energy&fuels
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pubs.acs.org/EF

Dynamic Variation of Fuel Properties of Tonkin Cane (*Pseudosasa amabilis*) during Maturation

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ABSTRACT: Bamboo is a potential feedstock for bioenergy production. *Pseudosasa amabilis* is a common bamboo species in south China and commonly known as Tonkin Cane. It has a high biomass yield, and its properties are outstanding compared to many other bamboo species as well as grasses and woody biomass for bioenergy applications. Bamboo can mature within 1 year, and its chemical composition changed slightly after the growth during the first year. To understand the effect of the maturation process on fuel properties, biomass materials of *P. amabilis* ranging from 0.5 m bamboo shoot to 1-year-old bamboo culm were investigated for chemical composition, crystallinity index (CrI), element contents (i.e., C, H, N, S, and O), heating values, and thermogravimetric characteristics. Except for the H content, which did not show an apparent changing trend, and the lignin content, which had a relatively stable increasing rate, the other tested properties changed significantly during the maturation process of the bamboo and rapidly before the age stage of high growth accomplishment of the bamboo. The CrI showed the same changing pattern with the cellulose content. In comparison to some grass and woody biomass materials, C and H contents of 1-year-old mature bamboo were higher, whereas N, S, and O contents were lower, which are advantageous for bioenergy utilization. The higher heating value of 1-year-old bamboo was more than 19 MJ/kg, even higher than some of the woody biomass feedstocks. The results from this study ensure that 1 year growth is enough for the Tonkin Cane to obtain a good quality biomass for biofuel production.

1. INTRODUCTION

Bamboo is a general term for more than 1250 species of woody grasses in 75 genera belonging to the family Poaceae and subfamily Bambusoideae, which is widely distributed all over the world.[1−4] Because of its large output of biomass, much faster growth rate than trees, and very similar chemical composition (50−70% holocellulose and 20−25% lignin) to wood,[2,5,6] bamboo is considered as a good substitute of timber in the wood industry. Recently, as an outstanding renewable plant resource, bamboo is receiving more and more attention to be used as a biomass resource for bioenergy and biofuel applications. Physical and chemical characterization and fuel properties of bamboo biomass from several species are reported elsewhere.[7−15]

Tokin Cane (*Pseudosasa amabilis*), a commonly known name, is a native bamboo species in south China. It has very good material properties, and traditionally, it has been used to make rods and strut. Tokin Cane rods (especially fishing rods and ski poles) have been exported from China to the United States and European countries since the 19th century.

Some studies of Tokin Cane have been performed with respect to biomass morphology and growth models,[16] the relationship between internode length and fiber length,[17] growth regularity,[18] growth of the bamboo rhizome,[19] biological characters, and high yield techniques.[20] However, there is still no study that talks about fuel properties of Tokin Cane and utilization of Tokin Cane for bioenergy and biofuel applications.

Former research about bamboo materials was all concentrated on matured bamboo (starting from 1 year old) culm, with the major species of the study being Moso bamboo (*Phyllostachys edulis*), and the studies have suggested that the chemical changes of bamboo culm after the growth during the first year are very low.[21−24] Meanwhile, an edible bamboo shoot can quickly grow up to a full height woody bamboo culm within its growth during the first year, which suggests that a major change in biomass properties can occur during that period. However, there is no study available in the literature on how the property changes during the growth of the first year in bamboo culm. The objective of this study was to investigate the fuel properties of Tokin Cane and to find out the influence of the first year maturation to its physical and chemical properties.

2. MATERIALS AND METHODS

2.1. Materials. Tokin Cane culm samples during the maturation process were collected between May 2012 and May 2013 in Jiangdu, Jiangsu, China (32° 29′ N and 119° 38′ E, 6 m above sea level). The climate of Jiangdu is a humid subtropical climate; the annual average temperature is 14.9 °C; and the annual average rainfall is 978.7 mm.[25] The soil type belongs to the alkaline-earth-element-enriched soil region in northern Jiangsu.[26]

The height of the mature bamboo culm was typically between 4 and 5 m. Both the bamboo shoots (new bamboo that is progressing its growth in height) ranging from 0.5, 1, 1.5, 2, 2.5, 3, to 4 m high and the bamboo culm (bamboo that already reached its matured height) ranging from 3 months, 6 months, 1 year, 2 years, and 3 years old were collected for this study. The sample numbers for 0.5 and 1 m shoots was 30 each, for 1.5 m shoots was 20, for 2 m shoots was 10, 5 each for two groups (one group was used for whole culm, and the other group

Received: December 2, 2014
Published: March 27, 2015

DOI: 10.1021/acs.energyfuels.5b00385
Energy Fuels 2015, 29, 2408−2415

was divided into four parts) of 1 year old, and 5 each for 2 and 3 years old. The duration between the 0.5 m shoot and 4 m shoot collection was 23 days. Considering that it may take 1−2 weeks for the new bamboo shoot to grow up to 0.5 m high from the ground, this number matched the previous finding, in which the study[20] reported that Tokin Cane can reach its mature height within 30−40 days. Considering the variation of the maturity level of the bamboo culm along the axial direction during the maturation process, all of the bamboo shoots and one group of 1-year-old culms were divided into four parts: bottom (the 1−3 internodes above ground), middle (the 4−7 internodes above ground), upper (the 8−11 internodes above ground), and top (the remainder). The division method for node and internode of bamboo culm is illustrated in Figure 1.

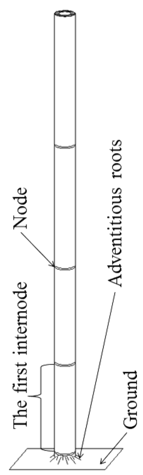

Figure 1. Schematic of the node and internode positions of bamboo culm.

All of the collected samples were cut into small pieces with stick scissors and oven-dried at 80 °C until there was no change in mass, ground by a micro plants grinder (model type FZ102), and subsequently sieved by mesh size that ranges between 0.25 and 0.425 mm. The samples with the particle size between 0.25 and 0.425 mm were selected for all of the characterizations and stored in plastic ziplock bags in the cool, dry, and dark preservation indoor environment until they were used. The bottom part of bamboo culm matures first, and the maturation processes of the other three parts were repetitions of the bottom part one after another. Therefore, data presented in this study for shoot and 3 and 6 month culm were only for the bottom part.

