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Full Length Research Paper

Drying characteristics and antioxidant properties of Java plum seed and skin waste

Amritpal Kaur, Dilpreet Singh, Harpreet Kaur and Dalbir Singh Sogi*

Department of Food Science and Technology, Faculty of Science, Guru Nanak Dev University, Amritsar 143005, India.

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Java plum seeds and skin wastes recovered after passing fruits through a pulper were separated manually and dried in tray/fluidised bed drier at 50, 70 and 90˚C or in freeze drier at -55°C at 4.4 torr. Drying behaviour of java plum seeds and skin followed falling rate period and described adequately by Page's model. Drying rate constant was higher for fluidized bed drier varying from 0.00163 to 0.255406 h^{-1} for seeds and 0.002042 to 0.004258 h^{-1} for skin followed by tray and freeze drier. Anthocyanin content of freeze dried java plum skin was 1944 mg/100g dry basis but high drying temperature resulted in lower anthocyanin retention in tray and fluidized bed driers. 'L' and 'b' value of java plum seeds increased but 'a' value decreased. Free radical scavenging activities of fresh java plum seeds and skin were 92.41 and 93.42% respectively which decreased after drying.

Key words: Java plum waste, drying, free radical scavenging activity, anthocyanin content, Page's model.

INTRODUCTION

Syzygium cumini also known as jambolao, black plum, jambolan, java plum or jamun is a member of Myrtaceace family (Veigas et al., 2007). Ripe Jamun fruit is about 2 to 3 cm long, oval shaped, purple-red to black peel and white to pink pulp with astringent taste (Benherlal and Arumughan, 2007). Fruit constitutes about 75% pulp and 25% seeds and skin. Fruit and seeds are used for treatment of various diseases such as antiscorbutic, diuretic, antidiabetic, and antidiarrohea (Achrekar et al., 1991; Chaturvedi et al., 2009). Java plum seeds and skin are the by-products of juice production containing high moisture level that limits their storage life and utilization. Drying is a simple preservation technique to extend storage life. In this investigation Java plum seed and skin waste was dehydrated using three techniques and its effect was analysed on pigment and antioxidant properties.

MATERIALS AND METHODS

Materials

Fresh java plum fruits were procured from local orchard located at Attari, Amritsar, India. Fruits were rinsed thoroughly with water and passed through pulper (Kalsi Industries, Ludhiana, India). The peel and seeds were separated manually. The seeds were cut in longitudinal and cross section direction using stainless steel knife.

Drying

Whole, longitudinal and cross section cut seeds and skin of java plum fruits were dried in tray drier (Narang Scientific Works, New

*Corresponding author. E-mail: sogids@gndu.ac.in.

Delhi, India) and fluidized bed drier (Endecotts, London, UK) at 50,70 and 90℃ whereas in freeze drier (Heto Power Dry, Allerod, Denmark) at -55°C at 4.4 torr pressure. Moisture content was observed at every 15 min interval to study drying characteristics. Page's model was used to describe drying behaviour of Java plum seeds and skin.

$$M.R = \frac{m - \mathrm{me}}{\mathrm{mo} - \mathrm{me}} = \exp(-\mathrm{kt}^{\mathrm{n}})$$

Where, M.R = moisture ratio
m = % moisture content at any given instant time t (% db)
me = equilibrium moisture content (% db)
mo = initial moisture content (% db)
k= drying rate constant (1/h)
n= dimensionless coefficient

Composition of java plum seeds and skin

Moisture, ash, crude fat, protein and fibre contents were measured following standard method of analysis (AOAC, 1990). Carbohydrate content was determined by difference.

Determination of anthocyanin content

Java plum skin was extracted with ethanolic HCl (85% of ethanol-95% and 15% of 0.1N HCl) and absorbance of extract was measured at 535 nm (Ranganna, 1986).

$$\text{Anthocyanin Content} = \frac{\text{OD at 535 nm} * \text{volume made} * \text{dilution factor}}{\text{weight of sample} * 98.2} * 100$$

Extinction factor = 98.2

Colour measurements

Ultra Scan VIS Hunter Lab (Hunter Associates Laboratory Inc., Reston, USA) was standardized using standard tiles, and *L, a* and *b* values were measured.

Free radical scavenging activity

Seeds/ Peel (100mg) was extracted with 1 ml of methanol for 2 h in shaker (LabTech, Namyangju, Korea), centrifuged at 10,000 xg for 8 min. 1 ml of supernatant was added to 3.9 ml of 0.1 mMol DPPH solution in brown glass vial. The reaction mixture was shaken and incubated in dark for 30 min. The absorbance was taken at 515 nm (Genesys 10S UV-VIS, Thermo Scientific, Massachusetts, USA) against a blank. The percentage of scavenging was determined by the formula:

$$\%\ \text{Inhibition} = \frac{\text{absorbance control} - \text{absorbance sample}}{\text{absorbance control}} * 100$$

Statistical analysis

One way analysis of variance (ANOVA) was applied on the data of proximate composition, anthocyanin content, free radical scavenging activity, coefficients of page's model and hunter colour parameters. Least significant difference values were calculated to find significant difference at p≤0.05. Mean values, standard deviation and ANOVA were computed using Mini Tab (Version 17) (Minitab Inc., State College, Pennsylvania, USA).

RESULTS AND DISCUSSION

Composition of java plum seeds and skin

Fresh java plum seeds contained 53% moisture, 6.4% protein, 1.5% ash, 4.53% fat, 16.4% fibre and 21.9% total carbohydrates (Table 1). Java plum skin contained 79% moisture, 0.91% ash, 0.80% fat, 0.12% protein and 15.35% total carbohydrates. Statistical analysis revealed that there was significant (p≤0.05) difference in moisture, fat, protein and total carbohydrates of java plum skin and seeds. Previous studies have reported 40.86 to 57.33% moisture, 2.42 to 5.05%, protein, 1.47 to 6.21% ash, 1.55 to 8.00% fat and 1.28 to 10.95% crude fibre in java plum seeds (Kochar et al., 2006; Swami et al., 2012). Present results of seed composition were close to previously reported values except for protein and fibre content which were higher. These differences might arise from the variation in variety, agricultural practices and climatic conditions. The composition of java plum skin could not be traced in the literature. Red grape skin had the moisture, fat and protein contents in the range of 74.6 to 73.2%, 3.35 to 6.33% and 11.26 to 12.12% respectively (Deng et al., 2011; Torres et al., 2010). Composition of java plum was quite different from red grape skin which contained low moisture but high protein and fat contents.

Drying curves

The initial moisture contents of whole, longitudinal cut and cross section cut java plum seeds were 113, 122 and 127% (dry basis - db) respectively (Figure 1). Tray and fluidized bed dried seeds had final moisture content of about 10% (db) and freeze dried seed had about 15% (db). The drying of java plum seeds took different time intervals in tray, fluidized bed and freeze drier operated at different temperatures.

The experimental data showed higher rate of moisture removal in the beginning of drying and later it slowed down with decrease in moisture content just like other biological materials. However, a considerable variation was observed in drying curves of whole, longitudinal cut and cross section cut java plum seeds. Drying rate increased significantly (p≤0.05) with increase in surface area due to size reduction. Similar results were reported for tomato seeds that drying rate decreased continuously indicating that drying of tomato seeds took place in falling rate period (Sogi et al., 2003).

The drying of the java plum skin took about 375, 105 and 75 min in tray drier while 75, 35 and 30 min in fluidized bed drier at 50, 70 and 90°C respectively (Figure 1) whereas it took about 300 min in a freeze drier. Drying rate was higher in the beginning but it became slow at the later stage in all the drying curves. Drying was rapid in fluidized bed dryer as compared to tray and freeze dryer.

The drying of java plum seeds and skin took place in falling rate period under experimental condition just like

Table 1. Proximate composition for fresh Java plum seeds and skin (n=3).

Parameters	Fresh java plum seeds	Fresh java plum skin
Moisture content (% wb)	53±1.21[b]	79.09±1.98[a]
Ash content (% wb)	1.5±0.23	0.91±0.01
Fat content (% wb)	4.53±0.68[a]	0.8 ± 0.15[b]
Protein content (% wb)	6.4±0.62[a]	0.12±0.01[b]
Crude fibre content (%wb)	16.4±0.36	ND
Total carbohydrates (by difference)	21.9±0.94 [a]	15.35±1.8[b]

Superscripts with different letters indicate significant difference p≤0.05 among treatments.

