Pulping of Bamboo using Supercritical Ammonia with Recovery and Reuse of the Ammonia

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Preliminary research on supercritical ammonia pulping of bamboo was completed using a differential thermal analyzer, scanning electron microscope, X-ray diffractometer, and an energy spectrometer. The results showed that ammonia can be recovered from bamboo raw materials under the supercritical condition of 185 to 190 °C. Compared with conventional kraft bamboo pulp, the separated bamboo pulp met the pulp quality requirements of industrial paper, achieving high efficiency and a multi-level utilization of biomass resources. Ammonia in the system can be recycled.

Keywords: Supercritical ammonia; Bamboo; Pulping

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INTRODUCTION

With the gradual improvement in living standards, the demand for energy will continue to increase. According to the latest "Energy Outlook Report" created by a group of USA oil and gas companies, global total energy demand will increase by 35% by the end of 2040 (ExxonMobil 2013). Fiber-based biomass feedstock is a relatively abundant class of renewable biomass resources. Improving the extraction of fiber raw materials has great research value and application prospects. According to the latest forecast from the International Energy Agency's World Energy Outlook report, biomass resources' applications will increase by a factor of four by the year 2035 (IEA 2012). Expectedly, the volume of trade between the international communities will continue to grow. Under such circumstances, the development of renewable energy has attracted global attention from scientific research institutions (Zhu and Zhuang 2012).

Generally speaking, biomass resources mainly refer to agricultural and forestry biomass resources, specifically the various organic substances produced by plants in nature using sunlight through the photosynthesis of living organisms (Feng 2010). Agriculture and forestry biomass are inexhaustible, renewable energy materials that can be continuously recycled. They can be converted into less polluting chemicals or fuels. Biomass energy is a special energy source in that its energy comes from the sun, or another form of solar energy. At the same time, it is also a carbon source for sustainable recycling. Biomass resources can be converted into fuel ethanol or useful energy such as high value-added bio-based chemicals (Li 2012).

Biomass resources are green plants that absorb CO_2 from the atmosphere and then convert inorganic CO_2 to an organic carbon source *via* photosynthesis. Finally, the biomass generates CO_2 after its use.

Therefore, biomass resource utilization does not substantially emit excess CO_2 and fiber-based biomass resources are generally less polluting and more sustainable than fossil fuels, such as petroleum. It is one of the most effective and feasible ways to address current energy and environmental problems (Ragauskas 2006). Hence, extracting fiber raw materials with high efficiency has become a key issue of research.

Supercritical fluid refers to a non-condensing high-density fluid that exceeds the critical temperature and critical pressure. Its physical and chemical properties fall in-between gas and liquid. It has the same density, high solubility, and heat transfer coefficient as liquid. It also has the same low viscosity and high diffusion coefficient as gas. All of these properties change with temperature and pressure and are extremely easy to control (Zhao *et al.* 2007).

Supercritical fluid extraction technology is active in many applications and has achieved good results. For example, in the application of woody biomass, McDonald and Stuthridge (1997) found that extraction efficiency has a great relationship with the polarity of the solvent. Supercritical extraction achieves better results. The extract contains resin acids, fatty acids, and lignin. In the supercritical state, lignin is not only soluble but also degradable.

In the selection of supercritical fluids, research on ammonia as a fluid has also been reported. Eckert *et al.* (1992) used CO_2, methanol, propane, and ammonia as supercritical fluids to extract residual lauryl alcohol in the reaction of synthetic polyoxyethylenelauryl ether. They found that CO_2 had best the selectivity, and ammonia had the largest capacity for extraction of residual lauryl alcohol. The reaction between ammonia and lignin has also been reported. He and Elder (1997) used ammonia reacted with a lignin model and found that the unsaturated bond of ammonia and lignin occurs in the 1,4 and 1,2 addition reaction, and the product is aminotoluene.

Given the performance of ammonia in the above examples, and taking the subsequent waste disposal issues into account, this study chose ammonia as the supercritical medium. The authors chose supercritical ammonia as the extraction medium. The aim of this work is to pulp bamboo fiber raw materials for papermaking. Compared with the conventional kraft (or “sulphate”) bamboo pulp, the separated bamboo pulp met the pulp quality requirements of industrial paper. For further application, bioenzyme hydrolysis an important methods involved in the bioconversion of lignocellulose to produce fermentable monosaccharides (Capolupo and Faraco 2016; Chen *et al.* 2018).

