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Research Article

Changes in physical and chemical properties during the production of palm sugar syrup by open pan and vacuum evaporator

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Abstract

Palm sugar syrup is obtained by heating palm sap until it is concentrated. In this study, palm sugar syrup was produced using two processing methods, including open pan (110°C) and vacuum evaporator under 70 and 80°C. The physical and chemical properties evaluated were colour (L* and a*), browning intensity (BI), fructose, glucose, sucrose content, HMF content and protein content. Samples were collected at 15 min (for open pan) and 10 min (for vacuum evaporator) intervals until the end of each process. The properties of each collected sample during heating were significantly different ($P<0.05$) in each sample. During each heating process, Maillard reaction and caramelization occurred as indicated by an increase in a* value, BI and HMF content and a decrease in L* value ($P<0.05$). An increase in reducing sugar with heating times in each process ($P<0.05$) was also observed due to the inversion reaction. Samples heated by open pan showed a higher non-enzymatic browning reaction and inversion reaction than samples heated by vacuum evaporator, indicated by a higher a* value, browning intensity, HMF, fructose, glucose and lower L* value and sucrose content than those heated by vacuum evaporator. Additionally, samples heated by vacuum evaporator under 80°C showed lower L* value and sucrose content and higher a* value, browning intensity, HMF, fructose, glucose than the samples produced by vacuum evaporator under 70°C.

Keywords: natural sweeteners, *Borassus flabellifer*, non-enzymatic browning, Maillard, Thailand.

Introduction

Palm sugar syrup is a natural product made from the sap of the Palmyra palm (*Borassus flabellifer* Linn.) and is widely grown in Africa, South Asia, South America, Australia and in other tropical countries [1]. In Thailand, especially the southern part, Palmyra palm is grown widely in Songkhla province. These large palms are planted on the dykes of rice fields for shading the rice, protecting the field from strong winds and for tapping the sap for cooking [2]. Traditionally, palm sugar syrup is produced by evaporating palm sap in a large open pan and heating using a wood fired stove until it becomes concentrated. The producer then determines the final product quality by its intensity of brown colour, thickness and viscous liquid during the on-going process. However, it requires a long time to evaporate water until the concentrate of total soluble solids reach 65^{o}Brix or above. Heat from the process, especially at high temperature and long heating time, will accelerate the inversion reaction and non-enzymatic browning reaction. Overheating during the process will alter its unique flavour and colour. If the syrup is dark it also affects the properties during storage. Therefore, vacuum evaporation under low temperature can be used as an alternative way to reduce thermal degradation of food properties.

Since quality is supremely important in food, deterioration has to be controlled during storage. Non-enzymatic browning may cause unacceptable nutritional and sensory effects in some stored food products and may be a limiting factor in the shelf life of products [3]. As a result, study of the processing methods that influence non-enzymatic browning reactions is very important for palm sugar syrup properties during production and storage. However, the property changes during concentration of palm sugar syrup have not yet been investigated. Therefore, this work is aimed at monitoring the property changes in palm sugar syrup during the heating process by both open pan and vacuum evaporator and comparing the properties of final syrup obtained from those two processes. The information obtained from this study could be used as a guideline for optimizing or designing thermal processes to reduce the quality loss of this product. In addition, more detailed knowledge of palm sugar syrup during processing and storage will be of benefit for producers and consumers.

Materials and Methods

Raw material

Palm sap was collected from farmers in Songkhla province. The sap was harvested after 12 hours of collection and included natural wood from the tapping process. The bottle of palm sap was kept in an icebox (4^{o}C) during transportation (30 minutes). The sample was filtrated by sheet cloth at room temperature and kept at 4-10^{o}C until used.

Production of palm sugar syrup

Palm sap (15 litres) was concentrated by using open pan (approximately 110^{o}C) and vacuum evaporator (70 and 80^{o}C). During the heating process, samples were collected at 15 minutes intervals until the total soluble solids reached 70^{o}Brix to obtain palm sugar syrup. Immediately after production, the physical and chemical properties of palm sugar syrup were determined.

Determination of physical properties

Colour measurement

Colour measurements of samples were carried out using a Hunter Lab Colorflex colourimeter. Instrumental colour data was provided as CIE system in terms of L* (lightness), a*(redness and greenness) and b*(yellowness and blueness).

Browning intensity

Browning intensity was determined by monitoring the absorbance at 420 nm. Prior to UV absorbance determination, samples were diluted with distilled water to obtain reliable absorbance readings [4].

