A STRATEGY FOR DETERMINING

THE CHEMICAL COMPOSITION OF RICE STRAW

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As rice is the staple food of most Asian countries, rice straw has become one of the largest agricultural wastes in Asia. It has not been subjected to adequate value additions yet. However, it has excellent potential to be converted to valuable materials, as it contains a significant amount of cellulose. Therefore, it would be beneficial in many ways to identify the cellulose yields of straws of different rice varieties. In general, the cellulose content of biomass is determined by wet chemical methods. Though these methods are accurate, they are not convenient to use under industrial conditions. This research work focuses on investigating the potential of thermal analysis as an alternative way to predict cellulose yields. For the study, rice straws of most frequently cultivated traditional Sri Lankan rice varieties: Suwandel and Raththal, as well as technically modified Sri Lankan rice varieties: BG300 and BG352, were selected. The results obtained by the proposed method were validated by an established three-step chemical extraction process.

Keywords: rice straw, cellulose yield, thermal analysis, agricultural industry

INTRODUCTION

Rice is the staple food in many Asian countries. Asian paddy fields account for over 90% of the total global rice cultivation area and that caters to one-half of the world's population.[1,2] Consequently, rice cultivation produces large amounts of agro-waste. Among them, the highest percentage is occupied by rice straw. According to the National Engineering Research and Development Centre of Sri Lanka, 800 GT of rice straw was produced in Sri Lanka in 2018.[3,4] In most cases, the rice straw is either left in the field as uncollected or subjected to open field burning. In 2019, several cities of India experienced a smog that originated from the burning of crop waste, including rice and wheat straw. It might affect nearby countries like Sri Lanka as well.[5,6] It has been reported that toxic emissions from the burning of rice straw result in air pollution, water pollution, soil degradation, and contribute to global warming. Most of these factors ultimately affect human health. Thus, it is high time to find better uses for this large agricultural waste.[7]

Rice straw is lignocellulose biomass that mainly consists of cell wall polymers: lignin, hemicelluloses, and cellulose.[8-10] Cellulose is known as the most abundant natural biopolymer on earth. It can be used as an excellent engineering material in a wide variety of high demand applications, such as the production of bio-composites, food packaging films, papers, and paperboards, *etc*. Further, rice straw is the most abundant source of cellulose out of all agricultural wastes, with approximately 32-47% cellulose content. Hence, the extraction of cellulose could be the right way of adding value to this agro-waste material. Nonetheless, it is vital to estimate the cellulose content of different rice straw varieties to find the types of rice straw that are capable of providing higher cellulose yields.[10-20]

Conventionally, the cellulose content of biomass is determined by wet chemical methods, which involve fractionation of biomass samples and further isolation of purified fractions, followed by quantification using conventional

analytical instruments.[21] Although these methods are accurate and robust, they cannot be used for industrial purposes, as they are costly and time-consuming. Therefore, the focus of this research work has been to utilize thermo-analytical methods and mathematical tools to find out the cellulose content of rice straw as a cost-effective method.

Thermogravimetric analysis (TGA) is a useful tool of quantitative analysis in evaluating compositions of mixtures, especially when the constituents' characteristic thermal decomposition temperature profiles are well separated.[22] However, the accuracy of results is questionable when a material has parallel chemical reactions and constituents with identical mass loss temperature profiles. The chemical composition of rice straw comprises, on average, 30-45% cellulose, 20-25% hemicelluloses, 15-20% lignin, and a number of minor organic and inorganic compounds. It has been reported that some of these constituents' mass temperature profiles are overlapping. Hence, in this study, we investigate a novel thermal analysis technique by introducing modifications to existing techniques, such as the TGA method, to obtain the cellulose composition of straws of different rice varieties.

The accuracy of the above technique was verified by isolating cellulose from the same rice straw varieties through the chemical purification processes mentioned in the literature.[23,24] Since there have been hardly any studies on evaluating and analysing the yields of cellulose from rice straws of various rice varieties, the method was used to evaluate the cellulose content of straws of several varieties of rice grown in Sri Lanka.

