ORIGINAL ARTICLE

Reverse Osmosis Integration into Nypa fruticans Palm Sugar (Gula Apong) Processing: Color Development Investigation Using L*, a*, and b* Parameter

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ABSTRACT- Color is one of the quality keys that define the acceptable appearance of the food product resulting from various processing methods. The aim of this study is to investigate the impact of non-thermal reverse osmosis process integration as a pre-concentration step into the existing conventional pan boiling process for *Nypa* sugar or *gula apong* making. The pH value and total acidity (%w/v) for the full pan boiling (FPB) and reverse osmosis-pan boiling (RO-PB) are consistent at every interval of total soluble solids (TSS) obtained. The Nypa sugar produced from both processes were further analyzed in terms of color development using the lightness L*, the greenness a*, and the yellowness* parameters. Overall, there are slight distinctions of each L*, a*, and b* parameter between FBP and RO-PB processes but statistically, are not significantly different (p-value>0.05). For the browning index (BI) and color difference derived from L*, a*, and b* values, the FBP process showed higher color changes than the RO-PB process with calculated values of 16.47 and 22.96, respectively.

KEYWORDS
Nypa sugar
Reverse osmosis
Pan boiling
Color
Browning Index

INTRODUCTION

Nypa sap is an extract that is produced from fruit stalks of the Nypa palm plant and is rich in chemical components including sucrose, glucose, fructose, and organic compounds with high concentrations of minerals, vitamins, and antioxidants activities that could be used for various purposes [1]. The sap comprised moisture contents around 84.96-87.20%, traces amount of crude protein, crude fat, ash contents (~less than 1%), and total acidity of 1.18% [2]. The local community in the Borneo region, particularly Sarawak, Malaysia utilizes the sap as fresh juice fermented drinks, syrup, and for the production of raw sugar or also known as *gula apong*[3]. This brown sugar is produced through conventional thermal evaporation or open-pan boiling method by boiling nypa sap for approximately 6 to 8 hours with continuous stirring to evaporate the water content until it is caramelized and thickened into a paste as shown in Figure 1.

The production of *gula apong* using a conventional heat process is a time-consuming procedure because of the high level of nypa sap moisture content. Overexposure to thermal treatment may affect the end product's quality in terms of physicochemical attributes and sensorial properties. Therefore, thermal-based processes application alternatively could be shortened with the replacement or integration of non-thermal processes such as reverse osmosis. Reverse osmosis is a pressure-driven process that has been widely utilized as for preconcentration process to eliminate moisture contents in liquid and semi-liquid foods. This method is favored because of its low capital investment, can be operated at low temperatures, and is energy efficient. Reverse osmosis has been used extensively in the food industry in several specific applications. The application includes purification of drinking water, pre-concentration of milk and whey, concentration and clarification of fruit and vegetable juices [4].

Food products can be assessed or appraised organoleptically using the senses of vision, sound, touch, odor, and taste [5][6]. These criteria of senses interpretation have become the foundation of today's standardization for food product development, testing, and innovation [7]. The first sense which is vision, optically evaluates food products' external appearance in color and texture. Color is a result of the natural appeal of food products in nature or a change that occurs during processing which may correlate with oxidation, pH fluctuation, light presence, oxidation exposure, and temperature [8][9].

Figure 1.*Gula apong* being caramelized and thickened in a wok

Physical quality evaluation practiced in many food industries, commonly conducted by appointed examiners or panels, is quite complicated and sometimes inaccurate due to its subjective nature [10]. More consistent evaluations using precise food inspection tools such as a chroma meter are favored as the parameter determination in terms of lightness L*, greenness a*, and yellowness* are easy to be interpreted. By using a 2D or 3D chroma diagram, the value obtained from the analysis can be mapped for visual assistance [11]. The value also conveniently be used for the browning index (BI) and color difference (ΔE^*) determination using calculation by equation methods.