Determination of chemical properties

Type and concentration of sugar

Type and concentration of sugar was determined using HPLC (Shimadzu, CR6A Chromatopac) with Shim pack CLC NH2 column and refractive index detector. The mobile phase used was the solution of acetonitrile and water (85:15), pumped at a flow rate of 1.5 ml/min and injection volume 20 µl. The samples were prepared by making appropriate dilutions with distilled water. All sample solutions were passed through a 0.45 µm syringe filter (Nylon) to remove particulates prior to HPLC analysis. D-glucose, D-fructose and sucrose were used as external standards [5].

5-hydroxymethylfurfural (HMF) content

Palm sugar syrup (5-10 g) was dissolved in deionized water up to 50 ml. After that, it was centrifuged at 5,000 rpm for 15 min. To determine the HMF content, 2 ml of supernatant was introduced into the tube. 2 ml of 12% trichloroacetic acid (TCA) and 2 ml of 0.025 M thiobabituric acid (TBA) were subsequently added and mixed thoroughly. The tube with the sample was then placed in water bath at 40°C. After incubating for 50 min, the tube was cooled immediately using water and the absorbance measured at 443 nm. A calibration curve of HMF was utilized to quantify the HMF concentration [6].

Protein content

Preparation of the dye

The dye solution was prepared monthly. Coomassie brilliant blue dye (100 mg) was dissolved in 50 ml of methanol followed by addition of 100 ml of phosphoric acid and made up to 1 litre with deionized water. The dye mixture was filtered twice through Whatman No. 1 filter paper.

Protein assay

Palm sugar syrup (2-5 g) was dissolved in deionized water and made up to 10 ml. Following this, 0.04 ml of sample was mixed with 2 ml of dye solution. The absorbance was measured at 595 nm. Bovine serum albumin was used as an external standard [7].

Statistical analysis

All analyses and measurements were performed in triplicate. The experimental design was a completely randomized design (CRD). Data was subjected to analysis of variance (ANOVA). Comparison of means was carried out by Duncan's multiple-range test [8]. Analysis was performed using a SPSS package (SPSS 6.0 for windows, SPSS Inc, Chicago, IL).

Results and Discussion

Physical properties

Figures 1A and 1B show the changes in L* and a* values during the production of palm sugar syrup by open pan and vacuum evaporator, respectively. During all heating methods, a significant decrease in L* and increase in a* values were found. The L* values decreased with heating times in all processing methods which reduced from 76.33 to 60.00, 58.64 and 57.78 for palm sugar syrup heated by open pan and vacuum evaporator at 70°C and 80°C, respectively. Since the L* value is a measurement of the colour in the light-dark axis, this falling value indicates that samples were turning darker. Similar results were obtained by various investigators and it has been reported that decreases in L* correlated well with increases in the browning of food materials [9].This result is in agreement with the decrease in L* value of pear puree, pineapple juice and cashew apple juice during heating [10,11,12].

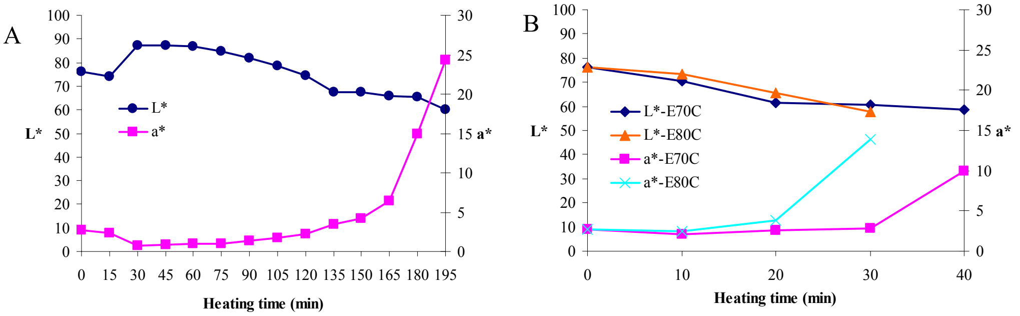

Figure 1. Changes in L*and a* values during the production of palm sugar syrup by open pan (A) and vacuum evaporator (B).

