The mineral composition and the effect of particle size of carbonized rice straw as colorant of a traditional cake kue jongkong Surabaya

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Abstract. Carbonized rice straw (CRS) is a term defined for the residue of incomplete combustion of rice straw. Utilization of CRS as a natural food coloring agent has been the local Indonesian wisdom. However, study of this local food coloring agent is rare in the literature. This study was aimed to determine the mineral composition of the CRS, and to investigate the effect of particle size of the CRS to the black color intensity of a traditional Indonesian cake called kue jongkong Surabaya. The mineral content of the CRS was analyzed using X-ray fluorescence (XRF). The CRS was grounded and sieved passing through different screen sizes (40, 80, 100, 120 and 200 mesh). The particle size distribution was measured using particle size analyzer. The CRS with different particle sizes were then applied as a natural coloring agent of the kue jongkong, from which the intensity of black color was determined using a color reader. It was found that the dominant minerals of the CRS were SiO₂, carbon, and K₂O. Other trace elements found were Cl, CaO, Na₂O, MgO, P, S, Fe, Al₂O₃ and Mn. The CRS which passed to the sieve of 40 mesh has particle size distribution of 28μm, 115μm, and 348μm for a standard of D₁₀, D₅₀, and D₉₀, respectively. However, CRS that passing through the sieve of 60-200 mesh have similar particle sizes (D₁₀: 12-14μm, D₅₀: 49-60μm, and D₉₀: 114-145 μm). The smaller of CRS particle size produced a darker color of the kue jongkong due to better molecule dispersion and wider surface area.

1. Introduction
The common harvesting technique of rice is cutting the top part of rice straw, then put it in the rice mill top separate the rice seed. This technique left the top part of the rice straw as a waste. The abundant quantity of this waste is expected due to the high rice production, particularly in Indonesia which among the top three of largest world rice producers after China and India[1]. A range of 0.7-1.4 rice straw waste is produced for every 1 kg of harvested rice [2]. In 2015, the production of rice in Indonesia reached 75 million tons [3] , leaving ≈52-105 million tons of rice straw in the process. However, the utilization of this large number of rice straw is limited.

One of the potential utilizations of rice straw is as a natural colorant, particularly black color. Popularity of natural colorants are increasing, since people pay more attention to the health safety issues of synthetic food colorants [4]. In Indonesia, rice straw has been used as a natural colorant for traditional food, such as kue jongkong Surabaya. Kue jongkong is a wet and gel-like cake, and has
black color. This cake is made from a mixture of rice flour, coconut milk, sugar, salt, and black colorant, all of which the batter is placed in a container then steamed.

To use the rice straw as a colorant, it requires carbonization process. Thus, the colorant product from rice straw is called carbonized rice straw (CRS). The products of carbonization are carbon and un-vaporized minerals. Thus, the benefit of using natural colorant is renewable and contains useful minerals. However, investigation of CRS is limited and a better understanding of this natural colorant particularly on its mineral properties is required. Therefore, in this research, the mineral components were studied using XRF.

Further investigation on its particle size is also required to study the effective mixture that can be formed by this natural colorant in a traditional food. Investigation of the particle size was aimed to meet the requirement of the Panel on Food Additives and Nutrient Sources added to Food [5]. Based on this standard, the smallest particle size allowed is no less than 275nm. In addition, this research studied the effect of particle size on the intensity of the black color which can provide a recommended particle size of CRS for the making of food colorant.

2. Method

Rice straw was burnt in a ceramic container, from which the CRS was collected. The sample was then analyzed using XRF to determine the mineral composition based on modified method of Hazra et al [6]. In brief, the rice straw was burn at a set furnace of 110 and 1000°C, and the loss on Ignition (LOI1000) was determined using a robotic TGA system. The sample was then investigated using XRF to determine its mineral properties.

For particle size analysis, the CRS collected from the ceramic container was then grinded and sieved at 40, 80, 100, 120 and 200 mesh. The size variation of the particles was then measured by using particle size analyzer (Cilas 1090). This method provided a standard of particle size analysis described in D-Values (D10, D50 and D90), which are the intercepts for 10%, 50% and 90% of the cumulative mass.

Application of different particle sizes which pass through the 40-200 sieves was then used as a colorant of kue jongkong. A 20g CRS was diluted with 50ml for 24h. The suspended solid was separated and the final CRS solution obtained. The kue jongkong was made from 230g rice flour, 20g tapioca starch, 800ml coconut milk, 125g sugar, 1.6g salt, 50ml CRS solutions. All of the ingredients were mixed and the batter then is placed on a 20x10x3 cm tray then steamed at 90±2°C for 30 minutes. Five different samples were created and triplicate based on the particle size of the CRS which through the sieves. Measurement of the color of the kue jongkong was done by using a color reader (Minolta CR-100). The colors of kue jongkong were measured based on the lab space color (L) where L=0 is the darkest and L=100 is the lightest. Data of L color of kue jongkong was statistically analyzed using Anova single factor and post hoc using Tukey (α=5%).

3. Results and Discussion

3.1. Mineral composition of CRS

Table 1 shows XRF result for the mineral composition of CRS. Silica is the highest component in CRS, followed by carbon, K₂O, and Cl. A few components such as CaO, Na₂O, MgO was found at concentration of <0.1%. There were no toxic chemicals, such as Pb and Co found in the CRS, suggesting that CRS suitable for food additive in low concentration. It has been reported that similar commercial product of bamboo charcoal powder (BCP) is declared safe to be consumed and no-observed-adverse-effect level (NOAEL) at daily consumption of 11.24 g/kg BW/day [7]. However, further research on toxicology of CRS is still required.