The primary objective of this study was to observe and discuss the color surface development in terms of L*, a*, and b* parameters of the palm sugar product processed using the pan boiling method with reverse osmosis (RO) integration. The comparison test was also highlighted which compares the browning index (BI) and color difference (ΔE^*) between pan boiling with RO integration product and conventional full pan boiling method product.

MATERIALS AND METHODOLOGY

Sap Sample Collection

The nypa fruticans saps were acquired from the local harvester in the Pusa area, a region in the middle of Sarawak that is recognized as the hub for active palm sugar production. The saps were harvested, chilled, and frozen to avoid major physicochemical attribute changes during transportation to the laboratory. The commercial nypa palm sugar or gula apong was also purchased from the same area for comparison tests with lab-produced nypa palm sugar.

Preparation of Nypa Palm Sugar

Freshly obtained nypa sap was filtered using clean and sterile muslin fabric and divided into two batches. The first batch was processed by using a conventional full open-boiling (FBP) method whereas the second batch was processed with a mixed combination of reverse osmosis and open-pan boiling (RO-BP) treatment as depicted in Figure 2. The first batch was heated in a heating *wok* at a temperature of 105° Celsius until the sap reached the final total soluble solids measurement of 80°Brix. For the second batch, the nypa sap sample was pre-concentrated using a membrane-driven process, a high-pressure reverse osmosis system as shown in Figure 3. The RO system has a threshold capacity of transmembrane pressure and salt rejection up to 80 Bar, and 99%, respectively [12]. The parameter controlled was the transmembrane pressure (TMP) of the system and the temperature of the nypa sap sample. According to a reverse osmosis optimization study, using the same system, the recommended transmembrane pressure setting is 60 bar and a temperature of 20°C (less than room temperature) for the sample. The nypa sap sample is concentrated up to 30 °Brix with a volumetric concentration factor of 2.9. and the total reduction of 67% of the original volume. After the pre-concentration by RO, the sap is heated by an open pan boiling until sugar with TSS of 80°Brix is formed. The time taken progress for both batches to reach intervals of total soluble solids of 30, 40, 50, 60, 70, and 80°Brix was tracked with a stopwatch.

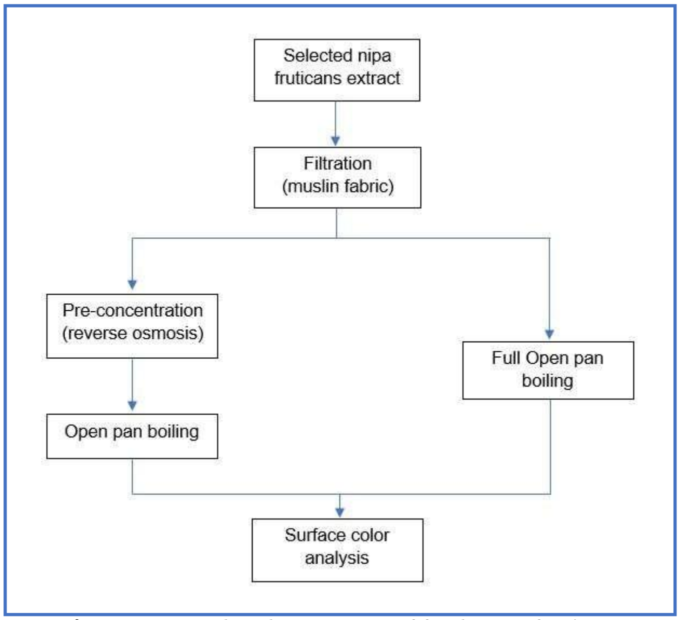

Figure 2. Two batch processes of fresh nypafruticans sap

Figure 3. Isometric view of high-pressure reverse osmosis concentration system

The pH, Total acidity (TA), and Total Soluble Solids (TSS)

