*Production and characterization of furanic bio-oil from Kawayan kiling (*Bambusa vulgaris *Schrad ex. Wendl) using molten citric acid in an open system*

JOHN GODWIN A. MALLARI AND RONNIEL D. MANALO

ABSTRACT: The burning of fossil fuels poses many threats to the environment. These predicaments have led to a continuous search for alternative sources and production of energy, and biomass is considered the most abundant renewable energy source.

In this study, the potential to produce furanic bio-oil from the cellulose of *Bambusa vulgaris* was explored. The proximate chemical analysis of bamboo was determined using TAPPI Standards. Cellulose was isolated through dewaxing, delignification, and alkaline treatments. The furanic bio-oil was produced by mixing cellulose and citric acid in a solvent-free environment. The effects of the digestion time (120 min, 180 min, and 240 min) on the yield and characteristics were determined. The chemical compositions were determined using Fourier transform infrared (FTIR) spectroscopy and gas chromatography-mass spectrometry (GCMS).

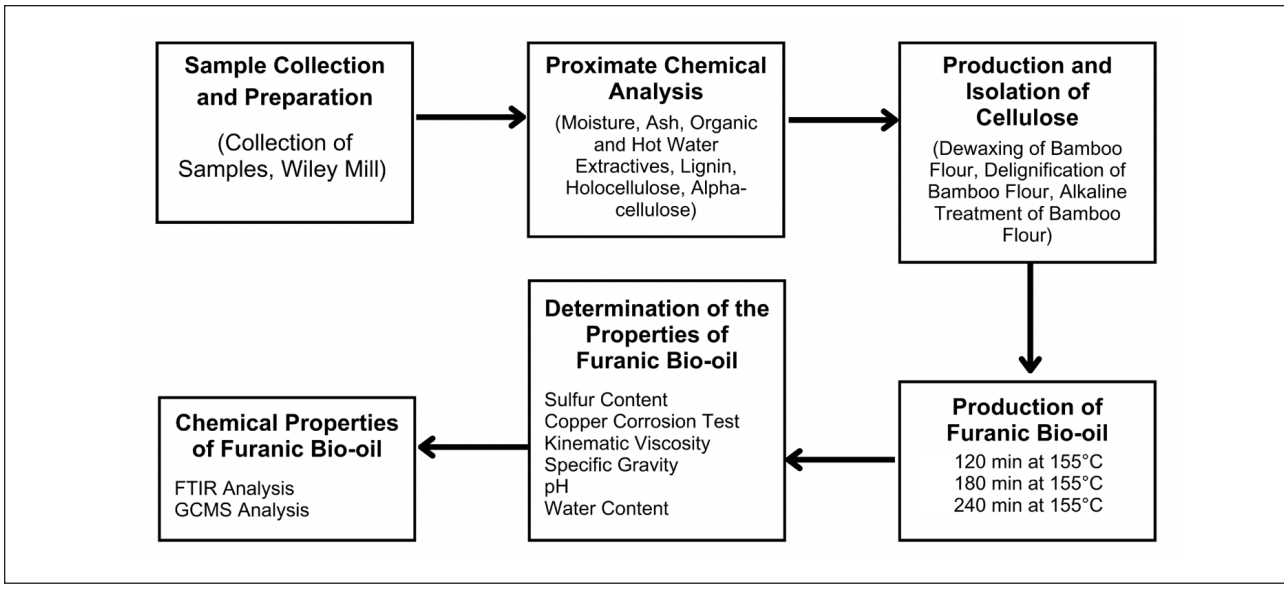
B. vulgaris has the following chemical composition: alpha-cellulose (57.42 ± 0.40), holocellulose (78.84 ± 0.52), lignin (28.85 ± 0.17), hot water extractives (3.99 ± 0.08), organic extractives (0.77 ± 0.04), ash (4.67 ± 0.02), and moisture (12.98 ± 0.22). The bio-oil yield was affected by the digestion time. The highest yield was obtained at 180 min, followed by 120 min, and 240 min with 88.59%, 59.28%, and 49.96%, respectively. The peaks in the FTIR spectra corresponded to the compounds determined by the GCMS analysis. The dominant chemicals were furans (29.19%), ketones (26.31%), and carboxylic acids (19.26%). The bio-oil obtained at 180-min digestion time has the following properties: sulfur content (0.032 wt%), kinematic viscosity (1.03 mm^2/s), specific gravity (0.925), copper corrosion test (No. 1a), pH (2.753), and water content (not detected). Overall, the obtained values from the properties and chemical characterization can be the basis for investigating its performance for biofuel production and utilization. This study is aligned with the Bamboo Industry's Strategic Science and Technology Plan for the Philippines to develop other value-added products from bamboo and to achieve Sustainable Development Goal 7 (SDG 7) as determined by the United Nations.

Application: This study explores the production of furanic bio-oil using a relatively new process. It offers an alternative option that uses readily available chemicals and does not require very high energy. This can be replicated in the laboratory and scaled-up. Other biomass can be explored. The product can be used as an alternative or as an additive to fossil fuels once a complete characterization has been done.

The burning of fossil fuels poses many threats to the environment, affecting land, air, and water components [1]. As a result, the demand for alternative renewable energy, i.e., biomass, has increased significantly in past years [2]. The biomass energy can be in the form of bioethanol, biodiesel, and bio-oil [1-3]. Bio-oil production is pivotal, as this liquid synthetic fuel can be a source of valuable chemicals. The most commonly used method for extracting bio-oil is pyrolysis [4]. However, its scalability is hampered by high energy costs due to elevated temperature requirements. In addition, it produces lots of by-products, including biochar, gas, and tar.

To address the shortcomings of pyrolysis, new methods are being introduced, one of which is the use of molten citric acid [5]. This method does not utilize potent inorganic compounds and does not require harsh conditions. Moreover, no by-products are formed [6]. Through this system, the use of Bronsted acid allows the conversion of cellulosic materials into furan-based compounds. The furan-based compounds are useful in industry, specifically for the production of biofuels, adsorbents, coatings, bio-pesticides, and polymers [4]. Furanic compounds can be manipulated or directly used for crucial processes. For instance, the dehydration of C6 carbohydrates can form 5-hydroxymethylfurfural (HMF) [7]. The HMF is considered a vital biorefinery building block, since this compound is crucial for synthesizing several valuable chemical intermediates and liquid fuels [5,6].

