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To cite this article: E S Murtini *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **230** 012025

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Comparison of characteristics of carbonized rice straw from various rice varieties and parts of rice straws as a source for natural black colorant

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Abstract. This study compared the characteristics of carbonized rice straw (CRS) made of a whole straw and *merang* (the half of the upper part of the rice stem until the panicle without leaves) of three different rice varieties. The yield, mineral components, carbon content, color, pH, and stability for heat and light were analyzed. The results showed that the yield of CRS ranged from 16.73 to 21.80% and there was no significant yield difference of CRS from different parts of straw and varieties of rice. The carbon content of *merang* was higher than that of rice straw, regardless rice varieties. The CRS of black glutinous rice had the highest carbon content, and the lowest silica content (31.69%) compared to the other rice varieties studied. The pH of the CRSs was ranging from 10.53 to 11.08. Exposed in light at 40 °C, the color and pH of the CRS filtrates were stable for 15 days of storage. The CRS from the *merang* of black glutinous rice had the darkest color due to its high carbon content and the low mineral content.

1. Introduction

Rice straw is a waste of rice harvesting, where 1.4 tons of the straws are produced per one-ton of un-hulled rice [1]. Rice straw as a source for lignocellulose is biomass that is widely available [1]. The rice straw is composed of cellulose ($34.89 \pm 0.36\%$), hemicellulose ($29.04 \pm 0.54\%$), lignin ($6.88 \pm 0.76\%$) and silica (5.88-8.20%) [2], and the present of cellulose, hemicellulose and lignin limit its practicality.

Rice straws have been utilized for food and compost, but the utilization value is too little compared to the production [3]. Only 20% of rice straws are used for bioethanol production, but the remaining 80% is a waste [4]. However, efforts to utilize rice straw have been recorded in the literature, such as a carbon source for the production of enzymes of *xylanase* and *endoglucanase* through degradation of rice straw using *Trichoderma reesei* and *Humicola insolens* [1]. Activated carbon from rice straw has been used for catalysts, electrochemical materials, and pollutant adsorbents [3]. Non-digestible oligosaccharides (NOS) were produced to improve the usage of rice straws.

Indonesia is one of the largest rice producing countries and has cultivated various rice varieties. Apart from the rice production for staple food, glutinous rice varieties, both black and white glutinous rice is grown for snacks / baking ingredients. Utilizations of rice straw in Indonesia are limited to animal feed and fertilizer. The rice straw produced from rice harvesting is usually the whole straw of rice, including leaves from the base straw until panicle. The part of rice straw that is widely used for other products is called *merang*, which is an upper part of the rice straw until the panicle (without leaves). The weight of the *merang* is approximately only 30-50% of the total weight of rice straw,



depending on the harvesting method. *Merang* is traditionally used as handicraft material, building materials, and the CRS are used as ingredients for black and traditional food coloring.

The use of CRS as traditional food coloring is local wisdom. Examples of traditional foods that use black dye from CRS are *dawet hitam* and *kue jongkong*. The CRS that is traditionally used as a colorant is derived from the *merang* part. However, there are no recommended rice varieties to produce the blackest color. Considering the production of straw is much more than the production of *merang*, it is interesting to study that the whole straw may also be used as a coloring material. This study compared the characteristics of ash produced from straw and *merang* from three different rice varieties, namely rice, black glutinous rice and white glutinous rice, aiming to produce ash with the highest carbon content and the lowest mineral content, especially silica.

2. Materials and Methods

The materials used in this study were rice straw and *merang* from rice, black glutinous rice and white glutinous rice. The materials were introduced into incomplete combustion, resulting in a black carbonized rice straw (CRS) which was mashed with a ball mill and sieved 200 mesh [6].