Determination of the pH, titratable acidity (TA), and total soluble solids (TSS) was done according to the AOAC method [13]. A calibrated pH meter (HACH®: USA) was used to determine the pH of palm sugar. First, the pH electrode was cleaned with distilled water, and excess water was wiped away with tissue. The pH meter was then calibrated using buffers with pH values of 4 and 7. The pH of the nypa palm sugar was measured in triplicate after calibration, and the average result was obtained. The titratable acidity was measured by dissolving 10 g of sample with 100 mL of distilled water. The homogenate was titrated with 0.1 M NaOH. The volume of base required to make the pH of the homogenate to pH 8.1 (end-point) was measured. The result was calculated as a percentage of lactic acid. The total soluble solids content of the nypa palm sugar product was measured using a handheld refractometer Atago (Japan) with a measurement spectrum of 0° to 50°Brix and 51° to 100°Brix. The result was expressed in terms of Brix percentage.

Surface Color Analysis

The surface color of the sugar was determined using a Minolta Chroma Meter (CR-A43, Japan). The color measurement was done in terms of the (CIE) Lab color space coordinate. There are three color parameters required to be measured namely L*, a*, and b*. L represents the degree of lightness which ranges from 0 (dark) to 100 (white), a* represents the degree of redness and greenness, and b* represents the degree of yellowness and blueness. The color of the three samples was measured in triplicates and the mean values and standard deviation were recorded. Before the color measurement, the chroma meter was calibrated on a calibration plate for standardization [14].

Color Difference and Browning Index

The browning index was determined to evaluate the brown color development of palm sugar due to process treatment on the sample according to the calculation formula below [15]:

$$x = \frac{a^* + 1.75L^*}{5.645L^* + (a^*) - 0.3012(b^*)} \quad (1)$$

$$\text{Browning Index, IB} = \frac{100(x - 0.31)}{0.17}, \quad (2)$$

Where,

x = chromaticity of x coefficient
L* = Lightness
a* = Greenness
b* = Yellowness

Meanwhile, the total color difference (ΔE^*) was determined to evaluate the effect of the color difference of the process treatment on the sample according to the calculation formula below [15]:

$$\Delta E^* = \sqrt{(L^*_f - L^*_g)^2 - (a^*_f - a^*_g)^2 - (b^*_f - b^*_g)^2} \quad (3)$$

Where,

L^*_f = Lightness of fresh nypa sap
L^*_g= Lightness of palm sugar
a^*_f = greenness of fresh nypa sap
a^*_g= greenness of palm sugar
b^*_f= yellowness of fresh nypa sap
b^*_g= yellowness of palm sugar

Statistical Test

The surface color analysis result was tested using t-test at $p \leq 0.05$ to check for significance differences between conventional full pan boiling nypa palm sugar and pan-boiling with RO integration product. All statistical analysis was carried out using SPSS version 23.0 (Statistical Package for the Social Science, IBM: United States) software.

RESULTS AND DISCUSSION

The nypa sap was concentrated at intervals of 30, 40, 50, 60, 70, and 80 °Brix, and the pH and the time taken to reach each interval were recorded as shown in Table 1. The initial pH of the nypa sap before process treatment is 5.57±1.22 and the progression of pH at each interval of TSS exhibits no significant difference $p>0.05$ for both full pan boiling (5.33±1.06-5.57±1.22) and RO-pan boiling process (5.39±1.535.57±1.22). Consistent measurement of values across the treatment suggests that thermal during open pan boiling and pressure applied during reverse osmosis has minimal influence and impact on the pH. A slight and minimal reduction in pH values is probably caused by the formation of organic acids for instance, tartaric, formic, acetic, and lactic acid [16][17][18] Freshly tapped nypa sap is about 7, but the value will decrease as a result of fermentation process occurrence during storage or downstream processing [19]. The natural quality of nypa sap deteriorates quickly with the presence of fermentative microbes which decrease the pH and increase the acidity level [20].