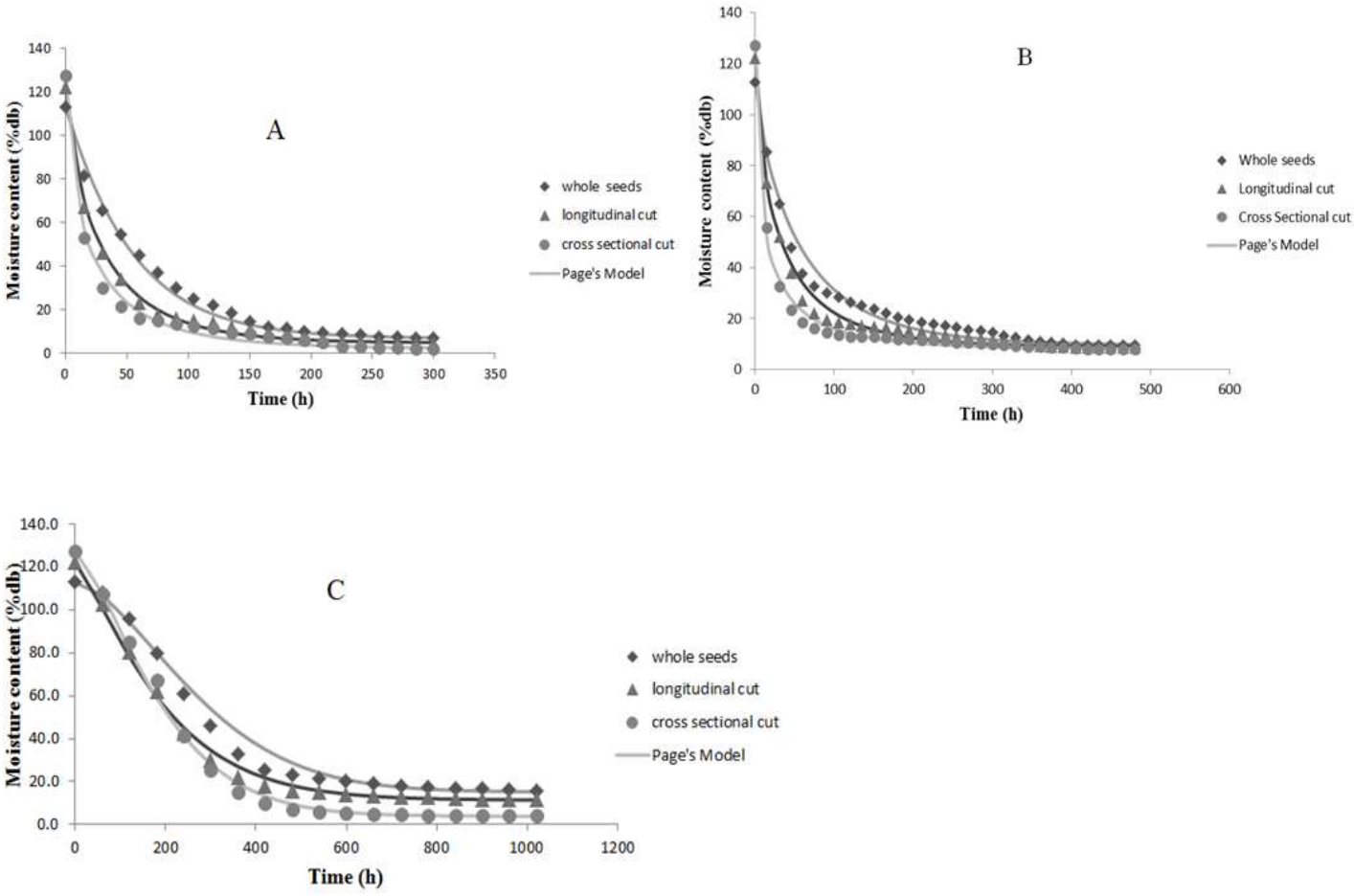

Figure 1. Drying curves of java plum seeds in Cabinet Drier at 70˚C (A), fluidised bed drier at 70˚C (B) and freeze drier (C) at -55˚C at 4.4 torr.

other biological materials. Drying of tomato skin took place in falling rate period as drying rate decreased during drying period. In fluidized bed drier, tomato skin dried in 108 min whereas in cabinet drier drying occurred in 1080 min (Kaur et al., 2006). Present results find support from previous studies on rate of drying of java plum seeds in different dryers.

Drying model

Drying data was analysed by using Page's model and its coefficients were computed. The drying rate constant (k) for seeds varied from 0.000374 to 0.004221 h^{-1} for tray dryer (Table 2). The drying rate constant was the highest for cross sectioned cut java plum seeds due to more

Table 2. Coefficients of Page's model for Java plum seeds (n=3).

Drier	Temperature	Java plum seed type	Drying rate constant K (1/h)	Dimensionless number (n)	R^2
		Whole seeds	0.000263±0.0001^{b}	0.9163±0.0003^{p}	0.982
	50˚C	Longitudinal cut	0.001342±0.0002^{f}	0.7088±0.0001^{i}	0.9661
		Cross section cut	0.002241±0.0001^{l}	0.4984±0.0002^{a}	0.8287
		Whole seeds	0.000374±0.00001^{c}	1.0358±0.0002^{q}	0.974
Tray	70˚C	Longitudinal cut	0.001131±0.0003^{e}	0.7873±0.0002^{k}	0.9509
		Cross section cut	0.002313±0.0002^{j}	0.6503±0.0002^{f}	0.8635
		Whole seeds	0.000620±0.00001^{d}	0.8794±0.0003^{o}	0.9196
	90˚C	Longitudinal cut	0.001731±0.0001^{i}	0.7224±0.0002^{j}	0.8945
		Cross section cut	0.002733±0.0001^{k}	0.6607±0.0002^{g}	0.9553
		Whole seeds	0.001663±0.0002^{h}	1.1595±0.0003^{r}	0.9722
	50˚C	Longitudinal cut	0.01371±0.0001^{m}	0.8441±0.00001^{n}	0.9451
		Cross section cut	0.103519±0.002^{q}	0.5025±0.0005^{b}	0.9385
		Whole seeds	0.03538±0.0001^{n}	0.8221±0.0004^{l}	0.9262
Fluidized bed	70˚C	Longitudinal cut	0.093621±0.0003^{p}	0.6776±0.00001^{h}	0.9175
		Cross section cut	0.255406±0.0001^{t}	0.5111±0.0001^{c}	0.8803
		Whole seeds	0.057908±0.0002^{o}	0.8301±0.0003^{m}	0.9773
	90˚C	Longitudinal cut	0.160365±0.0001^{r}	0.6402±0.00001^{e}	0.891
		Cross section cut	0.251553±0.0004^{s}	0.5615±0.0003^{d}	0.8562
		Whole seeds	0.0000926±0.000001^{a}	1.376±0.0003^{u}	0.9914
Freeze	-50˚C	Longitudinal cut	0.000632±0.00001^{d}	1.2339±0.0002^{t}	0.9858
		Cross section cut	0.001373±0.0001^{g}	1.6115±0.0002^{s}	0.9769

Superscripts with different letters indicate significant difference p≤0.05 among treatments.

surface area. The drying rate constant (k) for java plum seeds in fluidized bed drier varied from 0.00163 to 0.255406 h^{-1}. In fluidized bed drier the drying rate constant (k) for cross section cut was maximum 0.255406 h^{-1}.

In freeze drying, the drying rate constant (k) varied from 0.0000926 to 0.001373 h^{-1}. The dimensionless constant (n) varied from 0.4984 to 1.0358 in tray drier. Seeds dried in fluidized bed drier had dimensionless constant in the range of 0.5025 to 1.1595. The adequacy of fitness of any model can be judged by coefficient of determination (R^2). Its values decreased with increase in surface area of seeds during drying. Therefore, R^2 was the highest for whole seeds and the lowest for cross sectioned cut seeds in all three types of driers at all temperatures. The study showed that drying was rapid in fluidized bed drier followed by tray and freeze driers. Predicted values of moisture content during drying of java plum seeds in tray, fluidized bed & freeze drier has been shown in Figure 1.

Page's model was also used to study the drying behaviour of java plum skin (Table 3). The drying rate constant, k (h^{-1}) varied from 0.001867 to 0.003933 in tray dryer. The maximum value of drying rate constant in tray dryer was found to be 0.003933 h^{-1} at 90^{o}C for java plum skin. In fluidized bed dryer, the drying rate constant varies from 0.002042 to 0.004258 h^{-1} and maximum value was observed during drying at 90^{o}C. Drying rate constant of freeze drier was 0.000572 h^{-1}.

No systematic relation was observed for dimensionless number (n) during drying of java plum skin. The dimensionless number (n), varied from 0.555 to 0.814 for tray drier, 0.927 to 1.036 for fluidized bed drier, and 1.449 for freeze drier. The value of R^2 increased with increase in temperature in driers. The peak value of R^2 for tray and fluidized bed dryer was 0.8874 and 0.9964 respectively at 90^{o}C. The R^2 value for freeze dryer was found to be 0.9954. The coefficients of Page's model for tray, fluidized bed and freeze dryer are shown in Table 3. Drying rate constant (k) of tomato skin dried in cabinet and fluidized bed drier ranged between 0.074-0.528 and 0.937-2.482 respectively (Kaur et al., 2006). Page's model was applied for calculating the coefficients for watermelon pomace drying (Oberoi and Sogi, 2015).

Table 3. Coefficients of Page's model for Java plum skin (n=3).

