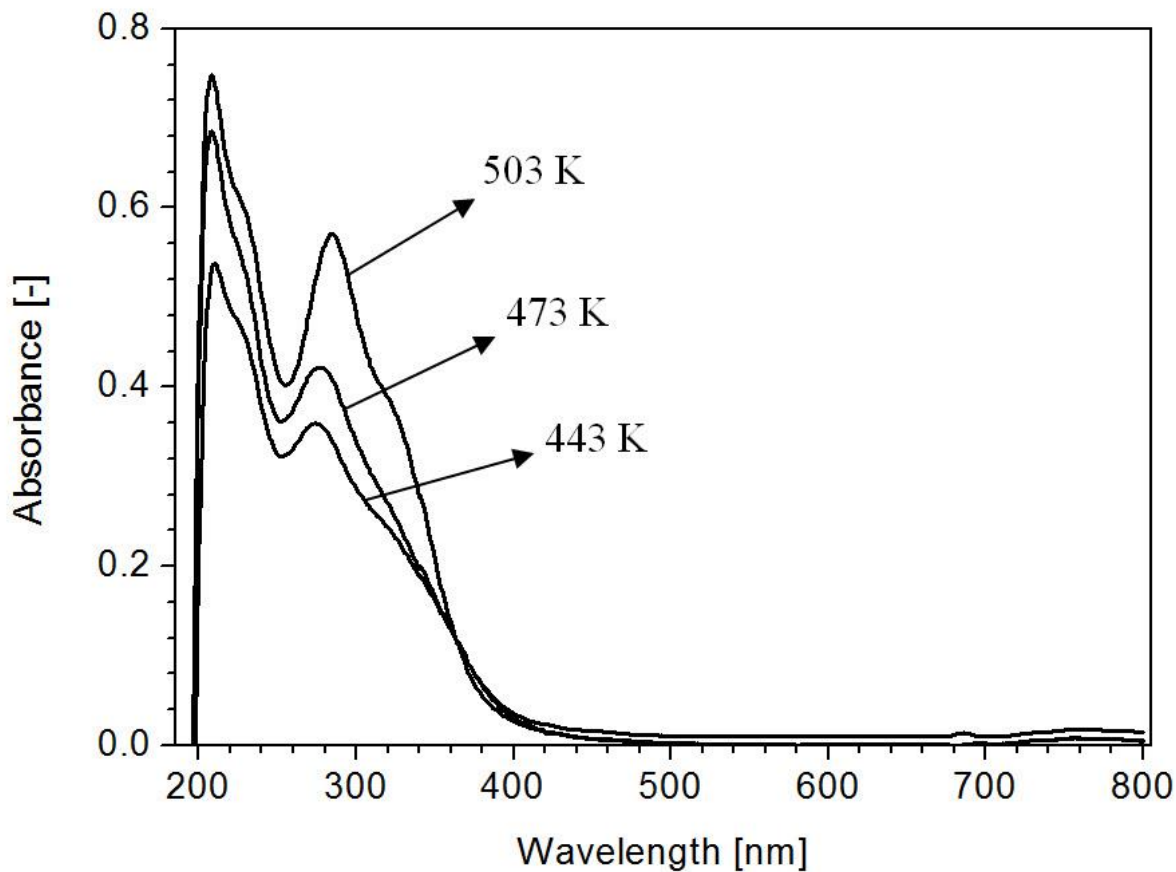


Fig. 3. UV-vis spectra of water soluble an extraction products.

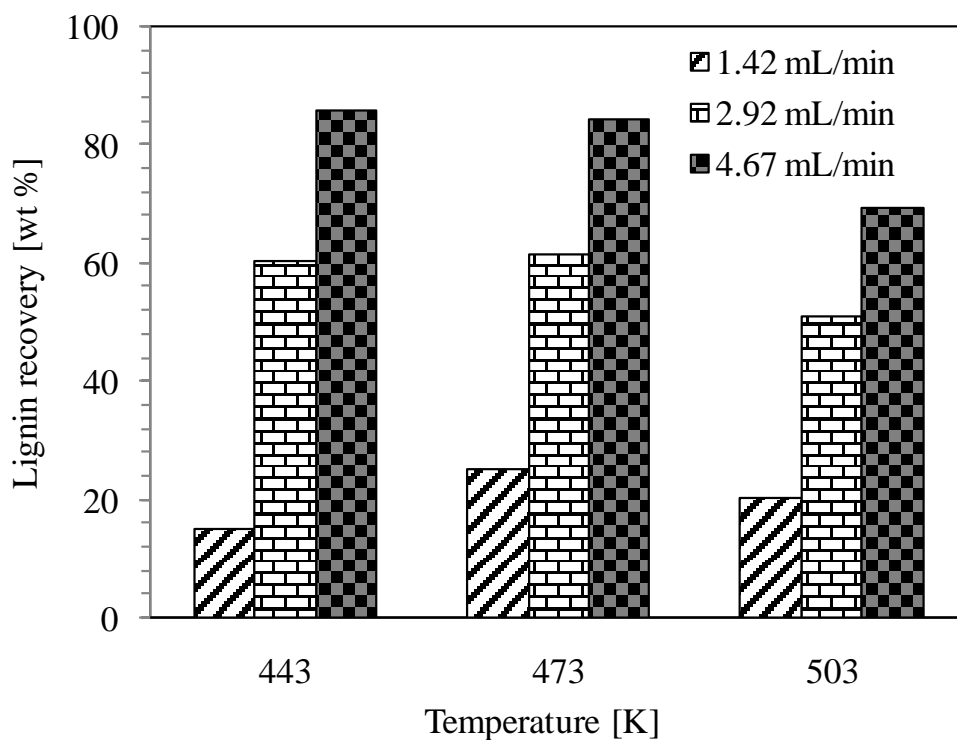


Fig. 4. Amount of lignin removal by hot compressed water from Japanese rice straw.

