

แบบจำลองเพื่อทำนายคุณภาพข้าวระหว่างการผลิต โดยใช้เนียร์อินฟราเรดสเปกโทรสโกปี

นางสาวสุนีย์ จีงธิรพานิช

จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

บทคัดย่อและแฟ้มข้อมูลฉบับเต็มของวิทยานิพนธ์ตั้งแต่ปีการศึกษา 2554 ที่ให้บริการในคลังปัญญาจุฬาฯ (CUIR)
เป็นแฟ้มข้อมูลของนิสิตเจ้าของวิทยานิพนธ์ ที่ส่งผ่านทางบัณฑิตวิทยาลัย

The abstract and full text of theses from the academic year 2011 in Chulalongkorn University Intellectual Repository (CUIR)
are the thesis authors' files submitted through the University Graduate School.

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต

สาขาวิชาเทคโนโลยีทางอาหาร ภาควิชาเทคโนโลยีทางอาหาร

คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

ปีการศึกษา 2559

ลิขสิทธิ์ของจุฬาลงกรณ์มหาวิทยาลัย

PREDICTIVE MODEL FOR STORED RICE QUALITIES USING NEAR-
INFRARED SPECTROSCOPY

Miss Sunee Jungtheerapanich



A Dissertation Submitted in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy Program in Food Technology
Department of Food Technology
Faculty of Science
Chulalongkorn University
Academic Year 2016
Copyright of Chulalongkorn University

สุนีย์ จีงธีรพานิช : แบบจำลองเพื่อทำนายคุณภาพข้าวระหว่างการเก็บโดยใช้เนียร์อินฟราเรดสเปกโทรสโกปี (PREDICTIVE MODEL FOR STORED RICE QUALITIES USING NEAR-INFRARED SPECTROSCOPY) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.จิรารัตน์ อนันตกุล, 116 หน้า.

งานวิจัยนี้มีวัตถุประสงค์เพื่อศึกษาการเก่าของข้าวที่มีปริมาณแอมิโลสสูงและต่ำในระหว่างการเก็บรักษาที่อุณหภูมิที่แตกต่างกัน และอธิบายการเปลี่ยนแปลงตามหลักการจลนศาสตร์ รวมถึงสร้างสมการแสดงความสัมพันธ์ระหว่างคุณภาพข้าวและสมบัติการสะท้อนแบบแปรของรังสีอินฟราเรดย่านใกล้ระหว่างเก็บรักษาที่อุณหภูมิต่างกัน วัตถุประสงค์ที่ใช้ในการทดลองเป็นข้าวแอมิโลสต่ำ 3 พันธุ์ ได้แก่ ข้าวขาวดอกมะลิ 105 ข้าวปทุมธานี 1 และข้าวกข 45 และข้าวแอมิโลสสูง 3 พันธุ์ ได้แก่ ข้าวกข 47 ข้าวชัยนาท 1 และข้าวพิษณุโลก 2 เก็บรักษาที่อุณหภูมิสิ่งแวดล้อม ($30\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$) นาน 9 เดือน และอุณหภูมิแช่เย็น ($8\text{ }^{\circ}\text{C} \pm 2\text{ }^{\circ}\text{C}$) นาน 18 เดือน และวิเคราะห์คุณภาพต่างๆ ในระหว่างการเก็บ ได้แก่ สมบัติของข้าวเปลือก คุณภาพการสี คุณภาพการหุงต้ม สมบัติของข้าวสุก และสมบัติของแป้งข้าว สำหรับข้าวใหม่ พบว่าข้าวแอมิโลสต่ำและแอมิโลสสูงมีสมบัติบางประการที่มีค่าใกล้เคียงกัน ได้แก่ ปริมาณไขมัน เส้นใยหยาบ เถ้า คาร์โบไฮเดรต เอนทัลปีของการเกิดเจลลิตินในเซชันของแป้งข้าว ค่าดัชนีความขาว ความยืดหยุ่นและการเกาะติดกันของข้าวสุก ข้าวแอมิโลสต่ำมีปริมาณ โปรตีน ปริมาณแอมิโลส อุณหภูมิการเกิดเพสต์ การคืนตัว เอนทัลปีของการหลอมผลึกสารเชิงซ้อนของแอมิโลสและไขมันของแป้งข้าว ปริมาณข้าวคั้น ปริมาณของแข็งที่สูญเสียระหว่างหุงต้ม ค่าความแข็งระดับความเป็นกาวยางหรือแป้งเปียกและพลังงานในการเคี้ยวของข้าวสุกต่ำกว่าข้าวแอมิโลสสูง แต่มีปริมาณน้ำที่ดูดซับระหว่างหุงต้ม ความหนืดสูงสุด ความหนืดที่ลดลง อุณหภูมิเริ่มต้น อุณหภูมิที่จุดสูงสุด อุณหภูมิสุดท้าย และช่วงอุณหภูมิในการเกิดเจลลิตินในเซชันของแป้งข้าว รวมถึงการเกาะติดผิวของข้าวสุกสูงกว่าข้าวแอมิโลสสูง การเก่าของข้าวส่งผลให้ปริมาณข้าวคั้น ระยะเวลาที่น้อยที่สุดที่ใช้ในการหุงต้ม ปริมาณน้ำที่ดูดซับระหว่างหุงต้ม การขยายปริมาตร ค่าความแข็ง การเกาะติดกัน ความยืดหยุ่น ระดับความเป็นกาวยางหรือแป้งเปียก และพลังงานในการเคี้ยวของข้าวสุก รวมถึงอุณหภูมิการเกิดเพสต์ของแป้งข้าวเพิ่มขึ้น ส่วนดัชนีความขาวของข้าวสาร ปริมาณของแข็งที่สูญเสียระหว่างหุงต้ม ความหนืดสูงสุดและการแตกตัวของแป้งข้าว และการเกาะติดผิวของข้าวสุกลดลง นอกจากนี้ สมบัติทางด้านความร้อน และรูปแบบน้ำหนักโมเลกุลของโปรตีนในแป้งข้าวมีการเปลี่ยนแปลงเพียงเล็กน้อยในระหว่างการเก็บรักษา ข้าวทั้ง 6 พันธุ์ที่เก็บที่ $8\text{ }^{\circ}\text{C}$ มีการเปลี่ยนแปลงช้ากว่าข้าวที่เก็บที่ $30\text{ }^{\circ}\text{C}$ Principal Component Analysis (PCA) ของข้อมูลทั้งหมดแสดงให้เห็นว่าสามารถจัดกลุ่มตัวอย่างได้เป็น 3 กลุ่ม ได้แก่ กลุ่มที่ 1 ข้าวแอมิโลสต่ำ (ข้าวขาวดอกมะลิ 105 ข้าวปทุมธานี 1 และข้าวกข 45) กลุ่มที่ 2 ข้าวแอมิโลสสูง (ข้าวกข 47 และข้าวพิษณุโลก 2) กลุ่มที่ 3 คือ ข้าวชัยนาท 1 สำหรับการสร้างสมการแสดงความสัมพันธ์ระหว่างคุณภาพข้าวและสมบัติการสะท้อนแบบแปรของรังสีอินฟราเรดย่านใกล้โดยใช้ partial least square (PLS) regression พบว่า มีเพียง 14 ค่าคุณภาพที่สามารถสร้างสมการการทำนายที่ดี ($R^2 > 0.7$) ได้แก่ ปริมาณข้าวคั้น ระยะเวลาที่น้อยที่สุดที่ใช้ในการหุงต้ม ปริมาณของแข็งที่สูญเสียระหว่างหุงต้ม ปริมาณน้ำที่ดูดซับระหว่างหุงต้ม การขยายปริมาตรของข้าวสุก อุณหภูมิการเกิดเพสต์ ความหนืดสูงสุด การแตกตัวและการคืนตัวของแป้งข้าว ความแข็งและการเกาะติดผิวของข้าวสุก อุณหภูมิเริ่มต้น อุณหภูมิที่จุดสูงสุดและอุณหภูมิสุดท้ายในการเกิดเจลลิตินในเซชันของแป้งข้าว และสามารถอธิบายการเปลี่ยนแปลงของค่าคุณภาพ 9 ค่าได้ด้วยแบบจำลองทางคณิตศาสตร์ first-order fractional conversion kinetic เมื่อเก็บรักษาข้าวที่ $30\text{ }^{\circ}\text{C}$ ($R^2 \geq 0.7$) ได้แก่ ปริมาณของแข็งที่สูญเสียระหว่างหุงต้ม ปริมาณน้ำที่ดูดซับระหว่างหุงต้ม การขยายปริมาตรของข้าวสุก อุณหภูมิการเกิดเพสต์ ความหนืดสูงสุด ความหนืดที่ลดลงและการคืนตัวของแป้งข้าว ความแข็งและการเกาะติดผิวของข้าวสุก สำหรับข้อมูลของข้าวที่เก็บรักษาที่ $8\text{ }^{\circ}\text{C}$ ไม่สามารถใช้สมการ zero-order kinetics หรือ first-order fractional conversion kinetic อธิบายการเปลี่ยนแปลงได้ เนื่องจากการเปลี่ยนแปลงเกิดขึ้นน้อยมาก

ภาควิชา เทคโนโลยีทางอาหาร

ลายมือชื่อ นิสิต

สาขาวิชา เทคโนโลยีทางอาหาร

ลายมือชื่อ อ.ที่ปรึกษาหลัก

ปีการศึกษา 2559

5472865123 : MAJOR FOOD TECHNOLOGY

KEYWORDS: RICE AGING / LOW AND HIGH AMYLOSE RICE / PHYSICOCHEMICAL PROPERTIES / NEAR-INFRARED SPECTROSCOPY / KINETIC MODEL

SUNEE JUNGTHEERAPANICH: PREDICTIVE MODEL FOR STORED RICE QUALITIES USING NEAR-INFRARED SPECTROSCOPY. ADVISOR: ASSOC. PROF. JIRARAT ANUNTAGOOL, Ph.D., 116 pp.

The objectives of this research are to study aging of high and low amylose rice during storage at different temperatures and explain the changes by kinetic model and to develop the predictive models between rice properties and NIR spectra in the diffuse-reflectance mode during storage at different temperatures. The samples used in this research included three varieties of low amylose rice, i.e. Khao Dawk Mali 105, Pathumthani 1 and Rice Department (RD) 45 and three varieties of high amylose rice, i.e. RD 47, Chai Nat 1 and Phitsanulok 2. Paddy rice in plastic woven sacks was stored at ambient temperature ($30\text{ }^{\circ}\text{C}\pm 2\text{ }^{\circ}\text{C}$) and chilled temperature ($8\text{ }^{\circ}\text{C}\pm 2\text{ }^{\circ}\text{C}$) for 9 and 18 months, respectively. The qualities determined during storage were paddy property, milling quality, cooking qualities, cooked rice properties and rice flour properties. Some qualities of all six rice varieties; namely fat content, fiber content, ash content, carbohydrate content, enthalpy of gelatinization of rice flour, whiteness index, springiness and cohesiveness of cooked rice, varied in a narrow range. However, low amylose rice varieties had lower protein content, amylose content, pasting temperature, setback, melting enthalpy of amylose/lipid complex of rice flour, head rice yield, solid loss, hardness, gumminess and chewiness of cooked rice but higher water uptake, peak viscosity, breakdown, onset temperature, peak temperature, conclusion temperature and gelatinization temperature range of rice flour as well as adhesiveness of cooked rice. Aging led to an increase in head rice yield, minimum cooking time, water uptake, volume expansion ratio, hardness, cohesiveness, springiness, gumminess and chewiness of cooked rice and pasting temperature of rice flour and a decrease in whiteness index of rice grain, solid loss, peak viscosity and breakdown of rice flour and adhesiveness of cooked rice. Thermal properties and MW distribution pattern of rice flour protein slightly changed during storage. The rate of changes for all rice varieties stored at $8\text{ }^{\circ}\text{C}$ was lower than that at $30\text{ }^{\circ}\text{C}$. Principal Component Analysis (PCA) of all observed variables classified the samples into three groups; low amylose rice (Khao Dawk Mali 105, Pathumthani 1 and RD 45, high amylose rice (RD 47 and Phitsanulok 2), and high amylose Chai Nat 1. The predictive models between rice properties and NIR spectra in the diffuse-reflectance mode were produced using partial least square (PLS) regression. Only 14 parameters, i.e. head rice yield, minimum cooking time, solid loss, water uptake, volume expansion ratio, pasting temperature, peak viscosity, breakdown and setback of rice flour, hardness and adhesiveness of cooked rice, onset temperature, peak temperature and conclusion temperature of rice flour, could be used to develop good prediction models ($R^2 > 0.7$). The first-order fractional conversion kinetic model reasonably explained the changes of nine variables, i.e. solid loss, water uptake and volume expansion ratio of cooked rice, pasting temperature, peak viscosity, breakdown and setback of rice flour, hardness and adhesiveness of cooked rice, during aging at $30\text{ }^{\circ}\text{C}$ ($R^2 \geq 0.7$). Changes in rice qualities during aging at $8\text{ }^{\circ}\text{C}$ were marginal, thus could not be explained by kinetic models.

Department: Food Technology

Student's Signature

Field of Study: Food Technology

Advisor's Signature

Academic Year: 2016

ACKNOWLEDGEMENTS

I would like to express the deepest sense of my gratitude to my advisor, Associate Professor Dr. Jirarat Anuntagool, for her help and guidance throughout my study. Without her scholarly advice and support, this dissertation would not have been completed.

I am deeply thankful to my examination committee; Professor Dr. Vanna Tulyathan, Associate Professor Dr. Kanitha Tananuwong, Assistant Professor Dr. Thanachan Mahawanich, and Dr. Sasikan Kupongsak, for their recommendation.

I would like to thank Chulalongkorn University for providing the 60/40 support for tuition fee throughout my study and the Agricultural Research and Development Agency (ARDA) and the National Research Council of Thailand (NRCT) for research funding during fiscal year 2012 and 2014 (grant number 2555NRCT716 and PRP5705021150).

I am also thankful to Pathumthani Rice Research Center, Agricultural Co-op Prachantakam, and Ratchaburi Rice Research Center for raw material support.

I would like to thank staff of Department of Food Technology, Chulalongkorn University for their assistance. In addition, I would like to thank all friends at the Department of Food Technology, Chulalongkorn University for their help and friendship.

Last but not least, I would like to thank my family for their support, encouragement and understanding.

CONTENTS

	Page
THAI ABSTRACT	iv
ENGLISH ABSTRACT.....	v
ACKNOWLEDGEMENTS	vi
CONTENTS.....	vii
LIST OF TABLES	x
LIST OF FIGURES	xi
ABBREVIATION LISTS	xv
CHAPTER I INTRODUCTION.....	1
CHAPTER II LITERATURE REVIEW	3
2.1 Rice	3
2.1.1 Low amylose rice	4
2.1.1.1 Khao Dawk Mali 105	5
2.1.1.2 Pathumthani 1	5
2.1.1.3 Rice Department 45	5
2.1.2 High amylose rice.....	5
2.1.2.1 Rice Department 47.....	6
2.1.2.2 Chai Nat 1.....	6
2.1.2.3 Phitsanulok 2	6
2.2 Structure of rice grain	7
2.3 Chemical compositions of rice	8
2.3.1 Starch.....	8
2.3.2 Protein	8
2.3.3 Lipids.....	9
2.4 Rice aging	9
2.5 Near Infrared Spectroscopy	12
2.5.1 Principle of Near Infrared Measurement.....	13
2.5.2 NIR calibration basic.....	15
2.5.3 Spectral data pre-processing.....	16

	Page
2.5.4 Multivariate data analysis	16
2.5.5 Application of NIR spectroscopy in foods	17
CHAPTER III MATERIALS AND METHODS	19
3.1 Materials	19
3.2 Methods	19
3.2.1 Sample preparation.....	19
3.2.2 Determination of fresh rice paddy qualities	20
3.2.2.1 Determination of moisture content of paddy.....	20
3.2.2.2 Determination of milling quality (head rice yield).....	20
3.2.2.3 Determination of physicochemical properties of milled rice	20
3.2.2.4 Determination of cooking quality.....	21
3.2.2.5 Determination of textural properties	22
3.2.2.6 Determination of pasting properties of rice flour.....	23
3.2.2.7 Determination of thermal properties of rice flour	23
3.2.2.8 Electrophoresis of rice protein.....	23
3.2.2.9 FT-NIR analysis	24
3.2.3 Determination of stored rice qualities	24
3.2.4 Chemometric analysis of FT-NIR data	25
3.2.4.1 Principal Component Analysis	25
3.2.4.2 Predictive model construction	25
3.2.5 Aging kinetics modeling	25
3.2.6 Statistical analysis	27
CHAPTER IV RESULTS AND DISCUSSION.....	28
4.1 Properties of freshly harvested rice	28
4.2 Properties of aged rice under controlled temperature environment.....	33
4.2.1 Changes in head rice yield during storage.....	34
4.2.2 Changes in whiteness index during storage	35
4.2.3 Changes in cooking qualities during storage.....	36

	Page
4.2.4 Changes in textural properties of cooked rice during storage	40
4.2.5 Changes in pasting properties of rice flour during storage	44
4.2.6 Changes in thermal properties of rice flour during storage.....	48
4.2.7 Changes in molecular weight distribution of rice protein from rice flour during storage	52
4.3 Principal Component Analysis	60
4.4 Chemometric analysis.....	61
4.5 Aging kinetics modeling.....	71
CHAPTER V CONCLUSIONS	79
REFERENCES	81
APPENDIX.....	89
APPENDIX A CHEMICAL ANALYSIS PROCEDURES	90
APPENDIX B PHYSICAL ANALYSIS PROCEDURES.....	99
APPENDIX C SUPPLEMENTARY DATA.....	100
VITA.....	116

LIST OF TABLES

		Page
Table 3.1	Rice varieties and cultivation area	19
Table 4.1	Physical properties, cooking qualities, pasting properties, textural properties, thermal properties and chemical properties of fresh rice (paddy, milled rice and rice flour)	29
Table 4.2	Range of composition variation in the samples used to develop PLS models	63
Table 4.3	PLS model statistics for rice qualities.....	64
Table 4.4	Kinetics model parameters (First order) for changes in rice and flour properties during storage at 8 °C and 30 °C.....	73
Table A.8.1	Composition of separating gel and stacking gel	98
Table A.8.2	Composition of electrode running gel buffer.....	98
Table B.1	Temperature profile (standard profile 1).....	99
Table C.4.1	Kinetics model parameters for changes in rice and flour properties during storage at 8 °C and 30 °C	108