Drier	Temperature	Drying rate constant K (1/m)	Dimensionless number (n)	R^2
Tray	50°C	0.001867±0.001[b]	0.555±0.001[a]	0.8777
	70°C	0.003624±0.001[d]	0.814±0.001[c]	0.878
	90°C	0.003933±0.001[e]	0.698±0.001[b]	0.8874
Fluidised bed	50°C	0.002042±0.001[c]	0.987±0.001[e]	0.964
	70°C	0.004074±0.001[f]	1.036±0.001[f]	0.9755
	90°C	0.004258±0.001[g]	0.927±0.001[d]	0.9964
Freeze	-50°C	0.000572±0.001[a]	1.449±0.001[g]	0.9954

Superscripts with different letters indicate significant difference p≤0.05 among treatments.

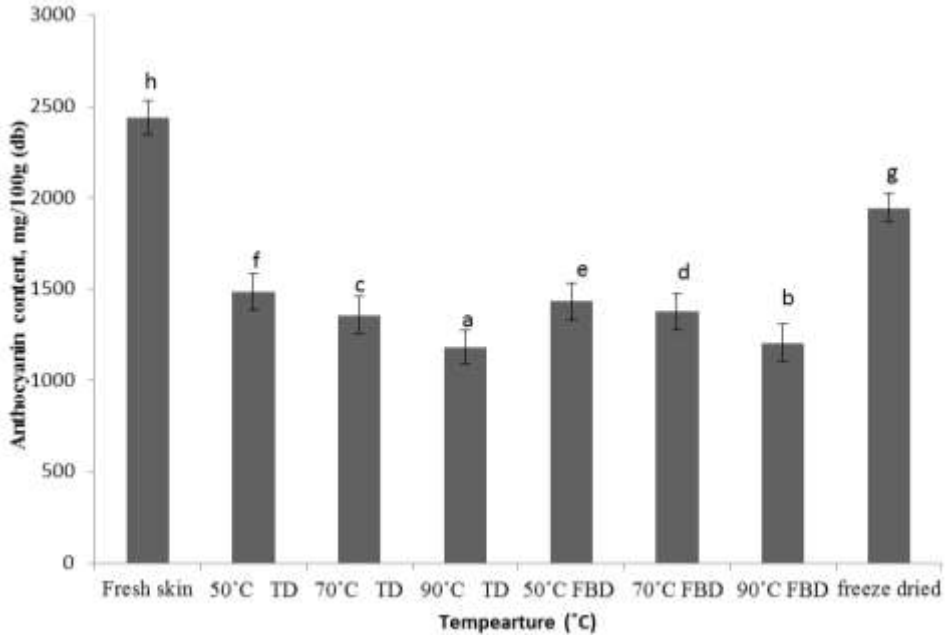

Figure 2. Anthocyanin content of fresh & dehydrated java plum skin. TD-Tray Drier; FBD – Fluidized Bed Dryer.

Although tomato and Java plum had thin peel or skin but the rate of drying was much higher for Tomato skin which might be due to the difference in soluble solids.

Anthocyanin content

The anthocyanin content of the fresh and dried java plum skin has been shown in Figure 2. Anthocyanin content of fresh java plum skin was 2438.10 mg/100g db. After dehydration, the java plum skin became moisture free due to which the anthocyanin content of the dried sample increased but at high temperature, degradation of anthocyanin occurred. The minimum value of anthocyanin content was 1180.97 mg/100g db when dried in a tray drier at 90°C while the maximum value was 1944.14 mg/100g db for freeze dried java plum skin. In fluidised bed drier, anthocyanin content of java plum skin varied from 1205.18 to 1432.60 mg/100g db. Sublimation effectively preserves the valuable food compounds than traditional methods of drying (Uddin et al., 2002). In previous studies, 731 mg/100g (wb) anthocyanin content in ripened java plum skin was reported (Sari et al., 2009). Bilberries contain 300 to 530mg/100g anthocyanin content (Prior et al., 1998). Anthocyanins colour and stability was affected by temperature, light and oxygen. Anthocyanin degradation was positively affected by air temperature and got reduced by 60 to 70% after drying

Table 4. Colour of fresh and dehydrated Java plum seeds and skin (n=3).

Drier	Temp (°C)	Java plum seeds			Java plum skin		
		L	a	b	L	a	b
Fresh	-	38.93±0.34^{a}	7.58 ±0.13^{f}	8.38 ±0.23^{b}	26.56±0.05^{f}	2.97±0.09^{d}	-1.03±0.05^{f}
Tray	50˚C	49.28±0.07^{d}	6.34 ±0.08^{c}	10.48 ±0.15^{f}	26.60±0.13^{g}	3.29±0.02^{f}	-0.52±0.03^{a}
	70˚C	48.31 ±0.8^{c}	6.04 ±0.005^{b}	9.79 ±0.2^{d}	25.90±0.04^{d}	2.85±0.01^{c}	-0.77±0.05^{d}
	90˚C	47.38 ±1.3^{b}	6.4 ±0.2^{c}	9.38 ±0.6^{c}	23.51±0.25^{a}	2.59±0.01^{b}	-1.25±0.03^{h}
Fluidized bed	50˚C	53.63 ±0.2^{e}	6.94 ±0.04^{e}	12.86 ±0.02^{h}	26.52±0.43^{e}	3.42±0.71^{g}	-1.07±0.02^{g}
	70˚C	53.97±0.1^{e}	6.36 ±0.01^{c}	10.9 ±0.03^{g}	25.42±0.39^{c}	3.05±0.17^{e}	-0.66±0.05^{c}
	90˚C	48.91 ±0.3^{c}	6.6 ±0.04^{d}	10.17 ±0.09^{e}	24.21±0.16^{b}	2.3±0.22^{a}	-0.62±0.04^{b}
Freeze	-50˚C	61.89 ±0.3^{f}	5.69 ±0.03^{a}	8.06 ±0.05^{a}	26.64±0.09^{h}	3.02±0.05^{d}	-0.89±0.04^{e}

Superscripts with different letters indicate significant difference p≤0.05 among treatments.

(Mussi et al., 2015). Freeze dried products retained the properties of raw material as compared to the air dried products (Michalczyk et al., 2009). It indicated that low temperature and vacuum helps in retaining the anthocyanin during drying operation.

Visual colour values

Fresh java plum seeds had ‘L’ value of 38.93 and dehydrated seeds had 47.38 to 61.89 (Table 4). Increase in ‘L’ value of java plum seeds on drying might be due to effect of thermal treatment as evident from the data which was found negatively correlated. In case of java plum skin the ‘L’ value was not affected by freeze drying as well as in tray and fluidized bed drying at 50^{o}C, however, it decreased at 70 and 90^{o}C.

The ‘a’ values of fresh java plum seed and skin were 7.58 and 2.97 respectively. Java plum seeds had higher ‘a’ value as compared to java plum skin due to pink pulp adhering on the surface. The ‘a’ value decreased due to the exposure of heat in fluidised bed and tray driers but in freeze dryer it might be due to prolong drying process. Java plum skin dried in freeze dryer, tray drier or fluidised bed drier at 70˚C had close ‘a’ values as in case of fresh peel but increased at 50˚C and decreased at 90^{o}C in tray and fluidized bed dryer. It might be due to browning at 50^{o}C and pigment degradation at 90^{o}C.

The ‘b’ value of fresh java plum seed and skin was 8.38 and -1.03 respectively. The ‘b’ value of java plum seeds increased on drying but showed low values at higher temperatures in tray and fluidised bed driers. The ‘b’ value of freeze dried seeds was close to the fresh seeds. Negative values of ‘b’ showed blueness in the java plum skin. The trend of ‘b’ values of skin was opposite in fluidised bed dryer and tray dryer where it decreased and increase respectively. The ‘b’ value of freeze dried skin was slightly lower than the fresh skin. Statistical analysis showed a significant (p≤0.05) change in colour values on drying in three dryers. Blanching and heating decreased brightness (L), redness (a) and yellowness (b) (Bao and Chang, 1994). ‘L’, ‘a’ and ‘b’ values of black currants varied between 22.01-23.63, -0.08-0.90 and -0.03-1.53 respectively (Ochmian et al., 2014). Thus previous results support the present findings on change in colour values due to heat involved during drying.

Free radical scavenging activity

The antioxidant activity of fresh and dried java plum seeds was measured from decolourizing of DPPH (2,2-diphenyl-1-picrylhydrazyl) solution in term of neutralizing free radical ability (Naik et al., 2003). The study showed that the free radical scavenging activity of java plum seeds reduced after drying. Free radical scavenging activity of fresh java plum seeds was 92.41% and it got decreased to 91.66, 90.99 and 88.65 at 50, 70 and 90^{o}C in the tray drier respectively, while freeze dried seeds had maximum (91.98%) activity after drying (Table 5).

The free radical scavenging activity of fluidised bed dried seeds varied from 90.64 to 91.92%. Statistical analysis depicted the significant difference (p≤0.05) in the free radical scavenging activity of java plum seeds after drying. Java plum seeds dried at 90^{o}C in the tray drier had lowest scavenging activity whereas freeze dried java plum seeds showed the highest free radical scavenging activity. The analysis showed that Java plum seeds are rich source of antioxidants but antioxidants got partially destroyed with the application of heat.

Java plum skin had high content of anthocyanins and contributed to high antioxidant properties. Fresh java plum skin had 93.42% free radical scavenging activity and it reduced to 92.97, 90.66 and 90.01% at 50, 70 and 90˚ C in tray drier respectively whereas in fluidised bed drier free radical scavenging activity decreased from

Table 5. Free radical scavenging activity of java plum seeds and skin (n=3).