Given these advantages, this new process has gained interest in recent years [5]. Previous studies focused on the production of furanic bio-oil from timber biomass, grass biomass, agricultural residues, and some algae. Specifi-



1. Schematic diagram of the production, extraction, and characterization of furanic bio-oil from bamboo (FTIR: Fourier transform infrared [spectroscopy]; GCMS: gas chromatography-mass spectrometry).

cally, sugarcane bagasse, softwood and hardwood species (i.e., pine and maple), and rice straw were common feedstocks used to produce and characterize furanic bio-oil [8,9]. The production of furanic bio-oil from bamboo using an open system in a solvent-free environment has yet to be studied, and the application of furanic bio-oil from bamboo is limited. There are approximately 1400 species of bamboo in the world [10]. Bamboos are fast-growing and can be harvested after 3–5 years.

To achieve the full potential of furanic bio-oil, it is important to ascertain the amount and nature of its chemical composition. This will pave the way for the synthesis of various valuable chemical intermediates and liquid fuels that may benefit the petrochemical industry, the transport sector, and other related sectors. The furanic bio-oil extraction from bamboo biomass is aligned with the Bamboo Industry Strategic Science and Technology Plan of the Philippines and is consistent with Sustainable Development Goals (SDGs) of the United Nations.

METHODOLOGY

Figure 1 provides a schematic flow diagram of the methods. The sample preparation, proximate chemical analysis, and production of bio-oil were done at the Department of Forest Products and Paper Science, College of Forestry and Natural Resources, University of the Philippines Los Baños. The characterization of the bio-oil was done in the laboratories of the Standards and Testing Division, Industrial Technology Development Institute (STD, ITDI), Advanced Device and Materials Testing Laboratory (ADMATEL) of the Department of Science and Technology and (DOST), the Energy Research and Laboratory Testing Services of the Department of Energy (ERLTS, DOE), and the Central Instrumentation Facility of the De La Salle University (CIF, DLSU).

Sample collection and preparation

Healthy mature poles of *B. vulgaris* were collected from the Bambusetum located at the Los Baños Experimental Station of the Ecosystem Research and Development Bureau of the Department of Environment and Natural Resources (ERDB-DENR) in the Mt. Makiling Forest Reserve, Los Baños, Laguna, Philippines. The skin and nodes of the bamboo poles were removed. The poles were reduced to chips and were then subjected to hammer milling. The particle size was reduced to powder using a Wiley mill, followed by manual sieving.

Proximate chemical analysis

The amounts of water, ash, cyclohexane-ethanol extractives, hot water extractives, alpha-cellulose, and lignin of *B. vulgaris* were determined following TAPPI Standard Test Methods, as shown in **Table I**. The holocellulose content was measured using a modified chlorite method [11]. The proximate chemical analysis was performed with three replicates.

Production and isolation of cellulose from B. vulgaris

Dewaxing of bamboo flour

Two-hundred grams (200 g) of bamboo flour was weighed and placed into a macro-soxhlet extractor containing 2800 mL cyclohexane-ethanol (2:1 v/v) solution. The extraction ran for 6 h with a constant temperature of 75°C. The dewaxed sample was washed with hot distilled water (dH_2O) several times to remove the organic solvents. It was then dried in the oven set at 70°C for 24 h.

Delignification of bamboo flour

Thirty grams (30 g) of dewaxed bamboo was subjected to 2 h digestion with solvent containing 82.3 g of 35 wt% hy-

Parameter	TAPPI Standard Test Method	Description
Moisture content	T 264 om-07	"Preparation of wood for chemical analysis"
Ash content	T 211 om-02	"Ash in wood, pulp, paper and paperboard: combustion at 525°C"
Organic extractives (cyclohexane-ethanol solubility)	T 204 om-07	"Solvent extractives of wood and pulp"
Hot water extractives	T 207 om-08	"Water solubility of wood and pulp"
Lignin content	T 222 om-02	"Acid-insoluble lignin in wood and pulp"
Alpha-cellulose content	T 203 om-09	"Alpha-, beta- and gamma-cellulose in pulp"

***I. TAPPI Standard Test Methods for proximate chemical analysis of* B. vulgaris.**

drogen peroxide (H_2O_2) and 106.2 g of 99.8 wt% acetic acid (CH_3COOH) with 0.5 grams of titanium (IV) oxide (TiO_2). The temperature was maintained at 130°C. The sample was washed with methanol until the filtrate became colorless. It was then dried in an oven set at 70°C for 24 h.

Alkaline treatment of bamboo flour

The sample was then digested with 300 mL of 6 wt% sodium hydroxide (NaOH). The mixture was heated at 80°C for 2 h with constant stirring. The digestion continued for another 6 h without heat. The sample was filtered and washed with dH_2O via suction filtration and was air-dried for 36 h.

Production of furanic bio-oil

Equivalent amounts (5 g) of alkali-treated cellulose and citric acid were mixed in a large test tube. This was done in triplicates. The samples were heated in a hot oil bath set at 155°C at varying reaction times (120 min, 180 min, and 240 min). After each cooking time, 60 mL of acetone was added. The suspended particles were filtered using a sintered glass. An additional 60 mL of acetone was used to wash the citrated cellulose. The volume of the collected liquid was reduced in a rotary evaporator to collect the furanic bio-oil. The furanic bio-oil yield was calculated using the following equation:

$$\frac{Vol_{oil}}{m_{cellulose}+m_{CA}} \quad (1)$$

where Vol_{oil} is the amount of furanic bio-oil (mL); $m_{cellulose}$ is the mass of cellulose (g); and m_{CA} is the mass of citric acid (g).

Determination of furanic bio-oil properties

The effects of the digestion time on the properties of furanic bio-oil were determined. The tests included copper corrosion, kinematic viscosity, specific gravity, pH, and water content. The values were compared with published literature that used pyrolysis.

Copper corrosion test

The produced furanic bio-oil was subjected to this laboratory analysis to determine its corrosiveness for 3 h at 40°C. The test method followed ASTM D130 "Standard test method for corrosiveness to copper from petroleum products by copper strip test" by immersing the polished copper strip into a 100 mL furanic bio-oil and heating it to 50°C for 3 h. The appearance of the color and tarnish of the copper strip was assessed based on the copper strip classification for petroleum products, as may be seen in **Table II**.