LIST OF FIGURES

		Page
Figure 2.1	Structure of rice grain	7
Figure 2.2	Changes as a function of aging process during rice storage	11
Figure 2.3	Spectral range of NIR region	13
Figure 2.4	Six vibrational modes of tri-atomic molecule	14
Figure 2.5	Principle of NIR instrument	14
Figure 2.6	Type of NIR measuring modes	15
Figure 2.7	NIR calibration and validation process	16
Figure 3.1	Pattern of (a) zero th order kinetic model and (b) the first-order fractional conversion kinetic model	26
Figure 4.1	(a) Atmospheric temperature and (b) relative humidity during storage	33
Figure 4.2	Moisture content (%) of paddy during storage at (a) 8 °C and (b) 30 °C.....	34
Figure 4.3	Head rice yield (%) of milled rice during storage at (a) 8 °C and (b) 30 °C.....	35
Figure 4.4	Whiteness index of milled rice during storage at (a) 8 °C and (b) 30 °C.....	36
Figure 4.5	Minimum cooking time of milled rice during storage at (a) 8 °C and (b) 30 °C.....	38
Figure 4.6	Solid loss of cooked rice during storage at (a) 8 °C and (b) 30 °C.....	38
Figure 4.7	Water uptake of cooked rice during storage at (a) 8 °C and (b) 30 °C.....	39
Figure 4.8	Volume expansion ratio of cooked rice during storage at (a) 8 °C and (b) 30 °C.....	39
Figure 4.9	Elongation ratio of cooked rice during storage at (a) 8 °C and (b) 30 °C.....	40
Figure 4.10	Cooked length-breadth ratio of cooked rice during storage at (a) 8 °C and (b) 30 °C	40
Figure 4.11	Hardness of cooked rice during storage at (a) 8 °C and (b) 30 °C	42

	Page
Figure 4.12 Cohesiveness of cooked rice during storage at (a) 8 °C and (b) 30 °C.....	42
Figure 4.13 Adhesiveness of cooked rice during storage at (a) 8 °C and (b) 30 °C.....	42
Figure 4.14 Springiness of cooked rice during storage at (a) 8 °C and (b) 30 °C...	43
Figure 4.15 Gumminess of cooked rice during storage at (a) 8 °C and (b) 30 °C ..	43
Figure 4.16 Chewiness of cooked rice during storage at (a) 8 °C and (b) 30 °C	44
Figure 4.17 Pasting temperature of rice flour during storage at (a) 8 °C and (b) 30 °C.....	46
Figure 4.18 Peak viscosity of rice flour during storage at (a) 8 °C and (b) 30 °C ..	46
Figure 4.19 Final viscosity of rice flour during storage at (a) 8 °C and (b) 30 °C..	47
Figure 4.20 Breakdown of rice flour during storage at (a) 8 °C and (b) 30 °C.....	47
Figure 4.21 Setback of rice flour during storage at (a) 8 °C and (b) 30 °C	47
Figure 4.22 Trough viscosity of rice flour during storage at (a) 8 °C and (b) 30 °C.....	48
Figure 4.23 Onset temperature (T_o) of rice flour during storage at (a) 8 °C and (b) 30 °C.....	49
Figure 4.24 Peak temperature (T_p) of rice flour during storage at (a) 8 °C and (b) 30 °C.....	50
Figure 4.25 Conclusion temperature (T_c) of rice flour during storage at (a) 8 °C and (b) 30 °C.....	51
Figure 4.26 Enthalpy of gelatinization (ΔH_g) of rice flour during storage at (a) 8 °C and (b) 30 °C	52
Figure 4.27 Rice protein pattern of low and high amylose rice during storage at (a, b) 8 °C and (c, d) 30 °C	54
Figure 4.28 Raw volume (%) of protein molecular weight distribution (MW > 150 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C	55
Figure 4.29 Raw volume (%) of protein molecular weight distribution (MW 100-120 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C	56

	Page
Figure 4.30 Raw volume (%) of protein molecular weight distribution (MW 75-100 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C	57
Figure 4.31 Raw volume (%) of protein molecular weight distribution (MW 40-55 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C	58
Figure 4.32 Raw volume (%) of protein molecular weight distribution (MW 25-30 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C	59
Figure 4.33 Raw volume (%) of protein molecular weight distribution (MW < 20 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C	60
Figure 4.34 Score plot of all parameter of rice during storage at 8 °C and 30 °C ..	61
Figure 4.35 Comparison of measured and predicted values for rice qualities of validation samples for (a) head rice yield, (b) minimum cooking time, (c) solid loss, (d) water uptake, (e) volume expansion ratio, (f) pasting temperature, (g) peak viscosity, (h) breakdown, (i) setback, (j) hardness, (k) adhesiveness, (l) onset temperature, (m) peak temperature and (n) conclusion temperature	69
Figure 4.36 Comparison of measured (\diamond = KDML105, \square = PTT1, Δ = RD45, x = RD47, $+$ = CNT1 and $*$ = PSL2) and predicted (- - -) values for rice qualities (30 °C storage) of the first-order fractional conversion kinetic model for (a) solid loss, (b) water uptake, (c) volume expansion ratio, (d) pasting temperature, (e) peak viscosity, (f) breakdown, (g) setback, (h) hardness and (i) adhesiveness	76
Figure 4.37 Steps to obtain age of rice by NIR models and kinetic models	78
Figure C.1.1 Gelatinization temperature range (T_c - T_o) of rice flour during storage at (a) 8 °C and (b) 30 °C.....	100
Figure C.1.2 Enthalpy of amylose/lipid complexes (ΔH_{al}) of rice flour during storage at (a) 8 °C and (b) 30 °C.....	101

Figure C.2.1	NIR spectra of rice grains during storage at 8 °C and 30 °C (a) Raw spectra (b) SNV preprocessing spectra for HRY (c) 1 st derivative preprocessing spectra for MCT (d) Moving average smoothing preprocessing spectra for SL (e) Savitzky-Golay smoothing preprocessing spectra for WU (f) 1 st derivative preprocessing spectra for VER (g) SNV preprocessing spectra for PT (h) SNV preprocessing spectra for PV (i) 1 st derivative preprocessing spectra for BD (j) 2 nd derivative preprocessing spectra for SB (k) 1 st derivative preprocessing spectra for H (l) 1 st derivative preprocessing spectra for Ad (m) 1 st derivative preprocessing spectra for T _o (n) 2 nd derivative preprocessing spectra for T _p (o) 2 nd derivative preprocessing spectra for T _c	102
---------------------	--	-----



ABBREVIATION LISTS

ARDA	Agricultural Research and Development Agency
AOAC	American Association of Official Analytical Chemists
APS	Ammonium persulfate
ANOVA	Analysis of variance
BD	Breakdown
CNT1	Chai Nat 1
R ²	Coefficient of determination
T _c	Conclusion temperature
DSC	Differential Scanning Calorimeter
DMRT	Duncan's multiple range test
$\Delta H_{\text{amylose/lipid complex}}$	Enthalpy of amylose/lipid complex
ΔH_g	Enthalpy of gelatinization
FV	Final viscosity
FT-NIR	Fourier-transform near infrared
HRV	Head rice yield
KAPI	Kasetsart Agricultural and Agro-Industrial Product Improvement Institute
KDML105	Khao Dawk Mali 105
MCT	Minimum cooking time
MC	Moisture content
MW	Molecular weight
NRCT	National Research Council of Thailand
NIR	Near infrared
TEMED	N,N,N',N'-Tetramethyl ethylenediamine
T _o	Onset temperature
PLS	Partial least square
PT	Pasting temperature
PTT1	Pathumthani 1
T _p	Peak temperature

PV	Peak viscosity
PSL2	Phitsanulok 2
PCA	Principal component analysis
ΔT_g	Range of gelatinization temperature
RVA	Rapid Visco Analyzer
RH	Relative humidity
RD45	Rice Department 45
RD47	Rice Department 47
RMSEC	Root mean square error of the calibration
RMSEP	Root mean square error of the prediction
SB	Setback
SDS	Sodium dodecyl sulfate
SDS-PAGE	Sodium dodecyl sulfate polyacrylamide gel electrophoresis
SL	Solid loss
SNV	Standard normal variate
TPA	Texture profile analysis
TAS	Thai Agricultural Standard
Tris-base	Tris (Hydroxymethyl) aminomethane
TV	Trough viscosity
VER	Volume expansion ratio
WU	Water uptake
W_C	Weight of cooked rice kernels
W_{UC}	Weight of uncooked rice kernels
WI	Whiteness index

CHAPTER I

INTRODUCTION

Rice is a primary dietary source of carbohydrates. Low amylose rice is mostly preferred for consumption as cooked rice as it yields soft and sticky texture while high amylose rice is good for processing into products such as rice noodle, dessert and others. Storage usually causes rice to become harder with reduced stickiness, thus perceived as undesirable process in preserving rice that is preferred for consumption as cooked grains. However, similar changes after aging result in desirable flour for further processing as it reduces adhesiveness. A number of chemical and physical changes occurring as a result of aging include changes in textural properties, pasting properties, thermal properties and others which can be referred to as cooking quality (Park *et al.*, 2012; Soponronnarit *et al.*, 2008; Zhou *et al.*, 2007). Mechanisms of rice aging involve starch, protein and lipids. Changes in protein results in reduced granule swelling which affects the consistency of cooked rice (Ramesh *et al.*, 2000; Zhou *et al.*, 2002a). Lipids can undergo changes in two possible paths; one involves lipids hydrolysis resulting in the production of free fatty acids which can complex with amylose resulting in increasing hardness; the other is the oxidation of lipids to produce hydroperoxides that can accelerate oxidation of protein and condensation with volatile carbonyl compounds causing off odor (Zhou *et al.*, 2002a). External factors, e.g. temperature, moisture content, storage time and packaging, play an important role in either slowing down or accelerating aging of rice during storage. By far, various studies have been carried out to assess the effect of some factors, e.g. time and temperature, on aging of rice. None has proposed a tool to assess the extent of rice aging.

Near Infrared (NIR) Spectroscopy is a powerful technique that has several advantages such as rapid, non-destructive, environmentally safe, minimal sample preparation and low cost. The method can be used to investigate several parameters within one scan (Bao *et al.*, 2007; Batten, 1998; Osborne, 2006; Posom and Sirisomboon, 2014; Sirisomboon *et al.*, 2013; Wu and Shi, 2004; Zhang *et al.*, 2011). NIR Spectroscopy can be used in both quantitative and qualitative analyses of food

products for instance determination of pH and soluble solids content of yogurt (Shao and He, 2009), total amino acids in oilseed rape leaves (Liu *et al.*, 2011), protein content in *Brassica oleracea* species (Szegedi *et al.*, 2012), spoilage of intact chicken breast muscle (Alexandrakis *et al.*, 2012), calcium content in powdered milk (Wu *et al.*, 2012), on-line screening of different dates varieties (Tavakolian *et al.*, 2013) and quantification of mildew damage in soft red winter wheat (Shahin *et al.*, 2014). In rice grain, flour and starch, NIR had been widely used to determine rice quality such as milled rice grade (Chen and Huang, 2010), grain weight (Wu and Shi, 2004), gel consistency and alkali spread value of brown rice and milled rice (Wu and Shi, 2007), swelling properties and water solubility in whole grain barley (Cozzolino *et al.*, 2013), identification of native maize, native wheat starches, high amylose maize starch, phosphorylated wheat starch, and their mixture (Hódsági *et al.*, 2012), thermal and retrogradation properties of rice starch (Bao *et al.*, 2007), amylose content (Bagchi *et al.*, 2016; Delwiche *et al.*, 1996; Himmelsbach *et al.*, 2001; Villareal *et al.*, 1994; Wu and Shi, 2004, 2007; Xie *et al.*, 2014), protein content (Bagchi *et al.*, 2016; Delwiche *et al.*, 1996; Himmelsbach *et al.*, 2001; Shao *et al.*, 2011; Xie *et al.*, 2014), amino acid in brown rice (Zhang *et al.*, 2011), and aflatoxigenic fungal contamination (Sirisomboon *et al.*, 2013). A study has shown satisfactory result in using NIR to detect rice adulteration (Osborne *et al.*, 1993b). Sirisomboon *et al.* (2013) reported the use of NIR in detection of aflatoxigenic fungal contaminated rice samples (jasmine rice, white rice and brown rice). From the literature reviewed, determination of rice aging using NIR spectroscopy is still scarce. Therefore, the first objective of this research was to study aging of high and low amylose rice so that the data on quality changes of rice could be collected systematically and aging kinetics could be assessed. The second objective was to develop the predictive models between rice properties and NIR spectra of rice during storage at different temperatures.

CHAPTER II

LITERATURE REVIEW

2.1 Rice

Rice can be classified into two species; *Oryza sativa* or Asian rice and *Oryza glaberrima* or African rice, which are significant for human consumption globally (Ricepedia, 2016). *Oryza sativa*, mostly cultivated and traded worldwide, can be classified into 3 types, which are Japonica, Javanica and Indica (Agricultural Research and Development Agency, 2016). Japonica rice, cultivated in the Northern, Eastern and Central of China, Japan and Korea, has short and spherical grains, low amylose content, moist and sticky texture after cook (Ricepedia, 2016; Rosell and Gómez, 2014). Javanica rice, cultivated in Indonesia, Philippines, Taiwan and Japan, has long, broad and large kernel, low amylose content and low productivity (Agricultural Research and Development Agency, 2016; Lu and Collado, 2010; Matsuzaki, 1995; Ricepedia, 2016). Indica rice, widely planted in Thailand, Vietnam, India, Bangladesh and Pakistan, has long and slender grain, high amylose content, drier and harder texture compared to japonica rice after cook (Juliano, 2005; Lu and Collado, 2010; Ricepedia, 2016; Rosell and Gómez, 2014).

Rice can also be classified by its cultivation area into 3 groups, which are upland rice, lowland rice and floating rice. Upland rice can be cultivated in both flat and slope area, but is mostly grown on the slope area in the Northern, Southern, Eastern and Northeastern regions of Thailand with cultivation area around 10% of total rice cultivation area of Thailand. Lowland rice can be cultivated in lowland of all regions in Thailand, thus it has the highest cultivation area around 80% of total rice cultivation area of Thailand. Floating rice can be cultivated in uncontrolled water level area, such as Ayutthaya, Suphanburi, Lopburi, Phichit, Angthong, Chainat and Singhburi province of Thailand and that governs around 10% of total cultivation area of Thailand (Thai Rice Foundation under Royal Patronage, 2006).

Besides, rice can be divided by cultivation season into 2 groups namely in-season rice and off-season rice. In-season rice is cultivated from May to October and

harvested before February. Photo period-sensitive rice is suitable to grow in this season. Off-season rice can be cultivated in January and harvested before April. Non photo sensitive rice is mostly grown in this season in the Central region of Thailand (Agricultural Research and Development Agency, 2016; Thai Rice Foundation under Royal Patronage, 2006). In Thailand, in-season rice is popular and is accounted for larger cultivation area around 62.83 Million Rai with the 2014/2015 average production yield of 439 kg per rai, while off-season rice governs around 16.14 Million Rai planting area with the 2014/2015 average production yield of 622 kg per rai (Department of Foreign Trade, 2016).

In term of amylose content, rice can be divided into 5 groups that are glutinous (0-2%), very low amylose (2-10%), low amylose (10-20%), intermediate amylose (20-25%) and high amylose rice (>25%) (Lu and Collado, 2010; Yu *et al.*, 2013). Low and intermediate amylose rice is mostly consumed as cooked rice because of their sticky, moist and soft texture (Cheapun *et al.*, 2005; Yu *et al.*, 2013). However, high amylose rice varieties, especially Indica rice, give a hard and crumbly texture when cooked thus it is used as healthy, gluten-free, functional flour in the production of rice noodles and bakery products (Kim *et al.*, 2010; Lu and Collado, 2010).

2.1.1 Low amylose rice

Low amylose rice is preferred for consumption as cooked rice as it gives sticky and soft texture (Cheapun *et al.*, 2005; Yu *et al.*, 2013). In general, low amylose rice has higher adhesiveness and lower hardness value when compared to high amylose rice. The flour from low amylose rice also has high peak viscosity, breakdown, swelling power, but low setback, final viscosity, and pasting temperature (Varavinit *et al.*, 2003; Woo *et al.*, 2015). Vast varieties of low amylose rice have been bred in Thailand, only few varieties are preferred for commercial production, i.e. Khao Dawk Mali 105, Pathumthani 1, Rice Department 15 and Rice Department 45 (Rice Department, 2016).

2.1.1.1 Khao Dawk Mali 105

Khao Dawk Mali 105 (KDML105) is also known as “Jasmine rice” as it yields shaded jasmine-like color whereas pandan-like odor. The recommended planting area for KDML105 is the Northern and Northeastern region of Thailand. KDML105 is wet season rain-fed crop (in-season rice). It is non-sticky rice with long transparent grain and slender shape which contains a natural fragrant aroma. KDML105 contains 12 to 17% amylose. Cooked KDML105 rice has soft texture and is highly fragrant. After aging, the rice yields cooked rice with less adhesiveness and reduced fragrant aroma (Rice Department, 2016).

2.1.1.2 Pathumthani 1

Pathumthani 1 (PTT1) is suitable for planting in the Central region of Thailand and gives high production return of around 650-774 kg of paddy rice per Rai. The plant is non-photo sensitive and tolerant to many diseases and pests. This non-glutinous rice is a bred variety of BKNA6-18-3-2/PTT85061-86-3-2-1. PTT1 contains 15 to 19% amylose, thus yields cooked rice with soft texture and natural fragrant aroma (Rice Department, 2016).

2.1.1.3 Rice Department 45

The recommended planting area for Rice Department 45 (RD45) are the Central and Eastern regions of Thailand. RD45 gives moderately high production yield around 520 kg of paddy rice per Rai. The plant is photo period sensitive. RD45 is non-glutinous rice with transparent kernel that was bred between PPCRBR83012-267-5 and KDML105. RD45 contains 16.35% amylose and has good milling quality. Cooked RD45 rice has soft texture and fragrant aroma (Rice Department, 2016).

2.1.2 High amylose rice

High amylose rice yields fluffy, hard texture and non-sticky cooked rice, hence suitable for processing into food products, especially noodle (Cheapun *et al.*, 2005; Juliano, 2005). In general, high amylose rice flour has low peak viscosity, break down, swelling power, but high setback, final viscosity, and pasting

temperature (Thanathornvarakul *et al.*, 2016; Varavinit *et al.*, 2003; Woo *et al.*, 2015). Similar to low amylose rice, many varieties of high amylose rice have been bred. Only a number of varieties, e.g. Rice Department 29 (Chai nat 80), Rice Department 31 (Pathumthani 80), Rice Department 47, Chai nat 1, Phitsanulok 2, Suphan Buri 1 and Suphan Buri 3, have been widely cultivated in Thailand (Rice Department, 2016).