For this study, two traditional Sri Lankan rice varieties, Suwandel and Raththal, together with two technically modified varieties, BG300 and BG352, were chosen. The BG varieties are hybrids with some favorable characteristics that the traditional rice varieties lack, such as higher yield potential, improved resistance to pest and disease, *etc.*[25] The chosen traditional rice varieties are cultivated according to conventional methods, while the hybrid BG rice varieties are grown using modern techniques. It is important to notice that there is a significant variation in agronomic, soil, and climatic conditions under which traditional and hybrid varieties are cultivated.[26] Therefore, it is expected to obtain significant differences in the cellulose contents of their straw.

EXPERIMENTAL
Rice straw materials and chemicals

Two types of rice straws, namely, technically modified and traditional rice varieties were selected for this analysis. They were obtained from local sources. The straws of technically modified rice verities: BG300 and BG352 were collected at maturity after harvesting in the 2016 Yala season (from May to end of August) from the Rice Research Center, Batalegoda, Kurunegala, Sri Lanka. The straws of the Raththal variety were gathered at maturity after harvesting in the 2016 Yala season from the Hela Suwaya paddy cultivation area, Padaviya, Anuradhapura, Sri Lanka. Finally, rice straws of Suwandel were obtained at maturity after harvesting in 2016 Yala season from a traditional paddy cultivation area, Kurunegala, Sri Lanka. The main chemicals used for cellulose extraction were toluene (C_6H_5CH3, $\geq99.7\%$, ACS), acetic acid (CH_3COOH, $\geq99.8\%$, ACS) and sulfuric acid (H_2SO_4, 95.0-97.0%, ACS). They were supplied by Sigma-Aldrich. Ethanol (H_3CCH_2OH, Min. 99.85%, ACS), hydrogen peroxide (H_2O_2, 50% (w/v), AR) and potassium hydroxide (KOH, $\geq85.0\%$, GR) were purchased from VWR Chemicals, Glorchem, and MERCK Chemicals, respectively.

Method of cellulose extraction

The details of the wet-chemical methods employed in isolating cellulose from rice straw are described in our previous research publications.[11,27,28] Approximately 200 g of rice straw from each variety was used for this extraction procedure. As an initial step, all foreign matter was sorted and removed from the rice straw. Then, dirt and water-soluble substances in the rice straws were removed by washing with warm distilled water. Air drying was carried out at room temperature for forty-eight hours, followed by oven drying at 60 °C for five hours to remove the moisture in the rice straw (Memmert GmbH, Germany). Then, the purified and dried rice straw was powdered by an Easy Blend grinding machine. After that, ground rice straw powder was subjected to a sieving process, with the use of 250 µm, 150 µm, 106 µm, 75 µm and 53 µm aperture sized sieves. A homogeneous blend of rice straw powder was prepared by mixing rice straw powder retained on the 150 µm, 106 µm, 75 µm and 53 µm aperture sized sieves.

The cellulose extraction process consists of three main steps: namely, dewaxing, delignification and silica and hemicelluloses removal. Rice straw powder (10 g) was introduced into the Soxhlet apparatus with a 2:1 v/v toluene/ethanol (450 mL) mixture and the reaction conditions were set as 400 °C temperature for 15 hours to remove wax, pigments and oils. This process was followed by oven-drying at 55 °C for 24 hours to convert dry mass. Then, measurements related to dewaxed materials were taken.