Drier	Temperature	Java plum seeds	Java plum skin
Fresh sample	-	92.41±0.73^{g}	93.42±0.49^{h}
Tray	50˚C	91.66±1.07^{e}	92.97±1.20^{g}
	70˚C	90.99±0.71^{c}	90.66±1.46^{c}
	90˚C	88.65±1.05^{a}	90.01±1.23^{a}
Fluidised bed	50˚C	91.92±0.85^{f}	92.54±0.77^{f}
	70˚C	91.48±1.39^{d}	91.43±1.42^{d}
	90˚C	90.64±0.88^{b}	90.17±1.37^{b}
Freeze	-50˚C	91.98 ±2.11^{e}	92.46 ± 0.51^{e}

Superscripts with different letters indicate significant difference p≤0.05 among treatments.

92.54 to 90.17%. Statistical analysis revealed significant ($p<0.05$) change in the free radical scavenging activity of java plum skin. During drying, heat damage occurred at high temperature which resulted in lowering the antioxidant activities.

Syzygium cumini fruits have high antioxidant activity (Afify et al., 2011). The antioxidant activity of fresh java plum seed and skin was 93.90 and 94.55% respectively (Shrikanta et al., 2015). Jamun seeds dried in sun, shade and freeze drier had 92.57, 93.48 and 96.27% antioxidant activity respectively (Shahnawaz et al., 2010). More losses of antioxidant and anthocyanins were found in the air dried serviceberries than freeze dried (Kwok et al., 2004). Previous findings are in accordance with the present results which reaffirm that java plum waste seeds and skin had excellent antioxidant activities.

CONCLUSION

Drying behaviour of java plum seeds and skin waste followed falling rate period pattern and was well described by Page's model. Anthocyanin retention of skin was higher in the freeze dryer but least in tray and fluidized bed drier at 90˚C. Drying rate was affected by size of java plum seeds, and higher drying rate was obtained in cross section cut seeds. Fluidized bed drier was efficient for the drying of java plum seeds and skin.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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Application of NIR-Spectroscopy to predict the harvesting maturity, fruit ripening and storage ability of Ca-chitosan treated baby kiwifruit

J. G. Kim[1,2*], Y. Park[3], M. H. Shin[1], S. Muneer[1], R. Lerud[4], C. Michelson[4], D. Il Kang[1], J. H. Min[5] and H. M. P. Chamidha Kumarihami[1,6]

[1]Department of Horticulture, College of Agriculture and Life Sciences, Gyeongsang National University, Jinju 52828, Korea.
[2]Institute of Agriculture and Life Science, Gyeongsang National University, Jinju 52828, Korea.
[3]Division of Special-Purpose Trees, Korea Research Institute, Suwon 16632, Korea.
[4]Felix Instruments, 1554 NE 3rd Avenue, Camas, WA, 98607, USA.
[5]Department of Horticultural Science, College of Agriculture and Life Science, Chungnam National University, Daejeon, 34134, Korea.
[6]Department of Crop Science, Faculty of Agriculture, University of Peradeniya, Peradeniya, 20400, Sri Lanka.

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In this study, near infrared (NIR) spectroscopy was performed to establish a non-destructive method to predict the harvesting maturity, fruit ripening and storage ability of Ca-chitosan treated baby kiwifruit. Destructive measurements of firmness, dry matter (DM), soluble solids content (SSC), and acidity was performed. The calibration range investigated for dry matter content (DM) and SSC using NIR reflectance spectrums were observed at 729-975 nm wavelengths. NIR predictions of those quality factors were calculated using the modified partial least square regression method. The predicted R^2 value for DM and SSC was 0.73, and the standard error deviation (SED) value was greater than 2. The correlation between the actual value and predicted model of DM were r = 0.74. The correlation between the predicted DM content and the actual SSC, using SSC model was r = 0.65. The correlation between the predicted value of SSC and the actual value of SSC (baby kiwifruits ripen with ethylene) was r = 0.48, which was lower than the actual SSC model. Further, Ca-chitosan pre-harvest treatment on baby kiwifruit showed considerable effects on baby kiwifruit quality. The actual DM content of untreated fruits was 21.4% and it was 22.3% in Ca-chitosan treated fruits. Also, the predicted DM content was significantly high in Ca-chitosan treated fruits (22.7%) compared to untreated fruits. NIR spectroscopy is an effective and efficient method to measure DM and SSC to determine the fruit harvest maturity hence, date of harvest and storability for quality baby kiwifruits from the marketing point of view.

Key words: Ca-chitosan, firmness, harvest index, maturation, nondestructive measurement.

INTRODUCTION

Actinidia arguta, a very promising species in genus *Actinidia* also known as baby kiwi, hardy kiwi, kiwi berry, or mini kiwi, is currently highly appreciated fruit by consumers for its delicious taste and health-promoting properties (Latocha, 2017). Moreover, the consumers are highly concerned on fruit quality indicators such as

ripeness, firmness, dry matter (DM), soluble solids content (SSC) and acidity (Wang et al., 2015). Kiwifruits are highly perishable and have a short shelf-life of 1-2 weeks depending on SSC, cell respiration and microbial spoilage. The decrease of flesh firmness and acidity, and conversion of starch to sugar are the prominent changes in kiwifruits during their maturation and ripening (Lee et al., 2012). The physiological, chemical and sensory changes that occurred during storage reduce the shelf life and quality of kiwifruits. The shelf life of kiwifruits can be increased considerably using edible coating materials such as polysaccharides, proteins, lipids and plant extracts. The coating materials decrease the gas exchange, oxidative reaction rates, respiration and moisture losses as well as suppress the physiological disorders. Chitosan combined with calcium chloride ($CaCl_2$; Ca-chitosan) can be used as an edible coating to increase shelf life of kiwifruits. Chitosan is a high molecular weight cationic polysaccharide produced by chemical deacetylation of the chitin found in arthropod exoskeletons. Chitosan has been actively used as an edible coating material for increasing the shelf life of fruits due to its edible, biocompatible, antimicrobial and nontoxic nature. Chitosan possesses excellent film-forming properties and inhibits the growth of a wide range of fungi and trigger defensive mechanisms in fruits (Kaya et al., 2016; Drevinskas et al., 2017). Calcium improves structural integrity and makes the cell wall less accessible to the enzymes that cause softening and controls fruit ripening, softening and decay. Further, calcium application enhances tissue resistance to fungal attack, maintains cell turgor, membrane integrity, tissue firmness and delays membrane lipid catabolism, maintains textural quality, hence extending shelf life of fruits (Kazemi et al., 2011; Shiri et al., 2016). Therefore, application of chitosan coating together with calcium might have positive effects on postharvest quality of kiwifruits.

Moreover, the firmness, DM, SSC and acidity are much important parameters in kiwifruit quality evaluation, but they currently require the destructive measurements. Hence, the development of reliable, nondestructive, and rapid method is required for the quality evaluation of kiwifruits. Near infrared (NIR) spectroscopy has been introduced as a rapid and nondestructive method to measure the internal fruit quality and potential replacement of existing methods which are highly subjective and time consuming (Maniwara et al., 2014; Wang et al., 2015). Further, the portable, handheld NIR spectroscopic instruments have drawn wide attention due to their potential for in-situ measurements, which enables the growers to obtain nondestructive measurements on pre-harvest maturation rates of fruits. However, to the best of our knowledge, no research has been reported in literature about NIR spectroscopy method used to predict the harvesting maturity, fruit ripening and storage ability of baby kiwifruit [(*A. arguta*) cv. Saehan] and about the combined effect of Ca-chitosan coating on postharvest qualities of baby kiwifruits. Hence, in this study, near infrared (NIR) spectroscopy was performed to establish a non-destructive method to predict the harvesting maturity, fruit ripening and storage ability of Ca-chitosan treated baby kiwifruit.

MATERIALS AND METHODS

Fruit material

Baby kiwifruits [(*A. arguta*) cv. Saehan] from the National Institute of Forest Science in Suwon, Republic of Korea were harvested at 108 days after full bloom (DAFB). Two consecutive harvests were collected on 24th September (1st harvest) and 8th (2nd harvest) October, in 2015. First harvest was used to predict the harvesting maturity based on NIR-spectroscopy and they were not pre-treated with Ca-chitosan. The second harvest consisted of pre-harvest Ca-chitosan treated kiwifruits and was used to measure the fruit quality parameters based on NIR-spectroscopy. All samples were packaged immediately in a plastic clamshell container (KMD-501, Go Pack, Republic of Korea), where twenty fruits were allotted per container and moved to the Laboratory of Fruit Science, Gyeongsang National University, Republic of Korea.

NIR method

NIR spectra of kiwifruit were measured using NIR-spectroscopy system F-750 spectrophotometer (Felix, WA, Camas, USA) with an internal white reference shutter to normalize collected data. The spectrophotometer scanned absorbance at 3 nm sampling wavelength intervals and partial least squares regression (PLSR) was performed on the second derivative of absorbance spectra. Owing to the temperature dependence of the spectral response (Peinado et al., 2006; Cozzolino et al., 2007), kiwifruits were stabilized at temperatures of 1, 15, and 25°C, prior to spectra measurements and a set of three representative scans for each sample was obtained.