2.1.2.1 Rice Department 47

Rice Department 47 (RD47) has been recommended for cultivation in the south of Northern region of Thailand. The variety has high and stable production yield and is not sensitive to photo period but sensitive to cold weather. RD47 is non-glutinous rice with transparent and slender shape kernel. It is a hybrid variety of Suphan Buri 1/IR64 and CNT1 86074-25-9-1. RD47, containing 26.81% amylose, has good milling quality. Cooked RD47 rice is crumble and has hard texture (Rice Department, 2016).

2.1.2.2 Chai Nat 1

Chai Nat 1 (CNT1) can be grown in all irrigated area of Thailand and is not sensitive to photo period. It is a hybrid variety of IR13146-158-1/IR15314-43-2-3-3 and BKN6995-16-1-1-2. CNT1, a non-sticky rice with 26 to 27% amylose, yields cooked rice with crumbly hard texture (Rice Department, 2016).

2.1.2.3 Phitsanulok 2

Phitsanulok 2 (PSL2) is also suitable for cultivation in all irrigated area of Thailand and not sensitive to photo period. The variety is crossbred between CNTLR81122-PSL-37-2-1/SPRLR81041-195-2-1 and IR56. It yields high production around 807 kg paddy rice per Rai. The rice contains 28.6% amylose, thus gives non-sticky, crumbly hard texture. It also possesses good milling quality (Rice Department, 2016).

2.2 Structure of rice grain

Paddy rice (Figure 2.1) composes of the hull, the outer protective covering, which is accounted for 16 to 28% (dry basis) and the rice caryopsis or kernel (Arendt and Zannini, 2013). The rice caryopsis consists of pericarp (1-2%), aleurone with seed coat and nucellus (4-6%), endosperm (89-94%) and embryo (2-3%) (Arendt and Zannini, 2013; Delcour and Hoseney, 2010; Hinton and Shaw, 1954; Zhou *et al.*, 2002b). The rice hull comprises lemma and palea which give protection for the rice kernel from fungal harm, insect agitation and environment, such as humidity oscillation (Arendt and Zannini, 2013; Marshall and Wadsworth, 1994). The pericarp is the layer inside the hull, which encompasses the endosperm. It is fibrous and has many thickness levels (Arendt and Zannini, 2013; Champagne *et al.*, 2004). The aleurone layer ranges from 1 to 5 cell layers, which encloses the endosperm and embryo. The cells encircle the endosperm are cuboidal that carry mostly protein bodies and lipid bodies, whereas the rectangular aleurone cells - around the embryo - contain fewer and smaller lipid bodies (Arendt and Zannini, 2013; Champagne *et al.*, 2004; Del Rosario *et al.*, 1968; Zhou *et al.*, 2002b). The embryo is set on one side of the endosperm near the lowest part of the caryopsis (Arendt and Zannini, 2013).

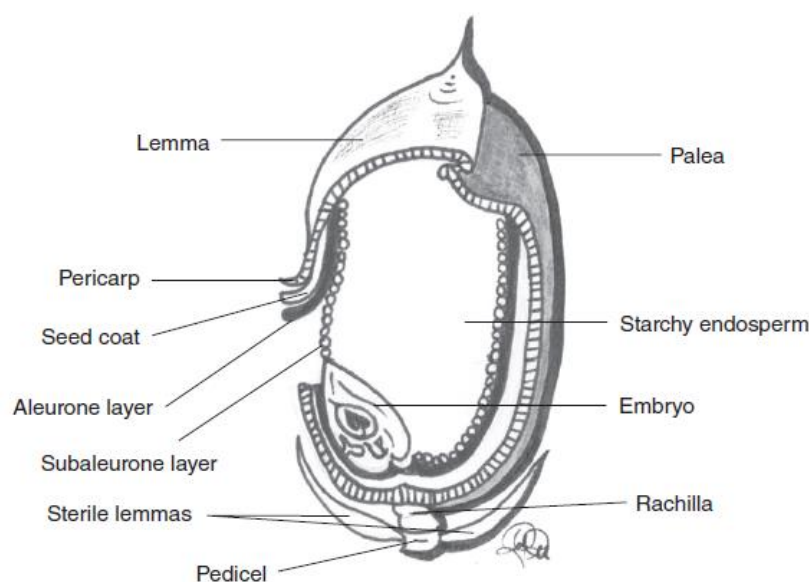


Figure 2.1 Structure of rice grain (Arendt and Zannini, 2013)

2.3 Chemical compositions of rice

The chemical components of rice and its fractions count on environment, soil, variety and processing conditions (Arendt and Zannini, 2013; Champagne *et al.*, 2004; Zhou *et al.*, 2002b). The three major compositions of the rice kernel are starch, protein and lipids (Arendt and Zannini, 2013).

2.3.1 Starch

Starch is the most abundant component of milled rice, accounting for around 90% of dry matters (Arendt and Zannini, 2013; Zhou *et al.*, 2002b). Rice starch granules, having 3-8 μm size range, are the smallest of starch from plant. The granules are irregular in shape but polygonal (Hayakawa *et al.*, 1980; Zhou *et al.*, 2002b). The starch granules comprises many starch molecules, which consist of amylose and amylopectin (Zhou *et al.*, 2002b). Amylose is a combination of long linear D - glucopyranosyl units linked by α - (1 \rightarrow 4) - linkages and a few of branched α - (1 \rightarrow 6) - bonded molecules (Arendt and Zannini, 2013; Ball *et al.*, 1996; Park *et al.*, 2013; Zhou *et al.*, 2002b). Amylose content exerts an effect on cooking quality, eating quality, water absorption, volume expansion and texture quality, such as hardness and stickiness of rice (Arendt and Zannini, 2013; Juliano, 1985, 2003; Zhou *et al.*, 2002b). Amylopectin is a much larger molecule (Park *et al.*, 2013; Rosell and Gómez, 2014). Amylopectin comprises α - (1 \rightarrow 4) - linkages D - glucosyl chains and has branches with α - (1 \rightarrow 6) - linkages (Arendt and Zannini, 2013; Buléon *et al.*, 1998). Higher amylose content in flour contributes to low peak viscosity, breakdown, and swelling power but high setback, final viscosity, and pasting temperature (Rosell and Gómez, 2014; Thanathornvarakul *et al.*, 2016; Varavinit *et al.*, 2003; Woo *et al.*, 2015; Zhu *et al.*, 2011).

2.3.2 Protein

Rice grain has protein as the second most plentiful composition. Normal rice contains 6.6% to 7.3% protein for brown rice and 6.2% to 6.9% for milled rice (Arendt and Zannini, 2013; Gomez, 1979; Kennedy and Burlingame, 2003; Singh, 1998; Zhou *et al.*, 2002b). The rice protein in milled rice composes of albumin (water-soluble proteins), globulin (salt-soluble proteins), prolamin (alcohol-

soluble proteins) and glutelin (alkali-soluble proteins), which is approximately 9.7-14.2%, 13.5-18.9%, 3.0-5.4% and 63.8-73.4%, respectively (Arendt and Zannini, 2013; Basak *et al.*, 2002; Juliano, 2003; Zhou *et al.*, 2002b). The peripheral layers of the grain have a large amount of rice protein. The protein content usually diminished after a rise in polishing level (Pal *et al.*, 1999; Zhou *et al.*, 2002b). Protein in rice has a large effect in the properties of cooked rice and rice flour. Higher protein content gives rise to harder cooked rice texture with lower stickiness and smoothness, higher pasting temperature of rice flour, and more cooking time (Arendt and Zannini, 2013; Mutters and Thompson, 2009; Shih, 2004).

2.3.3 Lipids

Most of rice lipids are placed in the bran and aleurone layer (Zhou *et al.*, 2002b). The lipids content in milled rice are low, accounting for about 2.2% of grain weight (Arendt and Zannini, 2013; Childs, 2004). Lipids in rice can be sorted into 2 groups which are starch lipids and non-starch lipids. Milled rice consists of 0.5% to 1.0% starch lipids, mainly monoacyl lipids such as fatty acids and phospholipids, which complex with amylose in the starch granules to form amylose-lipid complexes (Arendt and Zannini, 2013; Choudhury and Juliano, 1980; Ito *et al.*, 1979; Zhou *et al.*, 2002b). Non-starch lipids are reserved as lipid droplets, or spherosomes, and are dispensed to rice grain (Arendt and Zannini, 2013; Bechtel and Pomeranz, 1978; Choudhury and Juliano, 1980). The amylose-lipid complexes have an effect on rice properties, e.g. reducing the water-solubility in rice pastes and increasing pasting temperature (Arendt and Zannini, 2013; Kaur and Singh, 2000). The major fatty acids in rice are palmitic (C16:0) acids and linoleic (C18:2) (Arendt and Zannini, 2013; Kitahara *et al.*, 1997).

2.4 Rice aging

Aging of rice is a result of chemical changes of rice components, which, in turn, causes changes in its physical and functional properties. The change in physical and functional properties include textural properties, pasting properties, thermal properties and others (Faruq *et al.*, 2015; Park *et al.*, 2012; Soponronnarit *et al.*, 2008; Zhou *et al.*, 2007).

The factors that affect rice aging during storage can be sorted to internal and external factors. Internal factors are rice composition such as starch, protein and lipids. During the aging process, although starch, protein and lipid content in the rice grain remain unchanged, there are interactions among these components causing subsequent changes in other properties (Figure 2.2). Protein could bind onto starch granules, hence increasing the strength and inhibiting swelling of starch granule. As a result, the texture of cooked rice is altered. Lipids can undergo changes in two possible paths; one involves hydrolysis of lipid to produce free fatty acid which can complex with amylose resulting in a reduction of starch granule swelling and thus increasing hardness of cooked rice; the other is the oxidation of lipid to produce hydroperoxides that can accelerate oxidation of protein and condensation with volatile carbonyl compound causing off odor. Protein oxidation leads to formation of disulfide linkages between sulfhydryl groups that result in cystine. These changes in protein results in reduced swelling of starch granule which affects cooked rice texture (Ramesh *et al.*, 2000; Zhou *et al.*, 2002a).

External factors, e.g. temperature, moisture content, and packaging, play an important role in either slowing down or accelerating aging of rice during storage. At higher storage temperatures, changes in starch, lipid, and protein components have been shown to be more pronounced (Chrastil, 1990). Moisture content has secondary cause on changes of rice properties for example physical and thermal properties (Bhattacharya, 2011b; Cao *et al.*, 2004). According to Cao *et al.* (2004), who studied the effect of moisture on mechanical and thermal properties of brown rice, the glass transition temperature, melting temperature, maximum compressive, and tensile strengths of rice kernels increased with decreasing moisture content. In addition, Gujral and Kumar (2003) reported that accelerated aging of paddy at higher level of moisture resulted in increasing elongation, width expansion, water uptake, cooking time, hardness, cohesiveness and springiness but a decrease in solid loss and adhesiveness. Packaging is a significant element for rice preservation which offers protection of rice from encompassing environment (Li *et al.*, 2017). According to the studied of Norkaew *et al.* (2017), packaging unpolished black rice (Luem Pua and Kao Hom Nin) in nylon/LLDPE pouches flushed with nitrogen gas could preserve the

aroma compound (2-acetyl-1pyrroline), total phenolic and anthocyanin contents and reduce creation of off-flavor compounds. Besides, Li *et al.* (2017) found that antimicrobial nano-silver packaging prevents the changes in pasting properties and textural properties, hence shelf life extension of rice.

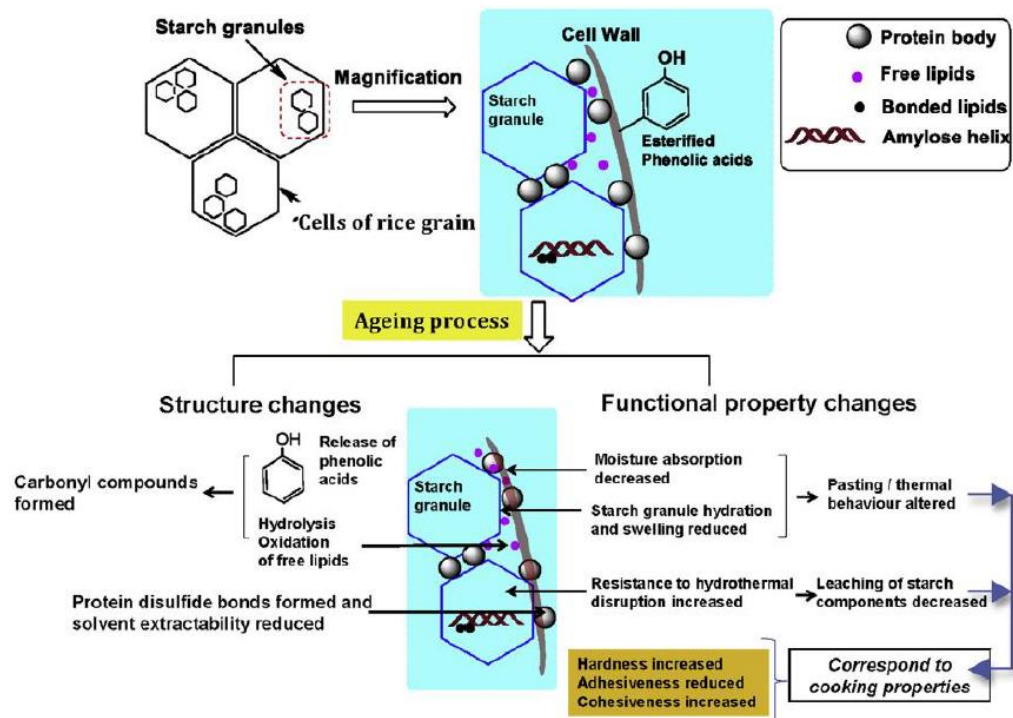


Figure 2.2 Changes as a function of ageing process during rice storage (Zhou *et al.*, 2015)

Zhou *et al.* (2007) studied aging of three rice varieties; Koshihikari, Kyeema and Doongara, that were stored at 4 and 37 °C and for 16 months. They reported that water uptake, hardness and cohesiveness of the rice increased while solid loss and adhesiveness decreased to a greater extent when stored at 37 °C. At 15 °C, aging effect was most significant during the first three to four months of storage (Perez and Juliano, 1981). Park *et al.* (2012) followed changes in Japonica rice stored at 4, 20, 30, and 40 °C for 4 months. The result from their study was consistent with other researches in that aged rice had reduced breakdown and adhesiveness and increased hardness, cohesiveness, and setback. They also found that the 40 °C/1 month aged rice had a similar texture with the 4 °C/4 month aged rice. Zhou *et al.* (2003) investigated

the influence of storage temperature on pasting qualities of milled rice grains that were stored at 4 and 37 °C for 16 months. The researchers measured pasting properties by Rapid Visco Analyzer and found that storage at higher temperatures decreased peak viscosity and break down to a greater extent. Zhou *et al.* (2003) probed the effect of temperature on thermal properties of milled rice grains stored for 16 months at 4 and 37 °C. They measured thermal properties by Differential Scanning Calorimetry (DSC) and found that storage at higher temperatures increased gelatinization enthalpy, onset temperature, peak temperature and conclusion temperature to a larger extent when compared to lower temperature storage. In addition, Soponronnarit *et al.* (2008) studied natural aging at room temperature in paddy rice for 6 months. The researchers found that head rice yield rapidly rised and reached the highest level after storage at 3 months and slowly decreased after that. Moreover, Jaisut *et al.* (2009) investigated the characteristics of natural aging of paddy rice that was stored at room temperature for 7 months. They found that water uptake, volume expansion, hardness, pasting temperature, final viscosity and setback increased with storage time while solid loss and peak viscosity decreased.

2.5 Near Infrared Spectroscopy

Near infrared (NIR) spectroscopy is a powerful technique that has several advantages such as rapid, non-destructive, environmentally safe, minimal sample preparation, low cost and can be used to investigate several parameters with one scan (Bao *et al.*, 2007; Batten, 1998; Osborne, 2006; Posom and Sirisomboon, 2014; Sirisomboon *et al.*, 2013; Wu and Shi, 2004; Zhang *et al.*, 2011). NIR spectroscopy has been used in both quantitative and qualitative analysis of foods and food products in recent year (Cen and He, 2007; Haughey *et al.*, 2013; Osborne *et al.*, 1993a). Fourier-transform near infrared (FT-NIR) spectrometer is one type of NIR devices used to obtain spectral data. FT-NIR has many advantages compared to conventional grating NIR spectroscopy, such as more signal-to-noise ratios, greatly high resolutions, rapid and precise frequency determinations (Armstrong *et al.*, 2006; Skoog *et al.*, 1998).

2.5.1 Principle of Near Infrared Measurement

NIR is a spectroscopic method which utilizes small region of spectral range from 780 to 2500 nm ($12,500\text{-}4,000\text{ cm}^{-1}$) (Figure 2.3) (Cen and He, 2007; Jha, 2010; McClure, 2007; Workman and Weyer, 2008). The NIR radiation reacts to C-H, O-H and N-H chemical bonds while these bonds relate to food compositions, i.e. water, protein, fat and carbohydrate (Cen and He, 2007; McClure, 2007).

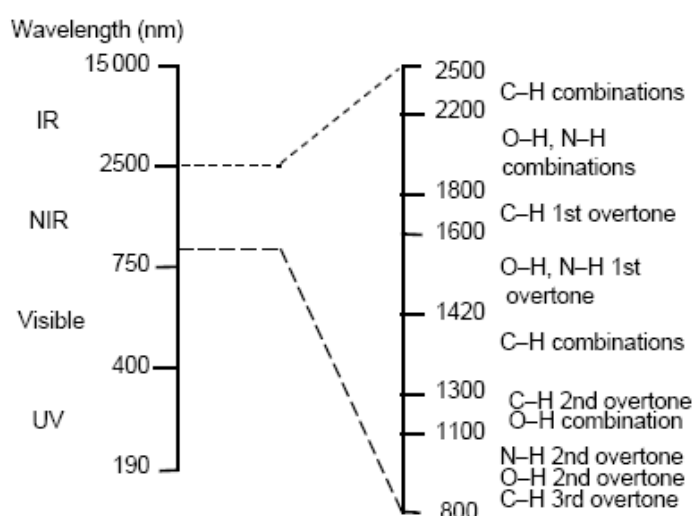


Figure 2.3 Spectral range of NIR region (Osborne, 2000)

Chemical linkages between atoms of molecules respond to the energy of the radiation in many ways and can be manifest by the resulting spectrum (a plot of energy versus wavelength) (Osborne, 2000). Figure 2.4 shows 6 vibrational modes, encompassing stretching and bending, in basic tri-atomic molecule (Jha, 2010).

NIR spectrometer composes of light source, wavelength selector, sample chamber, detector and computer (Figure 2.5) (Cen and He, 2007; Jha, 2010). In NIR determination, light comes from a source and interacts with the sample before it travels straight to a detector that responds to NIR light. Electrical data is then generated from the signal and later read by a computer (Ritthiruangdej, 2006). The light from a sample can be by either transmittance or reflectance (Figure 2.6). The transmittance procedure is appropriate for determination of internal data of sample

with large volume while the data from reflectance spectra is limited to the subsurface layer of samples (Tsuchikawa and McClure, 2007).