The main organic acids present in palm sugar are mainly lactic acid [16] and the total acidity is determined by calculation in equivalence of lactic acid, in terms of weight over volume percentage. Total acidity content for full-pan boiling and ro-pan boiling varied from 0.30 to 0.49%w/v and 0.27 to 0.49%w/v, respectively. The presence of traces amount of acidity suggests that there is a pre-spoilage of the fresh nypa sap likely during harvesting or storage. Fresh nypa sap is susceptible to bacteria or microorganism invasion, especially from surroundings once collected and the equipment for tapping can be a detrimental factor too. Overall, total acidity content across both process treatments showed no significant differences ($p>0.05$) as similar to pH value trends. However, it is important to note that acidity may contribute to the acceleration of the Maillard reaction and promote the browning of the palm sugar produced [21].

Table 1. Total soluble solids, pH, and time record stamps for full pan boiling and RO-pan boiling process

Process	Total soluble solids (°Brix)	pH	Total Acidity (%w/v)	Time (minutes)
Full pan boiling	17	5.57±1.22	0.41	0
	30	5.33±1.06	0.31	30
	40	5.42±0.93	0.35	38
	50	5.40±1.26	0.38	47
	60	5.46±1.44	0.34	54
	70	5.36±1.05	0.49	63
	80	5.47±1.21	0.30	72
RO-pan boiling	17	5.57±1.22	0.47	0
	30	5.39±1.53	0.49	12
	40	5.44±1.45	0.3	22
	50	5.52±0.63	0.36	28
	60	5.49±1.63	0.29	37
	70	5.44±1.77	0.39	48
	80	5.53±0.82	0.27	55

The total time taken for full pan boiling and RO-pan boiling process to reach the final TSS concentration of palm sugar of 80°Brix is 72 and 55 minutes, respectively. By comparison test, there are significant differences ($p<0.05$) in the time taken between both processes. The concentration of nypa sap to palm sugar using the RO-pan boiling process is much faster than full open-pan boiling with 27.78% time-saving. The preconcentration using reverse osmosis fastened the total time taken as the process alone managed to reduce the volume of fresh nypa sap by 67% and concentrate it up to 30°Brix which took just 12 minutes. As for full pan boiling, the concentration from 17 to 30°Brix took around 30 minutes and hence 18 minutes longer than the RO process.

For the concentration process from 30°Brix to 80°Brix, the total time taken RO-pan boiling is a bit longer than full-pan boiling. This is because the heat transfer mechanism and evaporation for RO-pan boiling start at minute 12. While the process is slowly gaining temperature momentum, the full pan boiling process is already at a consistent maximum temperature of a boiling point, 115°C. Having early temperature consistency gave an advantage to full pan boiling to dissipate sample moisture with a higher evaporation rate over time. Overall thermal exposure-wise, the RO-pan boiling process duration is 40.28% shorter than full pan boiling.

The surface color for nypa sap concentrated by both processes was investigated using Minolta Chroma Meter L*, a*, b* and plotted for color progression as depicted in Figure 3, Figure 4, and Figure 5. The lightness of both processes declines steadily as the nypa sap concentrated from 17 to 67°Brix. The total soluble solids value increases as a result of moisture content elimination by preconcentration of reverse osmosis and evaporation. The decrease in moisture content directly correlates with the decrease of L*, the lightness parameter which is a transformation of milky-white nypa sap into viscous thick dark-browny molasses. From 75°Brix to 85°C, the decreased rate of lightness almost reaches zero where the moisture content is extremely low for the evaporation to proceed. The substantial decrease of lightness over time is also influenced by high temperature and exposure time factor whereby it rapidly facilitates the hydrolysis of sucrose into reducing sugars. Reducing sugars are one of the primary substances in Caramelization reaction during thermal reaction. The presence of high reducing sugar content promotes the browning color caused by the Maillard reaction [22][23].