Sample preparation and measurement of DM and SSC

A total number of 100, even size fruits without wounds or mechanical damages were selected from the 1st harvest on 24th September, 2015 and stored at three different temperatures, that is, low temperature (1°C), medium temperature (15°C), and maximum temperature (25°C), respectively for 1 h. Three different temperatures were selected due to the temperature dependence of the spectral response and kiwifruits were stabilized at 1, 15 and 25°C, prior to spectra measurements. The spectra were nondestructively measured using F-750 at each temperature before making 2 cm thick destructive fruit cores at the scanned location. For DM reference values, fruit cores were oven dried for 48 h at 65°C. Fresh weight and dry weight was measured using a Voyager Pro balance (Ohaus Voyager, United Kingdom) with a scale at

*Corresponding author. Email: jgkim119@gnu.ac.kr Tel: +82-55-772-1918, C.P. +82-10-7711-4814. Fax: +82-55-772-1919.

0.001 mg resolution. The DM reference value of each fruit was correlated with the original spectral to create a calibration for F-750. For SSC calibration, another set of 100 baby kiwifruits was prepared and stored by following the same procedure described previously. Thereafter, fruits were ripened with 50 ppm exogenous ethylene (12 h, 18°C) in an environmental chamber. After 4-5 days, the SSC of ripened fruits were measured. The SSC reference value of each fruit was correlated with the original spectral to create calibration for F-750 which allows the pre-harvest estimation of SSC after ripening.

Calcium chitosan treatment and fruit storage conditions

High molecular weight chitosan (500,000 MW) and $CaCl_2$ (77%) were purchased from JS Logistics, Sejong and Samchun Pure Chemical Co., LTD., Pyeongtaek, Republic of Korea, respectively. Coating solutions were prepared by dissolving 2% chitosan and 2% $CaCl_2$ in 0.2 M acetic acid solution with 0.02% surfactant. Pre-harvest Ca-chitosan treatment was done for the baby kiwifruits through dipping method at three times, that is, 17th, 24th September and 1st October, 2015. The treated fruits were harvested on 8th October, 2015 and stored in a plastic container (2.1 L vessel, HPL826M, LocknLock, China) at 5°C and 95% RH for 7 and 14 days. After 7 days of storage, 10 fruits were subjected to ripening with 50 ppm ethylene for 5 days and SSC measurements were recorded. Similarly, after 14 days of storage, the rest of fruits were also subjected to ripening with 50 ppm ethylene for 5 days and SSC measurements were recorded.

Soluble solids content (SSC), titratable acidity (TA), and firmness

The SSC was measured using kiwifruit juice extractions from nine biological replicates. The extracted fruit juice was filtered through 4 layers of cheesecloth prior to analysis using PAL-1 Refractometer (Atago Co. LTD, Tokyo, Japan). Similarly, nine biological replicates were used for TA and firmness measurements. The titratable acidity (TA) of fruit juice was assayed by titration with 0.05 mol·L^{-1} NaOH using a professional benchtop BP3001 pH meter (Trans Instruments, Singapore). The TA content was expressed as citric acid equilibrium. The fruit firmness was measured using a rheometer (RHEO TEX SD-700, Sun Scientific Inc, Japan) with a round flat probe of 3 mm in diameter on a horizontal axis and the probe was inserted to the fruit up to 3 mm depth. The measurements were performed at the crosshead speed of 120 mm·min^{-1} at room temperature (20 ± 2°C).

Data analysis

All fruit samples were harvested randomly, and analysis was performed on three biological replicates. The data analysis was done with SAS 8.2 statistical software (SAS Inst., Cary. N.C., USA), following the analysis of variance (ANOVA) and Tukey's T-test. PLSR calibrations were done with the F-750 Model Builder software (Felix Instruments, WA, Camas, USA).

RESULTS AND DISCUSSION

NIR spectra calibration and prediction of physiochemical parameters

The NIR reaction wavelength range for soluble solids content (SSC) of kiwifruit has been reported as 800 – 1,100 nm (Lee et al., 2012) and for measuring carbohydrate content the wavelength range varies from 880, 900-930, and 970 nm. The spectra collected in the present study showed variations among fruit specimens (in 100 fruit samples) (Figure 1). The calibration range investigated for dry matter content (DM) and SSC using nondestructive predictions from F-750 Model Builder software (Felix Instruments) was observed at 729 - 975 nm wavelengths. The predicted R^2 value for DM and SSC was 0.73, and the standard error deviation (SED) value was greater than 2 (Table 1).

The baby kiwifruit cv. Seahan is known to be harvested at the beginning of October encompassing a full bloom date (108 DAFB). The change of fruit weight (FW) and maturity was observed for 2 weeks (Table 2). The SSC was increased by 1° Brix and the firmness was decreased by 3.7 N at the week before actual harvesting date. The correlation between the actual value and predicted model of DM were r = 0.74 (Figure 2). The predicted DM variation among the 384 harvested fruits is shown in Figure 3. Among 384 fruits, 71% fruits were shown 21 - 22% predicted DM, while 10% fruits were shown less than 21% predicted DM and 18% fruits were shown more than 23% predicted DM. Therefore, to prevent the accumulation of non-commodity acceptable fruits with unacceptable levels of SSC, it is necessary to study the uniformity of fruit quality in a sample through a nondestructive approach, such as NIR-spectroscopy.

The estimated SSC values in fruits for predicated DM were recorded as, 9.1° Brix for 20% DM, 9.6° Brix for 21% DM, 11.1° Brix for 22% DM, and 11.2° Brix for 23% DM (Figure 4). This infers that higher DM content at harvest correlates to higher SSC. The correlation between the predicted DM content and the actual SSC, using SSC model was r = 0.65 (Figure 5). The correlation between the predicted value of SSC and the actual value of SSC was r = 0.48, which was lower than the actual SSC model (Figure 6).

The use of NIR spectrometry to determine SSC, DM, and fruit firmness has been reported previously in kiwifruit (Schaare and Fraser, 2000; Clark et al., 2004). Park et al. (2003) found that the F-750 can be successfully used to predict SSC through spectra ranging from 800 - 1,100 nm in apple varieties, 'Gala' and 'Red Delicious' with a high accuracy (r = 0.97 and 0.96, respectively). Further, Angra et al. (2009) evaluated °Brix values of apple fruits with the wavelength that ranged from 800 - 1,600 nm. Similarly, Pissard et al. (2013) built models with NIR to predict °Brix in 150 apple genotypes. The present results obtained from F-750 and all other reports depicted that NIR is an accurate and reliable method to obtain physiochemical measurements particularly, SSC, °Brix, and starch content.