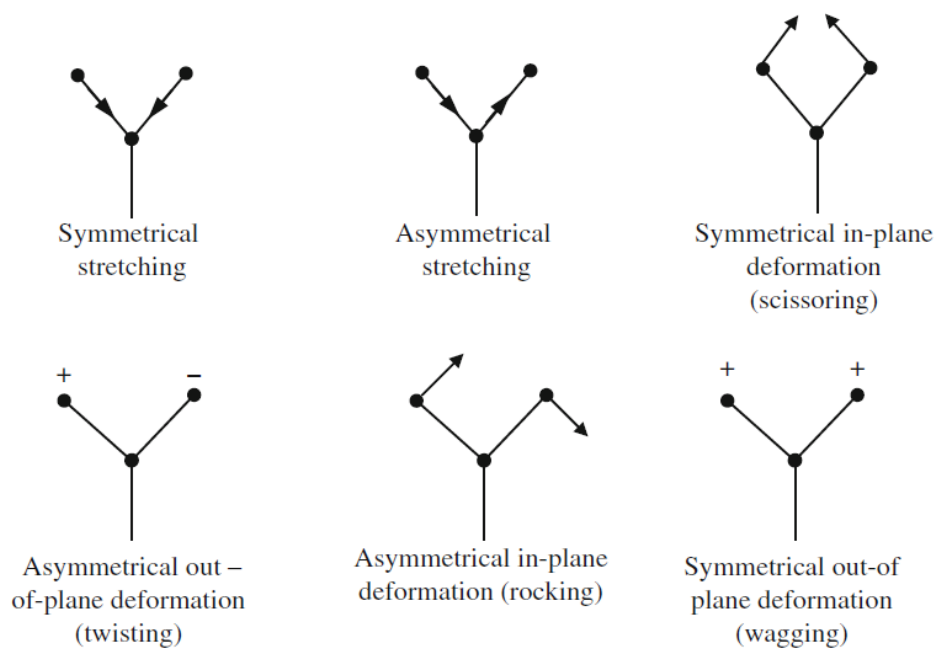


Figure 2.4 Six vibrational modes of tri-atomic molecule (Jha, 2010)

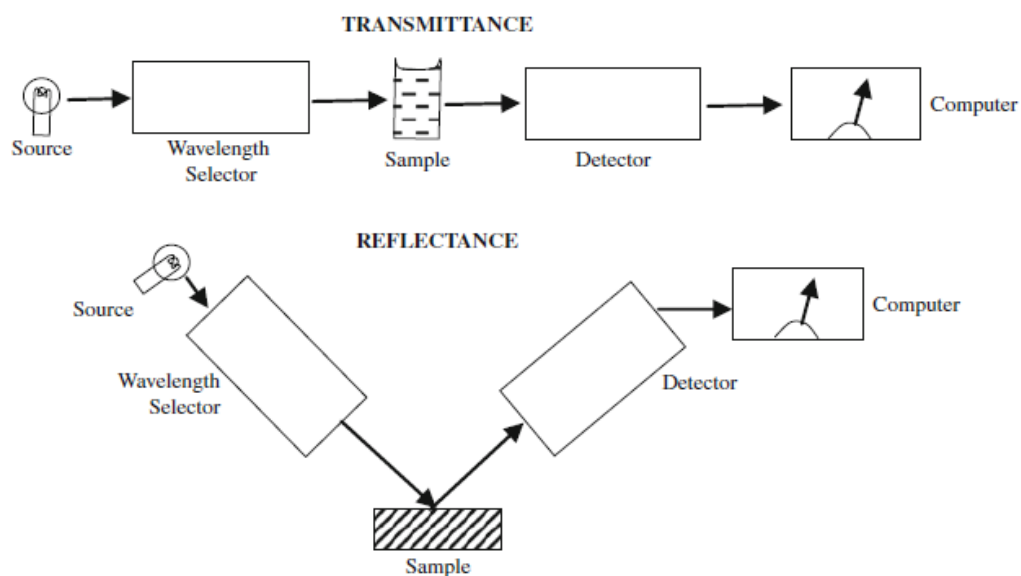


Figure 2.5 Principle of NIR instrument (Jha, 2010)

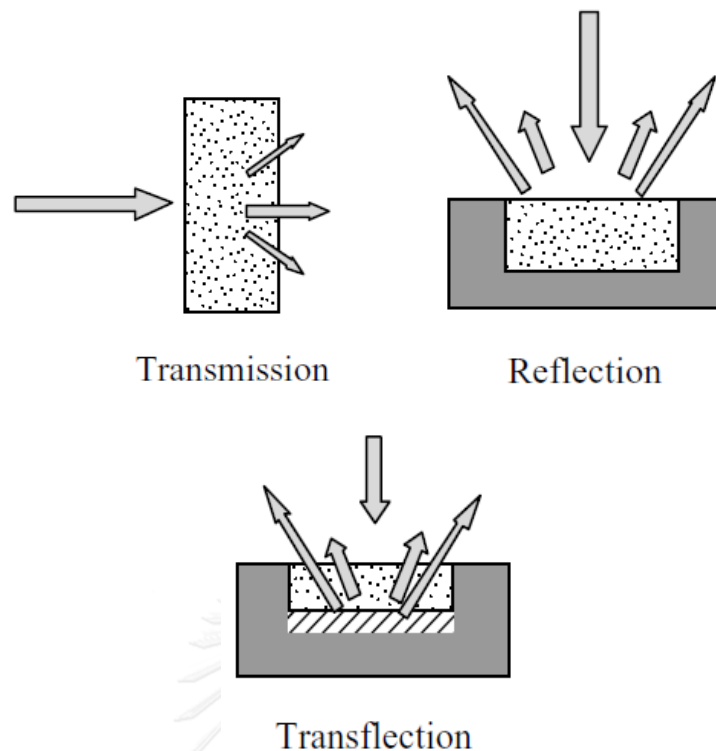


Figure 2.6 Type of NIR measuring modes (Tsuchikawa, 2007)

2.5.2 NIR calibration basic

It is very significant to generate a trustworthy and stable calibration model for quantitative or qualitative analysis in food investigation which concerns the prediction of separation and property for unknown samples (Cen and He, 2007). The calibration process is a multistep procedure which composes of collecting the samples, subjecting the samples to investigation by the reference method and by NIR instrument, developing calibration model and validation of the model (Figure 2.7) (Mark, 2001; Osborne *et al.*, 1993a).

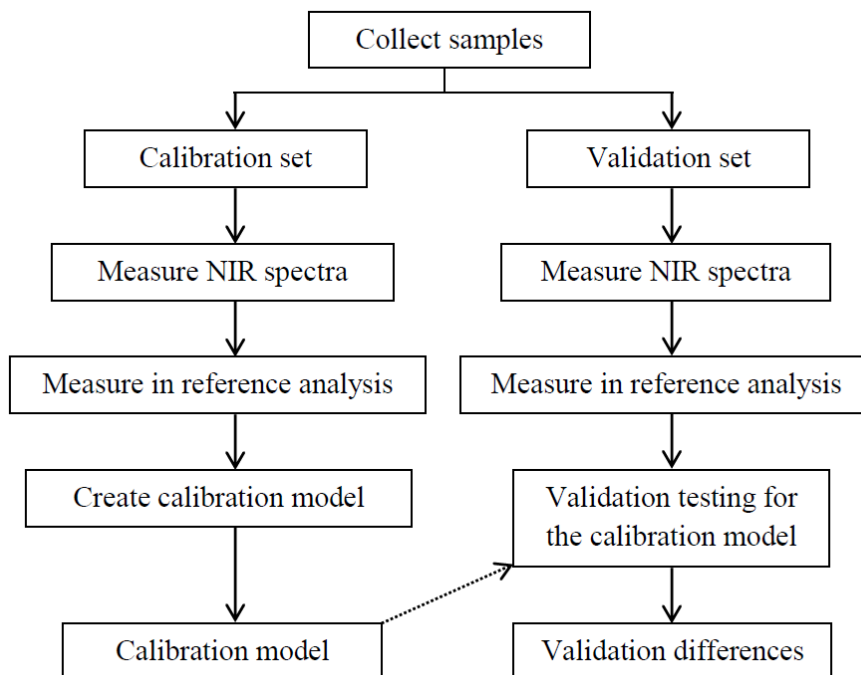


Figure 2.7 NIR calibration and validation process (Mark, 2001; Ritthiruangdej, 2006; Workman, 2001)

2.5.3 Spectral data pre-processing

The NIR spectra obtained from NIR spectrometer quite often contain background and noises. Therefore, it is very essential to pretreat spectral data before modeling. The pre-processing methods include smoothing, derivatization and standard normal variate (SNV). Smoothing can be done by moving average smoothing or Savitzky-Golay smoothing. These are the methods frequently used to get rid of noises. First- or second derivatization are used to delete background and enhance spectral resolution. SNV removes the multiplicative hindrance of scatter, particle size and the alteration of light length (Cen and He, 2007; Ozaki *et al.*, 2007).

2.5.4 Multivariate data analysis

The multivariate data analysis often used in quantitative NIR analysis are principal component analysis (PCA) and partial least square (PLS) regression (Naes *et al.*, 2002; Ritthiruangdej, 2006). PCA can be used to decrease the dimensionality of the information. The association of NIR spectra and PCA can be

used to classify the samples (Cen and He, 2007). PLS regression is the greatest popular multivariate technique and has been broadly applied in NIR analysis. PLS regression is a full-spectral calibration technique and based on compositions of the independent data and dependent data (Chalmers and Griffiths, 2002; Ritthiruangdej, 2006).

2.5.5 Application of NIR spectroscopy in foods

NIR spectroscopy can be used in both quantitative and qualitative analyses of foods and food products for instance measurement of soluble solids content and pH of yogurt (Shao and He, 2009), determination of total amino acids in oilseed rape leaves (Liu *et al.*, 2011), determination of protein content in *Brassica oleracea* species (Szgedi *et al.*, 2012), detection of spoilage of intact chicken breast muscle (Alexandrakis *et al.*, 2012), determination of calcium content in powdered milk (Wu *et al.*, 2012), on-line screening of different dates varieties (Tavakolian *et al.*, 2013) and quantification of mildew damage in soft red winter wheat (Shahin *et al.*, 2014).

In rice grain, flour and starch, NIR has been widely used to determine rice quality such as grain weight (Wu and Shi, 2004), gel consistency and alkali spread value of brown rice and milled rice (Wu and Shi, 2007), swelling properties and water solubility in whole grain barley (Cozzolino *et al.*, 2013), determination of native maize, native wheat starches, high amylose maize starch, phosphorylated wheat starch, and their mixture (Hódsági *et al.*, 2012), amylose content (Bagchi *et al.*, 2016; Delwiche *et al.*, 1996; Himmelsbach *et al.*, 2001; Villareal *et al.*, 1994; Wu and Shi, 2004, 2007; Xie *et al.*, 2014), protein content (Bagchi *et al.*, 2016; Delwiche *et al.*, 1996; Himmelsbach *et al.*, 2001; Shao *et al.*, 2011; Xie *et al.*, 2014), amino acid in brown rice (Zhang *et al.*, 2011) and identification between Basmati and other long grain rice samples (Osborne *et al.*, 1993b).

Delwiche *et al.* (1996) determined whole grain milled rice quality (amylose content in the range of 14-25%) from 196 U.S. rice samples by NIR spectroscopy in the 400-2498 nm region. They found that PLS was the most suitable technique for developing the best model. From their work, the relationship between

pasting properties versus NIR spectra of breakdown and setback had the R^2 of 0.719 and 0.737, respectively.

Bao *et al.* (2007) determined the thermal and retrogradation properties of rice grain and milled flour using NIR in the 1100-2498 nm region. They found that both grain and flour spectra gave the same precision in investigating the peak temperature and conclusion temperature of gelatinization. Nevertheless, the correlation between flour spectra and onset temperature ($R^2 = 0.80$) was better than the correlation between grain spectra and onset temperature ($R^2 = 0.73$).

Chen and Huang (2010) described a procedure to predict the grade of milled rice using surface lipid content, which was investigated using NIR. Sixty-six rice cultivars with different milling degrees were scanned by NIR in the range of 11,000-4,000 cm^{-1} . The calibration model was developed based on the PLS regression. The best model gave the root mean square error of the prediction (RMSEP) of 0.0248% and determination coefficient of 0.9905.

Sirisomboon *et al.* (2013) reported the use of NIR in detection of aflatoxigenic fungal contaminated jasmine rice, white rice and brown rice samples. One hundred and six (106) rice samples were scanned in the wavelength range between 950 and 1650 nm in reflectance mode. The calibration model was developed from the original and pre-processing spectra based on PLS regression. The original spectra gave the best model with the greatest accuracy in prediction ($r = 0.668$, SEP = 28.874% and bias = -0.101%).

CHAPTER III

MATERIALS AND METHODS

3.1 Materials

Paddy of rice from six varieties; three low amylose and three high amylose varieties, which were harvested in the 2012 crop year was used in this study. Table 3.1 shows the name and cultivation area for each rice variety.

Table 3.1 Rice varieties and cultivation area

Type	Variety	Cultivation area	Contributor
Low amylose (10.5-11.2%)	Khao Dawk Mali 105 (KDML105) or Jasmine rice	Prachinburi Province	Agricultural Co-op Prachantakam
	Rice Department 45 (RD45)	Prachinburi Province	
	Pathumthani 1 (PTT1)	Pathumthani Province	Pathumthani Rice
High amylose (26.3-27.9%)	Rice Department 47 (RD47)	Pathumthani Province	Research Center
	Phitsanulok 2 (PSL2)	Pathumthani Province	
	Chai Nat 1 (CNT1)	Ratchaburi Province	Ratchaburi Rice Research Center

3.2 Methods

3.2.1 Sample preparation

Rice paddy (10.2-13.1% moisture content) was packed in 1.5 kg plastic woven sacks. The packages were divided into two sets. The first set was stored at a controlled temperature of 8 ± 2 °C and 80% relative humidity (RH) for 18 months while the second set was stored at 30 ± 2 °C and 70% RH for 9 months. The rice qualities were determined at an interval of 2 months for the sample stored at 8 ± 2 °C and 1 month for that stored at 30 ± 2 °C. The experiment was conducted in two replications. Each replication was a sample from 1 plastic woven sack.

3.2.2 Determination of fresh rice paddy qualities

3.2.2.1 Determination of moisture content of paddy

The moisture content (MC) of rice paddy was determined using a grains moisture meter (GMK-303, G-WON Hitech CO., Ltd., Seoul, Korea). Three measurements were carried out per replication.

3.2.2.2 Determination of milling quality (head rice yield)

Head rice yield (HRY) was determined following the method of Thai Agricultural Standard (TAS) 4004-2012 (National Bureau of Agricultural Commodity and Food Standards, 2012). One hundred and twenty-five grams (125 g) of paddy were dehusked twice by a three-roller dehussing machine (Sinthavee garage, Lopburi, Thailand) to obtain brown rice which was then polished by a polishing machine (Sinthavee garage, Lopburi, Thailand) for 20 seconds to obtain milled rice. A roller sizing equipment (Sinthavee garage, Lopburi, Thailand) was used to separate broken rice kernels from head rice kernels. Head rice yield percentage was calculated from equation (1). Two measurements were carried out per replication.

$$\text{Head rice yield (\%)} = \frac{\text{Weight of head rice}}{\text{Weight of paddy}} \times 100 \quad (1)$$

3.2.2.3 Determination of physicochemical properties of milled rice

The color of milled rice was measured using a Chroma meter (model CR400 series, Konica Minolta, Tokyo, Japan). The whiteness index (WI) was calculated from L, a and b using equation (2). Three measurements were carried out per replication.

$$\text{Whiteness index} = 100 - [(100-L)^2 + a^2 + b^2]^{0.5} \quad (2)$$

The average breadth and the length of 100 whole rice kernels were determined by a micrometer following the method modified from Singh *et al.* (2005). Two measurements were carried out per replication.

The weight and volume per 1000 grains of whole rice kernels was determined following the method modified from Singh *et al.* (2005). One

thousands whole rice kernels were added into a graduated cylinder. The bulk density was calculated from the weight and the volume following the method modified from Singh *et al.* (2005). Three measurements were carried out per replication.

Proximate composition of milled rice, including moisture content, protein, fat, fiber, ash and carbohydrate was determined following the method in AOAC (2012). The method is elaborated in Appendix A.1-A.6. Milled rice was ground and sieved through a 100-mesh sifter prior to the analyses. The measurements were carried out by Thailand Institute of Scientific and Technological Research. Three measurements were carried out per replication.

Amylose content of milled rice was determined using the amperometric titration with potassium iodate solution method following the method of Takeda *et al.* (1987) and Gibson *et al.* (1997) with modification (Appendix A.7). The measurements were determined by Cassava and Starch Technology Research Unit, Kasetsart Agricultural and Agro-Industrial Product Improvement Institute (KAPI). Three measurements were carried out per replication.

3.2.2.4 Determination of cooking quality

One gram (1 g) of milled rice kernels was boiled in 10 mL of distilled water at 99 ± 1 °C in a glass test tube. The sample was retrieved at an interval of 1 minute and pressed between two microscope glass slides. The time required to fully cook rice kernels; the point when chalky center disappeared, was recorded as the minimum cooking time (modified method of Gujral and Kumar (2003). This minimum cooking time was further used for preparation of cooked rice for subsequent analyses.

For the determination of solid loss and water uptake, the sample held at the minimum cooking time was decanted. The liquid was transferred into a pre-weighed aluminum pan and dried at 105 °C for 24 hours in a hot air oven. The drained cooked rice was weighed to the third digit. Solid loss and water uptake was calculated from equation (3) and (4), respectively (Soponronnarit *et al.*, 2008). Two measurements were carried out per replication.

$$\text{Solid loss (\%)} = \frac{\text{Weight increase of aluminum pan}}{\text{Initial weight of rice sample}} \times 100 \quad (3)$$

$$\text{Water uptake (\%)} = \frac{W_c - W_{uc}}{\text{Initial weight of rice sample} - \text{solid loss (\%)/100}} \times 100 \quad (4)$$

where, W_{UC} and W_C are the weight of uncooked and cooked rice kernels, respectively.

The elongation ratio; defined as the length of cooked rice kernels divided by length of uncooked rice kernels (Soponronnarit *et al.*, 2008), of 10 cooked rice grains was measured and the average value was reported as elongation of rice from one measurement. Two measurements were carried out per replication.

The cooked length-breadth ratio; defined as the length of cooked rice kernels divided by breadth of cooked rice kernels (Singh *et al.*, 2005), of 10 cooked rice grains was measured and the average value was reported as cooked length-breadth ratio of rice from one measurement. Two measurements were carried out per replication.