2.2. Characterization Methods. *2.2.1. Chemical Analysis.* As shown in Table 1, moisture content, ash, hot-water extractives, alcohol−benzene extractives, holocellulose, and lignin of bamboo shoots and the four parts of 1-year-old bamboo culm were determined on the basis of the National Standard of People's Republic of China, whereas their cellulose content was determined on the basis of the nitric acid−ethanol method, as discussed elsewhere.[27]

Table 1. Methods Used for Major Chemical Analysis of Bamboo Shoots and the Four Parts of 1-Year-Old Bamboo Culm

chemical property	method
moisture content	GB/T 2677.2-93
ash	GB/T 2677.3-93
hot-water extractives	GB/T 2677.4-93
alcohol−benzene extractives	GB/T 2677.6-94
cellulose	nitric acid−ethanol method
holocellulose	GB/T 2677.10-1995
lignin	GB/T 2677.8-94

For the whole culm of 1-, 2-, and 3-year-old bamboo culm, the moisture content was measured using a moisture analyzer (Mettler Toledo, model MJ33), ash content was measured using the ASTM E1755-01 standard, ethanol extractives was measured using the ASTM E1690-08 standard, and cellulose, hemicellulose, and lignin contents were measured by following the National Renewable Energy Laboratory (NREL) Laboratory Analytical Procedure (LAP) of "Determination of Structural Carbohydrates and Lignin in Biomass".

2.2.2. Crystallinity Analysis. The crystallinity index (CrI) of the samples was carried out on an Ultima IV multipurpose X-ray diffraction system (λ = 1.5406 Å) at the continuous 2θ scanning mode with a scanning speed of 5°/min. Data were recorded every 0.05° from the angle range of 2θ = 5−50°. The CrI was calculated according to eq 1[28]

$$\mathrm{CrI} = ((I_{002} - I_{am})/I_{002}) \times 100\% \quad (1)$$

where I_{002} is the maximum peak intensity at 2θ = ∼22° and I_{am} is the intensity of the baseline at 2θ = 18°.

2.2.3. Ultimate Analysis. Elemental constituents based on dry materials were carried out on a PerkinElmer 2400 Series II CHNS/O elemental analyzer. Carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) contents were measured directly by the analyzer, whereas the oxygen (O) content was calculated by subtracting C, H, N, S, and ash from 100.[29]

2.2.4. Heating Value Analysis. Higher heating values (HHVs) were measured by an IKA C200 bomb calorimeter and calculated using eq 2 to present on a dry basis. The ash-free heating values (AFHVs) were also calculated using eq 3

$$\mathrm{HHV} = \mathrm{HV_t}/((1 - \mathrm{MC}\ \%)(1 - \mathrm{ash}\ \%)) \quad (2)$$

$$\mathrm{AFHV} = \mathrm{HHV}/(1 - \mathrm{ash}\ \%) \quad (3)$$

where HV_t is the heating value obtained by a bomb calorimeter and MC is the moisture content of the sample loaded in the bomb calorimeter.

2.2.5. Thermogravimetric (TG) and Derivative Thermogravimetric (DTG) Analyses. TG analysis was carried out on a Netzsch STA-449C system. The samples were heated from 20 to 750 °C at a heating rate of 10 °C/min while flowing N_2 at 20 mL/min.

3. RESULTS AND DISCUSSION

3.1. Chemical Composition. Moisture contents of all of the bamboo samples are listed in Table 2. All of the other chemical contents were calculated on the basis of the dry weight of biomass.

Table 2. Moisture Content of Tokin Cane Samples[a]

		location	moisture content (%)
bamboo shoot	0.5 m	bottom	8.96 ± 0.11
	1 m	bottom	7.10 ± 0.04
	1.5 m	bottom	5.42 ± 0.01
	2 m	bottom	7.56 ± 0.05
	2.5 m	bottom	5.65 ± 0.02
	3 m	bottom	6.99 ± 0.12
	4 m	bottom	7.80 ± 0.04
bamboo culm	3 months	bottom	5.22 ± 0.01
	6 months	bottom	2.51 ± 0.01
	1 year	bottom	4.72 ± 0.04
		middle	5.16 ± 0.01
		upper	5.10 ± 0.00
		top	4.87 ± 0.01
	1 year	whole	5.23 ± 0.41
	2 years	whole	5.20 ± 0.17
	3 years	whole	5.28 ± 0.16

[a]Data are presented as the mean ± standard deviation.

DOI: 10.1021/acs.energyfuels.5b00385
Energy Fuels 2015, 29, 2408−2415

Table 3. Mean Chemical Compositions of Tokin Cane with Maturation (on a Dry Weight Basis)[a]

		location	ash (%)	hot-water extractives (%)	alcohol−benzene extractives (%)	cellulose (%)	holocellulose (%)	Klason lignin (%)
bamboo shoot	0.5 m	bottom	9.26 h	53.33 j	25.6 g	10.50 a	23.98 a	0.70 a
	1 m	bottom	4.76 g	30.26 i	22.14 f	33.20 b	54.69 b	4.22 b
	1.5 m	bottom	2.67 f	14.91 g	10.96 e	43.27 d	72.53 d	6.31 c
	2 m	bottom	2.77 f	19.03 h	10.54 e	40.19 c	69.35 c	7.53 d
	2.5 m	bottom	2.32 e	10.88 e	8.85 cd	45.67 f	74.73 e	11.33 e
	3 m	bottom	1.95 c	12.55 f	9.44 d	44.76 e	72.85 d	13.32 f
	4 m	bottom	2.42 e	10.47 d	8.12 c	48.25 g	74.79 e	13.08 f
bamboo culm	3 months	bottom	2.15 d	7.37 b	4.52 a	45.92 f	75.31 e	19.28 g
	6 months	bottom	1.32 b	4.99 a	3.99 a	48.56 g	76.91 f	21.68 i
	1 year	bottom	0.90 aA	9.39 bcBC	5.76 bA	43.50 dB	73.35 dB	20.81 hB
		middle	0.97 B	8.88 B	5.53 A	44.55 C	74.23 B	20.13 A
		upper	0.97 B	8.08 A	5.46 A	44.78 C	74.00 B	20.07 A
		top	1.74 C	9.75 C	6.21 B	42.41 A	72.29 A	20.95 B

[a]Means with the same lowercase letter for a particular test for different ages or with the same capital letter for 1-year-old culm in different locations are not significantly different at $\alpha = 0.05$.