That covalent linkages between lignin and carbohydrates exist in wood is well-known. In the fractionation of plant biomass by hot compressed water, their separation is very important for complete and efficient utilization of substances which compose cell walls of plant biomass. The presence of water as the reactant leads to hydrolysis reaction and cleavage of bonds between hetero-atoms and carbon atoms. Non-requirement of additional chemicals and lower fabrication costs make this system attractive. Minowa *et al.* 1998 [38] reported that the decomposition of biomass components start at around 473 K or higher. Ko *et al.* 2014 [39] also investigated the fate of the lignin content in a hardwood biomass after treatment by liquid hot water at temperatures of 453–493 K. They reported that the percentage of lignin increased from 29.3 to 40.3% with increasing treatment temperature. They also explained that the higher treatment temperature (493 K) led to an increase in lignin recovery yield, which might be caused by the condensation reactions of lignin with other degradation products. Therefore, isolation of lignin is also possible at these range temperatures using hot compressed water. The amount of lignin from Japanese rice straw extracted by hot compressed water at a pressure of 4 MPa is shown in Fig. 4. Lignin recovery approached 85% when the extraction was performed at 443 and 473 K with a flow rate of 4.67 ml min⁻¹. The lignin extraction rate increased with increased flow rate at each temperature; the increased flow rate allowed the dissolved lignin to be swept from the reactor before it could react and precipitate, resulting in substantially higher lignin removal [40, 41]. Under the same conditions, the recovery of lignin decreased at 503 K, possibly explicable by cleavage of ether and C–C linkages as functional groups in the trans-*p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol existing in lignin structure units [29, 30, 42]. Demirbas *et al.* 2000 [36] reported that lignin is broken down by extensive cleavage of β -aryl ether linkages during steaming of wood at temperatures under 488 K. They explained that normal C–C bond energy is about 380 kJ mol⁻¹ and thermal excitation of the molecules becomes sufficient to break these bonds. These bonds, particularly the O–O bonds, are exceptionally weak and therefore can break at lower temperatures. Toor *et al.* 2011 [30] also explained that during hydrothermal degradation various phenols and methoxy phenols are formed by hydrolysis of ether-bonds (O–O bonds).

Table 1. Comparisons of different lignin extraction methods .

Material	Process	Condition	Yield [wt%]	Literature
Mixed hardwood	Liquid hot water	453–493 K; 10–15 min	81.8–97.4	Ko <i>et al.</i> 2014 [39]
Air-dried bio-ethanol production residue	Solvothermal	323–483 K; 15–120 min	41.60–74.14	Guo <i>et al.</i> 2013 [43]
Flax shives	High temperature and high pressure	493 K; 5.2 MPa, 130 min	26.0	Buranov <i>et al.</i> 2010 [44]
Bamboo (<i>Neosinocalamus affinis</i>)	Ultrasonic cell crusher	293 K; 0–50 min	13.4–16.4	Li <i>et al.</i> 2010 [45]
Maple wood flour	Ionic liquid solvent	263 K; 0.5–70 h	16–86	Lee <i>et al.</i> 2009 [46]
Wheat straw (Variety Riband)	Ultrasonic irradiation	308 K; 0–35 min	43.3–46.2	Sun <i>et al.</i> 2002 [47]
Wheat straw (Variety Riband)	Ultrasonic irradiation	333 K; 0–35 min	67.4–78.5	Sun <i>et al.</i> 2002 [48]

As introduced in introduction section that wood biomass consists of cellulose (40~45 wt%), hemicellulose (25~35 wt%) and lignin (15~30 wt%) as main components. This causes that wood biomass in general become attractive feedstock because of high polysaccharide content; however, it is not easy to use this biomass resources for ethanol and other chemicals production. Fractionation is often considered a pre-treatment process, prior to produce its biomass components. As shown in Table 1, there are several methods for performing the biomass fractionation especially to isolate lignin. However, the extraction methods are not easy to apply into large scale production due to the high cost or complex process. Sun *et al.* 2002 [48] conducted ultrasound-assisted extraction of wheat straw lignin in alkaline organosolv medium. They reported that applying sonication for 5–35 min resulted in an increasing yield of lignin by 61.0–78.5 of the original lignin in wheat straw. They said that the current results revealed that ultrasonic irradiation had a

significant effect on the delignification of wheat straw. Lee *et al.* 2009 [46] performed wood flour fractionation by using ionic liquids as pretreatment solvents to extract lignin from wood flour. They reported that ionic liquid such as [Emim][CH₃COO] did not dissolve the wood flour; conversely, facile extraction of the lignin was achieved. However, ionic liquid pretreatment also would result in a substantial decrease in the crystallinity of the cellulose. In other words, they demonstrated that the wood flour underwent delignification with substantially smaller losses of cellulose and xylan upon pretreatment in [Emim][CH₃COO]. Guo *et al.* 2013 [43] developed an adequate method to separate lignin from air-dried bio-ethanol production residue by using solvothermal methods. Benzyl alcohol, dioxane and ethanol were used as lignin solvent extraction at temperature of 323–443 K with 5–120 min reaction time. They concluded that benzyl alcohol and dioxane extraction could reach higher lignin yield of 71.55 and 74.14% when the experiments were conducted at 443 K and 323 K with reaction time 15 and 60 min reaction time, respectively. They explained that the chemical components and structure of lignin extracted by benzyl alcohol or dioxane was similar to that of lignin obtained with alkali-solution and acid-isolation method. Recently, Ko *et al.* 2014 [39] conducted experiments to remove lignin and its derived mixed hardwoods by liquid hot water at different severities. They reported that the isolated lignin from mixed hardwoods was 97.4% at 493 K with 15 min reaction time. In comparison with other methods (see Table 1), our work, hot compressed water extraction is simpler and could extract lignin around 85 % from Japanese rice straw. Here, the Japanese rice straw was directly fed in the extraction reactor as the starting material without any treatments. Under these conditions, water-soluble compounds (lignin) could be extracted from Japanese rice straw via autohydrolysis [15–17]. It could be said that this process is simple and versatile technique because of its capability and feasibility in the separation of large quantities of biomass.