Kinematic viscosity

The viscosity value of the produced furanic bio-oil was determined following ASTM D445 "Standard test method for kinematic viscosity of transparent and opaque liquids (and calculation of dynamic viscosity)." The sample (200 mL) was flown under gravity through the capillary of a calibrated viscometer under a reproducible driving head at 40°C.

Specific gravity

The specific gravity was measured following the ASTM D1298 "Standard test method for density, relative density, or API gravity of crude petroleum and liquid petroleum products by hydrometer method." A 500 mL sample was brought to a specified temperature of 15°C and the test portion was transferred to a hydrometer cylinder with the same temperature. The hydrometer and thermometer are lowered, and once the equilibrium is reached, the hydrometer scale is read, as well as the temperature.

pH value

The pH value was measured using a pH probe with a digital meter with a calibrated temperature of 29°C.

Sulfur content

The sulfur content was measured using ASTM D7039 "Standard test method for sulfur in gasoline, diesel fuel, jet fuel, kerosine, biodiesel, biodiesel blends, and gasoline-ethanol blends by monochromatic wavelength dispersive X-ray flu-

Classification	Designation	Description
Freshly Polished Strip		
1	Slight tarnish	a. Light orange, almost the same as a freshly polished strip b. Dark orange
2	Moderate tarnish	a. Claret red
	...	b. Lavender
	...	c. Multicolored with lavender blue or silver, or both, overlaid on claret red
	...	d. Silvery
	...	e. Brassy or gold
3	Dark tarnish	a. Magenta overcast on brassy strip
	...	b. Multicolored with red and green showing (peacock), but no gray
4	Corrosion	a. Transparent black, dark gray, or brown with peacock green barely showing
	...	b. Graphite or lusterless black
	...	c. Glossy or jet black

II. Copper strip classification for petroleum products.

orescence spectrometry," wherein a small amount of furanic bio-oil was taken. The sample was subjected to monochromatic, wavelength-dispersive X-ray fluorescence (MWDXRF) spectroscopy to determine the amount of sulfur in parts per million (ppm).

Water content

The water content of furanic bio-oil was determined using ASTM E203 "Standard test method for water using volumetric Karl Fischer titration." The sample was subjected to volumetric Karl Fischer titration to measure the free water and water of hydration in the furanic bio-oil.

Determination of furanic bio-oil chemical composition

The chemical composition of furanic bio-oil was determined using Fourier transform infrared (FTIR) spectroscopy and gas chromatography-mass spectrometry (GCMS) analysis. For FTIR, all of the samples were subjected to testing. The spectra were identified using the PerkinElmer Frontier FTIR spectrometer (PerkinElmer; Waltham, MA, USA) equipped with attenuated total reflectance (ATR). The absorption frequency spectra range from 4000 cm^{-1} to 600 cm^{-1} with 20 scans. The identity of the peaks was determined using published references.

Only the treatment that had the highest yield was subjected to GCMS analysis using an Agilent 8890 gas chromatograph (GC) system (Agilent Technologies; Santa Clara, CA, USA) coupled to an Agilent 5977B mass selective detector (MSD). The column used was an Agilent HP-5MS column with a length of 30 m, inner diameter of 0.25 mm, and film thickness of 0.25 µm. Helium gas (99.99%) was used as the carrier gas at a constant flow rate of 1 mL/min. The over-temperature was programmed from 35°C to 300°C at a heating rate of 25°C/min from 35°C to 125°C, and 7°C/min from 125°C to 300°C. The following operational conditions were used: MS ionization mode of 70 eV, acquisition mode through scanning, and mass range of 30 amu to 500 amu. The data processing and identification of peaks were done using an Agilent MassHunter Qualitative Analysis 10.00 and the NIST MS Search v2.3 database (National Institute of Standards and Technology; Gaithersburg, MD, USA), respectively.

RESULTS AND DISCUSSION

Proximate chemical analysis

The proximate chemical composition of *B. vulgaris* is presented in **Table III**.

Moisture content

B. vulgaris has an average moisture content of 12.73%. The typical %MC in tropical countries is between 10% and 15% [12]. The varying values can be attributed to the hygroscopicity of the material. The innate variability between samples of the same species can be attributed to the growth characteristics, weather conditions, and humidity in the area as well as the portion where the samples were obtained [13,14].

Ash content

The amount of inorganic components of *B. vulgaris* was 4.67%. This is higher than the value reported in [15] at 2.4%. In the same report, it was mentioned that *B. vulgaris* has the lowest percentage ash in comparison with other bam-

Chemical Composition	Average Values, %
Moisture content	12.98 ± 0.22
Ash content	4.67 ± 0.02
Organic extractives	0.77 ± 0.04
Hot water extractives	3.99 ± 0.08
Lignin content	28.85 ± 0.17
Holocellulose content	78.84 ± 0.52
Alpha-cellulose content	57.42 ± 0.40

***III. The proximate chemical composition of* B. vulgaris.**

boo species grown in the Philippines. The ash content may vary with the height of the bamboo pole and the season when it was collected. The typical minerals contained in the ash are calcium, potassium, sodium, magnesium, manganese, and phosphorus.

Extractives content

The amounts of cyclohexane-ethanol- and water-extractable materials were 0.77% and 3.99%, respectively. The values obtained were lower compared to those reported in other research [16,17]. The low organic extractive content indicates that the bamboo culm had fewer organic substances, such as phenolics, and flavonoids, while the higher value for water-soluble extractives indicates *B. vulgaris* had more tannins, gums, low molecular weight carbohydrates, dyes, and starch [16]. The organic extractives of *B. vulgaris* range from 0% to 5%, depending on the conditions of species, age, climate, and harvesting time [14,16]. The chemical composition of cell wall structures influences organic extractives, since bamboo fibers are suspended in a soft matrix mostly consisting of lignin and hemicelluloses.

Lignin content

B. vulgaris contains 28.85% lignin, which is higher compared to other research [15,16]. The variation in lignin content is attributed to the maturity of the bamboo and the portion of the bamboo sample. At a young age, the amount of bamboo decreases from bottom to top, which is reversed for mature ones [16,17]. Moreover, the top portion has a thicker middle lamella layer where the highest concentration of lignin can be found [18].