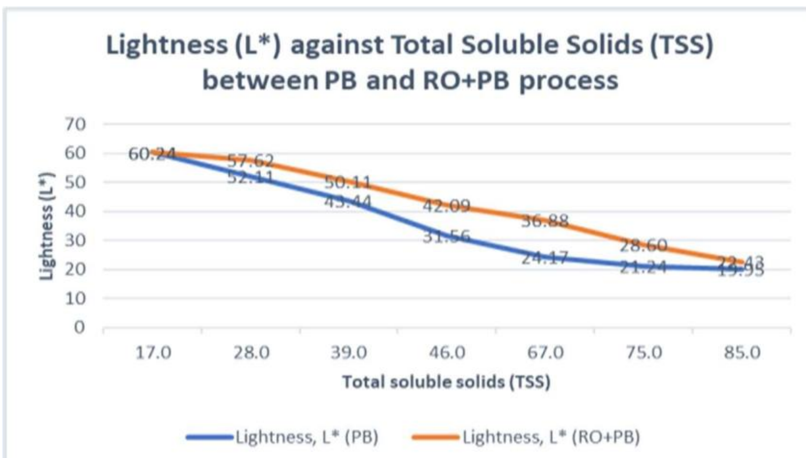

Figure 3. Lightness, L* measurement against total soluble solids (°Brix) percentage between FPB and RO-PB

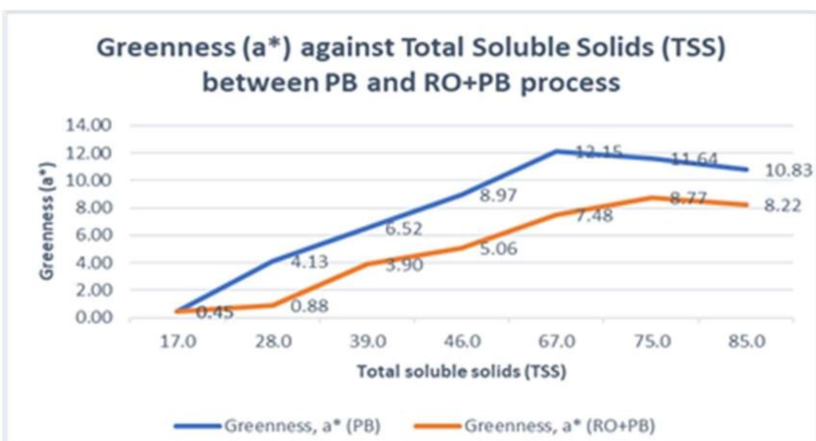

Figure 4. Greenness, L* measurement against total soluble solids (°Brix) percentage between FPB and RO-PB

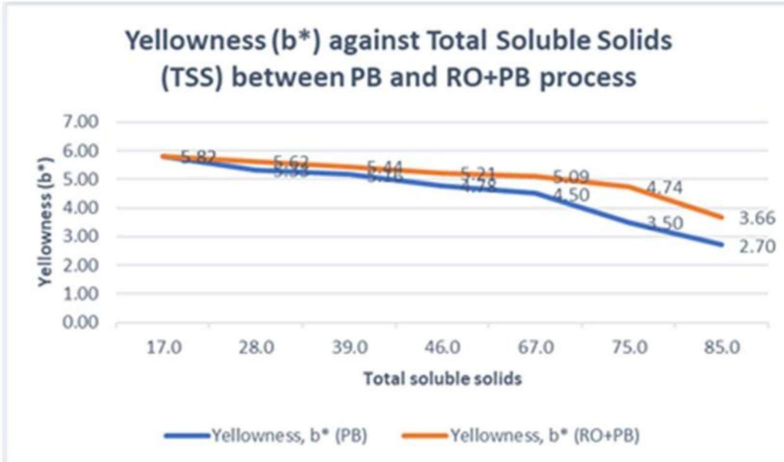

Figure 5. Yellowness, L* measurement against total soluble solids (°Brix) percentage between FPB and RO-PB