The dewaxed powder was subjected to the delignification process using a 3:10 v/v H_2O_2/CH_3COOH solution with the solid:liquid ratio of 1:60, g/mL, at 60 °C for 3 hours. H_2SO_4 was added as a catalyst for this reaction. Continuous stirring at 125 rpm was carried out for the extraction mixture. A thermostatically controlled water bath was used to heat the extraction mixture. This extraction process was designed in a flask with volumes two to three times those of the extraction mixtures to prevent oxygen evolution and substantial frothing during the initial stages. A vacuum filtration unit (Whatman 1, Maidstone, Kent, England) was used to remove the insoluble residue. Then, the product was subjected to washing with deionized water until the pH of the filtrate was neutral, followed by a drying process at 60 °C. After that, the content of the delignified rice straw material was calculated. After the delignification process, the product was subjected to a leaching process with 110 mL of 5% KOH at room temperature for 24 hours and then at 90 °C for 2 hours to remove hemicelluloses and silica. Then, the vacuum filtration process was carried out to remove the insoluble residue. The process was followed by washing with deionized water until the pH of the filtrate was neutral, and then it was oven-dried to remove water. Finally, the dry weight of the extracted cellulose was measured and calculated. The same methodology was followed for all four types of rice straw varieties in triplicate.

Characterization of extracted materials
Optical microscopy
An optical microscope (MT, Meiji Techno Co. Ltd., Japan), at 50x magnification, was used to observe the particle size of the rice straw powder samples. Image processing software was used to analyze the particle size distribution of rice straw powder for each variety. The obtained data were statistically analyzed by Math Lab software.

Thermal analysis
Thermal analysis was performed with about 5 mg of rice straw samples, using an SDT Q600 simultaneous thermal analyzer (TA instruments, Delaware, USA) and a heating rate of 10 °C/min, from ambient temperature to 600 °C, under high purity nitrogen atmosphere.

Fourier transform infrared spectroscopy (FTIR)
The samples were mixed with KBr (1:100 w/w) and pressed into pellets. FTIR spectroscopic analysis was performed using a Bruker ALPHA spectrometer (Bruker Corporation, Billerica, MA) under ambient conditions. The spectra were recorded in the transmittance mode, running 128 scans at 4 cm^{-1} resolution over the 4000-600 cm^{-1} range. This analysis was used to confirm the complete removal of non-cellulosic materials and the quality of the extracted cellulose from the four rice straw varieties.

Scanning electron microscopy (SEM)
A scanning electron microscope (EVO 18, Carl Zeiss AG, Germany) was used to examine the microstructural features and surface morphologies of the extracted cellulose materials from locally available rice straw varieties. The test samples were placed on aluminum stubs, fixed with conductive carbon tape and sputtered with gold under vacuum at 10 mA for 90 seconds (Sc7620 sputter coating system). The samples were observed and imaged at 14.5 mm working distance and 20 kV accelerating voltage.

RESULTS AND DISCUSSION
Particle size distribution of rice straw varieties
All four varieties of rice straws were subjected to the same mechanical grinding procedure and the powders obtained were studied using optical microscopes. This method involved spreading rice straw powder on a glass slide randomly to obtain a very thin layer of rice straw powder, followed by optical microscopy imaging.

These micrographs were analyzed using ImageJ image processing software, to obtain the particle size distribution for each rice straw variety, assuming that particle size is proportional to the projected area of the particles. Particle size distributions were fitted to a log normal curve using the Math Lab software. The mean values of particle sizes obtained for BG300, BG352, Suwandel and Ratthal varieties are 345.7±9.1, 346.6±9.2, 331.3±10.4 and 358.1±13.1 μm^2, respectively (Fig. 1).

Slow pyrolysis behavior of rice straw
The presence of two distinguishable stages of rice straw slow pyrolysis can be identified by the visual observation of the DTG thermograms. These two stages of slow pyrolysis of rice straw are illustrated in Figure 2 for the BG300 rice straw variety. These two stages can be elucidated as follows.

Stage I: Drying
Rice straw is hygroscopic.[29] Therefore, during this stage, evaporation of loose surface-bound water and inter-molecularly H-bonded water can be observed. Loss of light volatiles (wax – Stage I) also takes place during this stage.[10,12,30] Generally, this stage runs up to 120 °C.