Table 4. Weight, Length, and Linear Density of the Bottom Parts of 1.5 m Bamboo Shoots and 1-Year-Old Bamboo Culm[a]

	weight (g)	percentage of total weight (%)	length (cm)	percentage of total length (%)	linear density (g/cm)
1.5 m	73.18 ± 29.09	37.38 ± 6.51	37.57 ± 7.61	26.53 ± 5.96	1.92 ± 0.59
1 year	107.01 ± 20.97	13.71 ± 2.32	33.78 ± 6.30	7.20 ± 1.38	3.20 ± 0.47

[a]Data are presented as the mean ± standard deviation.

The ash content, hot-water extractives, alcohol−benzene extractives, cellulose, holocellulose, and Klason lignin of the bottom parts of bamboo culms in different maturation stages and the four different parts of 1-year-old bamboo culm were depicted in Table 3. Holocellulose (cellulose and hemicellulose) and lignin are the most important components in terms of biomass utilization and constitute the majority of the weight of the biomass. Ash and extractives are less useful for biomass utilization, but changes in their contents suggest some variations or formations of the main components in the growth process of the plants.

During the growth and maturation process from a 0.5 m bamboo shoot to a 1-year-old bamboo culm, profound changes occurred in all of the chemical components. The ash content and extractives in the bottom part decreased significantly in this period. Hot-water extractives showed the largest variation from 53.33 to 9.39%. Meanwhile, alcohol−benzene extractives decreased from 25.6 to 5.76%, and the ash content decreased from 9.26 to 0.90%. Contents of holocellulose, cellulose, and lignin increased in this period. Lignin displayed a slower rate of increase from 0.7 to 20.81%, whereas both the holocellulose and cellulose had faster rates of increase from 23.98 to 73.35% and from 10.50 to 43.50%, respectively.

For 1-year-old bamboo culm, there were more branches and leaves in higher positions and more physiological activities happened there; the variation of the content of its components by height were significant. The ash content continued to increase from the bottom to the top. The bottom and top parts had significantly higher contents of hot-water extractives and lignin than the middle and upper parts, whereas cellulose contents in the middle and upper parts were significantly higher than in the bottom and top parts. Contents of holocellulose and alcohol−benzene extractives did not change significantly from the bottom to the upper part; however, the holocellulose content was significantly lower and alcohol−benzene extractives were significantly higher at the top part. For a height lower than 1.5 m, the ash and extractives of bamboo shoots decreased rapidly, cellulose and holocellulose increased rapidly, lignin had a relatively stable increasing rate, and all of these changes were significant (Table 3). When the bamboo shoots were taller than 1.5 m, the rates of chemical change slowed but the overall trends did not change. When bamboo culm quickly grows to its full height, its meristematic tissue of the internodes moves with the growing parts upward like a telescope.[30] For this reason, the maturation process of bamboo culm is accomplished from the bottom to the top. Table 4 shows the weight, length, and linear density of the bottom parts of 1.5 m and 1-year-old bamboo culm. It is clear that the bottom parts of the culm had already completed their vertical growth when the whole culm reached the height of 1.5 m. From this point on, the culm no longer grows but continues its lignification and maturation. Considering that the lignification process may last up to several years,[21] it is reasonable for lignin to have a stable rate of increase.

The rate of vertical bamboo growth from the sprouting of the shoots to the completion of the young bamboo plants followed a "slow−rapid−slow" course.[24] The same pattern also occurs in the biomass accumulation.[31] This gradual and inconsistent maturation process leads to a stepwise mature rule of the bamboo culm described as follows. The bottom part of the culm begins its height growth with rapid chemical changes; after the completion of this growth, it switches to a process with slower chemical changes. The middle part of the culm then repeats this process, followed by the upper and the top. This rule also applies to all of the internodes.

Ash, ethanol extractives, cellulose, hemicellulose, and Klason lignin of 1-, 2-, and 3-year-old Tokin Cane culm are listed in Table 5. The percentage content of cellulose decreased significantly, but the amount was only 4.02% for the following 2 years of growth; this can be attributed to a considerable extent to the little increase of 1.45% in hemicellulose and 1.3% in Klason lignin during this period. The ash content increased

DOI: 10.1021/acs.energyfuels.5b00385
Energy Fuels 2015, 29, 2408−2415

Table 5. Mean Chemical Compositions of 1-, 2-, and 3-Year-Old Culm of Tokin Cane (on a Dry Weight Basis)[a]

	ash (%)	ethanol extractives (%)	cellulose (%)	hemicellulose (%)	Klason lignin (%)
1 year	1.03 a	4.63 a	45.77 b	22.79 a	20.62 a
2 year	1.17 b	4.64 a	42.11 a	23.38 ab	20.98 a
3 year	1.38 c	4.49 a	41.75 a	24.24 b	21.92 b

[a]Means with the same letter for a particular test for different ages are not significantly different at $\alpha = 0.05$.

significantly but only 0.35%, and ethanol extractives decreased 0.14% insignificantly. In comparison to the huge change in chemicals during the growth cycle of the first year, this change from 1 year old to 3 years old was very small. A similar result was reported by Zhang et al.[22] that the changes in the main chemicals of Moso bamboo from 1 year old to 8 years old were also very small (~4% at a maximum of lignin and ~3% at a maximum of holocellulose).

For being used as materials, Tokin Cane is usually harvested at about 3 years old, allowing for the culm to obtain a good mechanical property.[32] However, it is immaterial to consider about the mechanical property of biomass if they will be used as a feedstock for producing bioenergy and biofuels. These results also justify why the authors chose to study the properties of biomass for energy application during the rapid growth cycle and maturation process of Tokin Cane for the first year.