EXPERIMENTAL

Materials

The materials used in this study included an autoclave and circulation system, HYX-0.5G (Dalian Fourth Instrument Factory, Dalian, China); a differential thermal analyzer, DTA 200PC (Netzsch, Bavaria, Germany); a scanning electron microscope, S-450/PV9100 (Hitachi, Ltd., Tokyo, Japan); and an X-ray diffractometer (X`Pert PRO MPD; Philips, Amsterdam, Netherlands). Air-dried bamboo was obtained from Qingdao, Shandong Province, China. The bamboo’s chemical composition is shown in Table 1.

Table 1. Bamboo Raw Ingredients (%)

			Extraction						
Moisture	**Ash**	**Silica in Ash**	**Cold Water**	**Hot Water**	**Phenyl Alcohol**	**1% NaOH**	**Pentosan**	**Lignin**	**Total Cellulose**
13.00	0.79	0.15	5.14	7.93	1.92	25.49	20.78	24.99	72.98

Methods

Kraft pulping of bamboo

Conventional kraft cooking was used in this work for pulping of bamboo. The work was carried out in a high-pressure reactor (HYX-0.5G; Dalian Fourth Instrument Factory, Dalian, China). The bamboo had been air-dried before the cooking process. The cooking process conditions used 20% of alkali (calculated as Na_2O), a 20% degree of sulfidity, and a liquid ratio of water and oven-dried material of (5:1). First, the material was rotated for 20 min before heating. Then, the material was heated to 120 °C (this process took 50 min). Next, a small degree of degasification occurred, and this process took 2 min. Finally, the material was heated from 120 °C to 170 °C. This process took 90 min. The whole process took 162 min. After the cooking process, the resulting bamboo fiber was washed and then dried in preparation for papermaking.

Differential thermal analysis (DTA) of lignin

The bamboo pulp and the kraft black liquor prepared *via* the bamboo raw material and the kraft method were placed in a DTA200PC (Netzsch, Bavaria, Germany) instrument and subjected to differential thermal analysis. The operating conditions of the instrument were an initial temperature of 32 °C, final temperature of 250 °C, a heating rate of 10 to 15 °C/min, and a nitrogen flow rate of 60 mL/ min.

Supercritical ammonia pulping

Supercritical ammonia pulping of bamboo was carried out in a high-pressure reactor (HYX-0.5G), using the pressure difference between the cylinder and the reactor, and by pressing the liquid ammonia in the cylinder into the reactor. The reaction used a freezer to adjust the temperature of the reactor, controlling the amount of liquid ammonia entering the reactor. In the reaction kettle, the bamboo was in contact with the liquid ammonia. By raising the inside temperature of the reactor to reach and exceed the critical temperature of liquid ammonia, lignin was dissolved. After reaching the predetermined temperature, there was a cooling-down period, and then the reaction stopped. Separating the solids and liquids, the solids were bamboo fibers that had been separated into pulp. The liquid phase, which was the spent pulping liquor, can also be referred to as “black liquor”.

For the process conditions there was a liquid-to-solids ratio of 5:1 and a liquid ammonia initial pressure of 0.5 MPa. The experiment was conducted in accordance with the aforementioned experimental method, and the final heating temperature was 250 °C.

Bamboo pulp performance analysis

This study determined the beating degree, Kappa number, whiteness, tensile strength, tearing degree, and bursting resistance of the kraft bamboo pulp and supercritical ammonia bamboo pulp in accordance with GB/T 3332 (2004), GB/T 1546 (2004), GB/T 17749 (2008), GB/T 12914 (2008), GB/T 455 (2002), GB/T 454 (2002), respectively.

Electron microscopic observation and energy spectrum analysis of fiber morphology

A scanning electron microscope microanalyzer (S-450 energy spectrometer PV9100; Hitachi, Ltd., Tokyo, Japan) was used to observe the surface morphology of the supercritical ammonia bamboo pulp, as well as the full surface and end view of the normal temperature section and the frozen section. Energy spectrum analysis of the end face of the bamboo fiber of supercritical ammonia method was also performed.

X-ray diffraction analysis of fiber crystalline state

An X-ray diffractometer (model X`Pert PRO MPD; Philips, Amsterdam, Netherlands) was used to determine the X-ray diffraction patterns of the kraft pulp and supercritical ammonia bamboo pulp.

