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Structural Changes in Cooked Rice Treated with Cooling-Reheating Process and Coconut Milk Addition as Observed With FT-IR and ^{13}C NMR

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ABSTRACT

The molecular structural changes of food could be observed by the technique of FT-IR and ^{13}C NMR spectroscopy. This research was aimed to study the structural changes in cooked rice treated with cooling-reheating process and coconut milk addition using FT-IR and ^{13}C NMR. It was found that the cooling-reheating process and addition of coconut milk cause several structural changes of cooked rice. The IR analysis showed the bands at 3,400, 2,900, 1,018 and 856 cm^{-1} changed due to the retrogradation during cooling process. The spectrum of ^{13}C NMR showed the change of peaks at 100.28 and 100.10 ppm. These changes may be related to the addition of coconut milk during rice cooking.

Keywords: Coconut milk; cooked rice; spectroscopic method

INTRODUCTION

As a staple food of Indonesian people, rice was often mixed and cooked with other ingredients, such as coconut milk and pandan leaves. The addition of those ingredients aimed to give a unique taste and aroma for the cooked rice.

Previous studies showed that the physicochemical changes of rice during processing affects the functional properties of the cooked rice. During rice cooking, the gelatinization process was occurred and gives the starch was easily digestible. The in vitro digestion rate was increase with longer amylose branches (Patindol et al., 2010) and smaller ratios of long amylopectin and long amylose branches to short amylopectin branches (Syahariza et al., 2013). On the other hand, the in vitro digestion rate was decrease with retrograded starch (Frei et al., 2003; Chung et al., 2006; Vatanasuchart et al., 2009).

The molecular structural changes of starch could be observed with several techniques, such as differential scanning calorimetry (DSC) (Sodhi and Singh, 2003), X-ray diffractions (XRD) (Zhu et al., 2011), Fourier transform infrared (FT-IR) (Falade et al., 2014), Raman (FT-Raman) (Flores-Morales et al., 2012) and ^{13}C CP-MAS/NMR nuclear magnetic resonance (Zabar et al., 2009). The structural change of retrograded starch have been identified by the IR spectra on the band at 1,047 cm^{-1} while the band at 1,743 cm^{-1} associated to lipid and protein groups (Thygesen et al., 2003). Furthermore, amylose-lipid complexes could be identified from the NMR spectra. The fatty acids were trapped to both the acid form (COOH) and the salt form (COO^-) as can be inferred from the appearance of two signals at 177 ppm and 182 ppm (Zabar et al., 2009).

In this research, the techniques of the FT-IR and ^{13}C NMR were used to observe the structural changes of cooked rice mixed with coconut milk. The mixture rice and coconut milk were observed in fresh and treated with cooling and reheating process.

RESEARCH METHODS

Materials

The rice sample known as Setra ramos variety and purchased from local market in Yogyakarta, Indonesia. This

variety was chosen because of its amylose content (23.69 %) and resistant starch content (21.13 %). The commercial coconut milk fluid was purchased from market in Yogyakarta, Indonesia.

Preparation of Mixture of Rice and Coconut Milk

The preparation was done according to the method of Chung et al. (2006) and Rewthong et al. (2011) with modifications. Raw rice (100 g) was cooked with a 1.6 fold addition (w/v) of water and 50 mL (w/v) of coconut milk using home-style rice cooker until automatic shutoff (about 20 min). Fresh cooked rice samples were allowed to cool at room temperature for 15 min prior to analyses. The cooling and reheating process were treated to cooked rice samples for once and two times. The same procedure was done for cooked rice samples without addition of coconut milk.

FT-IR Measurements

The FT-IR measurements were done using the method of Falade et al. (2014). Samples (2 mg, dry basis) were mixed with 200 mg anhydrous KBr and pressed using a manual press for 20 min. Then, the pellets were transferred into FT-IR system. FT-IR spectra were recorded using a FT-IR Prestige 21 (Shimadzu Inc. USA). Each spectrum was recorded at a resolution of 4 cm^{-1} in a range 500-4,000 cm^{-1}.

^{13}C NMR Measurements

The ^{13}C NMR measurements were done according the method of Ai et al. (2013). Samples (10 mg, dry basis) were dissolved in 0.6-0.7 mL dimethyl sulfoxide. Then, the mixture was transferred into ^{13}C NMR system. The ^{13}C NMR spectra were recorded using ^{13}C NMR JEOL ECA-500 (USA). Each spectrum was recorded at room temperature at 500 mHz.