3.2. Cellulose Crystallinity. Bamboo shoots accumulate crystalline cellulose during their maturation to increase the stability of bamboo culm. The CrI of cellulose can be seen as a key predictor of the enzymatic hydrolysis rate of cellulose; indeed, the initial enzymatic rate continued to increase with a decreasing CrI.[33] As shown in Table 6, the CrI of the bottom part of the culm during the maturation process quickly increased from about 7.48 to 45.37% in bamboo shoots from 0.5 to 1.5 m. The CrI then continued to increase but at a slower rate from 45.37 to 51.41% in bamboo from 1.5 m shoots to 1-year-old culms. The pattern of CrI variation during the maturation process matched the increasing curve of the cellulose content very well. Furthermore, it agreed with the idea that the 1.5 m bamboo shoot stage can be a dividing point of the maturation process of the bottom part of the culm.

For 1-year-old bamboo culm, middle and upper parts have higher CrI than the bottom and top parts and this trend also repeats with the cellulose content. In a comparison among species, the CrI was about 41.16 and 37.50% in mature bamboo culm of *Phyllostachys edulis* (Syn. *Phyllostachys pubescens*) and *Bambusa emeiensis* (Syn. *Sinocalamus affinis*),[9] 53.8% in *Pinus massoniana*,[34] and 43.36, 41.90, 53.59, and 70.26% in the healthy wood of *Betula platyphylla*, *Picea koraiensis*, *Larix gmelinii*, and *Populus*.[35] Accordingly, the CrI of bamboo varies with different species and does not show a higher value than that of wood on average. This can be an advantage of using bamboo in biological conversion for renewable energy compared to wood.

3.3. Ultimate Analysis. The elemental content is an important fuel property of biomass. Basically, high contents of H and C and a low amount of O will increase the heating value of the biomass,[36] whereas N and S contents can contribute to undesired oxides of nitrogen (NO_x, principally as NO and NO_2) and sulfur (SO_x, principally as SO_2). These oxides are the primary pollutants of the combustion process.[37] The main elemental constituents of the culm are shown in Table 7. During the maturation process, N and S contents showed significant reduction, C and O contents displayed visible increase, but H did not have a clear trend of change. Table 5 also indicates that the "1.5 m bamboo shoot dividing point" discussed earlier divides the overall decreasing N trend into an early rapid stage and later slow stage; the trend of increasing O is similarly divided into an early rapid stage and a later stable stage.

In Table 8, C, H, and O contents are relatively stable as height varies in the 1-year-old bamboo culm but the N content is rather high at the top part of the culm. Considering that most of the leaves and branches are at the top part and that there are more physiological activities there, it is reasonable for the top part to have a higher N content. In comparison to other typical biomass samples in Table 9,[32−36] 1-year-old bamboo culm was ranked among the highest in terms of C and H contents, an advantage for its utilization as bioenergy. O, N, and S contents of bamboo culm were ranked in the middle, and N and S contents were lower than that of the other grass samples.

3.4. Heating Value. The heating value is one of the most important indicators of all materials to be used for energy. From Table 10, the HHV of the culm increased significantly during the maturation process, but the rate of increase was slowed when the bamboo culm grew to its total height. Additionally, there was no significant difference in HHV between different parts of 1-year-old bamboo culm. The trend of the AFHV is mostly the same as the HHV, except for an apparently high value at the 0.5 m bamboo shoot stage of the culm. Furthermore, the ash content is significantly higher in the 0.5 m bamboo shoot, but ash does not contribute anything to the heating value.

The heating value of bamboo culm is much higher than that of grass materials and is similar to woody materials.[43] Table 11[44,45] shows that Tokin Cane not only has higher HHV than corn stover and wheat straw but also has a higher HHV than hardwood (average), beech wood, and *Ailanthus* wood. In comparison to the HHV ranging from 18.1 to 19.6 MJ/kg of seven other several years old bamboo species,[7,9] 1-year-old Tokin Cane already showed the highest HHV; even bamboo shoots of Tokin Cane can stand at the same level with them. This strongly supports the utilization of the Tokin Cane for bioenergy application and directly indicates that 1 year of growth is enough for Tokin Cane to reach a high level of HHV to be used at a certain biomass.

3.5. TG and DTG. TG and DTG analysis is a widely used method for research about the pyrolysis characteristics and thermophysical properties of materials. The details of thermal decomposition processes of the bamboo culm in different ages

Table 6. CrI of Bamboo Culm of Tokin Cane (%)

0.5 m	1 m	1.5 m	2 m	2.5 m	3 m	4 m	3 months	6 months	1 year			
bottom	bottom	bottom	bottom	bottom	bottom	bottom	bottom	bottom	bottom	middle	upper	top
7.48	36.01	45.37	44.66	47.07	45.27	52.34	54.31	52.36	51.41	56.36	55.15	52.10

DOI: 10.1021/acs.energyfuels.5b00385
Energy Fuels 2015, 29, 2408−2415

Table 7. CHNS/O Contents of Tokin Cane (Bottom Parts) (%, on a Dry Weight Basis)[a]

	0.5 m	1 m	1.5 m	2 m	2.5 m	3 m	4 m	3 months	6 months	1 year
C	43.78 ± 1.00	45.34 ± 0.13	47.00 ± 0.12	46.97 ± 0.06	48.02 ± 0.37	48.36 ± 0.11	47.85 ± 0.12	48.83 ± 0.14	49.53 ± 0.15	49.68 ± 0.13
H	6.12 ± 0.25	6.26 ± 0.06	6.14 ± 0.02	6.06 ± 0.05	5.99 ± 0.05	5.90 ± 0.09	5.79 ± 0.06	5.74 ± 0.02	6.28 ± 0.04	6.08 ± 0.23
N	4.26 ± 0.02	1.43 ± 0.06	0.90 ± 0.06	1.52 ± 0.01	0.97 ± 0.00	0.52 ± 0.05	0.97 ± 0.06	0.74 ± 0.11	0.37 ± 0.03	0.25 ± 0.11
S	0.37 ± 0.01	0.34 ± 0.02	0.34 ± 0.00	0.33 ± 0.00	0.33 ± 0.01	0.29 ± 0.01	0.25 ± 0.02	0.28 ± 0.01	0.18 ± 0.00	0.19 ± 0.01
O	36.21 ± 1.24	41.89 ± 0.27	42.95 ± 0.08	42.35 ± 0.03	42.36 ± 0.43	42.98 ± 0.23	42.71 ± 0.02	42.27 ± 0.06	42.31 ± 0.14	42.90 ± 0.41

[a]Data are presented as the mean ± standard deviation.