Holocellulose content

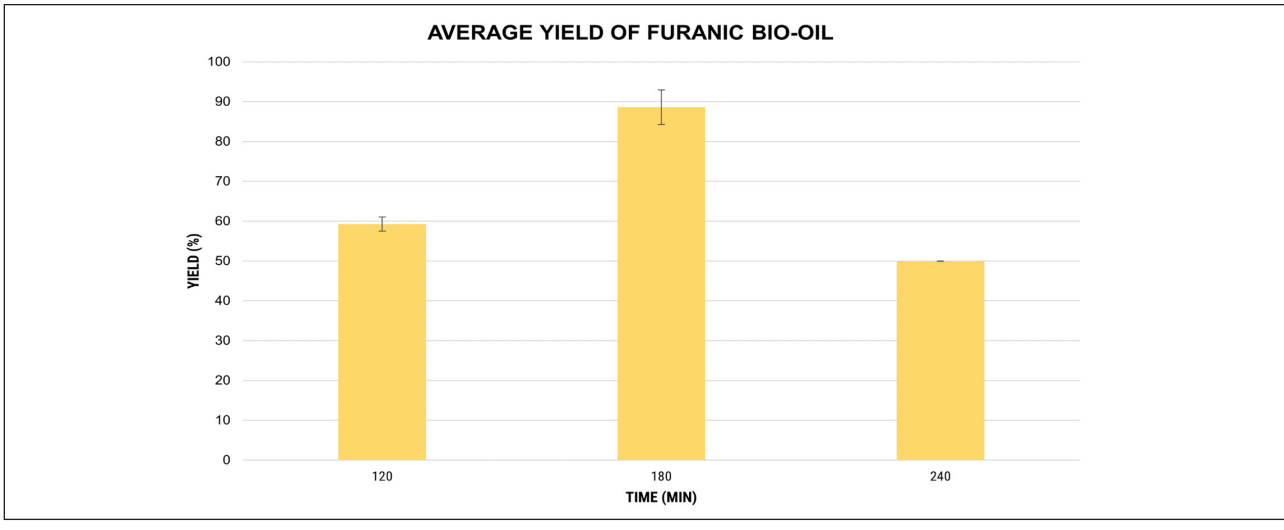
The amount of holocellulose in *B. vulgaris* was 78.84%. As with the other chemical components, the amount of holocellulose varies with the age and the portion of the bamboo sample. The top portion of young bamboo showed the highest percentage of holocellulose while the lowest percentage was at the top of mature bamboo [16]. This can be attributed to the anatomical structure of the top portion of young *B. vulgaris* that may have thickened the S1 layer from the secondary wall and is rich in sugar content on vascular bundles compared to the other portion, which is believed to have contained lots of holocellulose [16,19].

Alpha-cellulose content

The amount of alpha-cellulose obtained from *B. vulgaris* was 57.42%. This accounts for 78.84% of the total holocellulose content. The amount of alpha-cellulose in mature *B. vulgaris* was reported to be higher than in young ones at 58.50% and 52.93%, respectively [16]. In young *B. vulgaris*, alpha-cellulose increases with height while the highest value is at the middle portion in mature poles. It may be due to the anatomical structure, whereby the middle portion of mature age from *B. vulgaris* had a larger fiber size and length in the culm of the bamboo species [16,19].

Yield of furanic bio-oil

The amount of furanic bio-oil produced was affected by



2. Average yield of furanic bio-oil with corresponding standard error.

Parameters, unit	Furanic Bio-oil		
	120 min	180 min	240 min
S, wt%	0.033	0.032	0.032
Kinematic viscosity at 40°C, mm²/s	0.367	1.03	0.368
Specific gravity at 15°C	0.794	0.925	0.794
Copper corrosion test at 50°C for 3 h	No. 1a*	No. 1a*	No. 1a*
pH value	2.75	2.753	2.76
Water content	Not detected	Not detected	Not detected
*Light orange (see Table II, No. 1a); almost the same as freshly polished strip.			

IV. Properties of furanic bio-oil.

the length of time the cellulose was digested with citric acid, as shown in **Fig. 2**. The highest amount of furanic bio-oil was obtained from cellulose digested for 180 min followed by 120 min and 240 min at 88.59%, 59.28%, and 49.96%, respectively. The results were similar to the work of other researchers [5]. At 180 min, most of the cellulose has been depolymerized into glucose units and further dehydrated into furans. This was not achieved at 120 min since the cooking time was enough to break down the cellulose into glucose units. However, the yield declined after 180 min due to significant oxidation occurring within the furan-based compounds. The prolonged cooking time increased the oxidation and volatility of the furanic compounds, leading to the uncontrolled decomposition of organic compounds [5,20,21].

Furanic bio-oil is produced following the principles of hydrolysis and esterification. Cellulose hydrolysis occurs due to citric acid interacting with the glycosidic bonds of the cellulose chains and the oxygen in the pyranose rings [5]. The isolated cellulose is depolymerized to glucose units with the help of traces of water and the acids present in the carboxylic groups of citric acid. Furthermore, the traces of water present in the reaction are due to the open system conditions of the setup [5]. Once the glucose is formed, it reduces quickly due to the open system condition mechanism by losing three molecules of water, producing furan-rich bio-oil.

Once the furan-rich compound is produced, this can initiate a sequence of oxidation reactions that produce other furan compounds. The formation of moieties in carboxylic acids during the oxidation to furan compounds is confirmed by measuring the pH value of the compounds.