The a* value increased during the heating process in all palm sugar syrup samples. Initially the a* value of palm sugar syrup was 2.70. It was also observed that the finished samples were 24.35, 9.96 and 13.88 for palm sugar syrup heated by open pan and vacuum evaporator under 70°C and 80°C, respectively. Initially, there was slow change in the a* value in the first 120, 20 and 10 min of heating for palm sugar syrup. During heating, the a* value continued to change, and the colour of each sample changed towards orange-yellow, indicating the onset of caramelization and Maillard reactions. When the total soluble solids content reached approximately 40°Brix (at 135 min for open pan process, 30 min for vacuum evaporator at 70°C and 20 min for vacuum evaporator at 80°C), there were rapid changes in a* values, confirming the high rate of caramelization and Maillard reactions [13]. From these results, it was found that there was a higher change in a* and b* values for syrup heated by the open pan method than the syrup which was produced by vacuum evaporator. This is probably due to palm sugar syrup heated by open pan using higher heating temperature and longer heating time than syrup heated by vacuum evaporator. Generally, the rate of chemical reactions increases with increasing temperature and time [14]. The decrease of L* values and increased a* values may contribute to the non-enzymatic browning reaction during the heating process [3]. Therefore, these values can be used to indicate the rate of non-enzymatic browning reaction. The increase of a* value during heating was responsible for the brown colour that corresponded to a decrease in L* value.

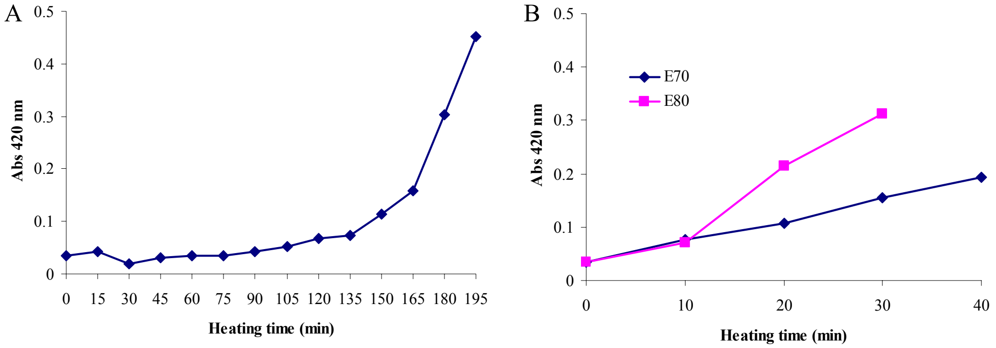

Figure 2. Changes in absorbance value at 420 nm during the production of palm sugar syrup by open pan (A) and vacuum evaporator (B).

Changes in browning intensity are shown in Figure 2A for open pan heating and 2B for vacuum evaporator heating. A significant increase in browning intensity was observed in all processing methods. The browning intensity of palm sugar syrup produced by open pan slightly increased within the first 90 min ($P \geq 0.05$). Following this, browning increased sharply with increasing time until 195 min ($P<0.05$). The browning intensity of palm sugar syrup heated by vacuum evaporator developed in the same manner as the samples heated by open pan, however, the browning intensity by vacuum evaporator increased rapidly after 20 min and 10 min for evaporation under 70°C and 80°C. The highest absorbance at 420 nm (0.401) was observed in palm sugar syrup heated by open pan, followed by vacuum evaporator under 80°C (0.313) and 70°C (0.194). These results indicated that during the heating process non-enzymatic browning, including Maillard and caramelization reactions, took place. Maillard reaction occurs between reducing sugars and amino acids or proteins [15]. Palm sap contains abundant sucrose and polar side chain amino acids, especially aspargine and glutamine that can react via Maillard reaction during the heating process [16]. Sucrose can be hydrolyzed during heating to obtain a reducing sugar, as a substrate of Maillard reaction. Reactive intermediates are formed by a variety of pathways yielding brown nitrogenous compounds of higher molecular weight called melanoidin pigments [17]. Additionally, at a higher temperature, the reaction rate is higher, thus allowing more non-enzymatic browning reactions to take place. This result corresponds to the decrease in L* value and increase in a* value.