Table 8. CHNS/O Contents of Tokin Cane (1 Year) (%, on a Dry Weight Basis)[a]

	bottom	middle	upper	top	average
C	49.68 ± 0.13	49.51 ± 0.12	49.41 ± 0.06	48.39 ± 0.83	49.25
H	6.08 ± 0.23	6.24 ± 0.07	6.32 ± 0.08	6.01 ± 0.14	6.16
N	0.25 ± 0.11	0.29 ± 0.07	0.26 ± 0.03	0.48 ± 0.03	0.32
S	0.19 ± 0.01	0.18 ± 0.01	0.19 ± 0.00	0.16 ± 0.02	0.18
O	42.90 ± 0.41	42.82 ± 0.23	42.85 ± 0.17	43.22 ± 0.94	42.95

[a]Data are presented as the mean ± standard deviation.

Table 9. CHNS/O Contents of Selected Biomass Types (%, on a Dry Weight Basis)[38−42]

	corn stover	rice husk	sugar cane bagasse	sugar cane bagasse	switchgrass	poplar	red cedar shaving	*Pinus* shaving	*Eucalyptus* shaving
C	42.5	36	44.8	46.8	46.7	48.4	50	49	48.2
H	5	5.1	5.4	6.3	5.9	5.9	6.3	6.7	6.4
N	0.8	$0.8_{\text{(N and S)}}$	0.4	$0.5_{\text{(N and S)}}$	0.8	0.4	$0.4_{\text{(N and S)}}$	$0.2_{\text{(N and S)}}$	0.2
S	0.2		0.01		0.19	0.01			
O	42.6	41.3	39.6	45.3	37.4	39.6	42.3	43.8	45

Table 10. Heating Value of Tokin Cane (Bottom Parts) (MJ/kg)[a]

age		HHV	AFHV
0.5 m	bottom	18.30 b	20.17 d
1 m	bottom	18.09 a	18.99 a
1.5 m	bottom	18.50 c	19.01 a
2 m	bottom	18.58 c	19.11 a
2.5 m	bottom	18.84 d	19.29 b
3 m	bottom	18.91 d	19.29 b
4 m	bottom	18.91 d	19.38 b
3 months	bottom	19.24 e	19.66 c
6 months	bottom	19.46 f	19.72 c
1 year	bottom	19.44 fA	19.62 cAB
	middle	19.33 A	19.51 A
	upper	19.47 A	19.66 AB
	top	19.44 A	19.79 B

[a]Means with the same lowercase letter for a particular test for different ages or with the same capital letter for 1-year-old culm in different locations are not significantly different at $\alpha = 0.05$.

Table 11. Heating Value of Some Typical Biomass Samples (MJ/kg)[44,45]

willow wood	19.7
softwood (average)	20.0
hardwood (average)	18.8
spruce wood	20.1
beech wood	19.2
Ailanthus wood	19.0
wood bark (average)	20.5
corn stover	17.8
wheat straw	17.0

are shown in Figures 2−5, and their parameters have been extracted and listed in Table 12. The whole thermal decomposition process can be divided into three steps.

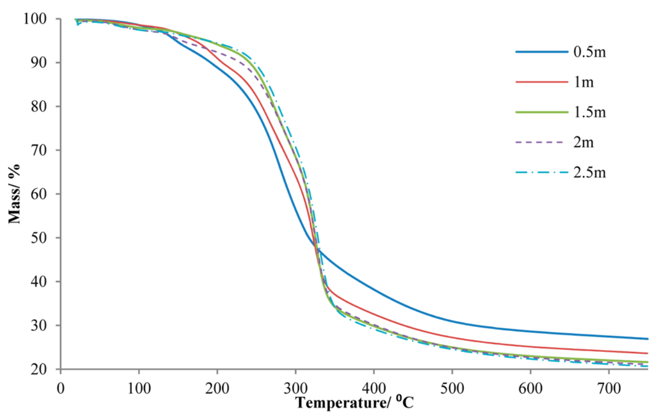

Figure 2. TG curve of Tokin Cane (0.5−2.5 m shoot, bottom part).

After the moisture evaporation process at below 100 °C, the first step of the pyrolysis process is the devolatilization of certain compounds and bound water between 105 and 150 °C. The main pyrolysis process (the second step) is signaled by an acceleration of the weight loss rate of biomass. As xylan and lignin start to decompose at a lower temperature (∼160 and 110 °C) compared to cellulose (∼225 °C),[46] the second step is a complex process that starts with the devolatilization of small molecules, proceeds through the decomposition of lignin and hemicellulose, and ends with the complete decomposition of cellulose. The third step is mostly a continuation of decomposition and carbonization of cross-linked sugar and lignin, which is the component mainly responsible for the char production.[46]

DOI: 10.1021/acs.energyfuels.5b00385
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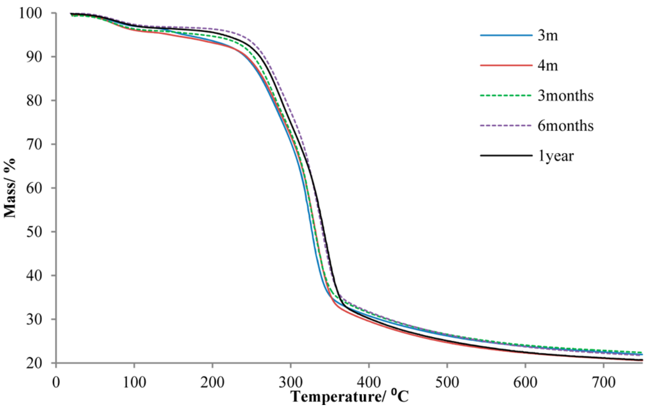

Figure 3. TG curve of Tokin Cane (3 m shoot−1-year-old culm, bottom part).