Properties of furanic bio-oil

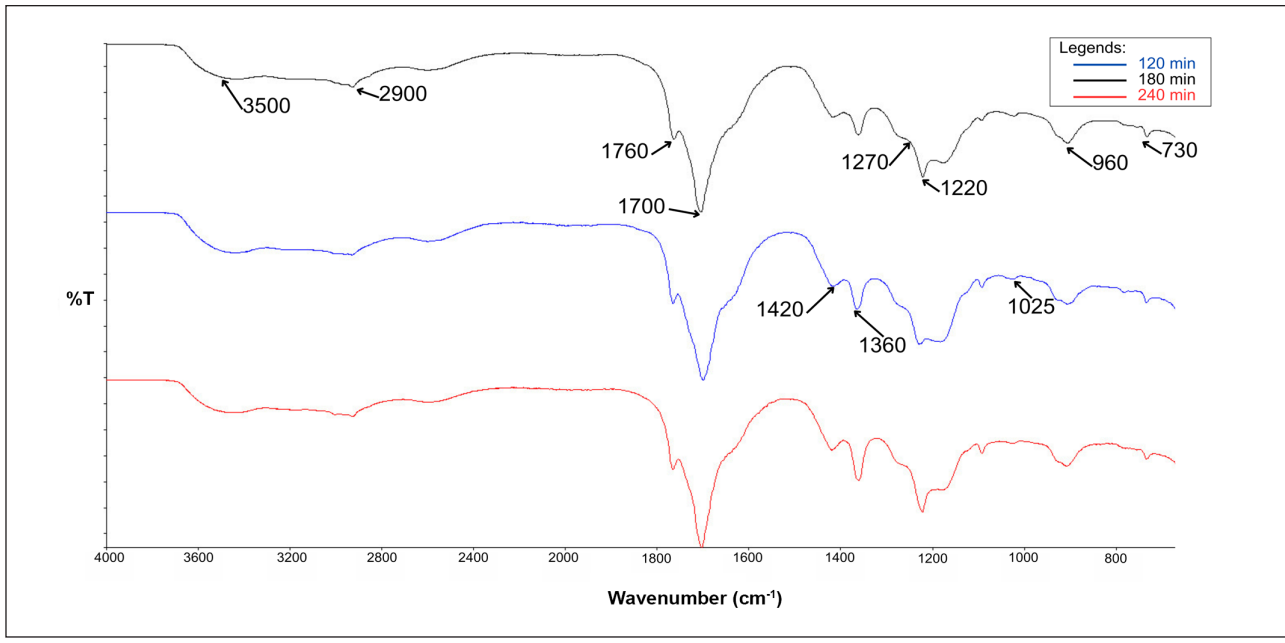
The properties of furanic bio-oil are presented in **Table IV**. The furanic bio-oil obtained at 180-min digestion time had the highest kinematic viscosity at 1.03 mm²/s. This was significantly higher than those produced at 120 min and 240 min at 0.367 mm²/s and 0.368 mm²/s, respectively. Compared with other species, the obtained values were lower. The kinematic viscosity of oil produced from thorny bamboo and long-branch bamboo via pyrolysis were 8.72 mm²/s and 7.52 mm²/s, respectively. The values for bamboo, however, were lower than that of rice husk at 13.2 mm²/s [22]. Kinematic viscosity is the ability of the liquid to resist when flowing. Lower kinematic viscosity values could improve fuel economy, since it would reduce greenhouse gas emissions [23]. Therefore, using furan-based bio-oil from bamboo would be more efficient and environmentally friendly.

The bio-oil produced after 180 min had a specific gravity of 0.925. This is higher compared to the ones produced at 120 min and 240 min at identical values of 0.794. In comparison, pyrolyzed bio-oil from thorny bamboo and long-branch bamboo were higher at 1.14 and 1.13, respectively. The specific gravity of bio-oil from rice husk is 1.14 [22].

In contrast to the commercially available diesel produced in the market, the achieved value for the 180-min furanic bio-oil is comparatively higher. Reported specific gravity values of the commercial automotive No. 2 diesel range from 0.820 to 0.860 [24]. The specific gravity indicates the energy value of the oil. Based on the values obtained, furan-based bio-oil has higher energy capacity compared to conventional fuels [25].

The sulfur concentration of furanic bio-oil ranged from 0.032% to 0.033%, which is similar to the findings obtained from the rice husks at 0.03% [22]. A lower concentration of sulfur imposes a positive trait since the sulfur content indicates the approximate amount of hazardous sulfur dioxide during the combustion process [22,25,26].

No water was detected in the produced bio-oil, regardless of the digestion time. In comparison, the water content of bio-oil obtained from pyrolysis of thorny bamboo, long-branch bamboo, and rice husk were 40.4%, 37.0%, and 28.0%, respectively [22]. The furanic bio-oil produced does not contain any moisture due to the nature of the process employed. Note that the process involved a solvent-free condition. Water content in furanic bio-oil can be attributed



3. The FTIR spectra of furanic bio-oil at different reaction times.

to the moisture of the biomass used and the method applied during the process of extraction [25].

The presence of water in bio-oil can form a separate layer of the aqueous phase and organic phase, which causes problems for its application in industry [27]. Moreover, higher moisture content in biofuel or biodiesel can impose severe problems in its application, such as the accumulation and growth of microorganisms in fuel tanks and transportation equipment [25,27,28].

All the bio-oil produced at different digestion times received a remark of No. 1a based on the copper corrosion test. This means that it can cause a slight tarnish to metal. In terms of the color appearance, a light orange was specified, which correlates to a freshly polished copper strip. The extracted furanic bio-oil is classified as non-corrosive as compared to other biodiesel or biofuel produced in the market. Biofuels can have drawbacks, as these products can cause metallic corrosion in some parts of the engine, such as fuel pumps, filter lines, and injectors [29]. The corrosion of metal can be due to sulfur content, amount of water, and degree of acidity [30,31].

No significant differences were observed in the pH of the furanic bio-oils at ~2.75. The pH value of the furan-based bio-oil can be influenced by various factors, such as the type of biomass used and the type of solvent used to extract the bio-oil [25]. The acidity of bio-oil can be reduced through the conversion of acids into esters through the process of esterification [31].

Chemical composition of furanic bio-oil

The chemical characterization of bio-oil is essential for the identification of important chemicals that can be the basis for further studies of furanic bio-oil.

Fourier transform infrared spectroscopy analysis

The IR spectra of furan-based bio-oil are summarized in **Fig. 3**. The peak assignments for the infrared spectra are summarized in **Table V**. The FTIR analysis is an analytical technique used in the characterization of functional groups in the bio-oil. The broad band of furan-based bio-oil between 3550 cm^{-1} and 3000 cm^{-1} denotes the presence of carboxylic acid due to the presence of COO-H stretching. On the other hand, the frequency range at 3000 cm^{-1} and 2840 cm^{-1} specifies the possibility of having carboxylic acid and alkane compounds with COO-H stretch and C-H stretch, respectively.