RESULTS AND DISCUSSION

The IR spectra of cooked rice treated with cooling and reheating process in Figure 1 showed identical characteristic bands among the treatments. The band at 3,400 cm^{-1} associated with –OH and the amplitude in the band changed with cooling and reheating process. The change of amplitude band was more pronounced for cooked rice treated with cooling and reheating process two times. Other change of characteristic band after cooling and reheating process was observed at 2,900 cm^{-1}. The cooling process could increase the intensity of crystalline matrix in retrograded rice. These findings agreed with Park et al. (2009) who reported that the retrogradation phenomenon was due to temperature conditions 4 °C. In addition, Flores-Morales et al. (2012) reported the changes of characteristic bands at 3,400 and 2,900 cm^{-1} were due to the phenomenon of retrogradation.

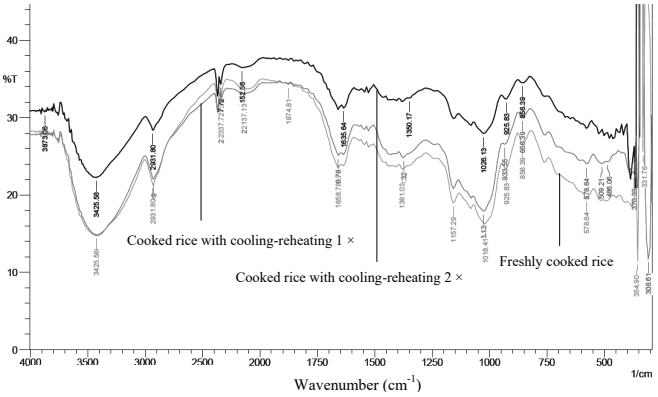

Figure 1. IR spectrum of cooked rice treated with cooling and reheating process

The bands at 1,018 and 856 cm^{-1} were also changed with the cooling and reheating process. These bands were more pronounced in the sample of cooked rice treated with cooling and reheating process two times than in the sample of freshly cooked rice and cooked rice with cooling and reheating process once time (Figure 1). Similar results were reported in previous studies. The region between 1,022 and 856 cm^{-1} were sensitive to changes in crystallinity and could be changed with retrogradation process (Falade et al., 2014; Falade and Christopher, 2015).

The peak at 1,743 cm^{-1} shown in the sample of cooked rice treated with cooling-reheating process and coconut milk addition (Figure 2). This result indicated the presence of lipid from coconut milk may form complex with the starch of cooked rice. The major component of coconut milk was lipid and the percentage of this lipid was varied between 15 and 40 % (Simuang et al., 2004; Naratarukса et al., 2010). Flores-Morales et al. (2012) reported that the band at 1,743 cm^{-1} was identified as the ester carbonyl group. Thygesen et al. (2003) and Derycke et al. (2005) reported that the amylose could form complex with the lipids.

The bands at 1,635, 1,373 and 1,242 cm^{-1} also changed due to retrogradation in the sample with coconut milk addition (Figure 2). These findings were consistent with Thygesen et al. (2003) and García-Rosas et al. (2009) who reported the changes of these bands due to retrogradation.

The signals that appear in the ^{13}C NMR spectra for freshly cooked rice and cooked rice treated with cooling-reheating process were similar (Figure 3). The peak at 99.79-99.81 ppm is identified for C-1, 71.39-73.01 ppm for C-2, C-3 and C-5, 78.65-78.68 ppm for C-4 and 60.37-60.40 ppm for C-6 of the glucose of starch. The spectrum of cooked rice treated with cooling-reheating process showed a decreased peak corresponding to C-1, C-2, C-3, C-4 and C-5. These findings supported by Flores-Morales et al. (2012) who

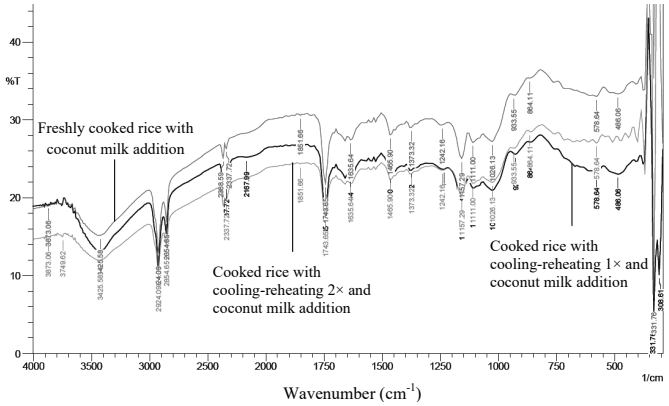

Figure 2. IR spectrum of cooked rice treated with cooling-reheating process and coconut milk addition

reported carbon chemical shift for starch has been identified in 101-106 ppm for C-1, in 72-76 ppm for C-2, C-3 and C-5, in 81-85 ppm for C-4 and in 62 ppm for C-6. Furthermore, as a comparison the retrograded of stored tortilla starch presents the additional peaks in C-1, the deformation peaks in C-6 and a decreased peak in C-2, C-3 and C-5.