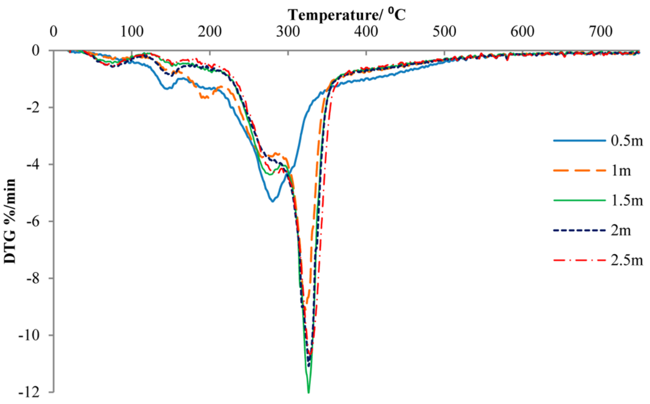

Figure 4. DTG curve of Tokin Cane (0.5−2.5 m shoot, bottom part).

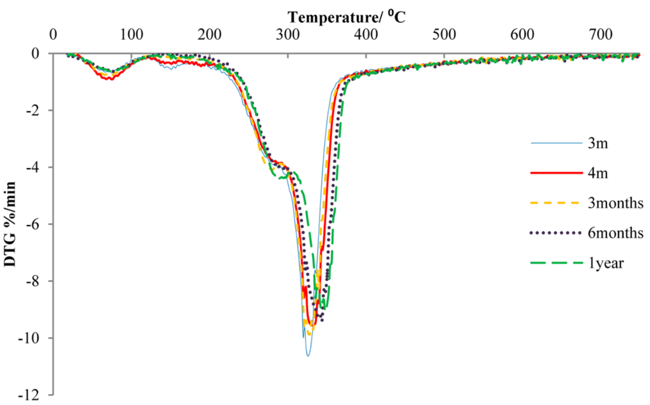

Figure 5. DTG curve of Tokin Cane (3 m shoot−1-year-old culm, bottom part).

In comparison to the other heights, the 0.5 m bamboo shoot has a different DTG pattern and a much lower second stage peak temperature (280 °C). Considering the lower cellulose content, higher ash content, and high extractives content of the 0.5 m shoot, extractives and ash contents were also important in this stage for the formation of the DTG peak. For the first step, a decreasing weight loss during the maturation process indicated reduction of volatile and light compounds, polymerization of small molecules, and lignification of the bamboo tissue, which are reasonable for the maturation process of bamboo.

The weight loss of the main pyrolysis process (the second step) was about 54% in the 0.5 m bamboo shoot, increased rapidly to more than 66% as the shoot grew to 1.5 m, then remained relatively stable between 64 and 67%. The temperature of the main peak increased between the 0.5 and 1 m shoot (from about 280 to 323 °C) compared to a relatively stable peak temperature between the 1 m shoot and the 3-month-old bamboo culm (at about a range of 323−332 °C). After 3 months old, the peak temperature of the culm began to increase again slightly and reached 348 °C at the 1-year-old stage. From the DTG data, the decomposition rate increased rapidly from 5.30 to 12.02%/min during the period from 0.5 m shoot stage to 1.5 m shoot stage and then gradually decreased to 9.06%/min at the stage of 1-year-old bamboo culm. Because cellulose with lower crystallinity will degrade at a lower temperature,[47] the increasing tread of the main peak temperature was the same as the CrI trend until the bamboo culm aged to 3 months old, when the lignin content almost reached the same level as the mature bamboo culm. Because the mutual interaction is significant in the pyrolysis process of cellulose and lignin,[48] the increase of the main peak temperature caused by lignin was then presented from the age stage of 3-month-old bamboo shoot. The weight loss of the third step was maintained around 10−15% for the culm at all ages. The 0.5 m shoot had the highest weight loss in this step, and the weight loss decreased up to the 1.5 m shoot. During the maturation process, younger bamboo always had a lower polymerization degree of macromolecules and a lower content of lignin, meaning that the pyrolysis is easier and less char is left. After the 1.5 m shoot stage, the polymerization degree of macromolecules and the lignin content increase but the lignin content is high enough to contribute to a higher weight loss during the third step of the thermal decomposition process.

As a comparison to some other woody and grass biomass materials,[49] the DTG peak temperature of 1-year-old Tokin Cane (348 °C) was closer to spruce and salix (both 337 °C) but much higher than straw (310 °C) and *Miscanthus* (304 °C) and the curve shape and DTG peak value were also closer to spruce and salix. Generally, the TG property of Tokin Cane is closer to woods (spruce and salix) rather than grasses (straw and *Miscanthus*).

The main pyrolysis process (second stage) of 1-year-old bamboo culm was also compared to the other two common bamboo species, *P. edulis* (Syn. *P. pubescens*) and *B. emeiensis* (Syn. *S. affinis*), in Table 13.[9] The onset temperature for the second stage of the three samples was at the same level, whereas the offset temperature of *B. emeiensis* was much lower than the other two species. Meanwhile, *B. emeiensis* had the biggest weight loss of the three. Of all three bamboo species, *P. amabilis* had the highest peak temperature.

4. CONCLUSION

On the basis of the continuous sample collection during the maturation process, changes of fuel properties of the biomass from Tokin Cane (*P. amabilis*) during its first year of growth were studied to investigate the effect of maturation on these properties.

During its maturation, main chemical components changed significantly, usually a rapid change at the beginning and followed by a slower change once it reaches the maximum growth. A linear relationship was found between CrI and cellulose content, and the CrI of 1-year-old bamboo culm can exceed 50%. Generally, the changes of the elements were not

DOI: 10.1021/acs.energyfuels.5b00385
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Table 12. Parameters of Thermal Decomposition from TG

	first step	second step			third step
	105−150 °C	150−370 °C			370−750 °C
	weight loss (%)	weight loss (%)	peak temperature (°C)	peak DTG (%/min)	weight loss (%)
0.5 m	3.76	54.14	280	−5.3	14.74
1 m	1.83	62.67	323	−9.12	11.51
1.5 m	1.02	66.22	326	−12.02	10.66
2 m	2.01	64.61	326	−11.08	11.71
2.5 m	0.99	66.87	328	−10.66	10.89
3 m	1.25	64.82	326	−10.64	11.26
4 m	1.08	65.72	332	−9.56	11.74
3 months	0.59	64.26	327	−9.88	11.87
6 months	0.45	64.27	343	−9.4	12.91
1 year	0.56	65.47	348	−9.06	12.60

Table 13. Parameters of Thermal Decomposition of the Main Process of Two Bamboo Species[9]

	P. pubescens	*S. affinis*	Tokin Cane
T_{onset} (°C)	157	157	160
T_{offset} (°C)	377	347	380
weight loss (%)	64.3	68.7	64.5
peak temperature (°C)	339	319	348

big. The C and O contents were increasing, whereas N and S were decreasing. In comparison to some other woody biomass and grasses, bamboo showed relatively higher C and H contents and lower N, S, and O contents. The higher heating value of Tokin Cane was increasing during the maturation and was already high enough when compared to other biomass to be used for bioenergy before the completion of its height growth.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by the Key Project of National Science and Technology Ministry (Grant 2012BAD23B05) and the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions Fund Program at Nanjing Forestry University, People's Republic of China. Also, Liang Cheng is thankful to the Department of Biosystems Engineering at Auburn University, Auburn, AL, for allowing him to perform part of the bamboo characterization work presented in this paper.