Stage II: Volatilization
This stage involves the release of major amounts of volatiles from cellulose and hemicelluloses, as well as small amounts of

volatiles from the lignin. Usually, these changes take place at temperatures above 180 °C. From the DTG thermogram, it can be observed that volatilization consists of two visible steps, and a flat tailing section. The lower temperature shoulder represents the decomposition of hemicelluloses, while the higher temperature peak indicates the decomposition of cellulose. The flat tailing section at higher temperatures of the DTG thermogram corresponds to the degradation of lignin.
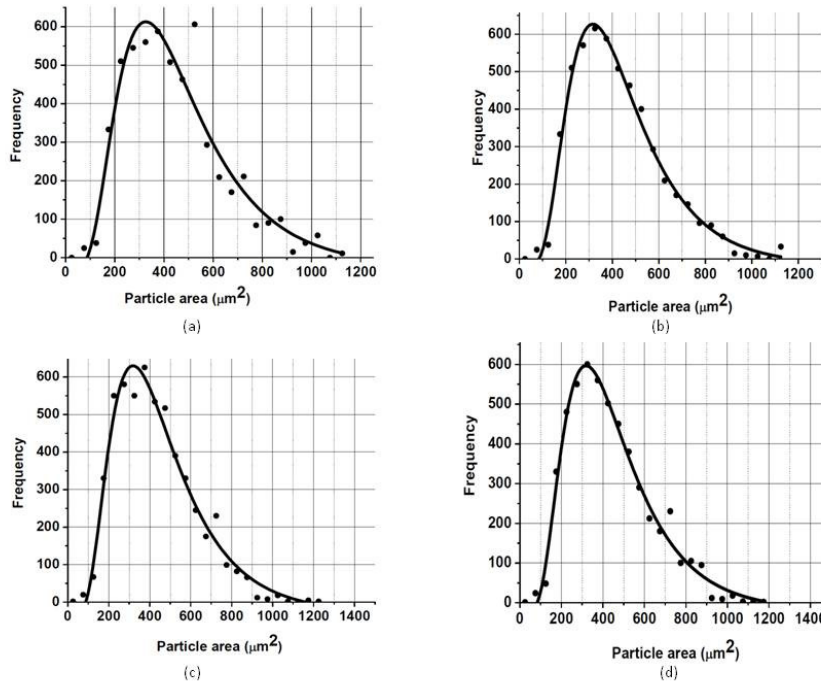

Figure 1: Particle area distribution of rice straw varieties BG 300 (a), BG 352 (b), Raththal (c) and Suwandel (d)
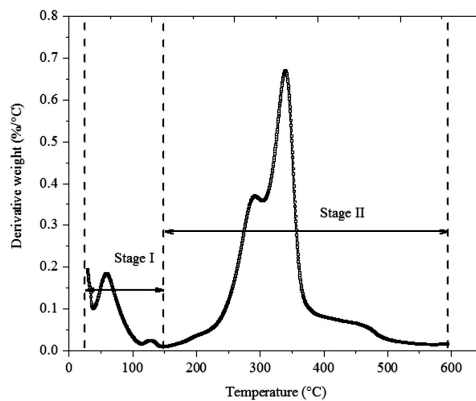

Figure 2: Stages of slow pyrolysis of rice straw for BG 300

Lignin is generally known to decompose slowly in a wide temperature range.[31,32] Moreover, melting of small amounts of extractives present in rice straw (wax – Stage II) also takes place during this stage.

Determination of chemical composition of rice straw
Principle
For a sample of rice straw, the mass loss with rising temperature can be expressed as:

$$\frac{dm}{dT} = \left(\frac{dm}{dt}\right)\left(\frac{dt}{dT}\right) \tag{1}$$

where m is the percentage mass of the sample (relative to initial mass), T and t are temperature and time, respectively.

Pyrolysis was carried out at a constant temperature ramp (dT/dt = β = 10 °C min^{-1}). This means each peak corresponds to a maximum rate of mass loss. It is reasonable to assume that different pyrolysis processes (or pyrolysis of different components) will have a different maximum rate of mass losses. To be more precise, the mass loss temperature profile of the constituents is more likely to be different.

The proposed method works only if it satisfies this condition:

$$\Delta m\,(T)_i = \int_{T_1}^{T_2}\left(\frac{dm}{dT}\right)_i dT \tag{2}$$

The above equation describes the mass loss of ith component with the time.