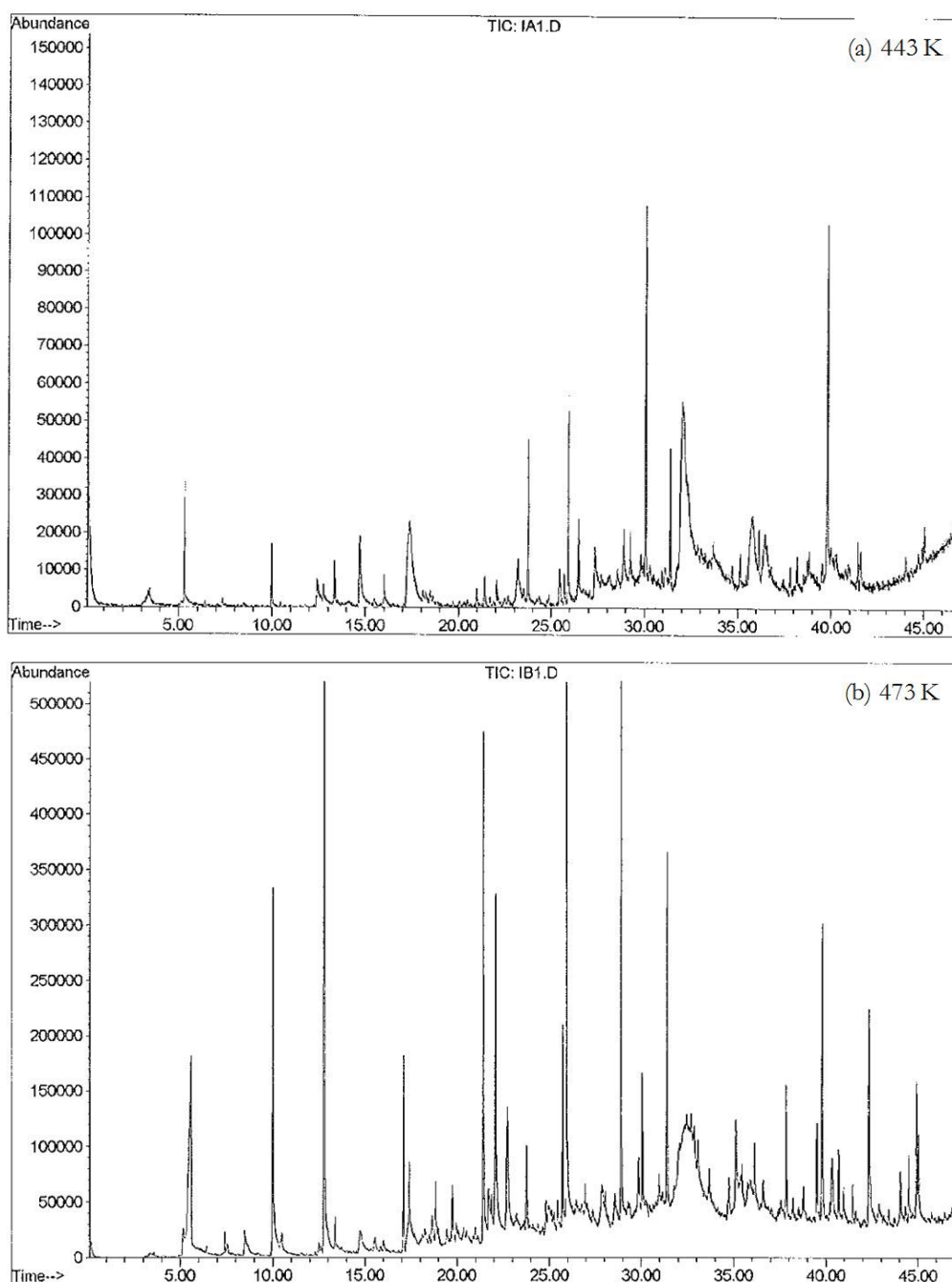
In order to identify the monomer derived from treatment of Japanese rice straw by hot compressed water, the collected aqueous effluent was diluted with methanol prior to analysis using GC–MS, a method which is well-known as a powerful tool to identify aromatic and aliphatic compounds. The identities of those compounds determined through a match of mass spectra in the GC–MS computer library, which contains a wide range of organic compounds, are reliable. Extraction with methanol gave organic compounds shown in Fig. 5, a typical GC–MS chromatogram of the products obtained at 443 K, 473 K, and 503 K with 2.92 ml min⁻¹ flow rate. It was well known that one of the most important parameters affecting hot compressed water extraction efficiencies is the extraction temperature. As the temperature increased, it was obviously decrease in dielectric constant, an increase in the diffusion rate and a decrease in the viscosity and surface tension. It should be noted that increasing the extraction temperature above a certain value also gives increase to the degradation of the extract components. In the case of hot compressed water extraction flow rate, only 2.92 ml min⁻¹ flow rate was presented. This condition was selected on the basis of the previous researcher's reports [49, 50]. Rangsrivong *et al.* 2009 [49] reported that the various extraction flow rates should affect the extraction rate but not the total amounts of the compounds extracted in the process. An increase in flow rate, it means that the mass transfer of the compounds extracted from the surface of the solid phase into the water phase regulated most of the extraction process. Increase in flow rate resulted in increase in superficial velocity, and thus, quicker mass transfer. As shown in Fig. 5, most of these compounds have been identified as lignin-derived compounds, sugar-derived compounds, and nitrogen-containing compounds. The lignin-derived compounds were clearly detected [51–53]. Klinka *et al.* 2002 [51] reported on a wide variety of phenolic compounds derived from alkaline wet oxidation of wheat straw at 458 K or 468 K with a pressure of 11–12 bar, vanillic acid and vanillin being the major components, followed by 4-hydroxybenzaldehyde, syringaldehyde, syringic acid, coumaric acid and guaiacol. However, the sugar-derived compounds detected by GC–MS increased with increased reaction temperature (473 K and 503 K). This phenomenon is most probably due to the partial degradation of cellulose at higher extraction temperatures. Yuan *et al.* 2009 [54] investigated the content of bio-oil obtained from the thermochemical liquefaction of straw by hot compressed water at temperature of 473–583 K. They reported that the bio-oil, a complex mixture containing carbon, hydrogen, and oxygen, is composed of acids, alcohols, aldehydes, esters, ketones, lignin derived phenols, and extractible terpene with multifunctional groups. The main compounds in those six samples were dibutyl phthalate and butylated hydroxytoluene, which is might be formed by the decomposition of lignin functional groups with some side reactions during the hydrothermal treatment. At 473 K, the main compounds in bio-oil obtained were butylated hydroxytoluene, dibutyl phthalate, and 1,2-benzenedicarboxylic acid, butyl 2-ethylhexyl ester. Similar to our result, when the temperature increased to 523, the composition of the oil became more complex, many high molecular compounds were produced as well, such as phorbol, 4-hydroxy octadecanoic acid methyl ester, and 17-pentatriacontene. Table 2 lists the data concerning the

compositional analysis under each experimental condition. Tymchyshyn and Xu 2010 [52] also reported that the oil derived from the liquefaction of lignin was the most concentrated with phenolic compounds. They explained that it is not surprising that the major compounds produced by the liquefaction of sawdust at around 523 K were phenolic compounds such as 2-methoxyphenol, 2-methoxy-4-methylphenol and 4-ethyl-2-methoxyphenol which comprise almost the phenolic/neutral oil. The major components of the phenolic/neutral oils derived from cornstalks are more varied. They said that substituted phenols and phenolic compounds comprise almost 74% of the phenolic/neutral oil collected from the liquefaction of lignin. In the case of cellulose, the major components of the cellulose-derived oil appeared to be esters of complex organic acids and long chain hydrocarbons, likely formed by dehydration of the cellulose.