The volume expansion ratio was the volume of cooked rice kernels divided by volume of uncooked rice kernels (Soponronnarit *et al.*, 2008). Two measurements were carried out per replication.

3.2.2.5 Determination of textural properties

For texture analysis, cooked rice was prepared by steaming for the minimum cooking time. After cooking, the rice was held in an aluminum bowl to cool down for 30 minutes. Textural properties were determined by texture profile analysis (TPA) using the Texture Analyzer (TA.XTplus Texture Analyzer, Stable Micro Systems, Ltd., UK). One (1) g of cooked rice were weighed and arranged in a single-grain layer on the platform of the Texture Analyzer. The sample was compressed using P100 probe at a speed of 1mm/second (Champagne *et al.*, 1998). Ten analyses were carried out for one measurement and two measurements were carried out for one replication.

3.2.2.6 Determination of pasting properties of rice flour

Milled rice was ground and sieved through a 100-mesh sifter. Pasting properties of rice flour were determined by a Rapid Visco Analyzer (RVA; Model 4D, Newport Scientific, Australia). Three (3) g of rice flour (12% moisture) in 25 mL of distilled water was subjected to pasting test using RVA standard profile 1 (Appendix B.1). Pasting temperature, peak viscosity, trough viscosity, final viscosity, breakdown and setback were reported. Two measurements were carried out for one replication.

3.2.2.7 Determination of thermal properties of rice flour

Thermal properties of the flour from milled rice samples were determined using Differential Scanning Calorimeter (DSC) (Model Diamond, Perkin-Elmer, Norwalk, CT, USA). Rice flour (3.5 mg) was weighed into a large volume stainless steel pan (Perkin-Elmer kit no. 03190218) and distilled water was added to give a flour-to-water ratio of 1:3 (w/w). Sample pans were hermetically sealed and equilibrated overnight at ambient temperature. The sealed pan and an empty reference pan were heated from 30 to 135 °C at a heating rate of 10 °C/minute. The onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), the range of gelatinization temperature (ΔT_g), enthalpy of gelatinization (ΔH_g), enthalpy of amylose/lipid complex ($\Delta H_{\text{amylose/lipid complex}}$) were recorded via PyrisTM software version 11 (Perkin-Elmer). One measurement was carried out for one replication.

3.2.2.8 Electrophoresis of rice protein

Molecular weight distribution of rice protein extracted from rice flour was determined using sodium dodecyl sulfate polyacrylamide gel electrophoresis (SDS-PAGE) using OmniPAGE electrophoresis (CVS10DSYS, Cleaver Scientific Ltd., UK). SDS-PAGE was run according to the method modified from Laemmli (1970) and Iida *et al.* (1993). Rice flour (40 mg) was weighed into an eppendorf and 700 μ L SDS-urea solution (8M urea, 4% Sodium dodecyl sulfate (SDS), 20% glycerol and 50 mM Tris-base, pH 6.8) was added. The samples were mixed using a vortex for 1 minute and left to stand overnight at room temperature. After that, the samples were centrifuged at 7000 \times g for 5 minutes to obtain rice protein

extract solution. Sample solution (200 μL) and 200 μL buffer (8M urea, 4% SDS, 20% glycerol, 1% bromophenol blue and 50 mM Tris-base, pH 6.8) were added into an eppendorf and mixed by a vortex. Sample (5 μL) was loaded onto SDS-PAGE (4% stacking gel and 10% separating gel, see appendix A.8) with Perfect ProteinTM markers, 10-225 kDa (Novagen®, Merck Millipore, USA) as the SDS-PAGE standard marker. After electrophoresis at 300 V and electric current 20 mA/gel, the gel was stained by staining solution (1 g of Coomassie brilliant blue R-250, 100 mL of glacial acetic acid, 500 mL of 95% ethanol and 400 mL of distilled water) for 1 hour and de-stained twice (30 minutes/time) in de-staining solution (100 mL of glacial acetic acid, 250 mL of 95% ethanol and 650 mL of distilled water). Molecular weight distribution of rice protein was analyzed using Gel documentation systems (InGeniusL, Syngene, UK) including GeneSnap software for taking gel photographs and GeneTools for protein molecular weight analysis. Finally, raw volume (%) of protein molecular weight distribution was calculated from equation (5). Two measurements were carried out per replication.

$$\text{Raw volume (\%)} = \frac{\text{Raw volume of specific band}}{\text{Sum of raw volume in similar lane}} \times 100 \quad (5)$$

3.2.2.9 FT-NIR analysis

The milled rice samples were analyzed using FT-NIR spectrometer (FT-NIR Antaris II, Thermo Scientific, USA) in the diffuse-reflectance mode. All diffuse-reflectance spectra were collected in the wavenumber range of 10000 to 4000 cm^{-1} (resolution: 8 cm^{-1} , number of sample scan: 32 scans). Twenty-five (25) g sample was filled in a quartz sample holder and scanned at 25 °C. Ten (10) spectra were collected on each sample. The spectra were then averaged to produce a single spectrum for each sample.

3.2.3 Determination of stored rice qualities

The qualities of stored rice paddy, milled rice and rice flour were determined following the detailed method in 3.2.2. It is noted that breadth and length of grain, weight and volume per 1000 grains, bulk density, proximate analysis and

amylose content were not determined on the assumption that the values were unchanged during storage.

3.2.4 Chemometric analysis of FT-NIR data

3.2.4.1 Principal Component Analysis

Principal Component Analysis (PCA) of 36 chemical and physical properties data from fresh and aged rice samples was carried out using the Unscrambler-® X version 10.3 software package (CAMO, Norway).

3.2.4.2 Predictive model construction

The measurement data and spectra were separated into 2 groups for calibration (n=153) and validation (n=75). The ratio of calibration samples to validation samples was 2:1 which the minimum and maximum values were calibration samples. It means that the range of values for the validation set fell within the calibration set range for all parameters. Spectra were pre-treated with smoothing, first derivative, second derivative using the Savitzky-Golay method and standard normal variate (SNV). Partial least square regression (PLS) was used to develop chemometric models using the Unscrambler-® X version 10.3 software package (CAMO, Norway) with full-spectrum analysis methods. Model performance was reported as the coefficient of determination (R^2) and Root Mean Square Error of Calibration (RMSEC) with each term calculated on the calibration set, Root Mean Square Error of Prediction (RMSEP), and bias (the average difference between modeled and reference values). The optimal model with lower RMSEC and higher R^2 was used to predict the sample properties in the validation set.

3.2.5 Aging kinetics modeling

The experimental data at each storage temperature were fitted using the first order fractional conversion model (equation 6) that was elaborated in Rizvi and Tong (1997). The model was reported by the researchers to have been used in modeling starch gelatinization that always follows first order kinetics (Lund, 1986), in which the reaction rate depends upon reactant concentration. In the first order fractional conversion model, the measured parameter at any time is a function of its

level at the beginning and the end multiplied by the exponential function of the reaction rate constant and the storage time.

$$A_t = A_\infty + (A_0 - A_\infty) \cdot e^{-kt} \quad (6)$$

where, t is storage time (week), A_0 and A_∞ is the measured parameter at the beginning of storage and that at equilibrium, respectively, and k is the reaction rate constant (week^{-1}). Rizvi and Tong (1997) noted that, to apply a first order fractional conversion kinetics model, the observation time should have been long enough so that the chosen property was no longer change with time. However, in many observed parameters recorded in present study, the changes during aging appeared linearly increasing or decreasing. A zeroth order reaction model (equation 7; Figure 3.1), where the progress of the reaction does not depend on the reactant concentration, could probably then be suitably applied.

$$A_t = A_0 + kt \quad (7)$$

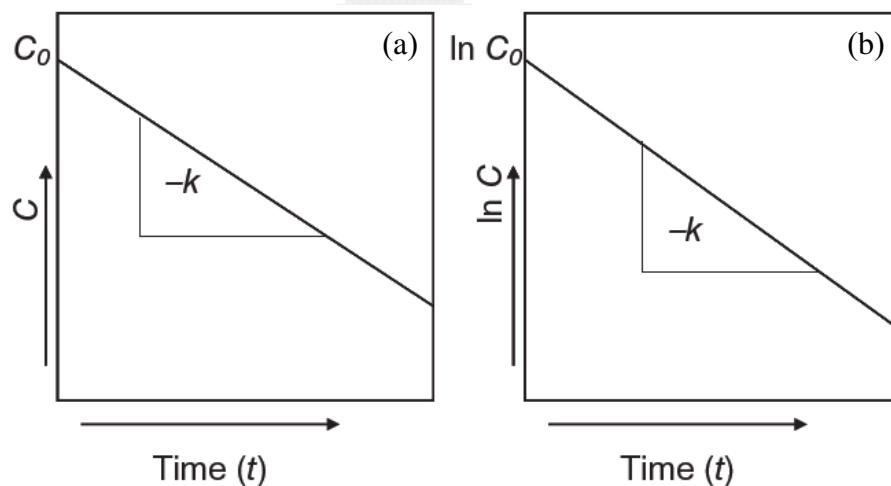


Figure 3.1 Pattern of (a) zeroth order kinetic model and (b) the first-order fractional conversion kinetic model (Ahmed *et al.*, 2012)

Therefore, all observed parameters were then fitted using both zeroth and first order fractional conversion kinetic models, and the regression coefficient of the fitted models was compared.

3.2.6 Statistical analysis

The experiments were carried out in two replications and the average value was reported. The data were analyzed by analysis of variance (ANOVA) with significance at $p \leq 0.05$. Duncan's multiple range tests (DMRT) were carried out for mean comparison. All statistical analyzes were performed using SPSS software (version 17, SPSS Inc., Chicago, USA).



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Properties of freshly harvested rice

Properties of six freshly harvested rice varieties in terms of physical properties of paddy rice, cooking quality, texture of cooked rice, and pasting properties of rice flour are shown in table 4.1. It was found that whiteness index (44.42-46.22), breadth of grain (1.98-2.22 mm), elongation ratio (1.38-1.52), cooked length-breadth ratio (3.19-3.69), bulk density (0.73-0.78), springiness (0.32-0.35), cohesiveness (0.38-0.41), enthalpy of gelatinization (7.48-11.55 J/g), fat (0.71-2.10% db), fiber (0.84-1.07% db), ash (0.39-0.91% db) and carbohydrate content (86.53-89.57% db) of low and high amylose rice varieties varied in a narrow range. High amylose rice showed higher head rice yield, length of grain, weight and volume/1000 grains, solid loss, pasting temperature, setback, hardness, gumminess, chewiness, enthalpy of amylose/lipid complex, protein content, and amylose content but lower water uptake (except CNT1), peak viscosity, breakdown, adhesiveness, onset temperature (except CNT1), peak temperature (except CNT1), conclusion temperature (except CNT1), gelatinization temperature range, than low amylose rice. In addition, no obvious relationship could be found between rice varieties with different amylose content and minimum cooking time, volume expansion ratio, final viscosity and trough viscosity. For example, CNT1, which is high amylose rice, yielded the longest minimum cooking time followed by RD45, which is low amylose rice. All other four varieties showed comparable minimum cooking time. Despite its high amylose content, CNT1 gave the highest volume expansion ratio, final viscosity and trough viscosity followed by low amylose rice varieties and the rest of high amylose rice varieties. This might be due to significantly high protein and relatively low fat content along with amylopectin fine structure and/or the interaction of these components thereof that needs further investigation.

Table 4.1 Physical properties, cooking qualities, pasting properties, textural properties, thermal properties and chemical properties of fresh rice (paddy, milled rice and rice flour)

Parameters	Low-amylose rice			High-amylose rice		
	KDML105	PTT1	RD45	RD47	CNT1	PSL2
Moisture content of paddy (%wb)	11.73 ^c ±0.14	10.78 ^c ±0.12	12.77 ^b ±0.14	13.13 ^a ±0.09	10.20 [±] 0.19	11.32 ^d ±0.02
Head rice yield (%)	34.70 ^b ±1.39	16.61 ^a ±0.39	28.54 ^c ±0.01	29.59 ^c ±0.58	47.27 ^b ±0.05	23.70 ^d ±0.09
Whiteness index	45.30 ^b ±0.27	45.40 ^b ±0.26	46.15 ^a ±0.05	44.58 ^c ±0.13	46.22 ^a ±0.30	44.42 ^c ±0.24
Breadth of grain (mm)	2.03 ^{cd} ±0.02	1.98 ^d ±0.01	2.22 ^b ±0.00	2.10 ^{bc} ±0.05	2.14 ^b ±0.00	2.08 ^{bc} ±0.01
Length of grain (mm)	6.95 ^c ±0.01	7.00 ^d ±0.00	6.87 ^f ±0.01	7.52 ^b ±0.00	7.49 ^b ±0.02	7.32 ^c ±0.01
Weight/1000 grains	19.53 ^c ±0.02	19.05 ^f ±0.03	21.00 ^d ±0.07	22.12 ^b ±0.16	22.53 ^b ±0.10	21.54 ^c ±0.09
Volume/1000 grains	26.58 ^c ±0.12	24.58 ^d ±0.35	27.50 ^b ±0.24	29.58 ^a ±0.12	29.33 ^b ±0.00	28.00 ^b ±0.24
Bulk density	0.73 ^b ±0.00	0.78 ^a ±0.01	0.76 ^a ±0.00	0.75 ^b ±0.00	0.77 ^b ±0.00	0.77 ^b ±0.00
Minimum cooking time (min)	17.00±0.00	18.00±0.00	21.00±0.00	18.00±0.00	24.00±0.00	18.00±0.00
Solid loss (%)	3.30 ^c ±0.04	3.43 ^d ±0.05	3.64 ^c ±0.03	4.18 ^b ±0.03	3.33 ^c ±0.03	4.54 ^a ±0.02

Note: KDML105 = KhaoDawk Mali 105; PTT1 = Pathumthani 1; RD45 = Rice Department 45; RD47 = Rice Department 47; CNT1 = Chai Nat 1; PSL2 = Phitsamulok 2

T_o = onset temperature; T_p = peak temperature; T_c = conclusion temperature; T_c-T_o = gelatinization temperature range; ΔH_g = enthalpy of gelatinization;

ΔH_{al} = enthalpy of amylose/lipid complexes

Mean values in a row with different superscripts are different significantly (p ≤ 0.05)

Table 4.1 Physical properties, cooking qualities, pasting properties, textural properties, thermal properties and chemical properties of fresh rice (paddy, milled rice and rice flour) (cont...)

Parameters	Low-amylose rice			High-amylose rice		
	KDML105	PTT1	RD45	RD47	CNT1	PSL2
Water uptake (%)	239.94 ^b ±7.68	239.41 ^b ±4.14	242.18 ^b ±1.82	204.45 ^c ±5.76	270.38 ^{cd} ±0.65	215.11 ^c ±4.93
Elongation ratio	1.52 ^a ±0.01	1.47 ^a ±0.00	1.38 ^b ±0.02	1.48 ^b ±0.01	1.52 ^b ±0.05	1.47 ^b ±0.01
Cooked length-breadth ratio	3.59 ^a ±0.07	3.19 ^b ±0.18	3.22 ^b ±0.22	3.68 ^b ±0.05	3.62 ^b ±0.04	3.69 ^b ±0.00
Volume expansion ratio	2.66 ^{ab} ±0.01	2.63 ^b ±0.03	2.57 ^{bc} ±0.08	2.60 ^{bc} ±0.11	2.84 ^b ±0.01	2.42 ^c ±0.10
Pasting temperature (°C)	74.26 ^d ±0.02	75.48 ^{cd} ±0.00	74.91 ^{cd} ±0.26	81.81 ^{ab} ±3.77	79.12 ^{bc} ±0.00	83.63 ^b ±0.60
Peak viscosity (Pa.s)	3.66 ^a ±0.12	3.58 ^b ±0.15	3.79 ^b ±0.09	1.70 ^c ±0.34	2.80 ^b ±0.05	1.36 ^c ±0.05
Final viscosity (Pa.s)	2.47 ^{cd} ±0.07	2.97 ^b ±0.10	2.77 ^{bc} ±0.05	2.63 ^{bcd} ±0.31	3.97 ^b ±0.06	2.25 ^d ±0.03
Breakdown (Pa.s)	2.12 ^a ±0.04	1.77 ^b ±0.08	2.10 ^b ±0.14	0.46 ^d ±0.14	0.91 ^c ±0.02	0.31 ^d ±0.04
Setback (Pa.s)	0.93 ^d ±0.01	1.15 ^c ±0.02	1.08 ^c ±0.00	1.38 ^b ±0.10	2.08 ^b ±0.03	1.20 ^c ±0.02
Trough viscosity (Pa.s)	1.54 ^b ±0.08	1.81 ^{ab} ±0.07	1.70 ^{ab} ±0.04	1.25 ^c ±0.21	1.89 ^b ±0.04	1.05 ^c ±0.01

Note: KDML105 = KhaoDawk Mali 105; PTT1 = Pathumthani 1; RD45 = Rice Department 45; RD47 = Rice Department 47; CNT1 = Chai Nat 1; PSL2 = Phitsanulok 2

T_o = onset temperature; T_p = peak temperature; T_c = conclusion temperature; T_c-T_o = gelatinization temperature range; ΔH_g = enthalpy of gelatinization;

ΔH_{al} = enthalpy of amylose/lipid complexes

Mean values in a row with different superscripts are different significantly (p ≤ 0.05)

Table 4.1 Physical properties, cooking qualities, pasting properties, textural properties, thermal properties and chemical properties of fresh rice (paddy, milled rice and rice flour) (cont...)