The total mass loss with the time, within the T_1-T_2 temperature window, is given by the following expression (Eq. (3)):

$$\Delta m(T)_{sample} = \sum_{i=1}^{n}\Delta m_i = \sum_{i=1}^{n}\int_{T_1}^{T_2}\left(\frac{dm}{dT}\right)_i dT \tag{3}$$

For any well-behaved function,

$$\frac{d}{dT}m(T)_{sample} = \frac{d}{dT}\sum_{i=1}^{n}\int_{T_1}^{T_2}\left(\frac{dm}{dT}\right)_i dT \tag{4}$$

This means that the sum of the DTG variations of each component is equal to the DTG signal obtained for the sample:

$$\frac{d}{dT}m(T)_{sample} = \sum_{i=1}^{n}\left(\frac{dm}{dT}\right)_i \tag{5}$$

Therefore, according to Equation (5), if the derivative thermograms (DTG) can be decomposed into pyrolysis processes of constituents, then, the fraction of each constituent present in the rice straw can be evaluated by the area under the corresponding deconvoluted curve, as suggested by Equation (2).

Data analysis

The predominant constituents in rice straw biomass are cellulose, hemicelluloses, and lignin.[33] In addition to that, rice straw consists of epicuticular wax, which functions as a protective layer on the plant surface.[34] The water-absorbing nature of rice straw also allows for the presence of minor amounts of free water and chemically bound water.[35]

After gaining a thorough understanding of the pyrolysis behavior of each major constituent, the DTG thermograms can be deconvoluted with the use of mathematical software, such as MATLAB. To achieve more realistic results, the non-linear least squares refinement with constraints (NLLSRC) approach was employed. As per Equation (5), when the DTG signal is broken down into the DTG signals of the constituents, the percentage of each constituent present in rice straw can be estimated by using Equation (2). The NLLSRC fitting procedure for decomposing DTG thermograms is illustrated by taking the DTG thermograms of the BG 300 variety displayed in Figure 3a. The deconvoluted DTG thermograms of BG352, Suwandel and Raththal varieties are also given in Figure 3.

The most direct information that can be acquired from this analysis is the chemical composition of rice straw. This can be attributed to the presence of three distinctive peaks in the DTG thermogram, corresponding to the degradation of hemicelluloses, cellulose and lignin in the temperature ranges of 200-400 °C, 250-400 °C and 100-600 °C, respectively.[36] Moreover, this study paved the way to estimating the percentage of additional constituents in rice straw varieties through interpreting their complicated pyrolysis behavior. Wax in rice straw is a complex mixture of different constituents, which melt over a wide temperature range. Certain constituents, namely, triacontanal (87 °C), 1-dotriacontanal (96 °C) melt in the temperature range of 50-100 °C, while others, such as stigmasterol (160-164 °C), campesterol (150-155 °C) and spinasterol (171-173 °C) melt over the temperature range of 150-300 °C.[37] Therefore, two stages of wax melting were identified, and computation was carried out accordingly. Free water and bound water percentages were also estimated as free water and bound water evaporation was found to occur around the temperature ranges of 50-90 °C and 120-130 °C, respectively. The chemical compositions predicted from the thermogravimetric analysis are summarized in Table 1. The high standard deviations are partially caused by the natural variation of compositions of paddy plants.

Validation of the proposed method

Cellulose was isolated from the chosen rice straw varieties through the three-step chemical purification process, as described in the literature.[40-42] The resultant white product obtained after this purification process was cellulose, and it was confirmed by FTIR spectra. The spectra also clearly show the sequential and complete removal of lignin, (1516 cm^{-1}, aromatic