From Table 2, the lightness mean value obtained from the RO-integrated pan-boiling process is slightly higher than the full pan-boiling standalone process. This indicates the product treated thermally with more time exposure will shift in greater magnitude towards a darker or brown color hue. Hence, darker color correlates with a substantial decrease in lightness, L* value. The observation is in line with Ho et al., 2007 [24] and Apriyantono et al 2002 [25] studies which observed browning of Maillard reaction and caramelization due to the processing of palm sugar using high temperature and longer process time exposure. However, the mean of both processes in terms of L*, lightness is statistically not significant, $p>0.05$ ($p=0.441$).

Table 2. Statistical analysis t-test on Hunter's parameter between FPB and RO-PB process

Criteria	Process	Mean (SD)	The p-value of the t-test
Lightness, L*	FPB RO-PB	36.1±1.26 42.6±2.23	0.441
Greenness, a*	FPB RO-PB	7.8±0.88 4.9±1.49	0.198
Yellowness, b*	FPB RO-PB	4.5±1.45 5.1±2.63	0.296

FPB – Full pan boiling, RO-PB – Reverse osmosis+pan boiling
*p-value <0.05 - The group is significantly different from each other

Overall, the detection of a* (greenness/redness) and b* (yellowness/blueness) are minimal and barely perceive by the chroma meter instrument as each color combination capacity is low in measurement value. For a* parameter, both processes of full pan boiling and RO-pan boiling showed a steadily increase pattern of greenness color capacity from the start until the end product formation with a detection range of 8.22 to 10.83. Similar trends were also observed for the b* parameter, where both processes steadily decrease in yellowness color capacity with end product formation with a detection range of 2.70 to 3.66. Statistically, the mean of parameters a* and b* for both processes are not significant, with a p-value of 0.198 and 0.296 ($p>0.05$), respectively (Table 2). The p-value for all the parameters, lightness, greenness, and yellowness criteria between the RO-integrated pan boiling and the full pan-boiling process is insignificant ($p>0.05$). The results reflect the effect of reverse osmosis integration as non-impactful in terms of Hunter's parameter evaluation when compared with the conventional method.

The brown color is the staple color and identity of most palm sugar and nypa palm sugar which differentiate it from some other sugar product. From Table 3, the browning index (BI) and color difference, $\Delta E^*$are higher for sugar produced by the full pan boiling process with 16.47 and 22.96, respectively. Generally, the samples that were heated at 100°C or above for a long time can cause a major shift in the product color from brown to darker intensity [21]. The darker color of the end product also heavily contributed by the decrease in L*, the lightness parameter which was observed higher for the full pan boiling process, and led to a higher rate of browning reaction during the heating process [25][26]. The exposure time of heat treatment has a direct correlation with the lightness parameter, browning index, and color difference where a higher time means a higher rate of non-enzymatic Maillard and browning reaction.

Table 3. Browning index and a color difference value between FPB and RO-PB process

Process	Browning Index (BI)	Color difference, ΔE^*
FPB	16.47	22.96
RO-PB	9.41	17.05

FPB – Full pan boiling, RO-PB – Reverse osmosis+pan boiling

CONCLUSION

The color investigation conducted on the palm or *gula apong* produced by full pan boiling and RO-pan boiling revealed variations and distinctions, particularly in terms of L*, lightness parameter, browning index (BI) and color difference, ΔE^*. Generally, the browning index and color difference value for full pan boiling process is higher than RO-pan boiling. This result indicates the impact of RO process integration capability in reducing the browning effect and overall color changes denoted by color difference. Moreover, less time exposure to heat treatments for the RO-pan boiling process shortens the browning color intensity due to non-enzymatic Maillard and over-caramelization. The findings of this research have the potential to be used for correlation studies with physicochemical attributes and color comparison similar sugar products from different sap sources.

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