Further, it could be said that cellulose, hemicellulose, and lignin as main components of Japanese rice straw underwent decomposition simultaneously during hot compressed water extraction process. Under these conditions, the cellulose degrades to low molecular weight aldehydes and ketones, then these aldehydes and ketones may then form aromatic compounds by condensation and dehydration. Hemicelluloses are also easily solubilized and hydrolyzed into various monosaccharides, including xylose, mannose, glucose and galactose, in water. As well as cellulose and hemicellulose, the decomposition of lignin was also occurred. It would be decomposed into various phenols and methoxy phenols by hydrolysis of ether-bonds during hot compressed water extraction. In this work, the reaction mechanism of cellulose, hemicellulose, and lignin are not presented.

The chemical structure of Japanese rice straw as a starting material and its major constituents, cellulose, xylan (hemicellulose) and lignin, were analyzed using FT-IR direct transmittance through KBr pellet technique. Infrared spectroscopy is an analytical technique that allows identification of unknown substances and of the types of chemical bonds the compounds in those substances contain. Rana *et al.* 2010 [55] explained that most of the observed peaks of wood represent major cell wall components such as cellulose at around 1154 and 898 cm^{-1} ; hemicelluloses at around 1738, 1024, 1057, and 1090 cm^{-1} ; and lignin at around 1596, 1505, and 1270 cm^{-1} . FT-IR spectra of Japanese rice straw, cellulose, xylan, and lignin are shown in Fig. 6 (a). It can be observed that cellulose, xylan and lignin as three components of biomass most likely consist of alkene, esters, aromatics, ketone and alcohol, with different oxygen-containing functional groups observed [4, 42, 50, 56]. As a reference, the peak positions of all infrared bands and their functional groups are summarized in Table 3. Each molecule is composed of many different chemical bonds, and these bonds are slightly elastic and can stretch, bend, or vibrate. Therefore, some differences exist at each FT-IR spectra due to their structure properties. The intensity of the absorbance due to the hydrogen bonded O-H stretching (3600–3000 cm^{-1}) could be found in each component. Strong IR spectra of C-O and C=O were found in lignin and xylan, while cellulose contained only high C-O compounds. At the region 1800–700 cm^{-1} , the IR spectra of lignin had high absorbance due to the presence of compounds containing methoxyl-O-CH₃, C-O-C stretching and C=C stretching (aromatic ring). Fig. 6 (b) shows the spectra for lignin and solid products from hot compressed water treatment at 443, 473, and 503 K, respectively. The peaks that point down represent the frequencies of light that the molecules absorb. Each spectrum is a spectral average of at least four scans. Most bands showed a shift in wave number for different solid products. The bands in the 3336.2–3356.9 and 2850.3–2937.7 cm^{-1} region were assigned to the hydrogen bonded O-H stretching and C-Hn stretching groups, respectively. In these regions, the peaks in (a) – (d) were clearly observed. As mentioned above, the fingerprint at the region 1800–700 cm^{-1} , indicating compounds rich in methoxyl-O-CH₃, C-O-C stretching and C=C stretching (aromatic ring), were also found at each solid product. These aromatic skeleton vibrations at around 1600, 1515 and 1426 cm^{-1} and the C-H deformation combined with aromatic ring vibration at 1462 cm^{-1} are common for all lignins, although the intensity of the bands may differ. In detail, Boeriu *et al.* 2004 [57] reported that common for the spectra of all lignins are a weak band at 1370–1375 cm^{-1} originating from phenolic OH and aliphatic C-H in methyl groups and a strong vibration at 1215–1220 cm^{-1} that can be associated with C-C plus C-O plus C=O stretching. Respect to lignin and sugar content in the samples and the amount of hydroxyl and carboxyl groups, they used the lignin content of samples varied between 64 and 99%. The aromatic C-H deformation at 1035 cm^{-1} appears as a complex vibration associated with the C-O, C-C stretching and C-OH bending in polysaccharides. Carbohydrate originating vibrations are associated also with other vibrations in the spectral region 1000–1300 cm^{-1} . The influence of polysaccharide impurities on the spectral profile is most visible for solid products when the extraction was conducted at higher temperature. As shown in Fig. 6(b), the spectral characteristics of the lignin and solid products are essentially the same, indicating that the three kinds of solid products obtained by hot compressed water extraction are within a similar functional group as lignin. However, the apparent difference between the

intensity of absorbances were found. It might be due to the loss of aliphatic and aromatic functional groups since further degradation occurs at higher temperatures. Ko *et al.* 2014 [39] reported that the intensity of isolated lignin functional groups decreased with increasing the pretreatment temperatures. The greater hydrolysis of isolated lignin functional groups at higher pretreatment temperatures can be attributed to the degradation of aromatic rings and breakage of ether linkages. Nevertheless, Yuan *et al.* 2009 [54] suggested that the main component including cellulose and hemicellulose of straw began to decompose at 473 K, but the lignin decomposed at 523–573 K. Judging from the results, it could be said that these range temperatures (443–503) are suitable to extract lignin from Japanese rice straw.