The CRS yield was calculated by comparing the weight of the CRS produced to the weight of the straw/*merang* used. The elemental components of the CRS were analyzed with ICP, while the mineral content was measured using X-Ray Fluorescence (XRF). Analysis on color and pH of the CRS were done by mixing a 2.5 g of CRS with 10 ml of distilled water and the solution was then measured using a color-reader (Minolta CR-100) and a pH meter (Ezdo PL-600). The yield, color and pH data were statistically analyzed using ANOVA to determine differences between treatments followed by least significant difference method ($\alpha = 5\%$). The stability of CRS was measured by exposing the CRS filtrate to heat and light [7]. A 2.5 g of CRS was diluted into 100 ml of distilled water. The solution then was filtered with a Whatman filter paper. The filtrate was then inserted in to the clear plastic bottle and placed in a 40°C oven heated by lamp for 15 days. Color observation and pH measurement were carried out on days 0, 3, 7, 11, 13 and 15.

3. Results and Discussion

3.1. CRS yield and elemental analysis with ICP

Table 1 shows that the CRS yield obtained from combustion of straw or *merang* of various varieties of rice ranged from 12.13 to 21.80%. However, the difference of CRS yields from various rice varieties was not statistically significant.

Table 1. The yield and element composition of CRS.

	Yield (%)	Elemental analysis using ICP			
		N (%)	C (%)	H (%)	S (%)
Rice <i>Merang</i> (RM)	18.06±0.02	0.39	17.89	2.06	18.68
Black glutinous <i>Merang</i> (BGM)	16.73±1.55	1.07	42.99	3.26	0
White glutinous <i>Merang</i> (WGM)	17.04±1.12	1.02	29.02	2.5	0.09
Rice straw (RS)	20.65±0.03	0.78	9.74	1.96	1.86
Black glutinous straw (BGS)	20.73±0.00	0.78	7.71	1.57	1.72
White glutinous straw (WGS)	21.80±0.00	0.85	11.07	1.91	17.6

The amount of CRS produced from the incomplete combustion of straw or *merang* was determined by the composition of the material, and composition of the three varieties of rice studied. The dry weight of rice straw contained 15.63-17.49% of ashes [2] and there was no significant yield difference on rice varieties studied ($p > 0.05$).

The results of the elemental analysis showed that carbon was the most abundance element found in CRS. The carbon content in the *merang* was higher than that of the straw. In the case of colorant making, the carbon content determines the intensity of the black color produced. The higher carbon content will produce the higher black intensity of colorant. Thus, *merang* was a better raw material than straw because of its higher carbon content. The amount of carbon in straw rice was 45% after pyrolysis at a temperature of 500°C [3].

The content of nitrogen, hydrogen and sulphur in CRS (except rice CRS and black glutinous rice CRS) is low. This is because the combustion of rice stems will eliminate nitrogen content, 20% potassium, 5-60% sulphur, depending on the method used. The content of hydrogen, nitrogen and oxygen decreased because decarboxilation, dehydration and demethylation take place during the combustion process [3].

Table 2. Mineral and carbon composition of CRS from various parts of straw and rice varieties.

	Limit detection	RM (%)	BGM (%)	WGM(%)	RS(%)	BGS(%)	WGS(%)
SiO ₂	0.01	48.09	31.69	45.34	64.46	72.33	69.93
Al ₂ O ₃	0.01	0.04	0.05	0.02	0.04	0.14	0.11
Fe ₂ O ₃	0.01	0.1	0.02	0.03	0.06	0.13	0.13
MnO	0.01	0.46	0.11	0.3	0.14	0.33	0.21
CaO	0.01	1.18	0.46	0.61	1.65	1.13	1.03
MgO	0.01	1.11	0.43	0.41	1.28	0.79	0.79
K ₂ O	0.001	18	8.03	9.815	12.42	10	7.65
Na ₂ O	0.01	0.06	nd	Nd	0.05	0.07	0.05
P ₂ O ₅	0.001	1.04	0.886	0.667	0.622	0.639	0.29
SO ₃	0.01	1.1	0.12	0.825	0.85	0.25	0.3
TiO ₂	0.01	nd	nd	Nd	nd	0.02	0.02
V ₂ O ₅	0.001	nd	nd	Nd	nd	nd	Nd
BaO	0.001	0.032	nd	Nd	0.024	0.002	0.019
As ₂ O ₃	0.001	nd	0.003	0.001	nd	nd	Nd
Cr ₂ O ₃	0.001	nd	nd	nd	nd	nd	Nd
CuO	0.001	0.003	nd	nd	0.005	0.004	0.002
NiO	0.001	nd	nd	nd	nd	nd	Nd
SrO	0.001	0.006	nd	nd	0.0095	0.002	Nd
PbO	0.001	nd	nd	nd	nd	nd	Nd
ZnO	0.001	0.029	0.005	0.0145	0.024	0.023	0.023
Co ₃ O ₄	0.001	nd	nd	nd	nd	nd	Nd
Cl	0.001	1.9	0.485	0.4025	1.69	1.445	1.69
LOI1000	0.01	28.7	58.3	42	18.55	14.1	19.6
C	0.01	17.1	44.7	30.4	9.21	7.07	10.8
C organic	0.01	13.5	41.7	27.9	8.12	6.09	9.68