RESULTS AND DISCUSSION

Thermal Analysis of Raw Materials and Determination of Reaction Temperature

The critical temperature of ammonia is 132.44 °C, so the reaction temperature should be higher to achieve supercritical extraction. Lignin was the object of extraction in this system, so it became an important factor in determining the temperature of the system.

Figures 1, 2, and 3, show the DTA chart of the bamboo raw material, kraft bamboo pulp, and its black liquor. The specimens were analyzed. Results are shown in Table 2.

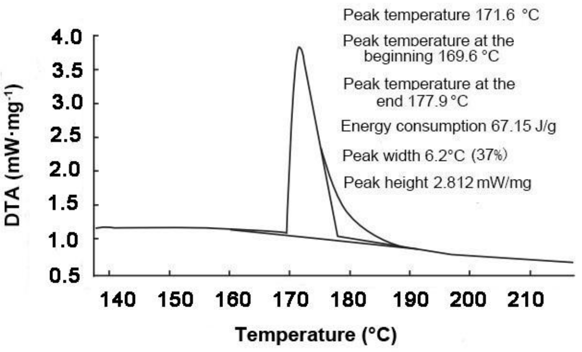

Fig. 1. DTA of bamboo raw materials

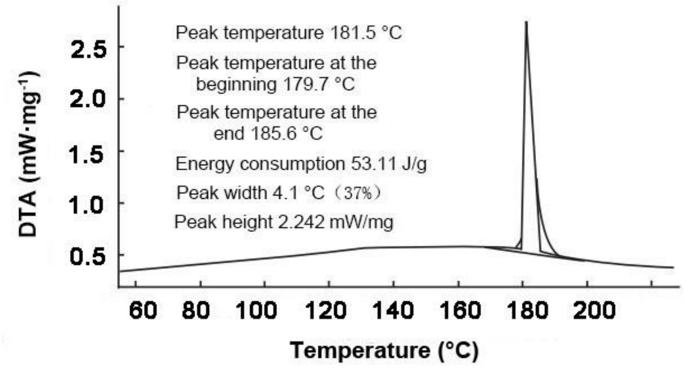

Fig. 2. DTA of kraft bamboo pulp

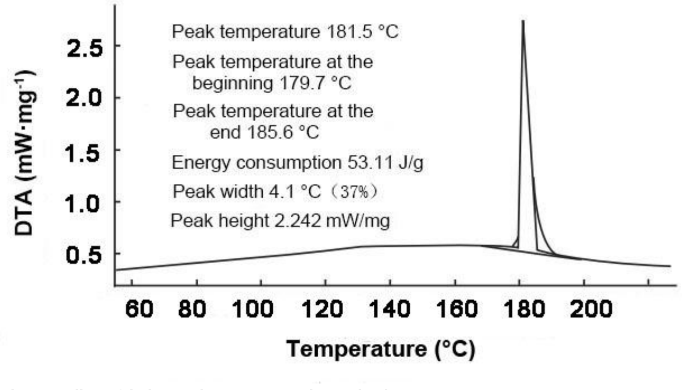

Fig. 3. DTA of sulphate (kraft) bamboo pulp black liquor

Table 2. DTA Analysis Results

Sample	Lignin Content (%)	Peak Temperature(°C)	Temperature at the End of the Peak (°C)	Sample Energy Consumption (J·g^{-1})	Lignin Energy Consumption (J·g^{-1})
Kraft bamboo pulp	1.93	181.5	185.6	53.11	27.52
Bamboo raw material	24.99	171.6	177.9	67.15	2.69
Kraft bamboo pulp black liquor	31.98	168.0	172.0	172.00	5.38

The endothermic peak was caused by the endothermic softening of lignin. The sulphate black liquor (also called kraft black liquor) had a high lignin content and therefore consumed the most energy. Although bamboo pulp had the lowest lignin content, it had low chemical activity, and through the process, bamboo's lignin remained in the pulp. The highest energy consumption required to soften the lignin was 27.5 J/g, which required high temperatures. As shown in Table 2, the maximum temperature for softening the lignin was 185.6 °C. Therefore, when the extraction temperature was established, it should have been higher than this temperature to maintain the dissolution and flow of lignin in the system.