Parameters	Low-amylose rice				High-amylose rice			
	KDML105	PTT1	RD45	RD47	CNT1	PSL2		
Hardness (kg)	11.45 ^c ±0.60	11.45 ^c ±0.49	10.61 ^c ±0.31	15.14 ^a ±1.13	12.06 ^{bc} ±0.16	13.63 ^{ab} ±0.15		
Cohesiveness	0.41 ^{ab} ±0.01	0.39 ^{abc} ±0.01	0.38 ^c ±0.00	0.41 ^a ±0.01	0.40 ^{ab} ±0.00	0.39 ^{bc} ±0.00		
Adhesiveness (kg.mm)	0.67 ^a ±0.05	0.69 ^a ±0.01	0.78 ^a ±0.03	0.14 ^c ±0.01	0.28 ^b ±0.07	0.21 ^{bc} ±0.03		
Springiness ^{ns}	0.34±0.02	0.32±0.01	0.34±0.00	0.34±0.01	0.35±0.03	0.35±0.01		
Gumminess (kg)	4.68 ^{bc} ±0.31	4.47 ^c ±0.27	4.04 ^c ±0.09	6.22 ^a ±0.60	4.84 ^{bc} ±0.03	5.33 ^b ±0.00		
Chewiness (kg)	1.62 ^{bc} ±0.03	1.42 ^c ±0.11	1.36 ^c ±0.04	2.14 ^a ±0.28	1.70 ^{bc} ±0.14	1.87 ^{ab} ±0.08		
T _o (°C)	64.20 ^c ±0.61	64.33 ^c ±0.54	66.58 ^b ±0.11	61.74 ^d ±1.68	73.42 ^a ±0.01	59.13 ^e ±0.72		
T _p (°C)	74.77 ^b ±0.72	74.70 ^b ±0.24	74.83 ^b ±0.38	70.60 ^c ±0.17	79.12 ^a ±0.01	69.72 ^c ±0.34		
T _c (°C)	83.80 ^a ±0.45	83.85 ^a ±0.50	87.12 ^a ±3.30	78.40 ^b ±0.59	85.80 ^a ±0.10	78.66 ^b ±0.20		
ΔH _g (J/g)	9.16 ^{ab} ±0.37	11.55 ^a ±1.21	9.38 ^{ab} ±0.83	7.48 ^b ±0.61	8.82 ^b ±1.04	9.46 ^{ab} ±1.20		
ΔH _{al} (J/g) ^{ns}	0.55±0.23	1.38±0.47	2.45±2.40	2.72±1.15	2.52±1.05	3.24±1.95		
T _c - T _o (°C)	19.60 ^a ±1.05	19.52 ^a ±1.05	20.55 ^a ±3.19	16.66 ^{ab} ±2.28	12.39 ^b ±0.09	19.53 ^a ±0.92		

Note: KDML105 = KhaoDawk Mali 105; PTT1 = Pathumthani 1; RD45 = Rice Department 45; RD47 = Rice Department 47; CNT1 = Chai Nat 1; PSL2 = Phitsanulok 2

T_o = onset temperature; T_p = peak temperature; T_c = conclusion temperature; T_c-T_o = gelatinization temperature range; ΔH_g = enthalpy of gelatinization;

ΔH_{al} = enthalpy of amylose/lipid complexes

Mean values in a row with different superscripts are different significantly (p ≤ 0.05)

Table 4.1 Physical properties, cooking qualities, pasting properties, textural properties, thermal properties and chemical properties of fresh rice (paddy, milled rice and rice flour) (cont...)

Parameters	Low-amylose rice			High-amylose rice		
	KDML105	PTT1	RD45	RD47	CNT1	PSL2
Moisture content of flour (%wb) ^{ns}	10.61±0.93	11.19±0.43	11.75±0.06	11.73±0.35	10.76±0.05	11.16±0.23
Protein content (%db)	7.62 ^d ±0.20	7.39 ^d ±0.10	8.39 ^c ±0.10	9.24^b±0.01	10.90^a±0.32	8.08^c±0.12
Fat (%db) ^{ns}	1.34±0.94	2.10±1.14	1.43±0.62	1.71±0.50	0.71±0.02	1.09±0.25
Fiber (%db)	1.07 ^a ±0.03	0.96 ^b ±0.03	0.90 ^{bc} ±0.01	0.88 ^{cd} ±0.03	0.97 ^b ±0.02	0.84 ^d ±0.01
Ash (%db)	0.39 ^b ±0.04	0.40 ^b ±0.04	0.43 ^b ±0.04	0.55 ^b ±0.18	0.87 ^a ±0.03	0.91 ^a ±0.04
Carbohydrate (%db)	89.57 ^a ±1.08	89.14 ^{ab} ±1.02	88.84 ^{ab} ±0.75	87.61 ^{bc} ±0.65	86.53 ^c ±0.35	89.08 ^{ab} ±0.34
Amylose content (% g/100 g carbohydrate)	11.18 ^d ±0.80	10.46 ^d ±0.28	12.55 ^c ±0.23	27.70^a±0.52	26.34^b±0.43	27.88^a±0.30

Note: KDML105 = KhaoDawk Mali 105; PTT1 = Pathumthani 1; RD45 = Rice Department 45; RD47 = Rice Department 47; CNT1 = Chai Nat 1; PSL2 = Phitsanulok 2

T_o = onset temperature; T_p = peak temperature; T_c = conclusion temperature; T_c-T_o = gelatinization temperature range; ΔH_g = enthalpy of gelatinization;

ΔH_{nl} = enthalpy of amylose/lipid complexes

Mean values in a row with different superscripts are different significantly (p ≤ 0.05)

4.2 Properties of aged rice under controlled temperature environment

Figure 4.1 shows the atmospheric temperature and relative humidity (RH) during storage of paddy rice at 8 °C and 30 °C. The RH of the storage environment was uncontrolled and, thus, reached the equilibrium RH according the psychrometric property of air. Chilling or refrigeration naturally gives rise to an increase in RH at a constant humidity ratio. Therefore, paddy rice stored at different temperatures experienced different environmental RH and hence equilibrated at different moisture contents. Figure 4.2 shows moisture content of paddy rice stored at 8 °C (10.2-14.6% range, 13.3% average) and 30 °C (10.2-13.9% range, 12.3% average). According to Soponronnarit *et al.* (2008), paddy rice can be well preserved when its moisture content does not exceed 16%.

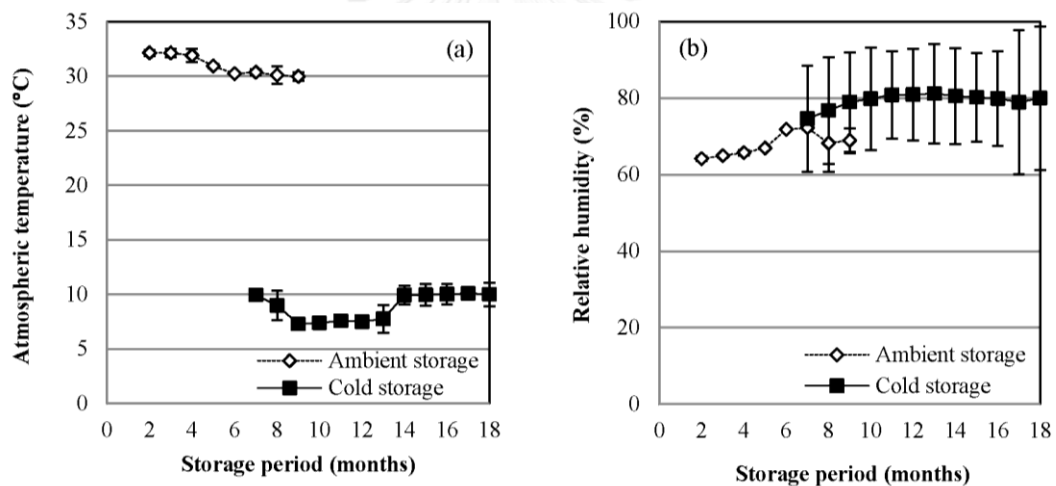


Figure 4.1 (a) Atmospheric temperature and (b) relative humidity during storage

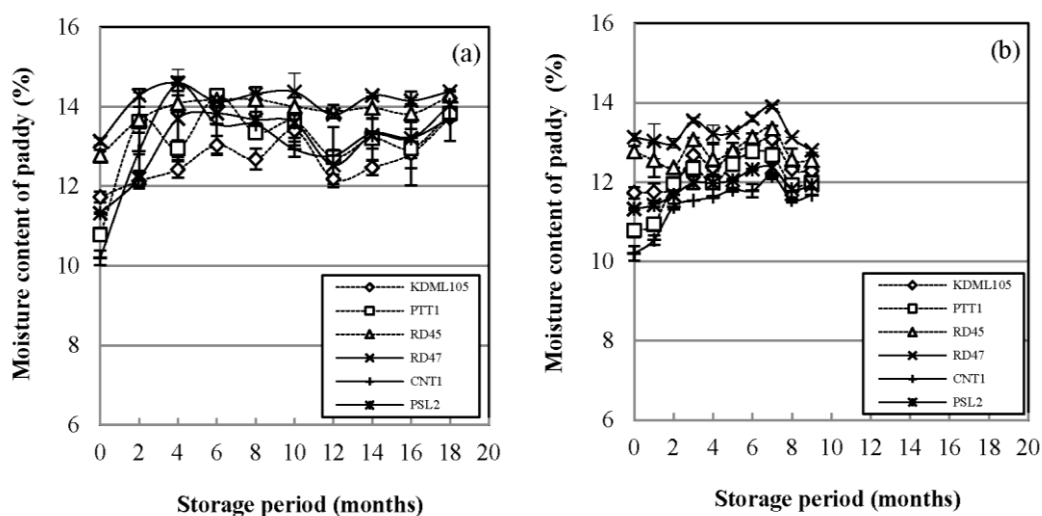


Figure 4.2 Moisture content (%) of paddy during storage at (a) 8 °C and (b) 30 °C

4.2.1 Changes in head rice yield during storage

Head rice yield (HRY) increased during storage as shown in Figure 4.3. In comparison, high amylose rice varieties had higher head rice yield throughout storage period. CNT1 had the highest HRY (45.91-54.21%) and PSL2 had the lowest HRY (23.70-36.24%) among three high amylose rice varieties. For low amylose rice, KDML105 had the highest HRY (34.70-39.08%) while PTT1 had the lowest HRY (16.61-21.87%). High amylose content results in high packing density of the starch, hence high density kernel (Juliano, 1972). This resulted in strengthened kernels that withstand wreckage during milling. Higher storage temperature had a greater effect on increasing HRY. This result was consistent with that reported by Soponronnarit *et al.* (2008) who determined head rice yield of KDML105 rice that was stored at ambient temperature for six months. The researchers found that head rice yield of rice increased within the first 3 months and decreased after that.

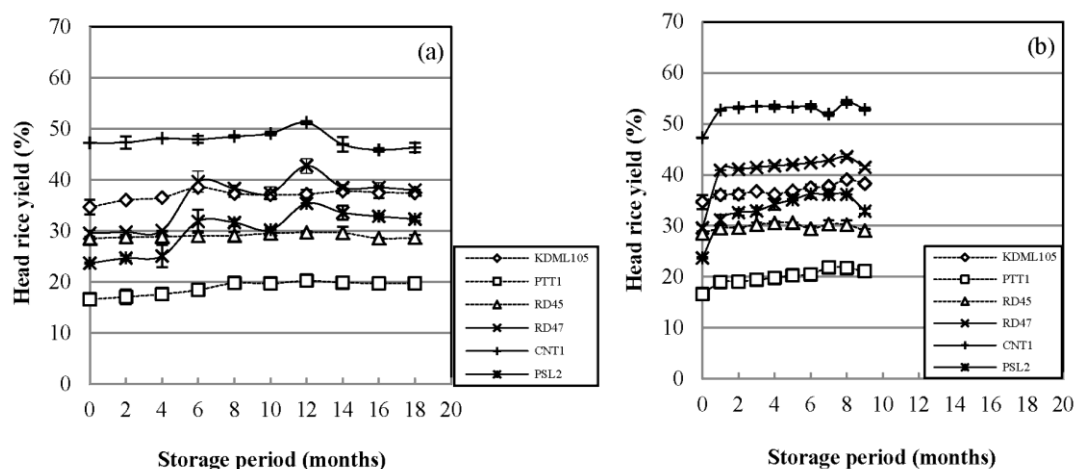


Figure 4.3 Head rice yield (%) of milled rice during storage at (a) 8 °C and (b) 30 °C

4.2.2 Changes in whiteness index during storage

Whiteness index of samples decreased during aging for both storage temperatures (Figure 4.4). High and low amylose rice varieties had comparable whiteness index (WI) which changed from 46.2 to 43.5 and 46.2 to 41.6 during storage at 8 and 30 °C, respectively. The reduction in WI was due to lipid oxidation (Kim and Cho, 1993; Park *et al.*, 2012). Decreasing whiteness index during storage has also been reported to arise from Maillard reaction (Kim *et al.*, 2004; Park *et al.*, 2012). The result from this study agreed with the study of Smanalieva *et al.* (2015) and Soponronnarit *et al.* (2008) who found that the whiteness of rice decreased with storage time. Moreover, storage at 30 °C caused the WI to decrease more rapidly in all rice varieties. This result is consistent with that reported by Park *et al.* (2012) who found that higher storage temperatures yielded rice with lower whiteness value compared to lower temperatures.

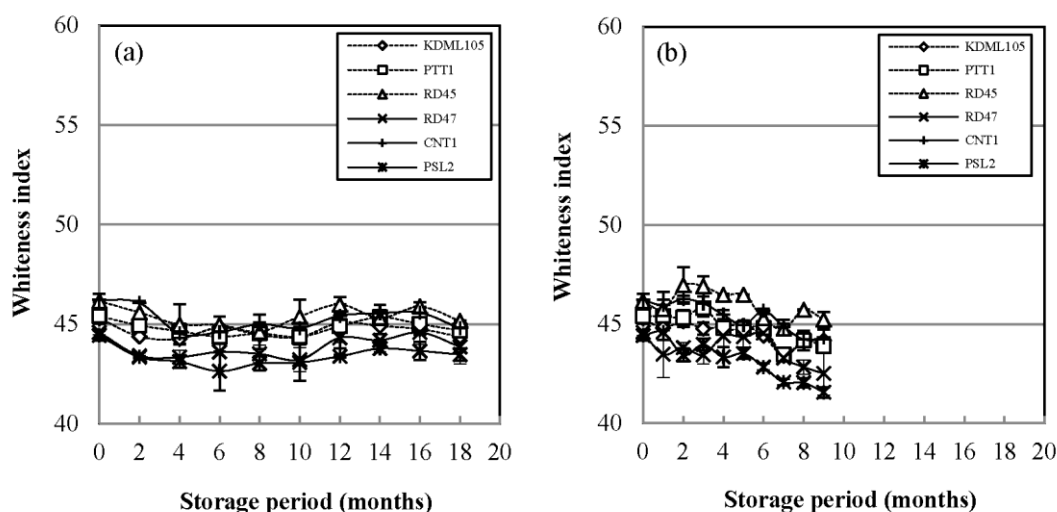


Figure 4.4 Whiteness index of milled rice during storage at (a) 8 °C and (b) 30 °C

4.2.3 Changes in cooking qualities during storage

During storage, minimum cooking time (MCT) of KDML105, RD45, RD47, CNT1 and PSL2 increased while that of PTT1 was almost unchanged for both storage temperatures (Figure 4.5). In comparative relation, high amylose rice varieties had higher MCT throughout storage time. CNT1 had the highest MCT (24-26 minutes) while RD47 and PSL2 had the same MCT (18-20 minutes). For low amylose rice, RD45 had the highest MCT (21-22 minutes) whereas KDML105 had the lowest MCT (17-18 minutes). Higher storage temperature had more pronounced effect on cooking time at the same storage period because aging proceeded faster at higher temperatures. As a result, cooking was slowed down and the best cooking time was extended (Sirisoontaralak and Noomhorm, 2007).

Consistently, solid loss of all samples decreased (Figure 4.6) and water uptake increased (Figure 4.7) during storage at both storage temperatures. High and low amylose rice varieties had comparable solid loss (SL) which changed from 4.54 to 3.11% and 4.54 to 2.60% during storage at 8 °C and 30 °C, respectively. For water uptake, both high and low amylose rice varieties had comparable water uptake (WU) which change from 204.4 to 310.7% and 204.4 to 303.9% during storage at 8 °C and 30 °C, respectively. In addition, storage at 30 °C caused the SL to decrease and WU

to increase more rapidly in all rice varieties. The result is consistent with the study of Soponronnarit *et al.* (2008) who reported that solid loss decreased whereas water uptake increased after storage. This could be due to the complex formation between amylose and free fatty acids that caused lower amount of water-soluble starch, hence reduced leaching of rice components from the granules. The result also agreed well with the study of Zhou *et al.* (2007) who reported that three rice cultivars (Koshihikari, Kyeema and Doongara) stored at 37 °C in air-tight glass bottles for 16 months had lower solid loss compared to that stored at 4 °C.

It was noted that the volume expansion ratio (VER) of the rice increased after storage (Figure 4.8). High amylose rice varieties had higher VER throughout storage time. CNT1 had the highest VER (2.84-3.59) while PSL2 had the lowest VER (2.42-2.83) among three high amylose rice varieties. For low amylose rice, KDML105 had the highest VER (2.66-2.95). Higher storage temperature had more pronounced effect on VER because aging proceeded faster at higher temperatures. The VER of the rice increased after storage due to a decrease in grain adhesion that, in turn, allows cooked rice to expand more freely (Bhattacharya, 2011a). The increase in grain strength due to amylose-lipid complex formation in aged rice and protein oxidation bring about more resistance of the rice grain to breakdown during cooking (Soponronnarit *et al.*, 2008). According to the stated reason, elongation ratio (Figure 4.9) and cooked length-breadth ratio (Figure 4.10) increased with storage time for both storage temperatures. Kaminski *et al.* (2013) also found that the elongation ratio of BR-IRGA 410 rice variety increased after storage at different temperature (0.5, 20 and 35 °C) for 180 days.

It is noted that CNT1 showed distinctive MCT, WU, and VER than the rice varieties in its own amylose class. As mentioned previously, this might be due to distinctive high protein that allows strengthening of the starch granules as well as reducing the adhesion between granules, hence higher level of MCT, WU, and VER. Its low fat content nature and amylopectin fine structure could also be held responsible for the notable properties of CNT1, hence further investigation is necessary.