By nature, silica is one of the most abundance components on earth as it is easily found in leafy green plants, which is the characteristics of rice straw. Silica may safely used directly in food according to FDA on Code of Federal Regulations Title 21. However, the recommended usage of silica is not more than 2wt% of the food as an anti-caking agent.
As the highest proportion of CRS, silica has the greatest effects on the properties of CRS. Silica has high surface area and easily adsorbs gas and oil [8], which suitable as food additive such as anti-caking agent [9] and bacterial anti-adhesion food-contact surface [10].

Carbon is the second largest proportion which determine the black color of the CRS as food additive. Purified carbon from plants combustion has been commonly used as a black colorant for food [7]. Table 3 shows that over 30wt% of CRS consist of carbon makes it potential source of food colorant.

### 3.2. Particle size of CRS

The CRS was grinded and sieved with 40-200 mesh size. Table 2 shows the particle size distribution of CRS. Overall, the particle that pass through of the 40mesh-sieve is larger compare to that of 80-200mesh-sieve. It is notable that the particle size decrease with increasing mesh value.

| Mineral   | Unit | Content   | Mineral   | Unit | Content   |
|-----------|------|-----------|-----------|------|-----------|
| SiO₂      | %    | 42.51±0.06| As        | %    | 0.00±0    |
| C         | %    | 36.92±0.09| TiO₂      | %    | 0.01±0    |
| K₂O       | %    | 17.16±0.01| Pb        | %    | 0.00±0    |
| Cl        | %    | 1.79±0    | Cu        | %    | 0.00±0    |
| CaO       | %    | 0.80±0    | Ba        | %    | 0.00±0    |
| Na₂O      | %    | 0.71±0    | V         | %    | 0.00±0    |
| MgO       | %    | 0.62±0.01 | Cr        | %    | 0.00±0    |
| P XRF     | %    | 0.32±0    | Ni        | %    | 0.00±0    |
| S XRF     | %    | 0.32±0    | Co        | %    | 0.00±0    |
| Al₂O₃     | %    | 0.19±0.01 | Sn        | %    | 0.00±0    |
| Fe        | %    | 0.12±0.01 | Sr        | %    | 0.00±0    |
| Mn        | %    | 0.09±0    | Zr        | %    | 0.00±0    |
| Zn        | %    | 0.02±0    |           |      |           |

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| Sieve (mesh) | D10  | D50  | D90  |
|--------------|------|------|------|
| 40           | 28.32| 115.37| 348.91|
| 80           | 10.31| 69.36| 145.41|
| 100          | 11.78| 66.83| 143.96|
| 120          | 14.83| 62.20| 135.10|
| 200          | 12.76| 49.13| 114.31|

The particle size of CRS from 40-200 sieve sizes is larger than the minimum EFSA requirement for vegetable carbon (E 153), which is not under 275 nm (0.275 μm), showing that CRS particle size complied with the EFSA requirement. However, compared to commercial black colorant, the E 153, the CRS particle was larger. The current standard, according to NATCOL (2011) in EFSA Panel on Food Additives and Nutrient Sources added to Food [5], the particle size distribution of the commercial available preparations is characteristically 10% < 2 μm, 50% < 5 μm, and 90% < 55 μm or 10% < 1 μm, 50% < 4 μm, and 90% < 10 μm for the finer product, with an absence of particles below 275 nm. Therefore, further research is required to reduce the particle size of CRS. Smaller particle size will effect on surface area. The smaller the particle, the wider the surface area and the particle will
easily to disperse in a solution at more stable state. The presence of silica in the CRS also assist the stability of the solution created.

3.3 The effect of particle size to kue jongkong Surabaya color
Table 3 shows the lab space color test (L) which show the darkness color of a material. Overall, higher sieve size, which produce smaller particle size of CRS, correspond to the darkness of kue jongkong. The CRS particles from 40mesh-sieve resulting on L value of 34 and the CRS particles obtained from 200mesh-sieve produce L value of 27 in the production of kue jongkong. This shows that smaller particles produced darker color of the kue jongkong.

Table 3. Effect of sieve size to L value of kue Jongkong Surabaya.

| Sieve size (mesh) | L value    | Tukey-test (\(\alpha=5\%\)) |
|-------------------|------------|-----------------------------|
| 40                | 34.43±2.12 | a                           |
| 80                | 32.93±0.26 | ab                          |
| 100               | 30.60±0.86 | bc                          |
| 120               | 28.63±0.70 | cd                          |
| 200               | 27.23±0.31 | d                           |

Kue jongkong Surabaya: commercial sample 30.53±0.14

The commercial kue jongkong L value was 30. Therefore, larger CRS particles collected from 40 and 80 mesh-sieve were not met the darkness standard commercial of kue jongkong. The CRS particle which pass through 100-200 mesh-sieve shows L color value that similar and lower than that of the commercial one when applied to kue jongkong, suggesting that 100 mesh-sieve is the minimum sieve size to be used for CRS sieving.

4. Conclusion
Incomplete combustion of rice straw produced carbonized rice straw (CRS) that can be used as food colorant. The CRS contained various minerals (63%) and carbon (37%). The CRS particles sieved with 40-200mesh-sieve produced particle size that comply with the standard for commercial vegetable carbon. When the CRS particle was applied to kue jongkong, a minimum of 100 mesh-sieve size was required for producing CRS particle which can match the standard of darkness of kue jongkong commercial.

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