Chemical properties

Changes in HMF content are shown in Figure 3A for open pan heating and 3B for vacuum evaporator heating. HMF is used as an indicator of heat stress to sugar based food such as honey and syrup because of its toxicological status. A significant increase in HMF content as heating increased was observed in all processing methods. HMF in fresh palm sap is approximately 0.6 mg/kg. At the end of each process, HMF in palm sugar syrup was approximately 21 mg/kg for a sample heated by open pan and 7 mg/kg for a sample heated by vacuum evaporator under 70°C and 9 mg/kg for a sample heated by vacuum evaporator under 80°C. From this result, HMF content of all samples was lower than the allowed maximum limit of 40 mg/kg as recommended by Codex Alimentarius [18]. During the production of palm sugar syrup by heating process, HMF can be formed. In the acid medium of this product, dehydration of carbohydrate, especially hexose, led to the formation of HMF. In addition, the Maillard reaction can also take place, giving rise to Amadori compounds during the first step of reaction, and HMF as a consequence of further reaction. Additionally, it is well known that HMF is a precursor of coloured compounds in the caramelization reaction [19]. Therefore, the considerable variations of HMF found in samples may be used as an indication of overheating during the production of palm sugar syrup. Normally, HMF content depends greatly on the processing method, degree of heating and acid condition, as well as storage condition.

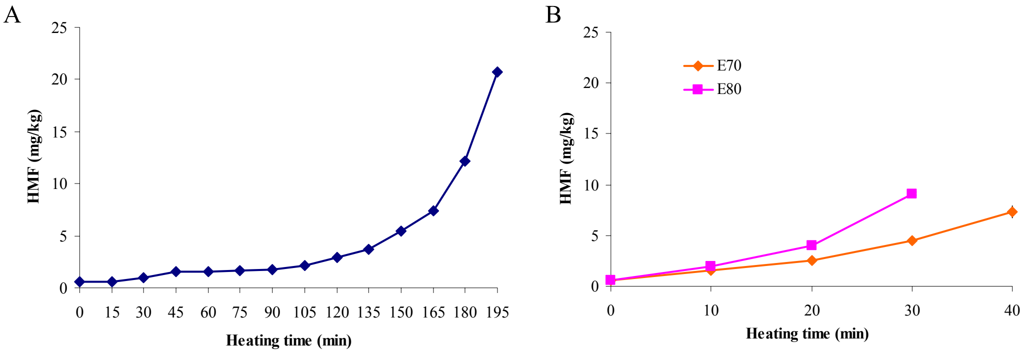

Figure 3. Changes in HMF content during the production of palm sugar syrup by open pan (A) and vacuum evaporator (B).

Figures 4A and 4B show the change of fructose, glucose and sucrose content during the production of palm sugar syrup by open pan and vacuum evaporator, respectively. A significant ($P<0.05$) increase in fructose, glucose and sucrose content was observed for palm sugar syrup produced by both open pan and vacuum evaporator. Initial fructose, glucose and sucrose contents of palm sap were 0.41%, 0.45% and 10.42%, respectively. The increase in fructose content, glucose content and sucrose content were slight in the first 90 min for open pan, 20 min for vacuum evaporator under 70°C and 10 min for vacuum evaporator under 80°C ($P<0.05$). Thereafter, a rapid increase in fructose content and glucose content occurred until the end of heating time (195 min for open pan, 40 min for vacuum evaporator under 70°C and 30 min for vacuum evaporator under 70°C) ($P<0.05$). The fructose, glucose and sucrose contents of finished palm sugar syrup were 4.71%, 4.76%, 61.18% for open pan process, 2.51%, 2.53%, 66.32% for vacuum evaporator under 70°C and 2.46%, 2.28% and 65.66% for vacuum evaporator under 80°C. In general, fructose and glucose contents should be reduced during Maillard reaction, but they increased in this observation. This unconformity may caused by sucrose inversion as heating temperature and heating time increased. This result may indicate that the reaction rate of sucrose inversion was greater than that of the Maillard reaction occurring [20]. In addition, the increase in fructose and glucose content was due to their being concentrated during the heating process, as well as the increase in sucrose content during the heating process ($P<0.05$). From this result, it was found that the major sugar found in palm sugar syrup was sucrose. Palm sugar syrup heated by vacuum evaporator can reduce the loss of sucrose more so than palm sugar syrup heated by open pan. This is probably due to this process using a lower temperature and a shorter time. Additionally, this process can also minimize sucrose inversion, therefore lower reducing sugar content is obtained than the production by open pan. The reducing sugar content is an important parameter that affects the properties of palm sugar syrup during storage since it can act as a substrate for Maillard reaction.