Frequency ranges from 2840 cm^{-1} and 2500 cm^{-1}, 1800 cm^{-1} and 1650 cm^{-1}, 1440 cm^{-1} and 1210 cm^{-1}, and 906 cm^{-1} and 880 cm^{-1} show the possible presence of carboxylic acid, aldehydes, and ketones, with the identified bonds of COO-H stretch, C=O stretch, and OC-OH stretch/C-OH stretch. Intense peaks were observed at 1700 cm^{-1} and 1760 cm^{-1} [5,32].

The peaks at 1220 cm^{-1} and 960 cm^{-1} and the range of 770 cm^{-1} and 720 cm^{-1} indicate the presence of alkanes with C-H skeletal vibrations. Furans may be present, as indicated by the peak at 960 cm^{-1} and 730 cm^{-1} and the peak at 1220 cm^{-1} and 1025 cm^{-1}, which correspond to C-H bending vibrations and =C-O-C= stretching vibrations in the furan ring, respectively [5,32].

As the reaction time increases, the IR spectra of bio-oil show interesting changes. Peaks at 1220 cm^{-1} at 180-min and 240-min are sharper and more intense peaks compared to the 120-min reaction time. The same can be observed at 1720 cm^{-1}. The relative increase could indicate stronger carboxylation, esterification, and oxidation, similar to the findings of other researchers [5,21].

Frequencies, cm^{-1}				Structure/Compound Type	Bonds
Standard Group Frequencies	Furanic Bio-oil				
	120 min	180 min	240 min		
3350–3000	3444.03	3425.00	3448.80	Carboxylic acid	COO-H stretch
3000–2840	2928.57	2928.57	2929.75	Carboxylic acid	COO-H stretch
				Alkane	C-H stretch
2840–2500	2603.57	2603.57	2603.57	Carboxylic acid, Ketones, Furans	COO-H stretch
1800–1650	1764.31	1763.14	1764.58		C=O stretch
	1699.22	1705.61	1703.55		
1440–1210	1417.19	1416.80	1418.86		OC-OH stretch/C-OH bend
	1363.99	1361.68	1361.74		
	1274.14	1272.35	1274.14		
	1227.77	1221.07	1223.57		
1210–960	1188.53	1177.83	1177.83	Furans, Alkane	C-H skeletal vibration
	1092.70	1094.01	1092.48		
	1028.02	1024.45	1026.24		
960–880	910.65	908.10	910.73	Carboxylic acid, Furans	OC-OH bend
770–720	734.20	733.27	733.96	Alkane, Furans	C-H skeletal vibration

V. Peak assignments in the infrared spectra of furanic bio-oil.

Gas chromatography-mass spectrometry analysis

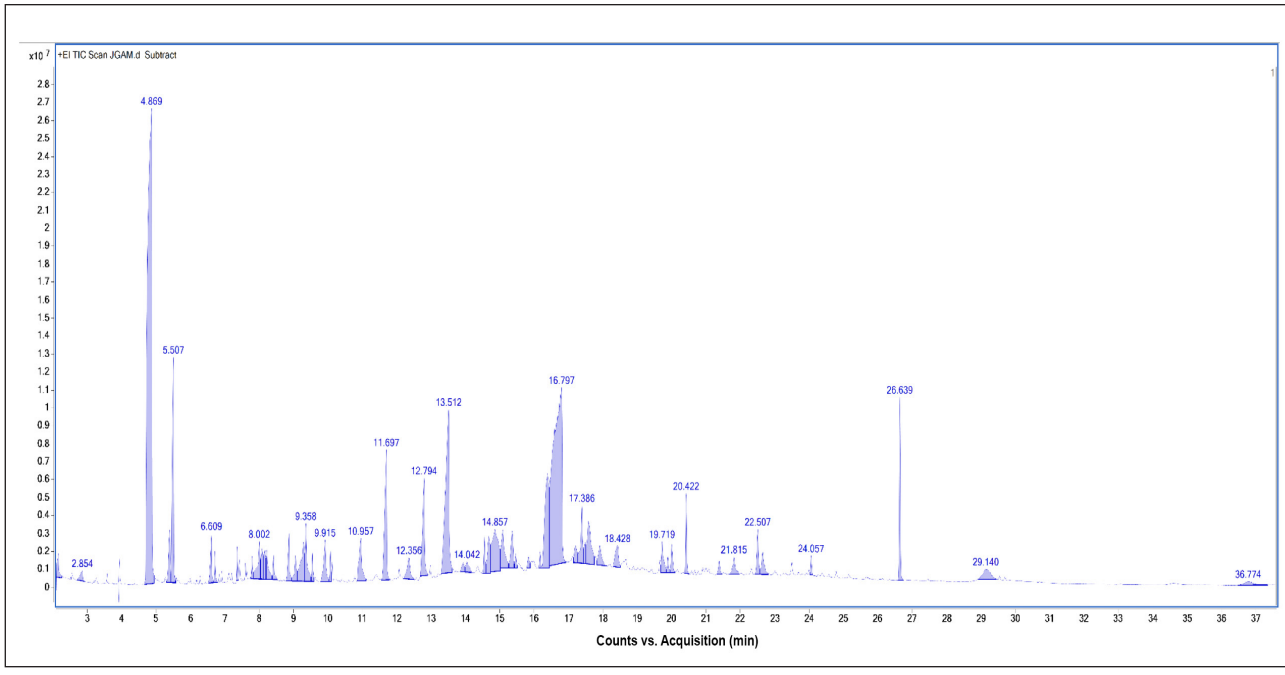
The GCMS was used to determine the relative composition of organic compounds in the bio-oil produced at 180 min. Over 70 compounds were detected in the mass spectrometry (**Table VI**). The major compounds are furans, ketones, and carboxylic acids at 28.19%, 26.31%, and 19.26%, respectively (**Fig. 4**).

The high concentration of furan compounds can be attributed to the polymerization brought about by citric acid acting as a Bronsted catalyst coupled with prolonged reaction time [32]. During the digestion process, cellulose was depolymerized to glucose units by traces of water and acidic carboxylic groups. This was followed by dehydration. The loss of three molecules of water gives rise to the formation of different furan compounds [5]. The innate structure of furfural causes a high probability of its polymerization. Some of the furanic derivative compounds identified in the furanic bio-oil are 3-methyl-2,5-furandione, dihydro-3-methylene-2,5-furandione, 3-methyl-4-propyl-2,5-furandione, and *trans*-2-(2-pentyl)furan.