Effect of calcium chitosan treatment on physiochemical parameters

The preharvest application of Ca-chitosan on baby

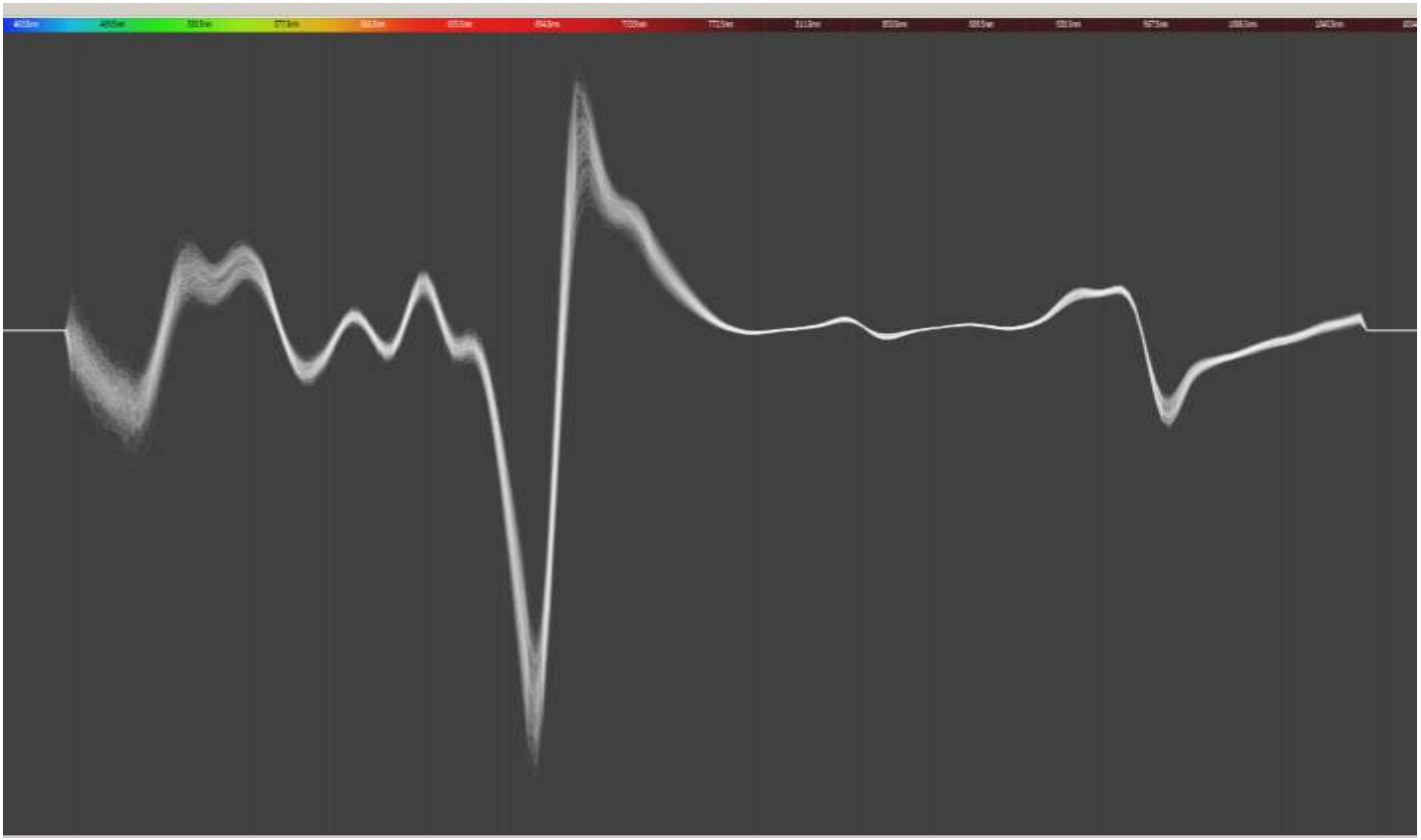

Figure 1. Screenshot of Model Builder Software displaying second derivative spectra collected from 100 fruits of baby kiwifruit cv. Saehan using F-750.

Table 1. NIR calibration values of dry matter content (DM) and soluble solid content (SSC) of baby kiwifruit cv. Saehan.

Quality Index	λ region (nm)	RMSECV[b]	RMSEC[a]	Principal component	Prediction R^2	Error/Deviation Ratio Predicted
DM (%)	729-975	0.46	0.41	7	0.73	3.38
SSC (^{o}Brix)	729-975	1.24	1.07	9	0.73	3.14

[a] Root mean square error calibration; [b] Root mean square error of cross validation.

Table 2. Characteristics of baby kiwifruit cv. Saehan at different harvest dates in 2015.

Harvest date	FW (g)	SSC (^{o}Brix)	TA (%)	Firmness (N)
24th September	13.3±0.5	7.8±0.2	1.4±0.1	21.6±0.4[a]
8th October	15.1±0.3	8.8±0.4	1.3±0.1	17.9±0.4

[a] Mean ± Standard error.

kiwifruit influences the metabolism and respiration of the preharvest fruits and may inhibit the maturation. Ca-chitosan treated baby kiwifruit cv. Saehan reported 9.5° Brix, which was significantly higher compared to untreated fruits with 8.4° Brix. The titrable acidity was not significantly different among Ca-chitosan treated and untreated fruits at p=0.05 level (Table 3). The Ca-chitosan treated fruits of baby kiwifruit cv. Saehan showed lower fruit weights (12.8 g) compared to the untreated fruits (14.9 g) (Table 3). The firmness of Ca-

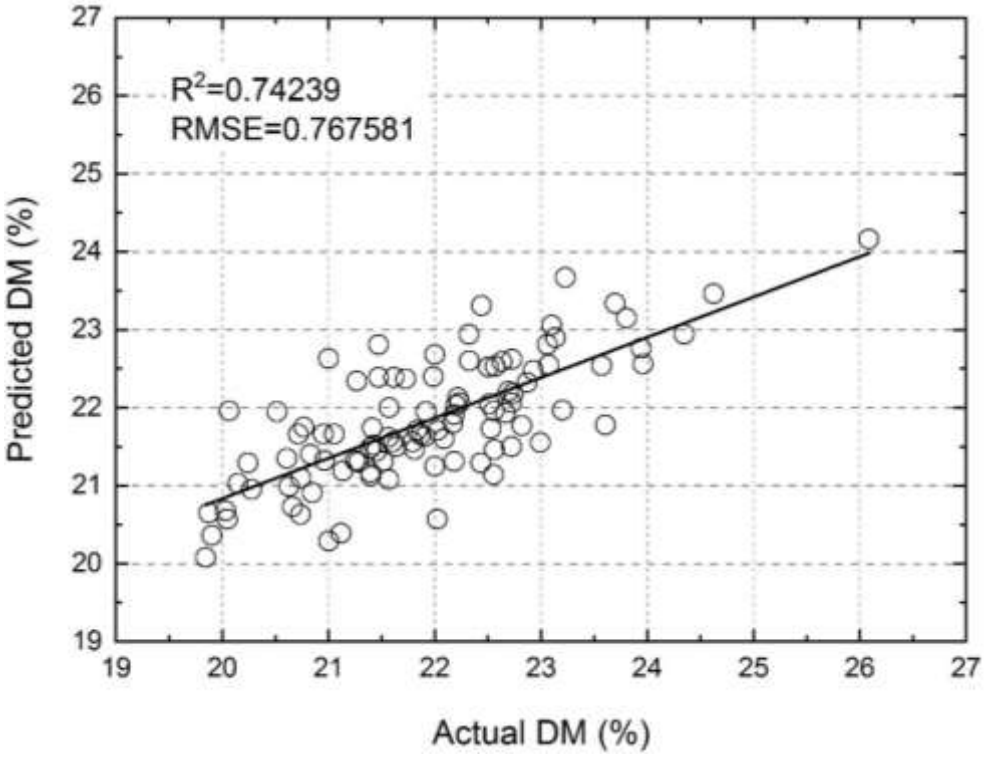

Figure 2. Correlation between actual and predicted dry matter content (DM) of baby kiwifruit cv. Saehan. Regression statistics (n=100, R^2=0.74239, RMSE=0.767581, STDy=0.93309).

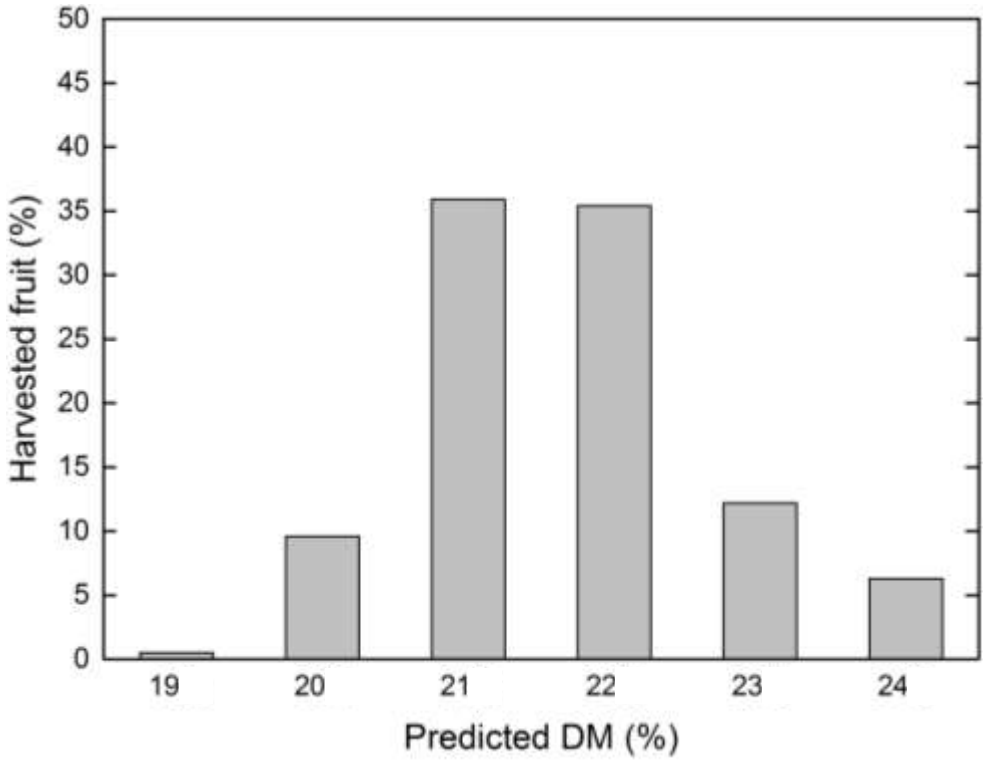

Figure 3. Distribution of dry matter content (DM) of all the harvested baby kiwifruit cv. Saehan on 8th October, 2015 analyzed by F-750 NIR.