■ REFERENCES

(1) Scurlock, J. M. O.; Dayton, D. C.; Hames, B. Bamboo: An overlooked biomass resource? *Biomass Bioenergy* **2000**, *19* (4), 229−244.
(2) Liese, W. Research on bamboo. *Wood Sci. Technol.* **1987**, *21* (3), 189−209.
(3) Zhou, F. C. The state of utilization, trade and strategies for the world bamboo industry. *World For. Res.* **1992**, *01*, 50−56.
(4) Jiang, Z. H. *Bamboo and Rattan in the World*; China Forestry Publishing House: Beijing, China, 2007.
(5) Sturkie, D. G.; Brown, V. L.; Watson, W. J. *Bamboo Growing in Alabama*; United States Department of Agriculture (USDA) Agricultural Experiment Station, Auburn University: Auburn, AL, 1968; Vol. 2, Bulletin 387.
(6) Liese, W. Progess in bamboo research. *J. Bamboo Res.* **1989**, *8* (2), 1−16.
(7) Kumar, R.; Chandrashekar, N. Fuel properties and combustion characteristics of some promising bamboo species in India. *J. For. Res.* **2014**, *25* (2), 471−476.
(8) Jiang, Z. H.; Liu, Z. J.; Fei, B. H.; Cai, Z. Y.; Yu, Y.; Liu, X. E. The pyrolysis characteristics of moso bamboo. *J. Anal. Appl. Pyrolysis* **2012**, *94*, 48−52.
(9) Liu, Z. J.; Fei, B. H.; Jiang, Z. H.; Cai, Z. Y.; Yu, Y.; Liu, X. E. A comparative study of thermal properties of *Sinocalamus affinis* and Moso bamboo. *J. Therm. Anal. Calorim.* **2013**, *111* (1), 393−399.
(10) Peng, H.; Wang, N.; Hu, Z. R.; Yu, Z. P.; Liu, Y. H.; Zhang, J. S.; Ruan, R. Physicochemical characterization of hemicelluloses from bamboo (*Phyllostachys pubescens* Mazel) stem. *Ind. Crops Prod.* **2012**, *37* (1), 41−50.
(11) Wen, J. L.; Xiao, L. P.; Sun, Y. C.; Sun, S. N.; Xu, F.; Sun, R. C.; Zhang, X. L. Comparative study of alkali-soluble hemicelluloses isolated from bamboo (*Bambusa rigida*). *Carbohydr. Res.* **2011**, *346* (1), 111−120.
(12) Shi, Z. J.; Xiao, L. P.; Deng, J.; Yang, H. Y.; Song, X. L.; Sun, R. C. Isolation and structural exploration of hemicelluloses from the largest bamboo species: *Dendrocalamus sinicus*. *BioResources* **2013**, *8* (4), 5036−5050.
(13) Wen, J. L.; Sun, S. L.; Xue, B. L.; Sun, R. C. Quantitative structural characterization of the lignins from the stem and pith of bamboo (*Phyllostachys pubescens*). *Holzforschung* **2013**, *67* (6), 613−627.
(14) Shi, Z. J.; Xiao, L. P.; Deng, J.; Sun, R. C. Isolation and structural characterization of lignin polymer from *Dendrocalamus sinicus*. *Bioenergy Res.* **2013**, *6* (4), 1212−1222.
(15) Sun, S. N.; Li, M. F.; Yuan, T. Q.; Xu, F.; Sun, R. C. Sequential extractions and structural characterization of lignin with ethanol and alkali from bamboo (*Neosinocalamus affinis*). *Ind. Crops Prod.* **2012**, *37* (1), 51−60.
(16) Zheng, J. S.; Cao, Y. H.; Xiao, S. P.; Chen, C. J.; Dai, Q. L. Study on the biomass models for different organs of *Pseudosasa amabilis*. *J. Bamboo Res.* **2001**, *20* (4), 67−71.
(17) Li, Q. On the relation between internode length and fiber length of *Pseudosasa amabilis* and *Bambusa pervariabilis*. *J. Bamboo Res.* **1984**, *3* (1), 89−94.
(18) Xiao, S. P. Research on bamboo growth regularity of *Pseudosasa amabilis* McCl. *J. Bamboo Res.* **2001**, *20* (4), 61−66.
(19) Chen, D.; Su, J. D.; Lin, L. N.; Zhang, R.; Zheng, W. P. Preliminary study on the growth law of *Pseudosasa amabilis* bamboo rhizome. *J. Fujian For. Sci. Technol.* **2002**, *29* (2), 37−39.

DOI: 10.1021/acs.energyfuels.5b00385
Energy Fuels 2015, 29, 2408−2415

(20) Dai, Q. L. *Studies on the High-Yield Techniques and Biological Characters of Pseudosasa amabilis McCl*; Fujian Agriculture and Forestry University: Fuzhou, China, 2002.

(21) Lin, J. X.; He, X. Q.; Hu, Y. X.; Kuang, T. Y.; Ceulemans, R. Lignification and lignin heterogeneity for various age classes of bamboo (*Phyllostachys pubescens*) stems. *Physiol. Plant.* **2002**, *114* (2), 296−302.

(22) Zhang, Q. S.; Guan, M. J.; jI, W. L. Variation of Moso bamboo chemical compositions during mature growing period. *J. Nanjing For. Univ., Nat. Sci. Ed.* **2002**, *29* (2), 4.