The addition of coconut milk in cooked rice treated with cooling-reheating process once time gave a further decreased peak compared to freshly cooked rice without coconut milk addition (Figure 4). When cooling-and reheating process repeated two times in cooked rice with addition of coconut

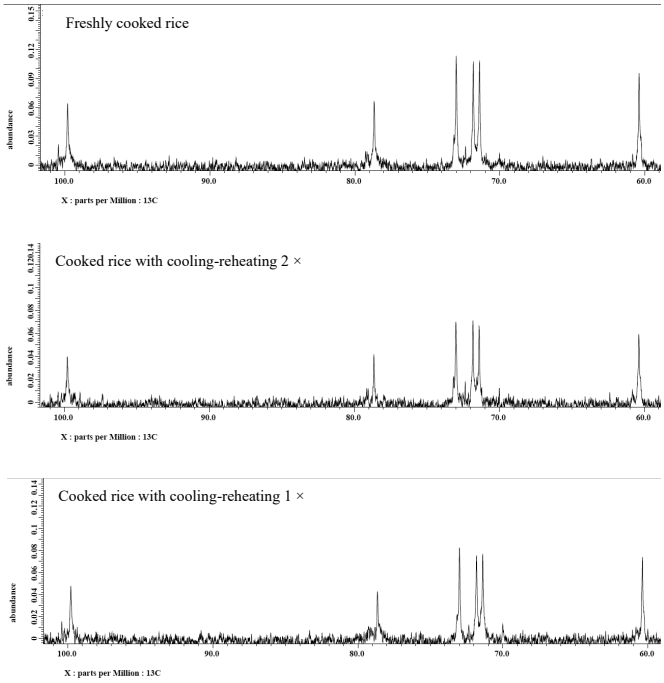

Figure 3. ^{13}C NMR spectrum of cooked rice treated with cooling and reheating process

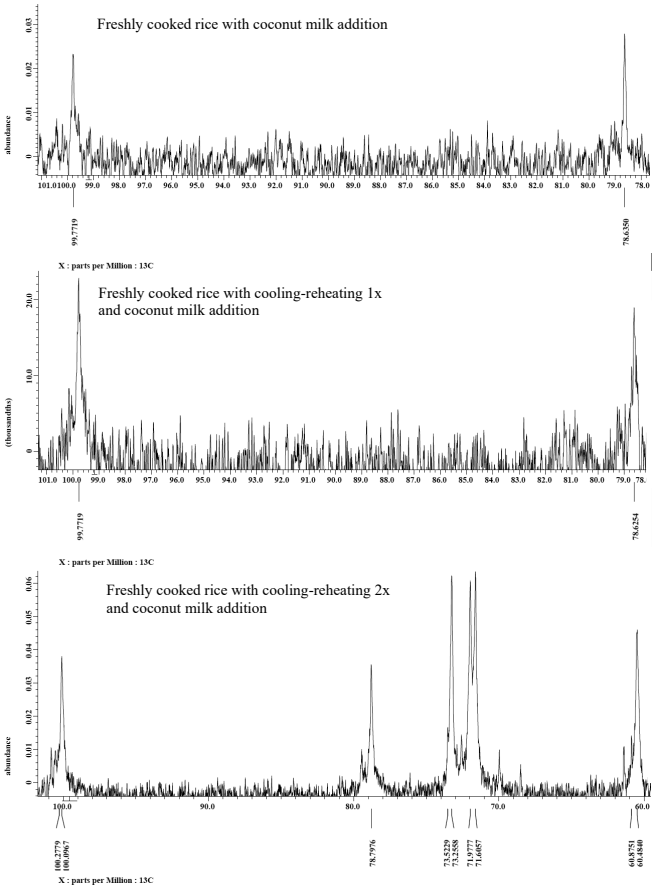

Figure 4. ^{13}C NMR spectrum of cooked rice treated with cooling-reheating process and coconut milk addition

milk, the peak showed increase and C-1 resonance exhibits two peaks at 100.28 and 100.10 ppm.

This result indicated that the addition of coconut milk could change the C-1 resonance. Primo-Martin et al. (2007) reported that the crystallinity and double helix symmetry of starch could be detected from multiplicity of the C-1 position of the glucose units. In addition Ai et al. (2013) reported that the formation of starch helical complex with lipids caused the downfield changes in the chemical shifts of C-1 and C-4 of the amylodextrin.

CONCLUSION

The technique of FT-IR and ^{13}C NMR spectroscopy showed structural changes in cooked rice treated with cooling-reheating process and coconut milk addition. The change of the band at 3,400 and 2,900 cm^{-1} indicated to retrogradation in cooked rice treated with cooling and reheating process. The peaks observed at 100.28 and 100.10 ppm indicate that the structural changes of C-1 position of the glucose units due to the addition of coconut milk in cooked rice treated with cooling-reheating process.

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