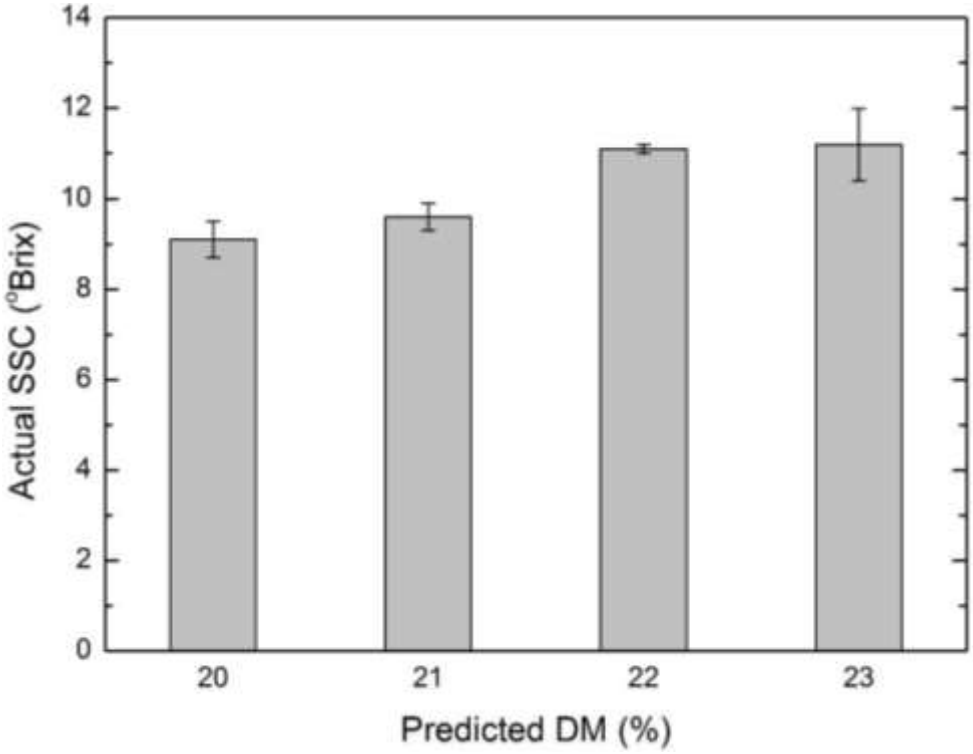

Figure 4. Soluble solid content (SSC) of predicted dry matter content (DM) in baby kiwifruit cv. Saehan analyzed by F-750 NIR.

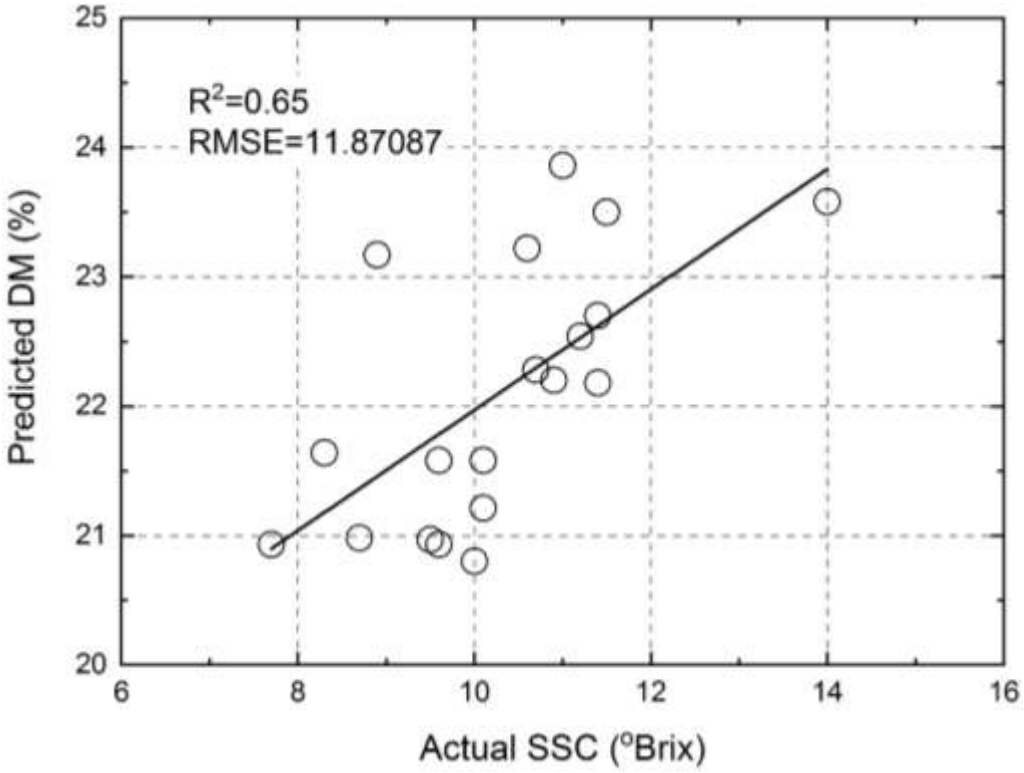

Figure 5. Correlation between predicted dry matter content (DM) and actual soluble solid content (SSC) after ripening of baby kiwifruit cv. Saehan.

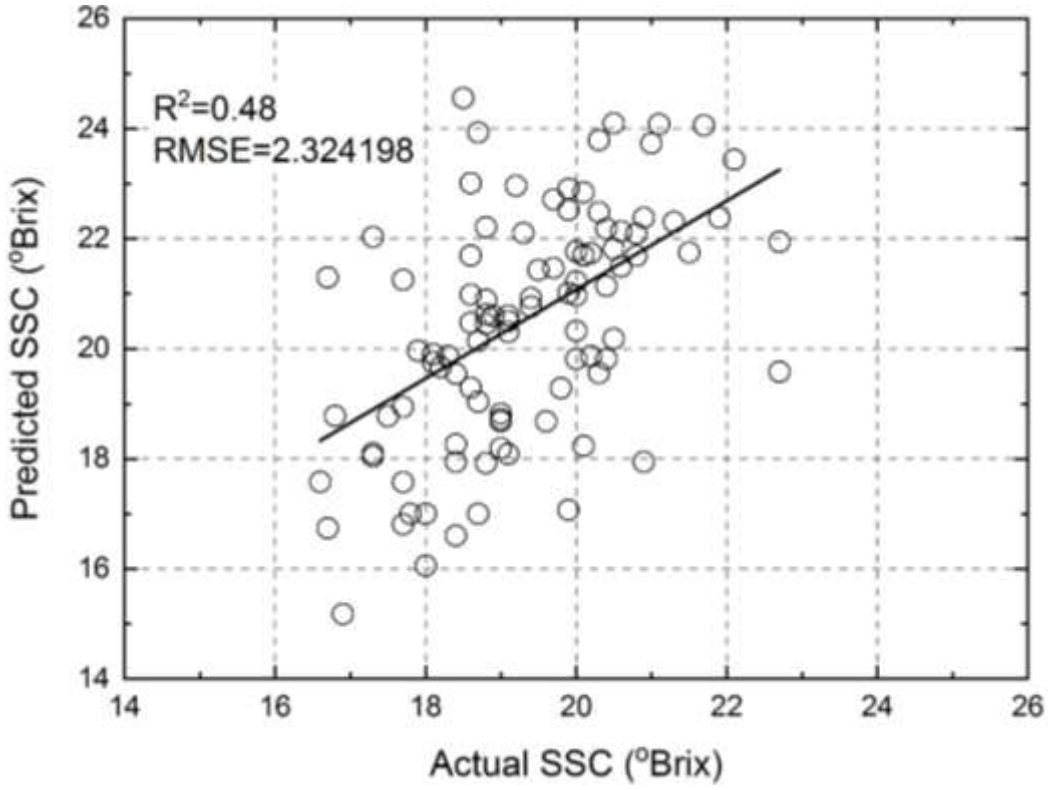

Figure 6. Correlation between actual soluble solid content (SSC) after ripening and predicted soluble solid content before ripening in baby kiwifruit 'cv. Saehan. Regression statistics (n=100) was used for every sampling.

Table 3. Effects of calcium chitosan preharvest treatment on quality characteristics of baby kiwifruit cv. Saehan.

Treatment	FW (g)	SSC (°Brix)	TA (%)	Firmness (N)	Predicted DM (%)	Actual DM (%)
Control	14.9±0.4	8.4±0.5	1.3±0.02	21.1±0.5	22.0±0.1	21.4±0.2[a]
Ca-Chitosan	12.8±0.7	9.5±0.2	1.2±0.04	21.9±0.4	22.7±0.1	22.3±0.2
T-test[b]	*				*	*

[a] Mean ± Standard error; [b] Tukey's test at the 0.05 level.

chitosan treated fruits and untreated fruits were 21.9 N and 21.1 N, respectively (Table 3). The actual DM content of untreated fruits was 21.4% and it was 22.3% in Ca-chitosan treated fruits (Table 3). Also, the predicted DM content was significantly high in Ca-chitosan treated fruits (22.7%) compared to untreated fruits (22.0%).

Both pre-harvest and postharvest applications of Ca have been widely used as a preservative and firming agent in fruits and vegetables and are known to increase fruit firmness and delay fruit decay (Chardonnet et al., 2003; Saftner et al., 2003; Madrid et al., 2004). Furthermore, Ca-chitosan has been reported to have fungicidal properties which work against fruit pathogen development (Bautista-Banos et al., 2003). The apparent relationship between the combined treatment of Ca and chitosan and increases in SSC content of kiwifruit are likely due to a decrease in the rate of ripening. This assertion agrees with reports obtained for strawberries (Eryani-Raqeeb et al., 2009; Petriccione et al., 2015). The SSC content in Ca-chitosan applied mango and banana was gradually increased with slow maturation, ripening, respiration and metabolism rates (Kittur et al., 2001; Li and Yu, 2001).