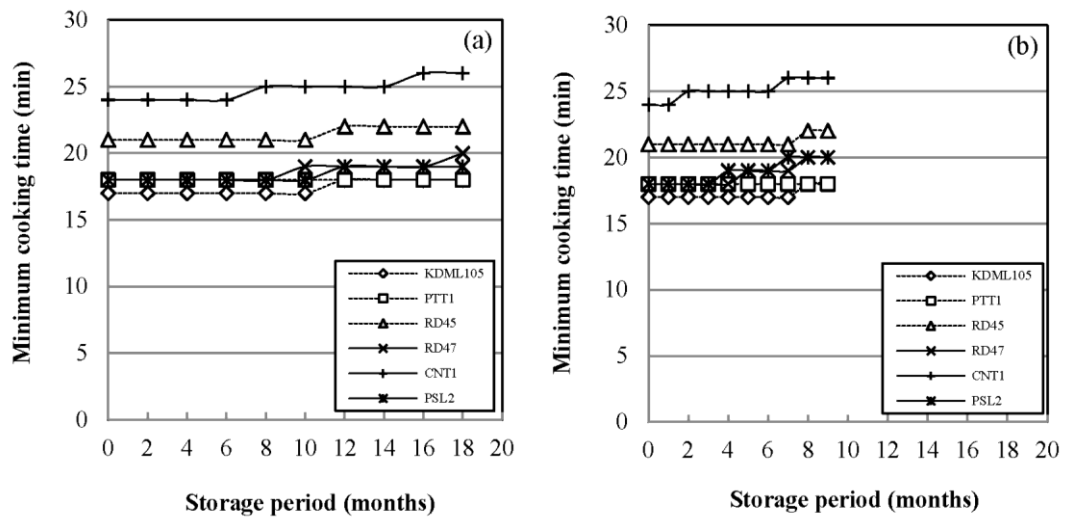


Figure 4.5 Minimum cooking time of milled rice during storage at (a) 8 °C and (b) 30 °C

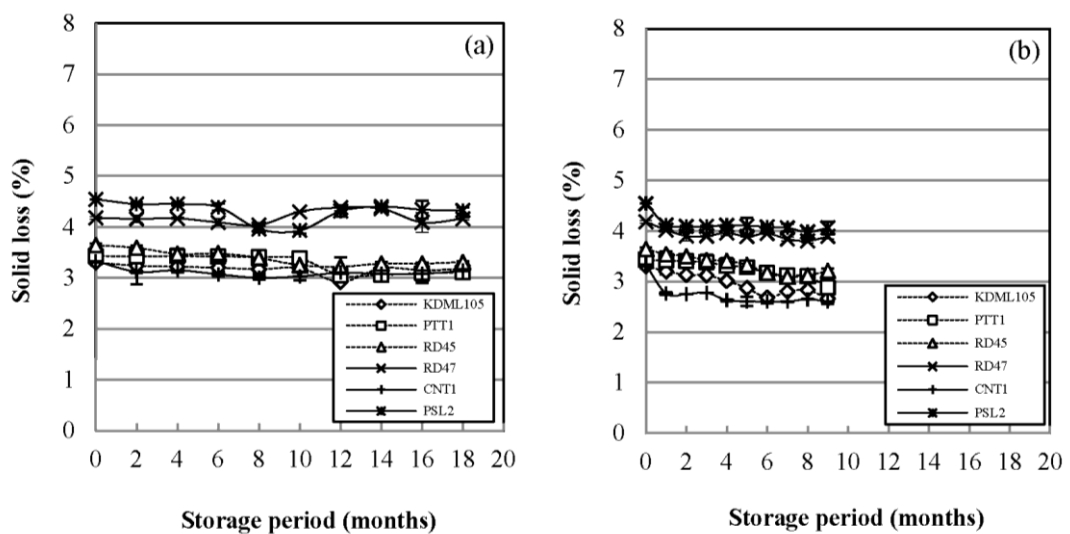


Figure 4.6 Solid loss of cooked rice during storage at (a) 8 °C and (b) 30 °C

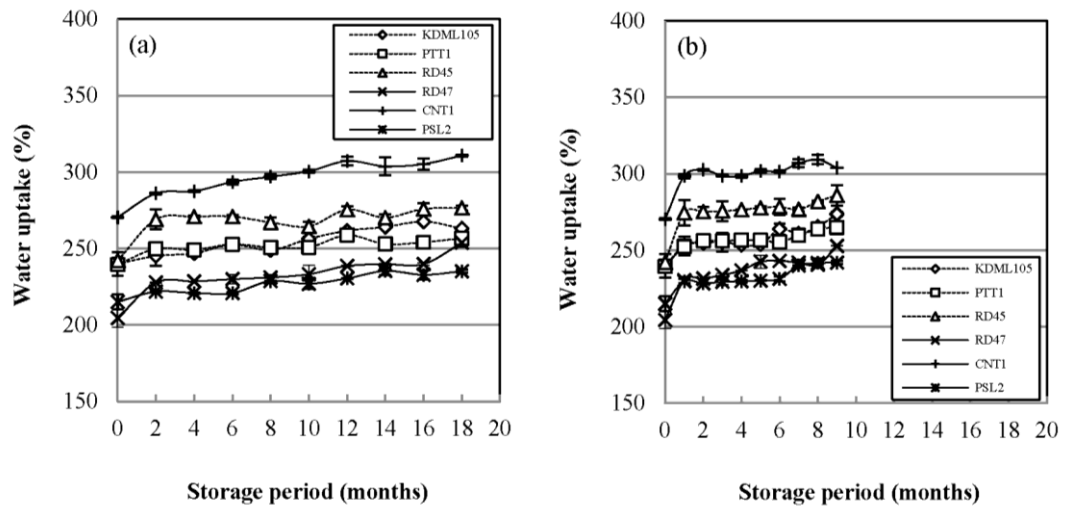


Figure 4.7 Water uptake of cooked rice during storage at (a) 8 °C and (b) 30 °C

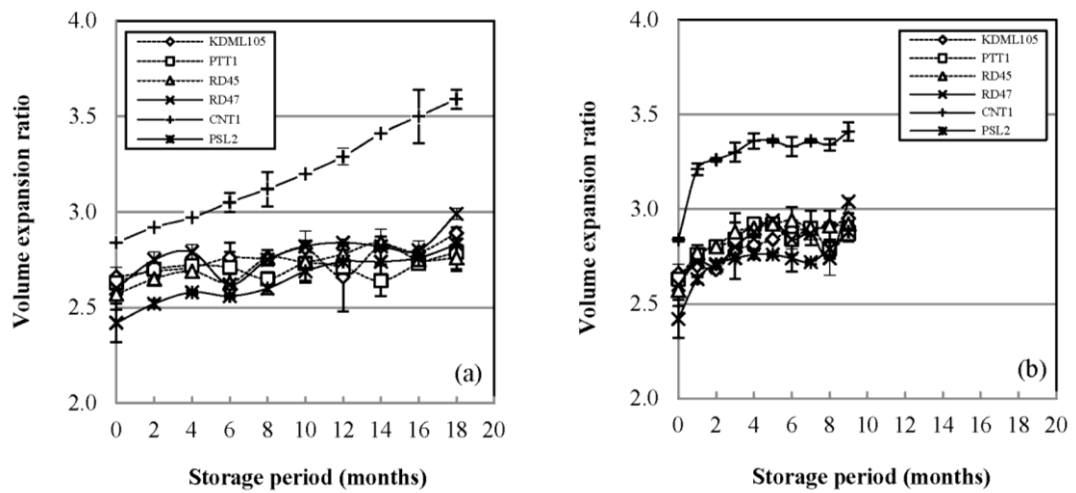


Figure 4.8 Volume expansion ratio of cooked rice during storage at (a) 8 °C and (b) 30 °C

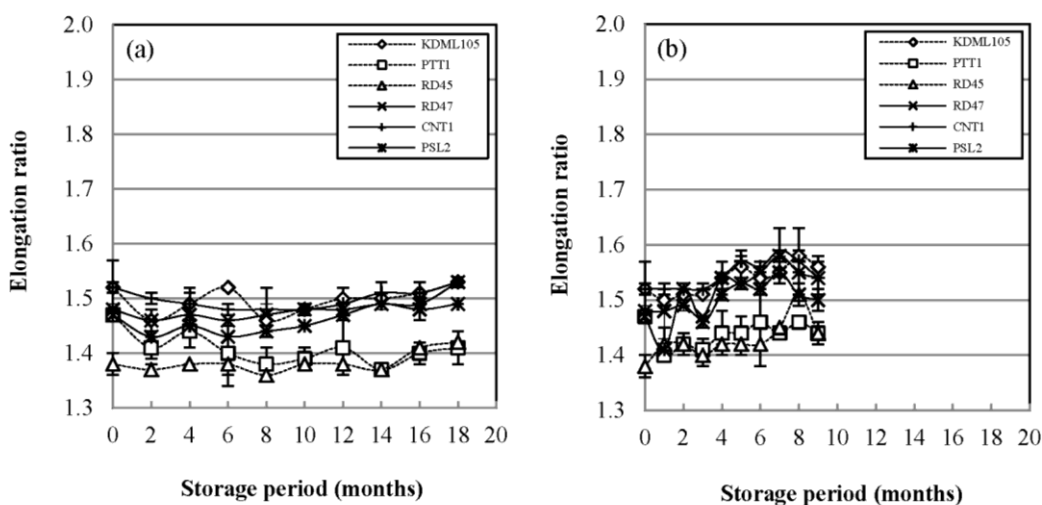


Figure 4.9 Elongation ratio of cooked rice during storage at (a) 8 °C and (b) 30 °C

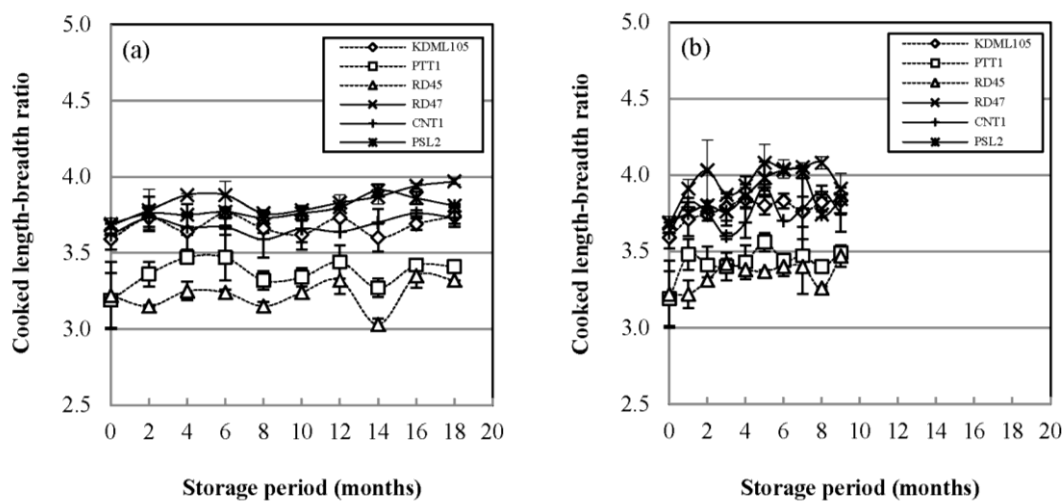


Figure 4.10 Cooked length-breadth ratio of cooked rice during storage at (a) 8 °C and (b) 30 °C

4.2.4 Changes in textural properties of cooked rice during storage

Changes in the textural properties of rice after aging at 8 °C and 30 °C were investigated. Hardness (Figure 4.11), cohesiveness (Figure 4.12), springiness (Figure 4.14), gumminess (Figure 4.15) and chewiness (Figure 4.16) of cooked rice increased, whereas adhesiveness (Figure 4.13) decreased clearly during storage at 30

°C. The changes observed at 8 °C were marginal. Among all textural properties of cooked rice, only adhesiveness clearly differed between low and high amylose rice varieties. Rice varieties with different amylose contents also showed differences in hardness, gumminess, and chewiness, except for CNT1 that always showed a value closer to that of low amylose rice varieties despite the fact that it contained amylose in the range of high amylose category. Low amylose rice varieties had marginal lower hardness, cohesiveness (except KDML105), springiness, gumminess, chewiness and higher adhesiveness than high amylose rice varieties. The increase in hardness and the decrease in adhesiveness of cooked rice during aging might be caused by the reduction in hydration ability of starch granules. This could be due to the formation of amylose-lipid complexes and the binding between rice protein in aged rice grains (Sodhi *et al.*, 2003; Tulyathan and Leeharatanaluk, 2007; Zhou *et al.*, 2007). From the results in Figures 4.11 to 4.16, it is also evidenced that higher storage temperature caused a faster increase or decrease of the observed variables. The pronouncing effect of temperature on aging of rice was previously reported by Zhou *et al.* (2007) who investigated texture of cooked rice from milled rice grain stored at 4 and 37 °C for 16 months. They found that higher storage temperature caused the hardness of cooked rice to increase and the adhesiveness to decrease more rapidly than lower storage temperature. In a more recent research, Park *et al.* (2012) reported that hardness of cooked rice increased while adhesiveness decreased with aging. Greater changes were found at higher storage temperatures. The increase of cooked rice cohesiveness after aging at higher storage temperature might be because starch granule has higher resistance to hydrothermal breakdown, hence an increase in insoluble contents, during cooking process which results in an ability to retain its form after compression (Gujral and Kumar, 2003; Park *et al.*, 2012).