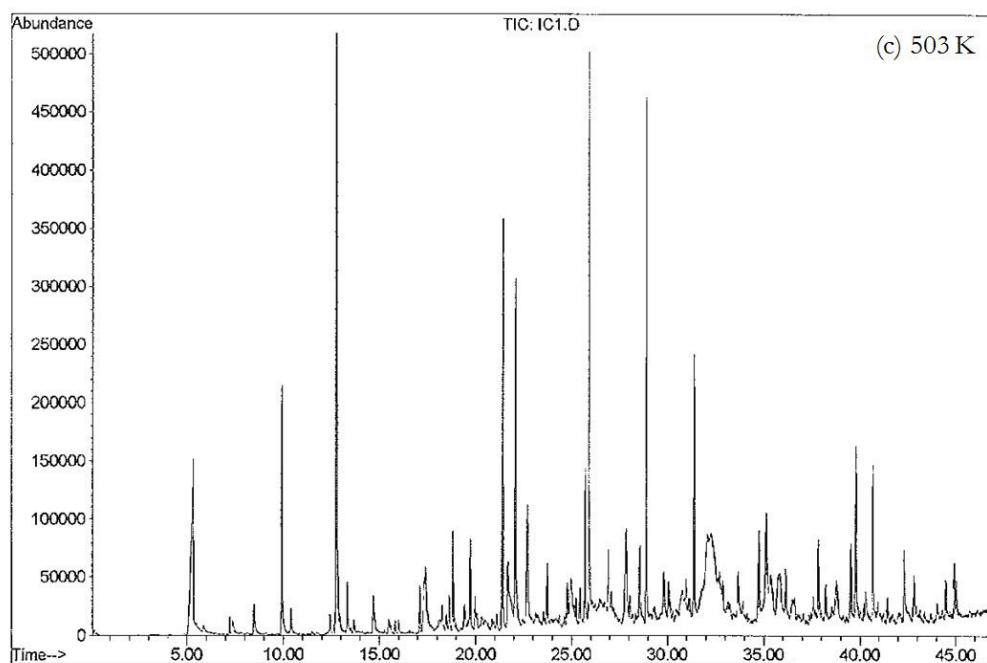


Fig. 5. GC–MS chromatogram of water soluble products recovered after treatment at (a) 443, (b) 473, and (c) 503 K with 2.92 ml min^{-1} water flowrate, respectively.

Table 2(a). List of GC–MS monomeric products in the water soluble fraction at temperature of 443 K with 2.92 ml min^{-1} water flowrate.

No	Retention time [min]	Compound name	Molecular weight	Compound formula
1	5.32	Urea	60.06	$\text{CH}_4\text{N}_2\text{O}$
2	9.98	3-Methylbutanal	86.13	$\text{C}_5\text{H}_{10}\text{O}$
3	12.46	Methyl nitrite	61.04	CH_3NO_2
4	12.76	2-Furancarboxaldehyde	96.08	$\text{C}_5\text{H}_4\text{O}_2$
5	13.35	2,5-Dihydro-3,4-dimethylfuran	98.14	$\text{C}_6\text{H}_{10}\text{O}$
6	14.72	Methylhydrazone acetaldehyde	72.11	$\text{C}_3\text{H}_8\text{N}_2$
7	16.02	2,3-Dihydro-5-methyl-2-furanone	98.10	$\text{C}_5\text{H}_6\text{O}_2$
8	17.36	Glycerin	92.1	$\text{C}_3\text{H}_8\text{O}_3$
9	18.24	Allyl alcohol	58.08	$\text{C}_3\text{H}_6\text{O}$
10	18.11	N-Methyloxazolidone	101.10	$\text{C}_4\text{H}_7\text{NO}_2$
11	18.49	Dihydropyran	84.12	$\text{C}_5\text{H}_8\text{O}$
12	20.99	Maltol	126.11	$\text{C}_6\text{H}_6\text{O}_3$
13	21.41	2-Nitro-2-butene	101.10	$\text{C}_4\text{H}_7\text{NO}_2$
14	22.05	2-Cyclohexenone	96.13	$\text{C}_6\text{H}_8\text{O}$
15	23.18	Sec-butylamine	73.14	$\text{C}_4\text{H}_{11}\text{N}$
16	23.74	3-Hydroxy-2,3-dihydromaltol	144.13	$\text{C}_6\text{H}_8\text{O}_4$
17	25.46	2,4-Dimethylhexane	114.23	C_8H_{18}
18	25.91	5-Hydroxymethylfurfural	126.11	$\text{C}_6\text{H}_6\text{O}_3$
19	26.46	Tetrahydro-3,4-furandiol	104.11	$\text{C}_4\text{H}_8\text{O}_3$
20	27.35	1,2-Heptanediol	132.20	$\text{C}_7\text{H}_{16}\text{O}_2$
21	28.87	Durenol	150.22	$\text{C}_{10}\text{H}_{14}\text{O}$
22	29.24	1,1-Diethoxydecane	230.39	$\text{C}_{14}\text{H}_{30}\text{O}_2$

23	30.06	Eugenol	164.20	C ₁₀ H ₁₂ O ₂
24	31.37	Vanillin	152.15	C ₈ H ₈ O ₃
25	32.01	Butyl glycolate	132.1577	C ₆ H ₁₂ O ₃
26	35.73	Methyl 2,2-dimethylvalerate	144.21	C ₈ H ₁₆ O ₂
27	36.45	Octadecanol acetate	312.53	C ₂₀ H ₄₀ O ₂

Table 2(b). List of GC–MS monomeric products in the water soluble fraction at temperature of 473 K with 2.92 ml min⁻¹ water flowrate.