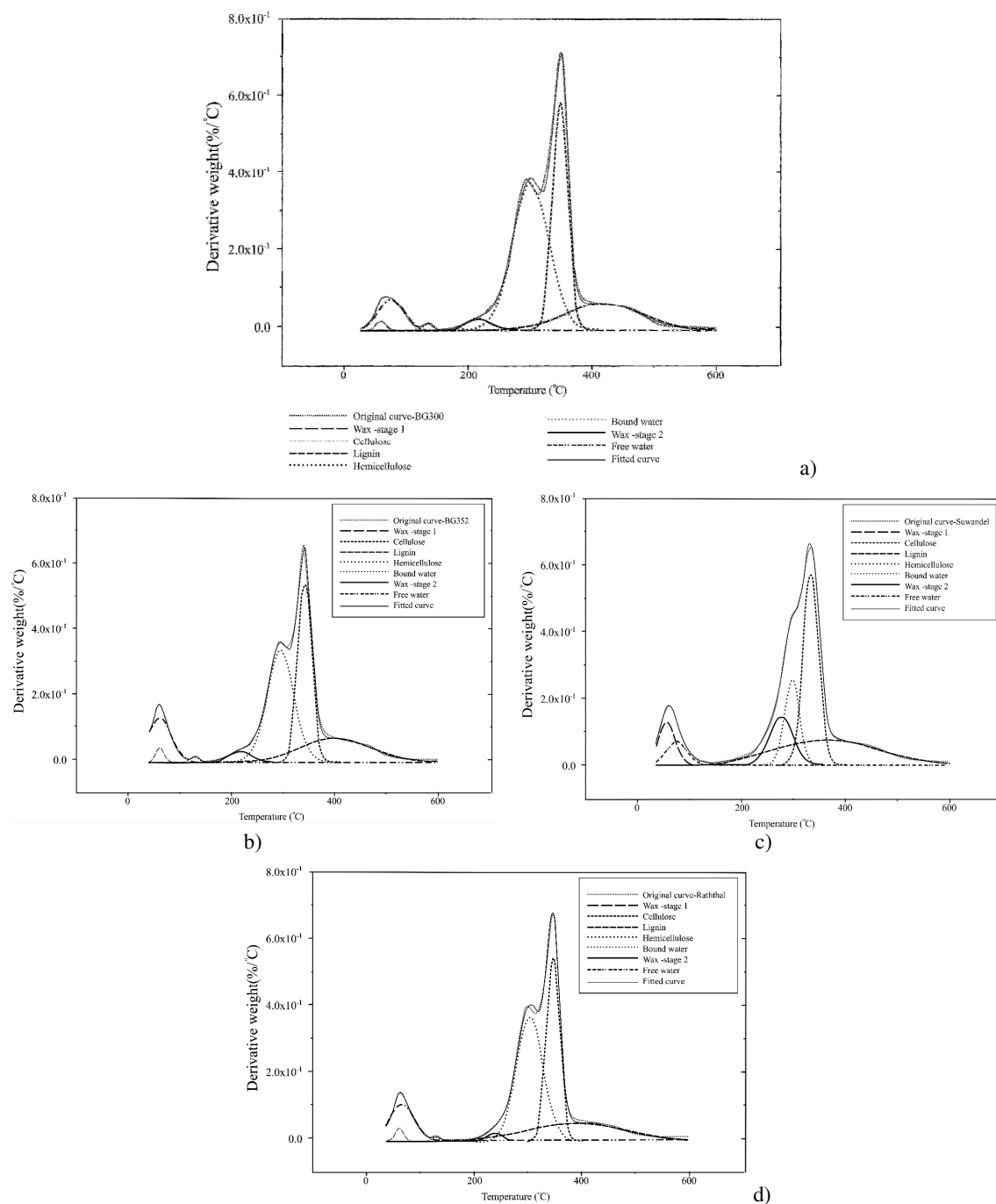skeletal vibrations) during peracetic acid treatment.[38]

Figure 3: Deconvoluted DTG thermograms of varieties BG300 (a), BG352 (b), Suwandel (c) and Raththal (d)

Table 1
Predicted chemical composition of rice straw varieties (5 TGA runs per sample was performed)