(23) Li, X. B.; Shupe, T. R.; Peter, G. F.; Hse, C. Y.; Eberhardt, T. L. Chemical changes with maturation of the bamboo species *Phyllostachys pubescens*. *J. Trop. Sci.* **2007**, *19* (1), 6−12.

(24) Li, Y. F.; Zhou, G. M.; Jiang, P. K.; Wu, J. S.; Lin, L. Carbon accumulation and carbon forms in tissues during the growth of young bamboo (*Phyllostachy pubescens*). *Bot. Rev.* **2011**, *77* (3), 278−286.

(25) Liu, S. G.; Zhang, Y. P.; Gao, H.; Wu, B.; Gong, X. X.; Zeng, H. Y. Evaluation of soil environment quality of paddy field in Jiangdu district of Yangzhou city. *Chin. Agric. Sci. Bull.* **2014**, *30* (32), 201−208.

(26) Liao, Q. L.; Liu, C.; Jin, Y.; Hua, M.; Zheng, L. C.; Pan, Y. M.; Huang, S. S. On geochemical regionalization of soils in Jiangsu. *J. Geol.* **2011**, *35* (3), 225−235.

(27) Shi, S. L.; He, F. W. *Analysis and Detection of Pulp and Paper*; China Light Industry Press: Beijing, China, 2003.

(28) Segal, L.; Creely, J. J.; Martin, A. E.; Conrad, C. M. An empirical method for estimating the degree of crystallinity of native cellulose using the X-ray diffractometer. *Text. Res. J.* **1959**, *29*, 786−794.

(29) Bech, N.; Jensen, P. A.; Dam-Johansen, K. Determining the elemental composition of fuels by bomb calorimetry and the inverse correlation of HHV with elemental composition. *Biomass Bioenergy* **2009**, *33* (3), 534−537.

(30) Liese, W.; Weiner, G. Ageing of bamboo culms. A review. *Wood Sci. Technol.* **1996**, *30* (2), 77−89.

(31) Xu, Y.; Wong, M. H.; Yang, J. L.; Ye, Z. Q.; Jiang, P. K.; Zheng, S. J. Dynamics of carbon accumulation during the fast growth period of bamboo plant. *Bot. Rev.* **2011**, *77* (3), 287−295.

(32) Yun, H.; Tu, D. Y.; Ou, L. F.; Guo, Q. Guangdong *Pseudosasa amabilis* performance analysis and its development and utilization. *For. Mach. Woodwork. Equip.* **2013**, *41* (9), 14−16.

(33) Hall, M.; Bansal, P.; Lee, J. H.; Realff, M. J.; Bommarius, A. S. Cellulose crystallinity—A key predictor of the enzymatic hydrolysis rate. *FEBS J.* **2010**, *277* (6), 1571−1582.

(34) Sun, C. Z.; Xie, G. E.; Ruan, X. G.; Yin, S. C. Studies on the relative crystallinity in the wood cellulose of *Pinus massoniana*. *Sci. Silvae Sin.* **1984**, *20*, 290−298.

(35) Zhang, X. L.; Wang, L. H.; Gao, S. Crystallinity of healthy and rotten wood of several tree species in Xiaoxing'an Mountain. *J. Northeast For. Univ. (Chin. Ed.)* **2010**, *38*, 83−84.

(36) Demirbas, T.; Demirbas, C. Fuel properties of wood species. *Energy Sources, Part A* **2009**, *31* (16), 1464−1472.

(37) Jenkins, B. M.; Baxter, L. L.; Miles, T. R.; Miles, T. R. Combustion properties of biomass. *Fuel Process. Technol.* **1998**, *54* (1−3), 17−46.

(38) Demirbas, A. Combustion characteristics of different biomass fuels. *Prog. Energy Combust. Sci.* **2004**, *30* (2), 219−230.

(39) Protasio, T. D.; Bufalino, L.; Tonoli, G. H. D.; Guimaraes, M.; Trugilho, P. F.; Mendes, L. M. Brazilian lignocellulosic wastes for bioenergy production: Characterization and comparison with fossil fuels. *BioResources* **2013**, *8* (1), 1166−1185.

(40) Paul, W. C.; Buchele, W. F. Development of a concentric vortex agri-residue furnace. *Agric. Energy* **1980**, *2*, 349−356.

(41) Ebeling, J. M.; Jenkins, B. M. Physical and chemical properties of biomass fuels. *Trans. ASAE* **1985**, *28* (3), 898−902.

(42) Tillman, D. A. Biomass cofiring: The technology, the experience, the combustion consequences. *Biomass Bioenergy* **2000**, *19* (6), 365−384.

(43) Nordin, A. Chemical elemental characteristics of biomass fuels. *Biomass Bioenergy* **1994**, *6* (5), 339−347.

(44) Ledin, S. Willow wood properties, production and economy. *Biomass Bioenergy* **1996**, *11* (2−3), 75−83.

(45) Demirbas, A. Calculation of higher heating values of biomass fuels. *Fuel* **1997**, *76* (5), 431−434.

(46) Orfao, J. J. M.; Antunes, F. J. A.; Figueiredo, J. L. Pyrolysis kinetics of lignocellulosic materials—Three independent reactions model. *Fuel* **1999**, *78* (3), 349−358.

(47) Wang, Z. H.; McDonald, A. G.; Westerhof, R. J. M.; Kersten, S. R. A.; Cuba-Torres, C. M.; Ha, S.; Pecha, B.; Garcia-Perez, M. Effect of cellulose crystallinity on the formation of a liquid intermediate and on product distribution during pyrolysis. *J. Anal. Appl. Pyrolysis* **2013**, *100*, 56−66.

(48) Hosoya, T.; Kawamoto, H.; Saka, S. Cellulose−hemicellulose and cellulose−lignin interactions in wood pyrolysis at gasification temperature. *J. Anal. Appl. Pyrolysis* **2007**, *80* (1), 118−125.

(49) Butler, E.; Devlin, G.; Meier, D.; McDonnell, K. Characterisation of spruce, salix, miscanthus and wheat straw for pyrolysis applications. *Bioresour. Technol.* **2013**, *131*, 202−209.

DOI: 10.1021/acs.energyfuels.5b00385
Energy Fuels 2015, 29, 2408−2415