The pyrolysis analysis of woody biomass by scholars from South China University of Technology (Li and Chen 2000) shows that high molecular substance is broken down into small molecular groups during the heating process. Mainly liquid products, but also phenol, oxymethyl phenol, and ethylene benzene gas escape from black liquor. In fact, the organic matter was cleaved at 230 °C. Avoiding excessive temperature during the extraction process helped to maintain the pulp's strength. Therefore, it is recommended that the temperature of supercritical ammonia extraction should not exceed 200 °C.

The authors determined that a suitable temperature range of the supercritical ammonia fiber raw material extraction was between 185 and 200 °C.

Supercritical ammonia extraction of bamboo fiber raw materials

The physical indexes of the supercritical ammonia method and the kraft method for bamboo pulp are shown in Table 3.

Table 3. Comparison of Physical Properties between Supercritical Ammonia Method and Kraft Method Bamboo Pulp

	Initial Temp. (°C)	Temp. Reflex (°C)	Freeness (°SR)	White Degree (%)	Yield (%)	Tensile Strength (KN•M^{-1})	Tear Degree (Mn)	Burst Resistance (KPa)	Kappa No.
SAP	15	199	16.0	8.50	43.8	4.69	1143.6	554.7	50.3
	8	189	17.5	8.30	45.6	4.29	1071.4	571.4	52.6
SBP	_	_	13.5	17.6	47.7	4.55	1303.8	497.3	_

*Note: SAP- supercritical ammonia pulping; SBP- sulphate bamboo pulp

The results show that the performance of the supercritical ammonia bamboo pulp was similar to sulphate bamboo pulp when the reaction temperature was 189 °C. After the reaction temperature was raised, the tensile strength and the burst strength decreased. Therefore, the temperature of the supercritical ammonia pulping should not exceed 190 °C.

In Fig. 4, the morphology of the supercritical bamboo pulp fiber revealed that the bamboo pulp fiber was well dissociated (a). The surface of the fiber was slightly golden yellow, indicating that the lignin had dissolved and a small part of the lignin adhered to the surface of the fiber. Due to supercritical fluid refers to a non-condensing high-density fluid that exceeds the critical pressure, and it has high solubility as liquid. The pressure is released rapidly causing the biomass to expand, so that the lignin had been dissolved (Bradshaw *et al.* 2007; Balan *et al.* 2009). The cryosection (b and c) and room temperature sections (d and e) showed that the fiber retained its softness under the action of supercritical ammonia.

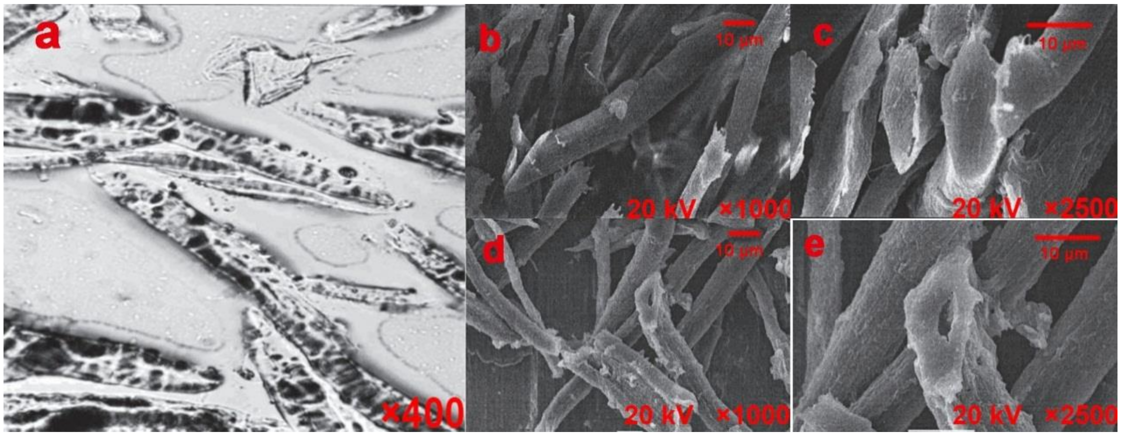

Fig. 4. Electron microscopic observation of supercritical bamboo pulp fiber. a: morphology of supercritical bamboo pulp fiber; b: supercritical bamboo pulp at room temperature; c: supercritical method bamboo pulp normal temperature, slice end face; d: supercritical bamboo pulp frozen section; e: supercritical bamboo pulp frozen section end face

For the end energy spectrum of bamboo pulp fiber, Fig. 5 shows that the C element content was 48.86%, O was 46.6%, and Mn was 3.84%. A lower content of Mn indicated that the lignin in the cell wall was largely dissolved.