Ketonic compounds, on the other hand, were formed due to the presence of acetone used in the extraction of the furanic bio-oil. Derivatives of ketone, i.e., methyl ethyl ke-

No.	Functional Group/ Organic Compound	Relative Composition, %
1	Furans	28.19
2	Ketone	26.31
3	Carboxylic acid	19.26
4	Fatty acids	7.50
5	Ester	6.44
6	Amine	3.87
7	Carbohydrates	2.22
8	Sulfhydryl	1.72
9	Alcohol	1.54
10	Aldehyde	0.95
11	Sesquiterpenoids	0.59
12	Alkyl halides	0.55
13	Acid anhydride	0.32
14	Diazo	0.31
15	Alkane	0.21

VI. The proportions of individual-compound functional groups of the 180-min produced furanic bio-oil.



4. Total ion chromatogram for the 180-min produced furanic bio-oil (*B. vulgaris*) at 300°C.

tones (MEKs), are the main ingredients in fuel production [33]. Some of the ketonic compounds identified in the mass spectrometry are 2-methylidenecyclohexan-1-one, 3-methyl-4-penten-2-one, 4-penten-2-one, 6-methoxy chromanone, and 3-methylene-1-oxaspiro(3.5)nonan-2-one. Carboxylic acid and its derivatives were formed as a result of prolonged reaction time. Once the furan compounds are formed, several of them commence a sequence of consecutive oxidation reactions, leading to the formation of carboxylic moieties [5].

Other organic compounds present in the furanic bio-oil are fatty acids (7.50%), esters (6.44%), amines (3.87%), carbohydrates (2.22%), sulfhydryl (1.72%), alcohol (1.54%), aldehyde (0.95%), sesquiterpenoids (0.59%), alkyl halides (0.55%), acid anhydride (0.32%), diazo (0.31%), and alkane (0.21%).

Differences in the chemical composition of feedstocks and process conditions will result in variations in the relative amounts of compounds formed during digestion. Carboxylic acid, furans, and ketones were identified in various pyrolyzed feedstocks, with average values of 20%, 17%, and 15%, respectively [34]. The relative amounts of ketones, carboxylic acids, and furans in thorny bamboo were 29.51%, 22.59%, and 10.08%, respectively [35]. The same group reported that the proportions of the same compounds in long-branch bamboo were 19.83%, 11.72%, and 8.94%.

CONCLUSION

Bambusa vulgaris contains a relatively high amount of cellulose at 57.82%. The cellulose was digested with citric acid in a solvent-free environment to form bio-oil after washing with acetone. The effects of varying digestion time on the yield and properties of the bio-oil were determined. The highest yield was obtained at 180 min, followed by 120 min and then 240 min at 88.58%, 59.27%, and 49.96%, respectively.

The bio-oil has the following characteristics: sulfur content (0.032% to 0.033%); kinematic viscosity (0.367 mm²/s to 1.03 mm²/s); specific gravity (0.794 to 0.925); pH (2.75 to 2.76); water content (0%); and copper corrosion test rating (No. 1a). The FTIR analysis suggested the presence of carboxylic acids, furans, and ketones, along with aldehydes and alkanes. The GCMS analysis revealed that the dominant compounds in the bio-oil digested at 180 min were furans (29.19%), ketones (26.31%), and carboxylic acids (19.26%).

Due to the presence of these compounds and owing to its properties, furanic bio-oil from *B. vulgaris* produced via citric acid digestion in an open system can be a potential replacement for conventional fuels or as additives in the refining process of petroleum products. **TJ**

ACKNOWLEDGMENTS

The authors would like to acknowledge the Department of Science and Technology-Philippine Council for Industry, Energy, and Emerging Technology Research and Development (DOST-PCIEERD) for the research subsidy provided under the DOST Facilities and Laboratory Access Grant (FLAG) program. Appreciation is expressed to STD, ITDI, ADMATEL, DOE and CIF, DLSU for the conduct of various analyses. This study was supported by the Department of Science and Technology, Philippine Council for Agriculture, Aquatic and Natural Resources Research and Development (DOST-PCAARRD) through the project titled "Production, characterization, and potential applications of biodegradable plastic from bamboo."

LITERATURE CITED

1. Cheng, L., Adhikari, S., Wang, Z., et al., *J. Anal. Appl. Pyrolysis* 116: 215(2015). https://doi.org/10.1016/j.jaap.2015.09.008.
2. Ma, Y., Jiang, J., Tan, W., et al., *BioResources* 11(4): 9520(2016). https://doi.org/10.15376/biores.11.4.9520-9532.
3. Dai, L., Wang, Y., Liu, Y., et al., *Environ. Res.* 182: 108988(2020). https://doi.org/10.1016/j.envres.2019.108988.
4. Park, H.C. and Choi, H.S., *Renewable Energy* 143: 1268(2019). https://doi.org/10.1016/j.renene.2019.05.072.
5. Romeo, I., Olivito, F., Tursi, A., et al., *RSC Adv.* 10(57): 34738(2020). https://doi.org/10.1039/D0RA06542K.
6. Zhao, S., Liu, M., Zhao, L., et al., *Ind. Eng. Chem. Res.* 57(15): 5241(2018). https://doi.org/10.1021/acs.iecr.8b00593.
7. Kohli, K., Prajapati, R., and Sharma, B.K., *Energies* 12(2): 233(2019). https://doi.org/10.3390/en12020233.
8. Wang, Y., Zeng, Z., Tian, X., et al., *Bioresour. Technol.* 269: 162(2018). https://doi.org/10.1016/j.biortech.2018.08.067.
9. Torri, I.D.V., Faccini, C.S., Huff, R., et al., *Bioresour. Technol.* 200: 680(2016). https://doi.org/10.1016/j.biortech.2015.10.086.
10. Yeasmin, L., Ali, M.N., Gantait, S., et al., *3Biotech* 5: 1(2014). https://doi.org/10.1007/s13205-014-0201-5.
11. Erickson, H.D., *Tappi* 45(9): 710(1962).
12. Nunes, L.J.R., Matias, J.C.O., and Catalão, J.P.S, *Torrefaction of Biomass for Energy Applications: From Fundamentals to Industrial Scale*, Elsevier/Academic Press, Cambridge, MA, USA, 2018, pp. 1-43. https://doi.org/10.1016/B978-0-12-809462-4.11001-6.
13. Williams, C.L., Emerson, R.M., and Tumuluru, J.S., "Biomass compositional analysis for conversion to renewable fuels and chemicals," in *Biomass Volume Estimation and Valorization for Energy* (J.S. Tumuluru, Ed.), InTechOpen, Rijeka, Croatia, 2017, Chap. 11. https://doi.org/10.5772/62678.
14. Sreeja Devi, P.S., Jijymol, K.K., Neethu, S., et al., *JABScience* 3(1/2): 15(2016).
15. Semana, J.A., Escolano, J.O., and Mosalud, M.R., *Tappi* 50(8): 416(1967).
16. Sulaiman, M.S., Ramle, S.F.M., Geng, B.J., et al., *Eur. Int. J. Sci. Technol.* 5(9): 27(2016).