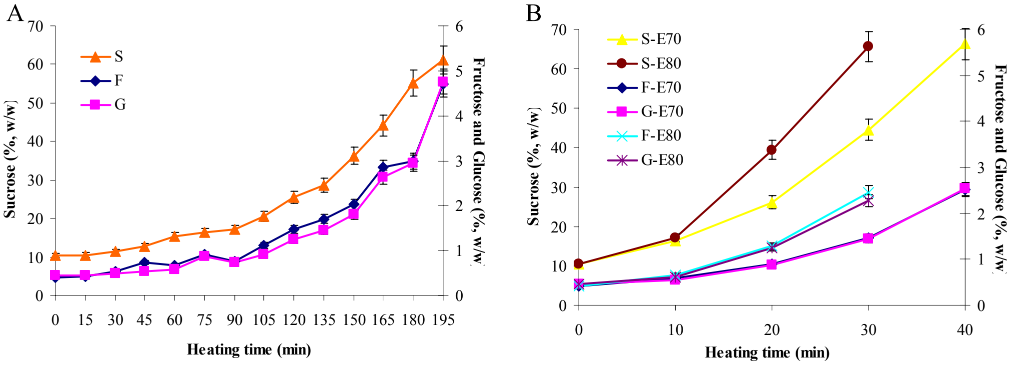

Figure 4. Changes in fructose, glucose and sucrose content during the production of palm sugar syrup by open pan (A) and vacuum evaporator (B).

Protein content in all palm sugar syrup samples was monitored during the heating process as shown in Figure 5A for open pan and 5B for vacuum evaporator. Protein content tended to increase as the heating time increased up to 195 min for open pan process, 40 min for vacuum evaporator under 70°C and 30 min for vacuum evaporator under 80°C. Protein content of palm sugar syrup initially was 0.42 mg/g. At the end of the heating process, protein content of palm sugar syrup was 1.42 mg/g, 1.51 mg/g and 1.45 mg/g for sugar syrup produced by open pan, vacuum evaporator under 70°C and 80°C, respectively. A slow increase in protein content was observed for the first 90 min of the open pan process, 20 min for the vacuum evaporator under 70°C and 10 min for the vacuum evaporator under 80°C ($P<0.05$). Following this, a marked increase in protein content was observed until the end of heating time for all palm sugar syrup samples ($P<0.05$). However, there was not significant protein content in all samples at the end of each process. In general, Maillard reaction is one of the major reactions that is responsible for browning during the heating process of palm sugar syrup. Protein content should decrease during Maillard reaction, but it was shown to increase in this study. This is probably due to the palm sugar syrup being concentrated during the heating process, indicating that the rate of concentration was higher than the rate of Maillard reaction.

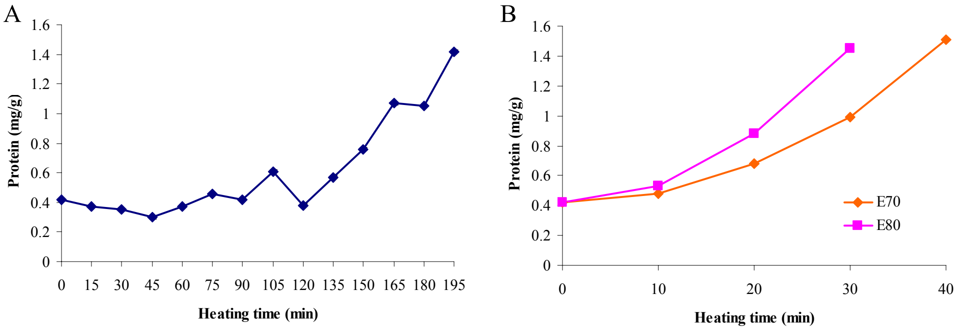

Figure 5. Changes in protein content during the production of palm sugar syrup by open pan (A) and vacuum evaporator (B).

Conclusion

Concentration of liquid food is a vital operation in many food processes. Traditionally, the production of palm sugar syrup uses both high temperature and long duration. During the heating process, non-enzymatic browning reaction and inversion reaction can take place. These reactions affect the properties of palm sugar syrup. According to the results obtained, palm sugar syrup heated by open pan provides for a higher rate of non-enzymatic browning than palm sugar syrup produced by vacuum evaporation, as evidenced by the decrease in L* values and increase in a* values and browning intensity. Moreover, concentration by vacuum evaporation can retain sucrose and lower reducing sugar content, mainly fructose, glucose and HMF content more so than the traditional open pan process. Both sugars are the substrates of Maillard reaction, following the non-enzymatic browning reaction of samples. It could thus be considered that concentration by vacuum evaporation is an improvement method for palm sugar syrup production since this method can minimize the loss of quality and the degradation of product due to the heating process. These results also suggest that heating temperature is the main factor affecting the quality of palm sugar syrup.

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