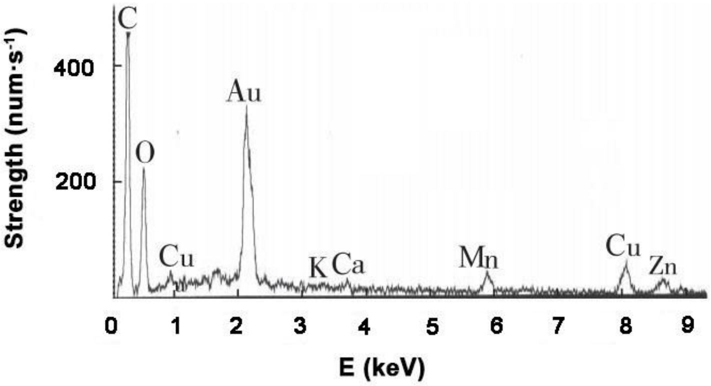

Fig. 5. Surface energy spectrum of bamboo pulp by supercritical extraction

Figures 6 and 7 show the X-ray diffraction patterns of the kraft bamboo pulp and supercritical extraction bamboo pulp. The figures show that the fiber crystalline state of the two kinds of bamboo pulp was not much different.

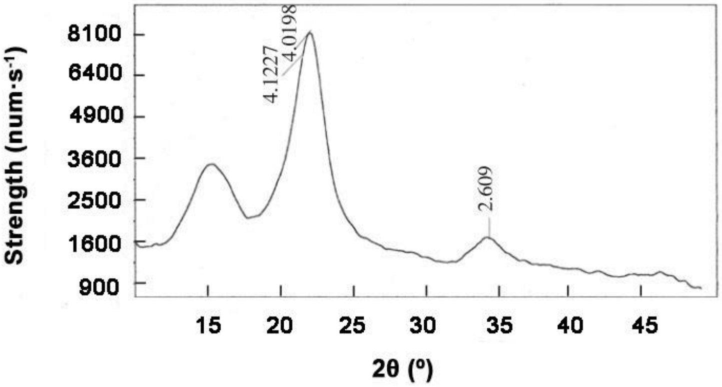

Fig. 6. X-ray diffractogram of sulphate bamboo pulp

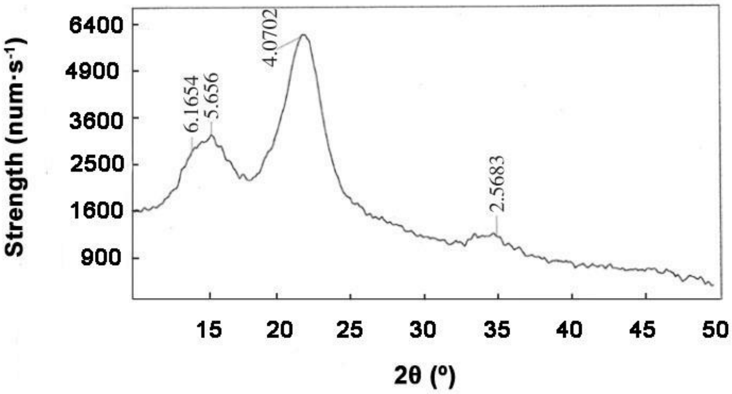

Fig. 7. X-ray diffractogram of supercritical bamboo pulp

Ammonia in the studied system can be recycled. Compared with the conventional kraft bamboo pulp, Supercritical ammonia pulping can reduce the consumption of water resources. Due to these two reasons, supercritical ammonia pulping have more potential for papermaking.

CONCLUSIONS

1. At a temperature of 185 to 190 °C, ammonia reached a supercritical state in which lignin became dissolved in the supercritical ammonia. After the lignin was dissolved, the fibers separated, thereby realizing the extraction of bamboo fiber raw materials.
2. Ammonia in the studied system can be recycled. As was the case for the conventional kraft bamboo pulp, the papermaking results met the quality requirements of paper.
3. For further application of fibers, bioenzyme hydrolysis an important methods involved in the bioconversion of lignocellulose to produce fermentable monosaccharides.

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