No	Retention time [min]	Compound name	Molecular weight	Compound formula
1	5.59	Urea	60.06	CH ₄ N ₂ O
2	8.53	Dicyclomine	309.49	C ₁₉ H ₃₅ NO ₂
3	10.01	3-Methylbutanal	86.13	C ₅ H ₁₀ O
4	12.76	2-Furancarboxaldehyde	96.08	C ₅ H ₄ O ₂
5	17.10	Trimethyloxazole	111.14	C ₆ H ₉ NO
6	17.41	5-Methyl-2-furaldehyde	110.11	C ₆ H ₆ O ₂
7	18.83	2,4-Imidazolidinedione	114.10	C ₄ H ₆ N ₂ O ₂
8	21.42	N-Ethylpropanamide	101.15	C ₅ H ₁₁ NO
9	22.07	Furan	68.07	C ₄ H ₄ O
10	23.74	3-Hydroxy-2,3-dihydromaltol	144.13	C ₆ H ₈ O ₄
11	25.71	Dihydrobenzofuran	120.15	C ₈ H ₈ O
12	25.92	5-Hydroxymethylfurfural	126.11	C ₆ H ₆ O ₃
13	28.89	2,4,6-Trimethyl-m-phenylenediamine	150.22	C ₉ H ₁₄ N ₂
14	30.06	Eugenol	164.20	C ₁₀ H ₁₂ O ₂
15	31.37	Vanillin	152.15	C ₈ H ₈ O ₃
16	32.07	D-Arabinose	150.16	C ₅ H ₁₀ O ₅
17	32.28	D-Galactose	180.16	C ₆ H ₁₂ O ₆
18	35.12	Vanillic acid	168.15	C ₈ H ₈ O ₄
19	37.82	Syringaldehyde	182.17	C ₉ H ₁₀ O ₄
20	39.51	Homovanillic acid methyl ester	196.20	C ₁₀ H ₁₂ O ₄
21	39.77	Eugenol methyl ether	178.23	C ₁₁ H ₁₄ O ₂
22	40.67	1-Phenyl-1H-indene	192.26	C ₁₅ H ₁₂
23	42.31	3-Methoxy-4-hydroxycinnamic acid	194.18	C ₁₀ H ₁₀ O ₄
24	44.48	Methyl diphenylacetate	226.27	C ₁₅ H ₁₄ O ₂
24	44.91	4-allyl-1,2,6-trimethoxybenzene	208.25	C ₁₂ H ₁₆ O ₃
26	45.03	4b,10a-Dihydrobenzo[3,4]cyclobuta[1,2-b][1,4]benzodioxine	210.23	C ₁₄ H ₁₀ O ₂

Table 2(c). List of GC–MS monomeric products in the water soluble fraction at temperature of 503 K with 2.92 ml min⁻¹ water flowrate.

No	Retention time [min]	Compound name	Molecular weight	Compound formula
1	5.33	Urea	60.06	CH ₄ N ₂ O
2	8.50	3-Pentanone	86.13	C ₅ H ₁₀ O
3	9.90	3-Methylbutanal	86.13	C ₅ H ₁₀ O
4	10.39	1-Hydroxy-2-butanone	88.11	C ₄ H ₈ O ₂

5	12.75	2-Furancarboxaldehyde	96.08	C ₅ H ₄ O ₂
6	13.32	2-Furanmethanol	98.10	C ₅ H ₆ O ₂
7	14.66	Unknown	-	-
8	17.10	Trimethyloxazole	111.14	C ₉ H ₉ NO
9	17.34	Glycerin	92.1	C ₃ H ₈ O ₃
10	17.40	2,3,5-Trimethylfuran	110.15	C ₇ H ₁₀ O
11	18.81	2,4-Imidazolidinedione	114.10	C ₄ H ₆ N ₂ O ₂
12	19.73	2,5-Piperazinedione	114.10	C ₄ H ₆ N ₂ O ₂
13	21.40	1-Methylmorpholine	101.15	C ₅ H ₅ NO
14	22.07	Furan	68.07	C ₄ H ₄ O
15	22.70	Styrene	104.15	C ₈ H ₈
16	23.73	3-Hydroxy-2,3-dihydromaltol	144.13	C ₆ H ₈ O ₄
17	24.78	Pyrocatechol	110.11	C ₆ H ₆ O ₂
18	24.96	2,5-Piperazinedione	114.10	C ₄ H ₆ N ₂ O ₂
19	25.44	Persicol	184.28	C ₁₁ H ₂₀ O ₂
20	25.71	Dihydrobenzofuran	120.15	C ₈ H ₈ O
21	25.91	5-Hydroxymethylfurfural	126.11	C ₆ H ₆ O ₃
22	26.92	2-Methyl-1-butene oxide	86.13	C ₅ H ₁₀ O
23	27.83	4,8-Dimethylundecane	184.36	C ₁₃ H ₂₈
34	28.55	Valproic Acid	144.21	C ₈ H ₁₆ O ₂
25	28.88	2,3-Diethyl-5-methylpyrazine	150.22	C ₉ H ₁₄ N ₂
26	29.80	2,6-Dimethoxyphenol	154.16	C ₈ H ₁₀ O ₃
27	31.37	Vanillin	152.15	C ₈ H ₈ O ₃
28	32.07	D-Arabinose	150.16	C ₅ H ₁₀ O ₅
29	32.14	D-Galactose	180.16	C ₆ H ₁₂ O ₆
30	32.27	D-Mannose	180.16	C ₆ H ₁₂ O ₆
31	33.67	4-Acetylguaiacol	166.17	C ₉ H ₁₀ O ₃
32	34.74	3-Ethylphenyl acetate	164.20	C ₁₀ H ₁₂ O ₂
33	35.11	Vanillic acid	168.15	C ₈ H ₈ O ₄
34	35.36	Xanthosine	284.24	C ₁₀ H ₁₂ N ₄ O ₆
35	35.81	Phenylacetylene	102.15	C ₈ H ₆
36	36.13	p-Methoxybenzaldoxime	151.16	C ₈ H ₉ NO ₂
37	37.82	Syringaldehyde	182.17	C ₉ H ₁₀ O ₄
38	39.51	Homovanillic acid methyl ester	196.20	C ₁₀ H ₁₂ O ₄
39	39.77	Eugenol methyl ether	178.23	C ₁₁ H ₁₄ O ₂
40	40.66	Perhydrophenanthrene	192.34	C ₁₄ H ₂₄
41	42.30	3-Methoxy-4-hydroxycinnamic acid	194.18	C ₁₀ H ₁₀ O ₄
42	44.47	Methyl diphenylacetate	226.27	C ₁₅ H ₁₄ O ₂
43	44.90	Asarone	208.25	C ₁₂ H ₁₆ O ₃

Table 3. The main functional groups of the major constituents of Japanese rice straw.

Wave number [cm ⁻¹]	Functional groups	Compounds
3600 – 3000	O–H stretching	Acid, methanol
2860 – 2970	C–H _n stretching	Alkyl, aliphatic, aromatic
1700–1730, 1510–1560	C = O stretching	Ketone and carbonyl

1632	C = C	Benzene stretching ring
1613, 1450	C = C stretching	Aromatic skeletal mode
1470–1430	O–CH ₃	Methoxyl–O–CH ₃
1440–1400	O–H bending	Acid
1402	C–H bending	
1232	C–O–C stretching	Aryl-alkyl ether linkage
1215	C–O stretching	Phenol
1170, 1082	C–O–C stretching vibration	Pyranose ring skeletal
1108	O–H association	C–OH
1060	C–O stretching and C–O deformation	C–OH (ethanol)
700–900	C–H	Aromatic hydrogen
700–650	C–C stretching	

Table 4. Elemental analysis results of solid residues analyzed by CHN analyzer, on average.