3.2. Mineral and carbon composition of CRS

The XRF results showed that the mineral composition of CRS from both the straw and the *merang* were dominated by silica (31-72%). Rice straws contain 82.51-84.37% volatile solid, 15.63-17.49% ashes, 37.27-42.61% cellulose, 10.12-15.35% hemicellulose, 9.26-11.89 % lignin, 29.22-31.34% cellular content, and 5.88-8.20% silica [2]. In the process of incomplete combustion of rice straw to CRS, other volatile and organic components were lost in flames, leaving carbon and minerals including silica. Silica is a mineral that is resistant to high temperature and is not easily destroyed even though using a heating temperature of 1000°C [8]. Silica is an ingredient that may be added directly in

food, but not more than 2%. Besides silica, CRS also contained several important minerals such as K, Ca and Fe. The amount of K was probably beneficial in addition to the CRS main function as a dye.

Vegetable carbon dyes are fine carbon produced by the activation of ash from plants [9]. The commercial black carbon vegetable dye requirement (E 153) is set by JECFA, one of which is having a minimum purity of 95% [9]. Meanwhile commercial purity vegetable carbon from bamboo charcoal powder (BCP) is 95.5% (carbon)[10]. Therefore, to be used as a commercial vegetable carbon, the mineral content, especially the silica in CRS must be reduced to comply with the standard. Among the materials tested, it appeared that the CRS of black glutinous rice was the most potential material to be developed as a source of black colorant, due to the lowest mineral content, especially silica, and the highest carbon content.

The carbon content of *merang* and straw from three rice varieties also varies greatly between 7 - 45% (Table 2). In general, the carbon content produced from the *merang* was more than rice straw. Among the three varieties of straw, the black rice glutinous rice was the most potential to be used as a raw material for black colorant because of its high carbon content (44.7%).

3.3. Characteristics of CRS filtrate

Table 3 shows the color and pH measurement of various varieties and parts of rice straws after conversion into CRS and soaked overnight.

Table 3. Color and pH of the CRS.

CRS type	Color			pH
	L	A	b	
BGM	28.97±0.06 e	7.38±0.03 c	5.32±0.05 b	10.53±0.03 e
WGM	29.38±0.05 d	7.38±0.02 c	5.04±0.03 c	10.99±0.01 b
RS	32.60±0.04 c	7.67±0.02 b	5.01±0.02 c	11.08±0.04 a
BGS	33.59± 0.10 a	7.53± 0.12 bc	5.39± 0.08 b	10.85± 0.02 c
WGS	32.84± 0.04 b	8.16± 0.02 a	5.68± 0.04 a	10.59± 0.03 d

3.3.1. Color and pH of the CRS solution

The color of the CRS solution was influenced by the material (the *merang* and rice straw from three rice varieties). It can be seen that the darkest color of the CRS solution was the *merang* of black glutinous rice, followed by CRS filtrate from the straw of black glutinous rice. This can be attributed to carbon content, where the highest order of carbon content to the lowest was BGM>WGM>RM>WGS>RS>BGS.

Table 3 shows that pH was also influenced by the origin of the material. The order of lowest pH to the highest was BGM<WGR<BGR<WGM<RM. Generally, pH ranges from 10-11, which means the pH was alkaline. This alkaline property was caused by the total mineral content of CRS ranging from 42% (BGM) to 87% (BGS), including minerals that are included in alkaline and alkaline earth classes, such as Ca, Mg, K and Na, which total ranges between 11% (WGS) to 27% (RM). When compared to the black color bamboo charcoal powder (BCP), which has a pH of 9.7[10], the pH of the CRS solution was slightly higher.