ABOUT THIS PAPER

Cite this article as:
Mallari, J.G.A. and Manalo, R.D., *TAPPI J.* 23(8): 419(2024). https://doi.org/10.32964/TJ23.8.419

DOI: https://doi.org/10.32964/TJ23.8.419

ISSN: 0734-1415

Publisher: TAPPI Press

About this journal

ABOUT THE AUTHORS

My (Mallari) fascination with bamboo served as the impetus for this study. Although *B. vulgaris*, like all bamboo species, has diverse applications, I wanted to explore its potential as a source of energy. As I was doing the systematic review, I came across the production of bio-oil. I learned that, aside from pyrolysis, the bio-oil can be produced with the use of a commonly available chemical such as citric acid. The method does not require high amounts of energy and forms less by-products.

The most difficult part of this study was the sourcing of funds both for chemicals that were used, as well for the analyses. I am grateful that I was part of the Forest Bio-Material Research Laboratory, a research group in the department. I also received a grant from the government that funded most of the analyses.

From the results of the study, we found out that bio-oil can be produced by digesting bamboo cellulose with dry citric acid in an open system. The bio-oil was separated by washing with acetone, leaving the residue as citrated cellulose. The yield of bio-oil was affected by the digestion time. The highest amount of bio-oil was obtained at 180 min. The digestion time also affected the properties of the bio-oil. The bio-oil contains furans, ketones, and carboxylic acids.

Given the large amounts of residues/wastes produced from bamboo sawmills, these industries can potentially utilize their wastes and convert them to valuable products, such as bio-oil. The bio-oil can be used as a source of energy. In addition, the bio-oil and its derivatives can serve as precursors for other value-added products. With the method used in the study, it would also be interesting to ascertain the effects of other acids, the ratio of cellulose and acid, the temperature, and other bamboo species on the yield and properties of the bio-oil.

Mallari

Manalo

Mallari is a teaching associate and Manalo is an assistant professor in the College of Forestry and Natural Resources at the University of the Philippines in Los Baños, Laguna, Philippines. Email Mallari at jamallari1@up.edu.ph.

17. Maulana, M.I., Marwanto, M., Nawawi, D.S., et al., *IOP Conf. Ser.: Mater. Sci. Eng.* 935: 012028(2020). https://doi.org/10.1088/1757-899X/935/1/012028.
18. Panshin, A.J. and de Zeeuw, C., *Textbook of Wood Technology*, 4th edn., McGraw-Hill, New York, 1980.
19. Babayemi, J.O., Dauda, K.T., Nwude, D.O., et al., *BioResources* 5(3): 1384(2010). https://doi.org/10.15376/biores.5.3.1384-1392.
20. Zhao, Y., Wang, S., Lin, H., et al., *RSC Adv.* 8(13): 7235(2018). https://doi.org/10.1039/C7RA13387A.
21. Kassanov, B., Wang, J.M., Fu, Y., et al., *RSC Adv.* 7(49): 30755(2017). https://doi.org/10.1039/C7RA05020H.
22. Lu, Q., Yang, X., and Zhu, X., *J. Anal. Appl. Pyrolysis* 82(2): 191(2008). https://doi.org/10.1016/j.jaap.2008.03.003.
23. Sondakh, R.C., Hambali, E., and Indrasti, N.S., *IOP Conf. Ser.: Earth Environ. Sci.* 230: 012071(2019). https://doi.org/10.1088/1755-1315/230/1/012071.
24. Williams, R.N., Pettinen, R., Ziman, P., et al., *Sustainability* 13(14): 7985(2012). https://doi.org/10.3390/su13147985.
25. Ahmad, F., Kalam, M.A., Zhang, Z., et al., *Energy Convers. Manage.: X* 14: 100222(2022). https://doi.org/10.1016/j.ecmx.2022.100222.
26. Yesilyurt, M.K., Cesur, C., Aslan, V., et al., *Renewable Sustainable Energy Rev.* 119: 109574(2020). https://doi.org/10.1016/j.rser.2019.109574.
27. Fregolente, P.B.L., Fregolente, L.V., and Maciel, M.R.W., *J. Chem. Eng. Data* 57(6): 1817(2012). https://doi.org/10.1021/je300279c.
28. He, B., Thompson, J.D., Routt, D.W., et al., *Appl. Eng. Agric.* 23(1): 71(2007). https://doi.org/10.13031/2013.22320.
29. Milano, J., Umar, H., Shamsuddin, A.H., et al., *Front. Energy Res.* 9: 778801(2021). https://doi.org/10.3389/fenrg.2021.778801.
30. Jung, H., Kittelson, D.B., and Zachariah, M.R., *Environ. Sci. Technol.* 40(16): 4949(2006). https://doi.org/10.1021/es0515452.
31. Lian, X., Xue, Y., Zhao, Z., et al., *Int. J. Energy Res.* 41(13): 1798(2017). https://doi.org/10.1002/er.3726.
32. Sokolowska, M., Grzebyta-Nowak, J., Stachowska, E., et al., *RSC Adv.* 13(32): 22234(2023). https://doi.org/10.1039/d3ra03885h.
33. Ahmad, S.F.K., Ali, U.F.M., Isa, K.M., et al., *Clean Energy* 6(2): 297(2022). https://doi.org/10.1093/ce/zkac012.
34. Lyu, G., Wu, S., and Zhang, H., *Front. Energy Res.* 3(28): 1(2015). https://doi.org/10.3389/fenrg.2015.00028.
35. Lin, Y.J., Ho, C.L., and Wu, S.R., *Taiwan J. For. Sci.* 8(4): 203(2011).