Temperature [K]	Flow rate [ml min ⁻¹]	Ultimate analysis [wt. %, DAF]				Atomic ratio [-]	
		H	C	N	O*	H/C	O/C
Room ⁺	-	5.98	39.89	0.81	53.32	0.15	1.34
	1.42	5.89	43.29	0.79	50.03	0.14	1.16
443	2.92	6.02	42.87	0.97	50.14	0.14	1.17
	4.67	5.99	43.02	0.97	50.02	0.14	1.16
473	1.42	6.19	43.89	0.91	49.01	0.14	1.12
	2.92	6.20	44.31	1.28	48.21	0.14	1.09
	4.67	6.32	43.98	1.13	48.57	0.14	1.10
	1.42	6.21	44.70	1.32	47.77	0.14	1.07
503	2.92	6.43	44.90	0.98	47.69	0.14	1.06
	4.67	6.33	44.40	1.23	48.06	0.14	1.08

*The content of oxygen was determined by difference.

+Original sample.

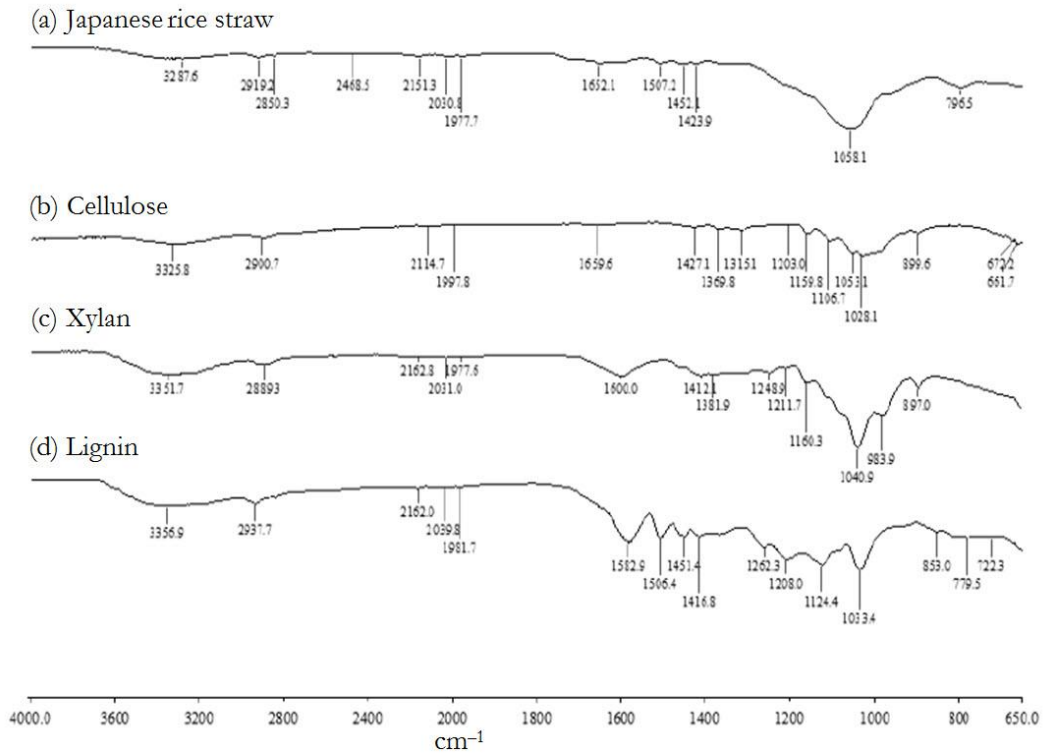


Fig. 6(a). FT-IR spectrum of Japanese rice straw and its major constituents.

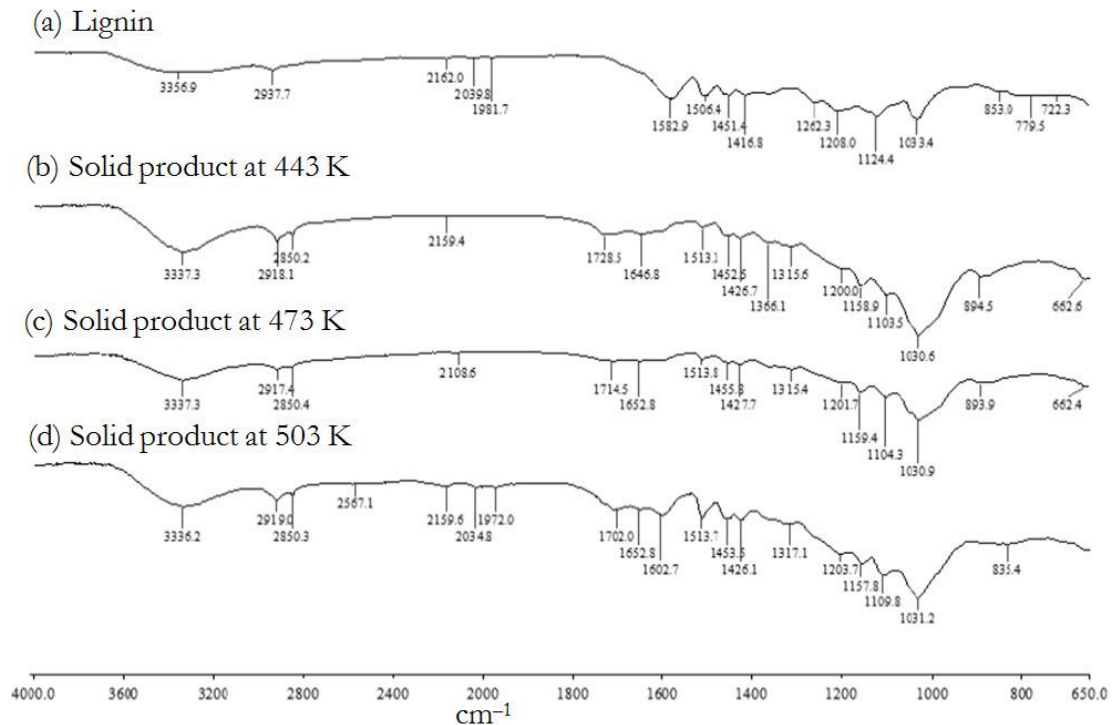


Fig. 6(b). FT-IR spectrum of solid products from Japanese rice straw extraction (a) 443, (b) 473, and (c) 503 K with 2.92 ml min⁻¹ water flowrate.