3.3.2. Stability of the CRS filtrate to heat and light

In traditional applications, CRS is soaked in water overnight and then filtered, and this filtrate is used as a black food colorant. One of the criteria for a high quality dye is stable to heat and light. Stability against heat is needed, because generally the cake that uses black coloring is processed by involving heat such as boiling, steaming and drying.

Figure 1 shows the color stability and pH of the CRS soaked filtrate stored for 15 days in a lighted oven at 40°C. In general, the color and pH of the CRS filtrate were constant for 15 days of storage in hot conditions and under the light. Regarding the application, this is exciting because generally other natural dyes derived from plants are easily damaged due to their instability and sensitive to external factors such as pH, temperature, light, oxygen, solvents, enzymes and the presence of metal ions. Such natural colorant includes anthocyanin components, beet groups (*betacyanins* and *betalains*), carotenoids, *phenolics* and chlorophyll [11].

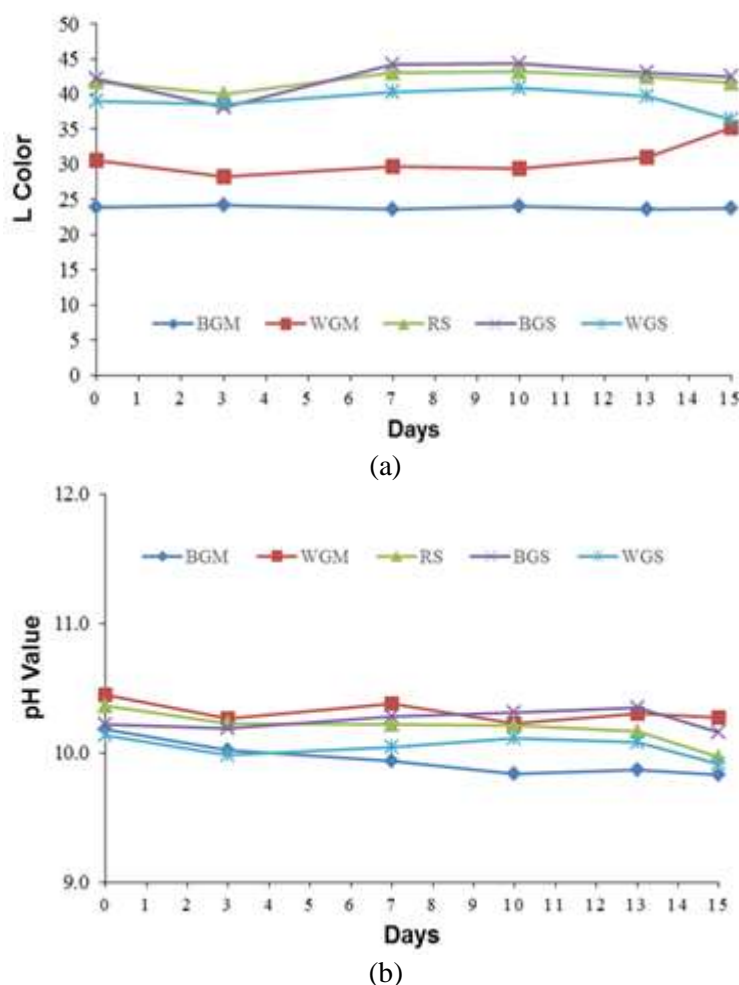


Figure 1. (a) L color and (b) pH stability of the soaked CRS filtrate for 15 days of storage.

4. Conclusion

The yield of CRS from *merang* and straw were not statistically different, but from the elemental composition, and mineral and carbon content, *merang* was more likely to be used as a black colorant than the rice straw. From the rice variety perspective, the black glutinous rice was the most potential material to be developed as a black vegetable colorant, because it has the highest carbon content, the lowest silica content and the darkest solution color. The color and pH of the filtrate from the soaking of black glutinous rice straw also had good stability against heat and light.

Acknowledgement

This article is part of the Insinas-2018 research project funded by the Ministry of Research, Technology and Higher Education

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