In peaches and golden kiwifruit, pre-harvest Ca-chitosan spray increased the internal CO_2 of fruit, probably resulting in the delay of ripening and ethylene activity (unpublished data). Hence, it is essential to have further studies on Ca-chitosan applications for insightful understanding of their effects on fruit maturation and ripening.

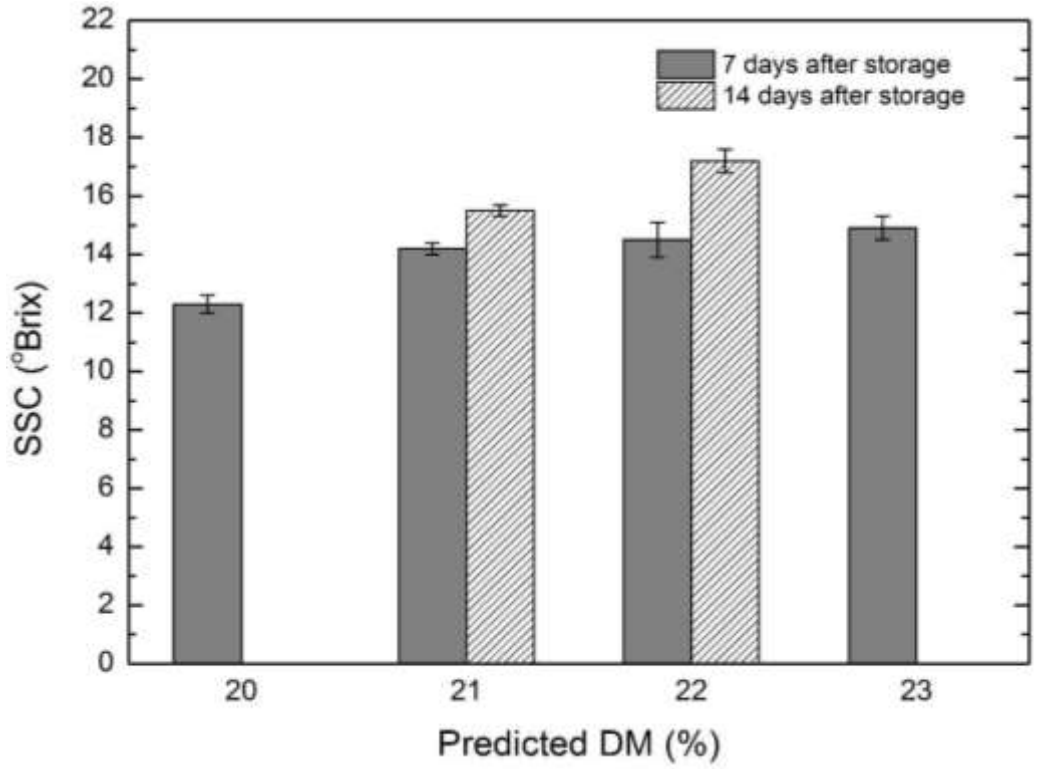

Figure 7. Changes in actual soluble solids content (SSC) during storage period at 5°C vs predicted dry matter content (DM) in baby kiwifruit cv. Saehan. Due to an insufficient quantity of fruits, DM data was not collected on 14th day reported for 20% and 23% DM.

Changes in physiochemical parameters during storage

The SSC of baby kiwifruit cv. Saehan, 7 days after storage was measured as °Brix and compared to the DM at harvest. Kiwifruit at 12.3° Brix had a 20% predicted DM at harvest. Additionally, at 14.2° Brix, 14.5° Brix, and 14.9° Brix showed predicted DM as 21, 22 and 23%, respectively (Figure 7). On the 14th day of kiwifruit storage, 15.5° Brix was aligned with 21% predicted DM, which was 43% higher than value observed at harvest. At 22% predicted DM, 17.2° Brix was observed, which was 49% higher than the day of harvest. As shown by Liu et al. (2010), the fruit with a higher DM at time of harvest correspond with a higher °Brix value after ripening. The firmness of baby kiwifruit cv. Saehan at the time of harvest was 17.9 N. After 7 days of storage at 5°C, the predicted DM and firmness (N) correlated as follows: 20% predicted DM with 18.5 N, 21% predicted DM with 15.5 N, 22% predicted DM with 14.6 N, and 23% predicted DM with 14.1 N, showing a reduction in firmness. On the 14th day of storage at 5°C, the DM and firmness correlated as follows: 21% DM with 12.6 N firmness, which was 30% lower than the harvest date; and 22% DM with 9.3 N firmness, which was 48% lower than the harvest date (Figure 8). According to Fisk et al. (2006), harvest maturity (6.0, 8.7, and 15.1 average SSC) affects the fruit quality after ripening and the storability of baby kiwifruit cultivar 'Ananasnaya'. They suggested that 'Ananasnaya' baby kiwifruit should be harvested at SSC > 8% and stored at low temperatures to achieve fruits with high consumer preference. Baby kiwifruit cv. Saehan is suggested to be harvested at over 21% DM content with a higher SSC; hence DM can be used as a maturity index for non-destructive quality prediction of baby kiwifruits based on NIR-spectroscopy.

Conclusion

Based on present findings it can be concluded that, the NIR-spectroscopy is an effective and efficient method to measure DM and SSC to determine the fruit harvest maturity hence, date of harvest and storability of quality baby kiwifruits. In addition, preharvest Ca-chitosan application can be implemented as a better strategy to improve the postharvest quality and shelf life of baby kiwifruits. The quality of NIR-spectroscopy method is cultivar specific with special emphasis on the different fruit quality indices. Moreover, the DM of unripe baby kiwifruits at harvest is very important factor affecting eating quality (SSC) of ripe baby kiwifruits. Ripe baby

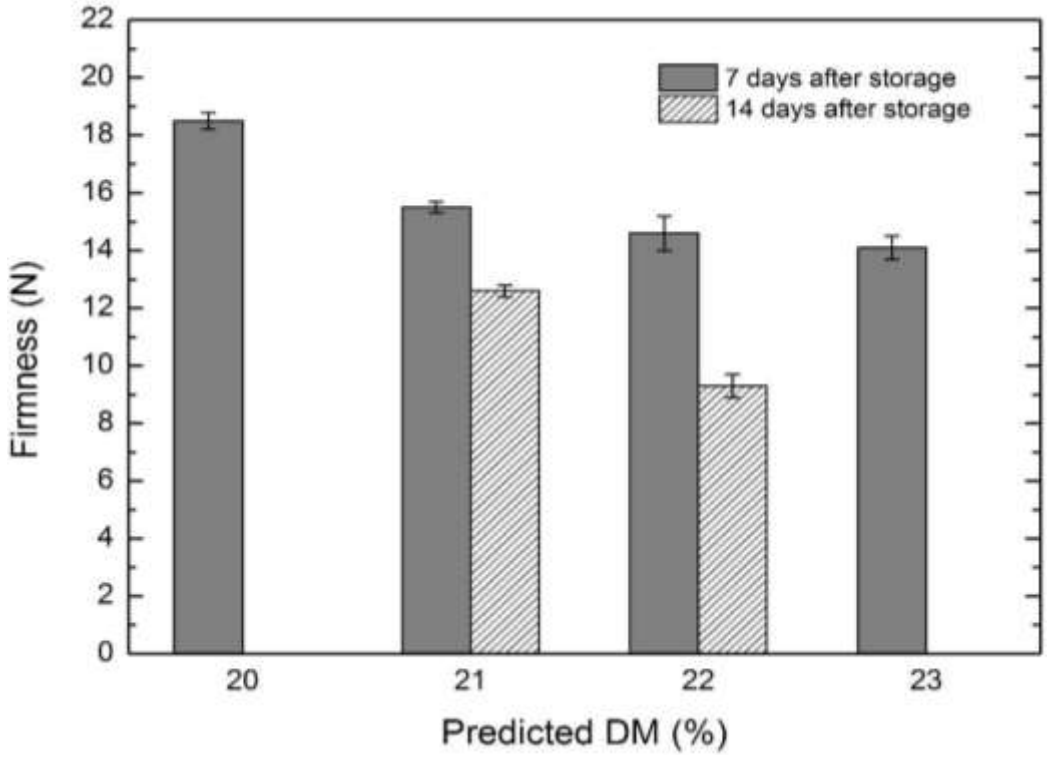

Figure 8. Changes in fruit firmness during storage period at 5°C vs predicted dry matter content (DM) in baby kiwifruit cv. Saehan. Due to an insufficient quantity of fruits, DM data was not collected on 14th day reported for 20% and 23% DM.

kiwifruits would have excellent eating quality with high SSC if they contained sufficient amounts of DM at harvest. By the NIR-predicted DM of unripe baby kiwifruits, the SSC of ripe baby kiwifruits could be precisely predicted at time of harvest. Hence, the development of a NIR-spectroscopy technique to predict eating quality of ripe baby kiwifruits from its quality at harvest or unripe stage is very important from the marketing point of view.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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