Table 4 shows the ultimate analysis of solid residue content in weight percent dry and ash free material (wt% DAF). The concentration of carbon increased gradually with increased water extraction flow rate at 443, 473, and 503 K, respectively. The loss of hydrogen and oxygen in the solid residues is reflected in the decrease in hydrogen and oxygen content. These observations are in good agreement with results obtained by infrared spectroscopy of solid products, which shows an increase in the intensity of absorbance due to

the hydrogen bonded. These results showed that dehydrogenation and deoxygenation occurred during the extraction process under these conditions [58–61]. It was reported by Nishimiya *et al.* 1998 [58] that the dehydrogenation and deoxygenation during the carbonization process of wood charcoal begin under dry conditions. Inoue *et al.* 2002 [59] also treated wood in hot compressed water to obtain charcoal, and then compare with dry conditions under a nitrogen atmosphere. They suggested that charcoal could be obtained from wood and that the dehydrogenation and deoxygenation in wood occurred during treatment with the hot compressed water. This indicates applicability of hot compressed water to such high-moisture biomass as Japanese rice straw, and that energy would be saved due to lack of necessity of drying.

As mentioned above, several methods, such as ultrasonic/microwave extraction, solvothermal extraction, ionic liquids solvent extraction, and liquid hot water extraction, were introduced to the extraction and separation of lignin as a one of the main components in biomass. Due to the complex process and less capacity of them, the development of extraction and separation technique for biomass components, such as lignin, is necessary. To reduce the use of organic solvent and improve the lignin extraction methods from plant biomass, hot compressed water extraction was applied at 443–503 K and 4.0 MP. It is a powerful technique at temperatures between 373 and 647 K and pressure high enough to maintain the liquid state leading to increased extraction efficiency through improvements in mass transfer and changes in the polarity of water. Under these conditions, water simultaneously acts as, reactant and catalyst. At conditions close to the critical point, water has several very interesting properties. Among them are low viscosity and high solubility of organic substances, which make hot compressed water an excellent medium for fast, homogeneous and efficient reactions. Hot compressed water was also called autohydrolysis, hydrothermal treatment, hydrothermolysis, liquid hot water, subcritical water, aquasolve process, aqueous processing and pressure-cooking in water [24]. Ruiz *et al.* 2013 [24] explained that hot compressed water has been considered a cost-effective pretreatment and in general, the major advantages of this process are: (1) the process does not require the addition and recovery of chemicals different from water, (2) limited equipment corrosion problems, (3) simple and economical operation.

Table 5. Properties of water under different conditions.

Fluid	Ordinary water	Subcritical water	Supercritical water	
Temperature (K)	298	523	673	673
Pressure (bar)	1	50	250	500
Density, ρ (g cm ⁻³)	1	0.80	0.17	0.58
Dielectric constant, ϵ	78.5	27.1	5.9	10.5
Ionic product, pK_w	14.0	11.2	19.4	11.9
Heat capacity (kJ kg ⁻¹ K ⁻¹)	4.22	4.86	13.0	6.8
Dynamic viscosity, η (mPa s)	0.89	0.11	0.03	0.07
Heat conductivity, C_p (mW m ⁻¹ K ⁻¹)	608	620	160	438

The hot compressed water (subcritical water) behaves very differently not only from water at room temperature but in some aspects also from supercritical water (see Table 5) [10]. The ionic product of water (K_w) is relatively high in the subcritical range (10^{12} compared to 10^{14} at ambient conditions). The high levels of H^+ and OH^- at subcritical conditions mean that many acid- or base-catalyzed reactions, such as biomass hydrolysis, are accelerated [30, 10]. Furthermore, the density of subcritical water is in the range between those of ambient and supercritical conditions. Despite the high-temperature, the compressibility is still rather low. The relatively high density combined with the high dissociation constant of subcritical water, favors ionic reactions. Shi *et al.* 2012 [62] also explained that the extraction is, thus, based on the changing dielectric constant of water with temperature, which modifies the polarity of water making it capable of extracting different compounds. Also, the use of pressure of around 5 MPa would be high enough to prevent the water from vaporizing at temperatures from 373 to 523 K. Once pressure is high enough to keep water in a liquid state, additional pressure is not necessary as it has limited influence on the solvent characteristics of water. Increasing the water temperature from 298 to 573 K causes similar changes in dielectric constant, surface tension, and viscosity. They also explained that the hot compressed water extraction process has the ability to selectively extract different classes of compounds, depending on the temperature used. The selectivity of hot compressed water extraction allows for manipulation of the composition of the extracts by changing the operating parameters, with the more polar extracted at lower

temperatures and the less polar compounds extracted at higher temperatures. For that reason, the hot compressed water extraction can be considered an environmentally friendly fractionation process. In addition, this technique is also suitable for processing high-moisture (wet) biomass since water is used as the extraction medium, and thus the biomass can be directly converted without an energy consuming drying step.

4. Conclusions

Hot compressed water extraction of lignin from the Japanese rice straw was studied at temperatures of 443–503 K and pressure of 4.0 MPa using a flow-through system. Under these conditions, thermal softening of the Japanese rice straw occurred, allowing the removal of the lignin protecting other constituents in Japanese rice straw. UV–vis spectrum revealed strong absorption peaks distributed at wavelengths in the region of 200–210 nm due to the high lignin content in extracted products. Lignin recovery approached 85% when the extraction was performed at 443 and 473 K with a flow rate of 4.67 ml min⁻¹; recovery increased with increased flow rate at each temperature. By ultimate analysis of solid residues, the concentration of carbon increased gradually with increased water extraction flow rate at 443, 473, and 503 K, respectively. The loss of hydrogen and oxygen in the solid residues is reflected in the decrease in hydrogen and oxygen content. Based on these results, it is proposed that hot compressed water treatment is applicable to isolate lignin from other types of biomass.

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