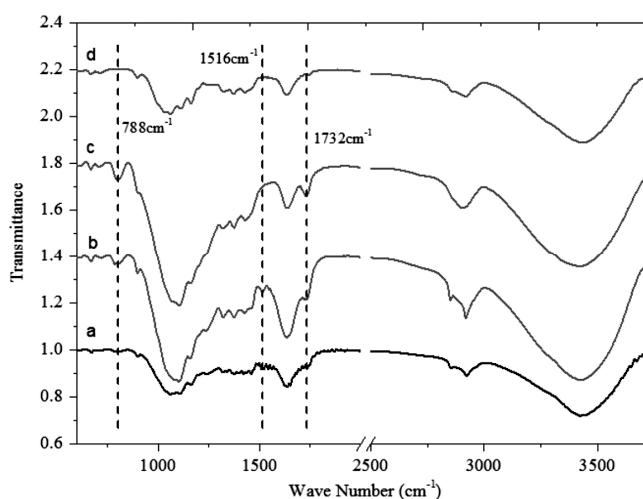| Constituent	Rice straw variety			
	BG300	BG352	Suwandel	Raththal
Cellulose percentage	30.0 ±1.5	29.5 ±1.4	33.9±1.8	28.5±1.6
Hemicellulose percentage	44.3 ±2.3	35.8 ±2.0	14.1±0.9	38.3±2.2
Lignin percentage	16.9 ±0.8	20.6 ±1.1	28.1±1.4	20.2±1.3
Wax (Stage I) percentage	2.3 ±0.1	2.7 ±0.2	12.2±0.3	1.5±0.2
Wax (Stage II) percentage	0.6±0.1	1.3±0.1	6.6±0.3	1.2±0.1
Free water percentage	6.0±0.8	9.6±0.5	5.3±0.5	9.0±0.6
Bound water percentage	0.5±0.1	0.4±0.1	0.1±0.05	0.4±0.1

Figure 4: FTIR spectra of rice straw during chemical purification process following: (a) cleaning,
(b) dewaxing, (c) delignification and (d) hemicelluloses and silica removal

It also shows the leaching of hemicelluloses (1732 cm^{-1}, carbonyl stretching) and silica (788 cm^{-1}, Si–O–Si stretching) during the alkaline treatment (Fig. 4).[23,39] The results obtained by the proposed TGA method are in a very good agreement with the results obtained by the chemical isolation method. The highest cellulose yield was obtained for Suwandel variety (35.2%). Further, the rice straw of the Raththal variety had the lowest yield of cellulose (25.1%), while the yields from the rice straws of BG300 (27.9%) and BG352 (29.3%) were intermediate as per the above results.

The degree of accuracy of the TGA method was ascertained by calculating the percentage variation between predicted and experimental yields (Table 2).

Table 2
Comparison of predicted and experimental cellulose yield

Variety	Method	Cellulose weight percentage
BG300	TGA predicted	30.0 ±1.5
	Chemical isolation	28.2±1.7
BG352	TGA predicted	29.5 ±1.4
	Chemical isolation	29.9±1.5
Suwandel	TGA predicted	33.9±1.8
	Chemical isolation	35.6±1.6
Raththal	TGA predicted	28.5±1.6
	Chemical isolation	26.4±1.5

For all four varieties, the percentage variation was less than or equal to 5%, which showed the suitability of this method to predict the cellulose yield from rice straw. However, only the predicted cellulose yield will be validated during this research. A significant variation of the chemical composition among rice straw varieties can be observed in the study. The genetic and agronomic diversity among the rice varieties selected might be the reason behind this variation. Principally, these observations predict that the highest cellulose yield could be obtained from the Suwandel variety.

CONCLUSION

The agreement between the experimentally obtained results and the predicted results based on the proposed TGA analysis (described in detail above) confirms that the three major constituents of rice straw will have different mass loss temperature profiles. Therefore, thermogravimetric analysis can be effectively utilized to predict cellulose yield of Sri Lankan rice straw varieties, with a relatively high level of accuracy. The study also shows that, among the investigated varieties, the highest cellulose yield was provided by the rice straws of Suwandel, a traditional variety. Further, this study showed that the potential of the TGA method to determine the minor constituents in the composition of rice straw.

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