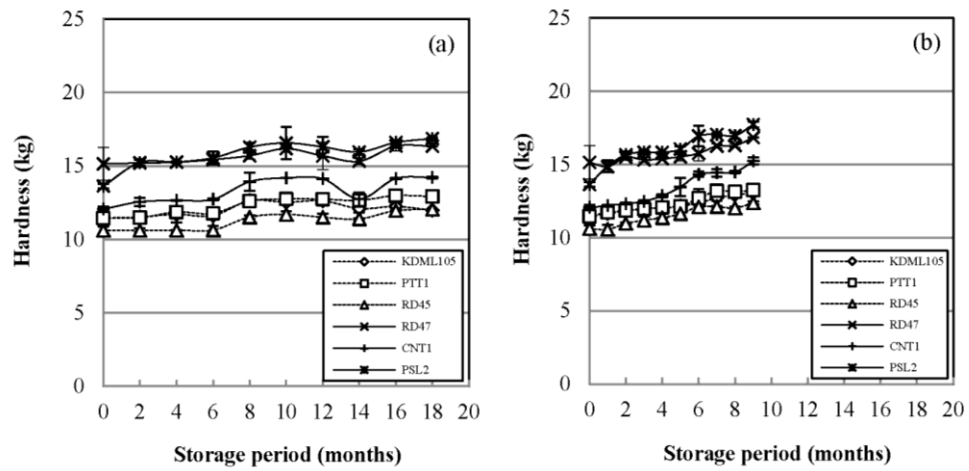


Figure 4.11 Hardness of cooked rice during storage at (a) 8 °C and (b) 30 °C

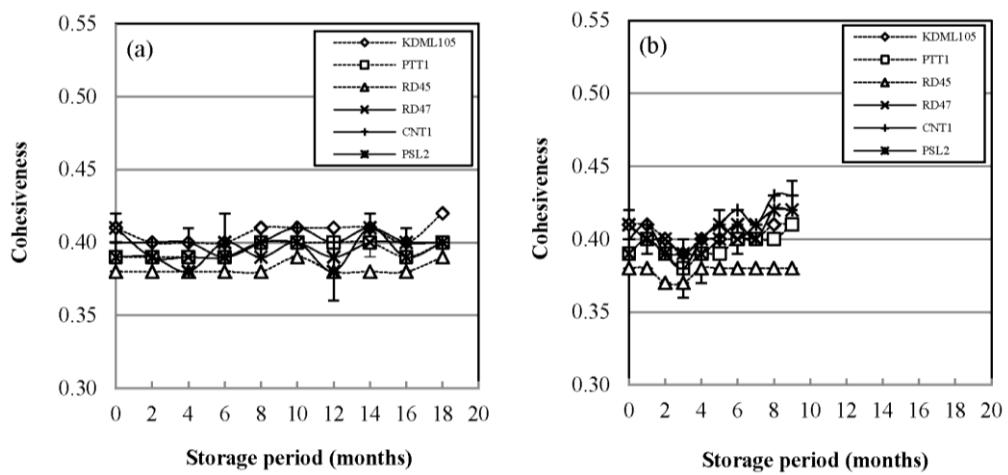


Figure 4.12 Cohesiveness of cooked rice during storage at (a) 8 °C and (b) 30 °C

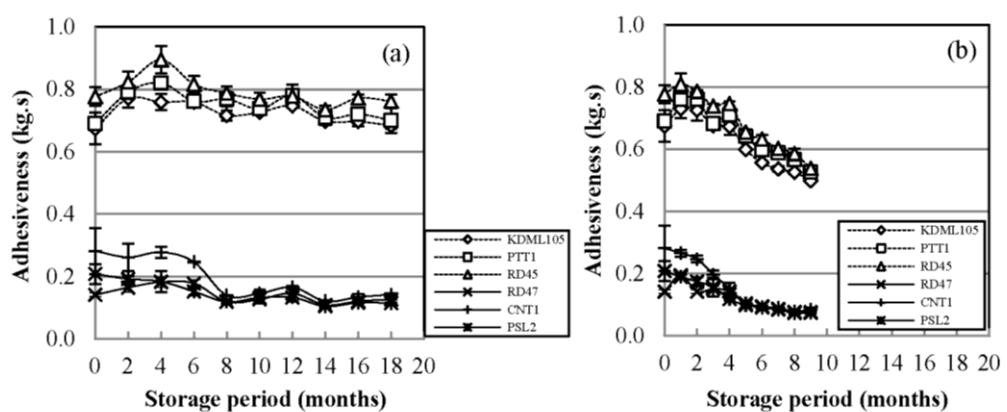


Figure 4.13 Adhesiveness of cooked rice during storage at (a) 8 °C and (b) 30 °C

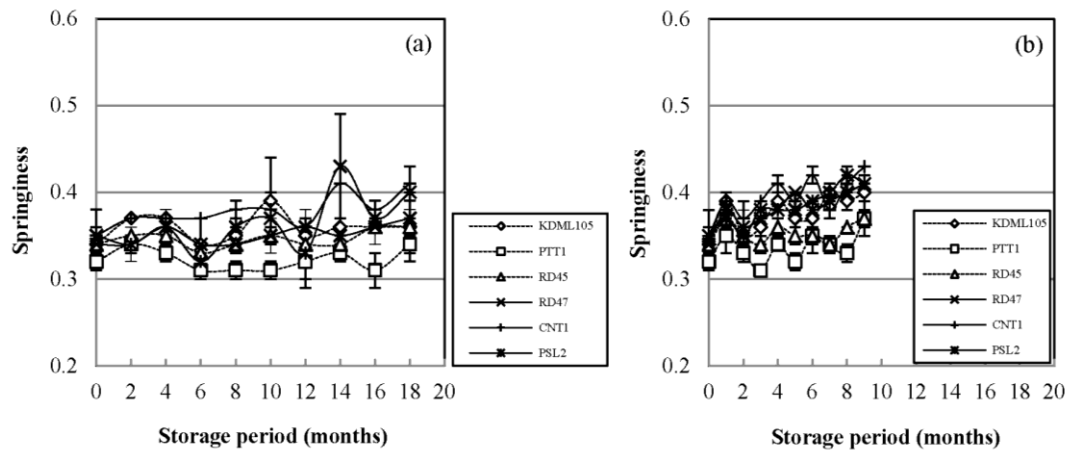


Figure 4.14 Springiness of cooked rice during storage at (a) 8 °C and (b) 30 °C

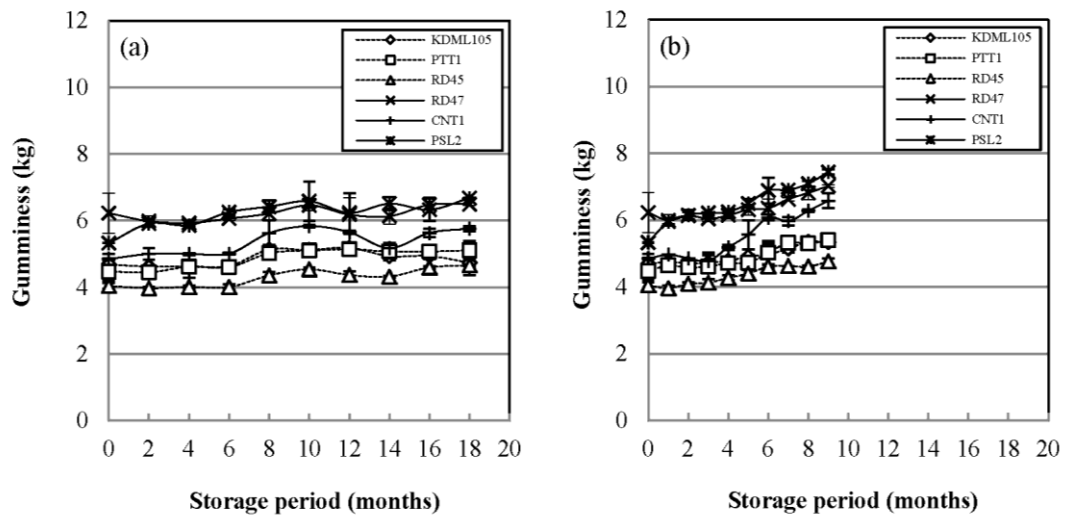


Figure 4.15 Gumminess of cooked rice during storage at (a) 8 °C and (b) 30 °C

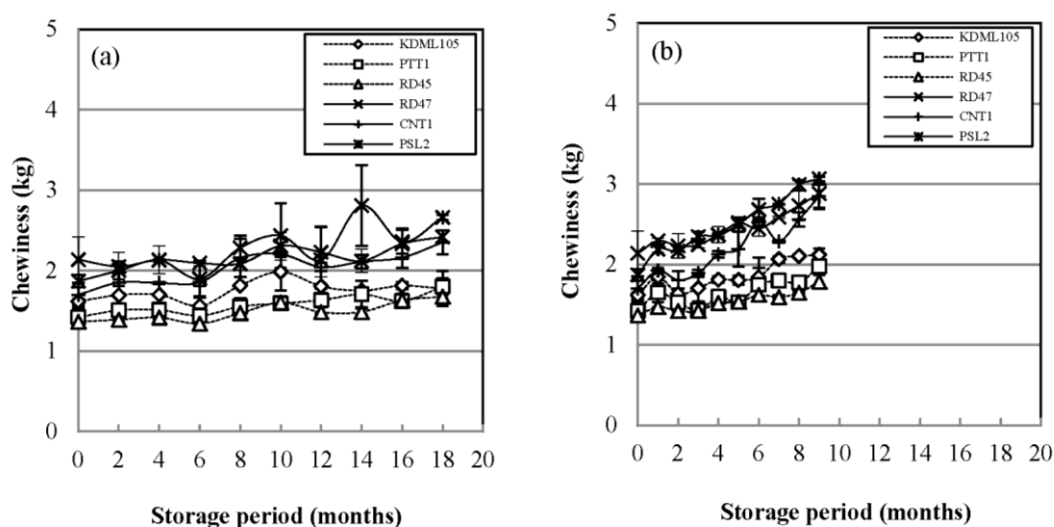


Figure 4.16 Chewiness of cooked rice during storage at (a) 8 °C and (b) 30 °C

4.2.5 Changes in pasting properties of rice flour during storage

Changes in pasting properties of rice flour at 8 °C storage were barely explicable (Figures *a* of 4.17-4.22). During aging at 30 °C, pasting temperature (PT) increased (Figure 4.17b) while peak viscosity (PV) (Figure 4.18b) and breakdown (BD) (Figure 4.20b) of all rice varieties decreased. In term of setback (SB) and final viscosity (FV), high and low amylose rice varieties showed distinctive changes; that is high amylose rice showed a decrease in SB and FV while low amylose rice showed the opposite behavior during aging. Trough viscosity (TV) of all rice varieties stored at 30 °C showed an increase values during the first 4 months of storage and decreased thereafter.

In comparison, high amylose rice varieties had higher PT throughout storage period. PSL2 had the highest PT (83.63-88.34 °C) and CNT1 had the lowest PT (79.12-86.90 °C) among three high amylose rice varieties. For low amylose rice, PTT1 had the highest PT (75.46-83.04 °C) and KDML105 had the lowest PT (74.20-78.96 °C). An increase in PT of aged rice was due to retardation to water absorption and reduced granule swelling of starch granules (Likitwattanasade and Hongsprabhas, 2010). This result agreed with the study of Tananuwong and Malila (2011) who

determined pasting properties of the rice flours from organic red fragrant rice which were stored at ambient temperature and 15 °C for 12 months. The researchers found that PT of the samples increased after storage at ambient temperature for six months while the changes in pasting properties of aged rice were retarded when stored at lower storage temperature. The result of our study was in accord with that reported by Paraginski *et al.* (2014) who found that PT of maize flour increased after 12 months of storage times at 5, 15, 25 and 35 °C. The researcher suggested that an increase in PT indicates the restriction of starch granule to swell and lower water uptake during hydration, heating and shearing process. Moreover, increasing disulfide linkages in protein that binds to starch granules may slow down the swelling of starch granule.

PV and BD of samples decreased during storage for both storage temperatures. Both high and low amylose rice varieties had comparable PV, which changed from 3.79 to 1.24 Pa.s and 3.79 to 0.98 Pa.s, and BD, which changed from 2.12 to 0.28 Pa.s and 2.12 to 0.09 Pa.s, during storage at 8 °C and 30 °C, respectively. The decrease in peak viscosity was due to the occurrence of disulphide bonds in protein molecules that caused large and strong protein networks and might retard water absorption of starch granules. Decreasing breakdown shows that the capacity of the granules to break after heating decreased significantly after storage (Katekhong and Charoenrein, 2014; Noomhorm *et al.*, 1997; Tulyathan and Leeharatanaluk, 2007; Zhou *et al.*, 2003). The result from this study was consistent with the previous research of Tulyathan and Leeharatanaluk (2007) who determined pasting properties of Khao Dawk Mali 105 rice during storage at ambient temperature for 8 months. The authors found that peak viscosity and breakdown of rice flour decreased with longer storage period. Furthermore, the result also agreed with the study of Park *et al.* (2012) who found that breakdown of samples decreased with storage time after storage at 4, 20, 30 and 40 °C.

For storage at 30 °C, low amylose rice showed an increase in SB, TV and FV, while high amylose rice showed the opposite behavior. The increase in these properties of low amylose rice was related to the more rapid and greater reduction of BD compared to that of high amylose rice (Figure 4.20). This could be mainly

attributed to the restricted leaching and swelling of amylopectin, which is the major component of low amylose rice starch, caused by reduced protein solubility and strengthened starch granules as mentioned earlier. On the other hand, high amylose rice's SB decreased which could be related to the interaction between protein and starch and increasing molecular weight of rice protein as previously stated. Those large and strong protein networks might retard water absorption, limit swelling of starch granules and lower amylose leaching (Likitwattanasade and Hongsprabhas, 2010) thus decrease paste SB.

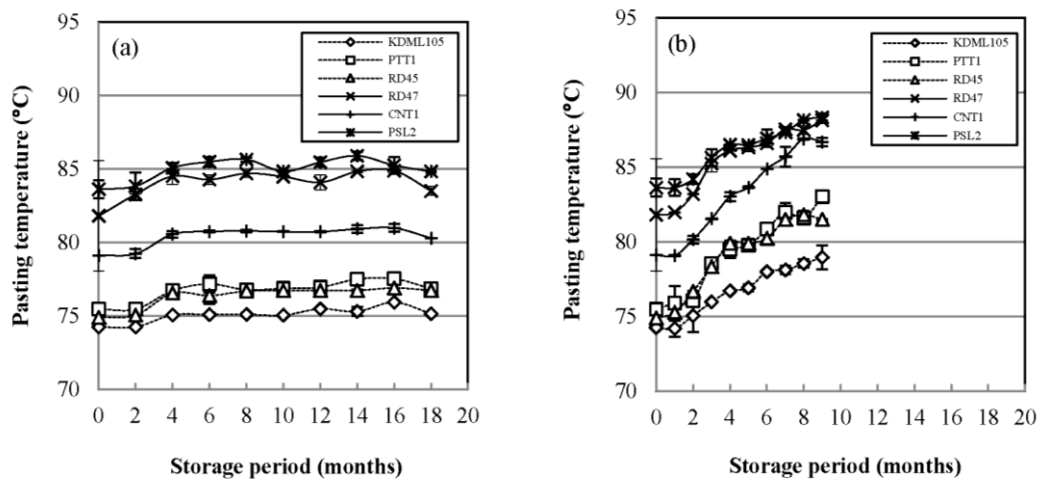


Figure 4.17 Pasting temperature of rice flour during storage at (a) 8 °C and (b) 30 °C

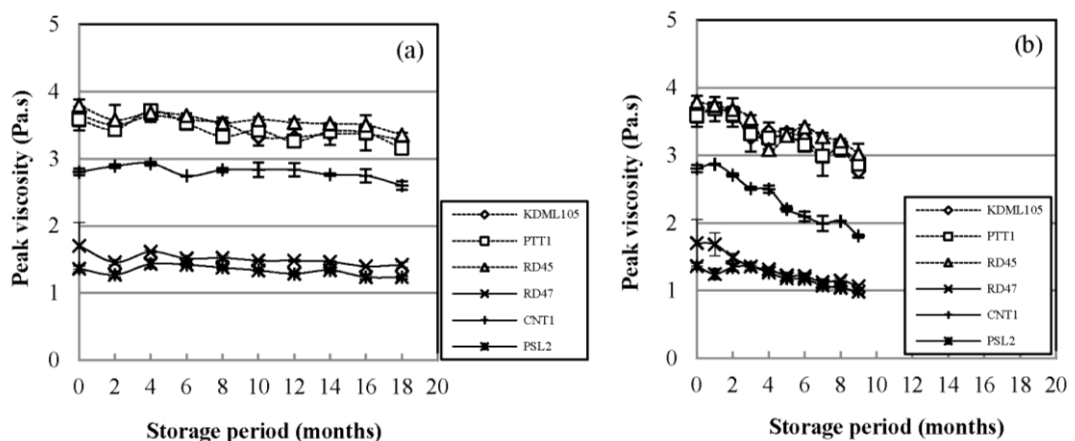


Figure 4. 18 Peak viscosity of rice flour during storage at (a) 8 °C and (b) 30 °C

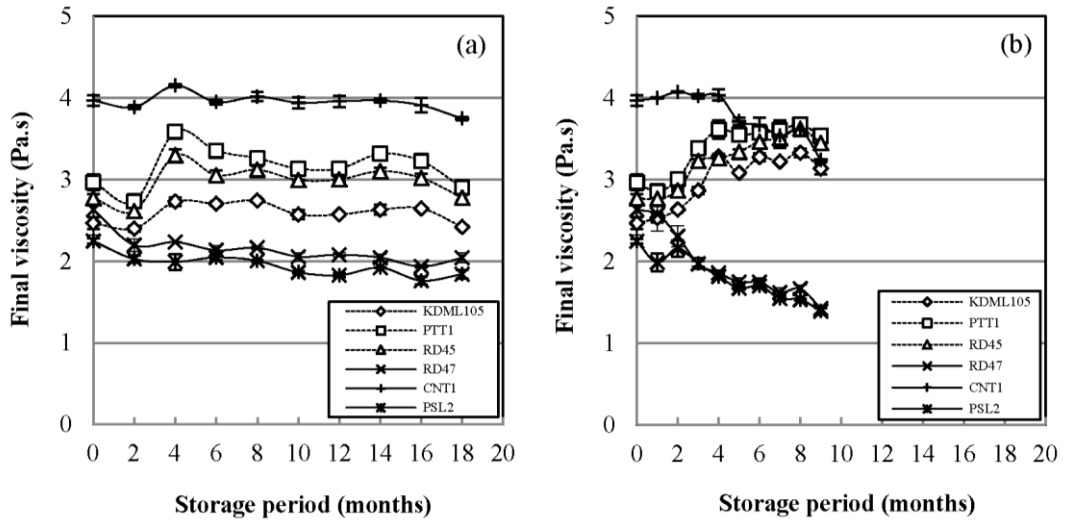


Figure 4.19 Final viscosity of rice flour during storage at (a) 8 °C and (b) 30 °C

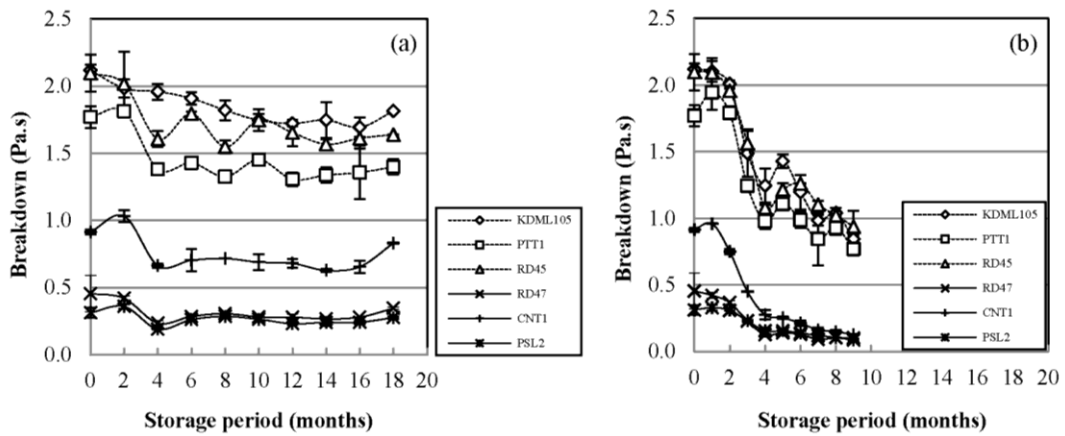


Figure 4.20 Breakdown of rice flour during storage at (a) 8 °C and (b) 30 °C

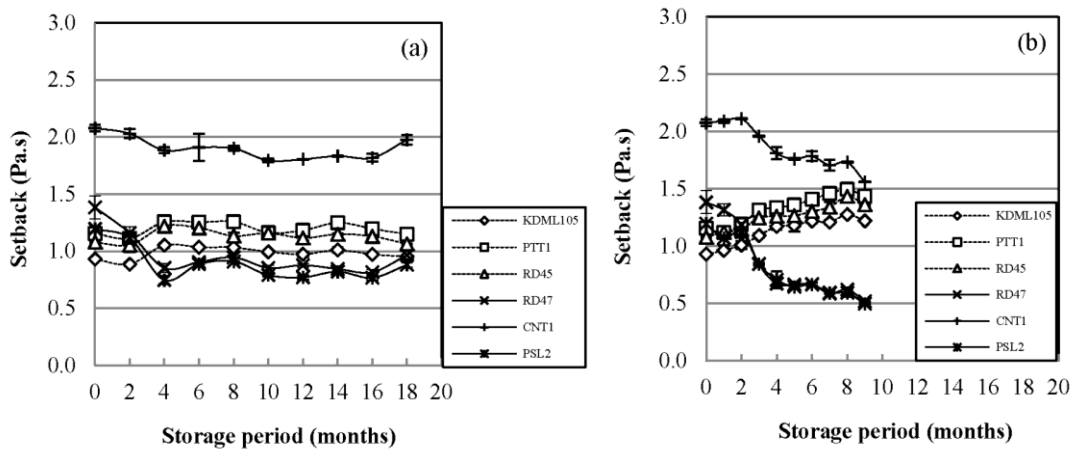


Figure 4.21 Setback of rice flour during storage at (a) 8 °C and (b) 30 °C

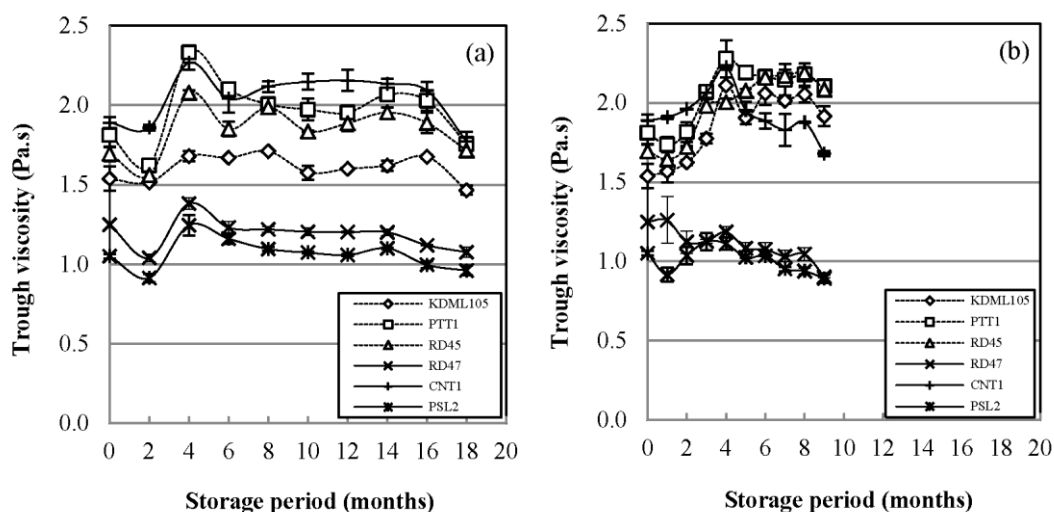


Figure 4.22 Trough viscosity of rice flour during storage at (a) 8 °C and (b) 30 °C

4.2.6 Changes in thermal properties of rice flour during storage

Thermal properties of rice after storage at 8 °C and 30 °C are shown in Figures 4.23-4.26. Onset temperature (T_o), peak temperature (T_p), conclusion temperature (T_c), gelatinization temperature range (Figure C.1.1, Appendix C.1) and enthalpy of amylose/lipid complexes (Figure C.1.2, Appendix C.1) of all varieties fluctuated and did not correlate with storage time for both storage temperatures. In comparison, low amylose rice varieties had higher T_o (63.37-67.24 °C), T_p (73.11-75.50 °C) and T_c (81.20-87.12 °C) than high amylose rice varieties (except CNT1). CNT1 had the highest T_o (71.27-73.65 °C), T_p (78.83-80.55 °C) and T_c (85.12-88.71 °C) among six rice varieties during storage. The reduction in enthalpy of gelatinization (ΔH_g) was more dramatic during the first 3 and 4 months of storage at 30 °C and 8 °C, respectively. The value tended to change slightly thereafter. The result in gelatinization enthalpy reduction was consistent with the change in pasting properties, which was a result of disulphide formation, as explained earlier. In a previous research, Zhou *et al.* (2010) reported that T_p and T_c of rice flour from milled rice grain of three varieties stored at 37 °C increased more than that stored at 4 °C for 12 months. Moreover, Teo *et al.* (2000) found that both temperature and time of storage affected the thermal properties. T_o , T_p and T_c shifted to higher temperature with increasing storage period.

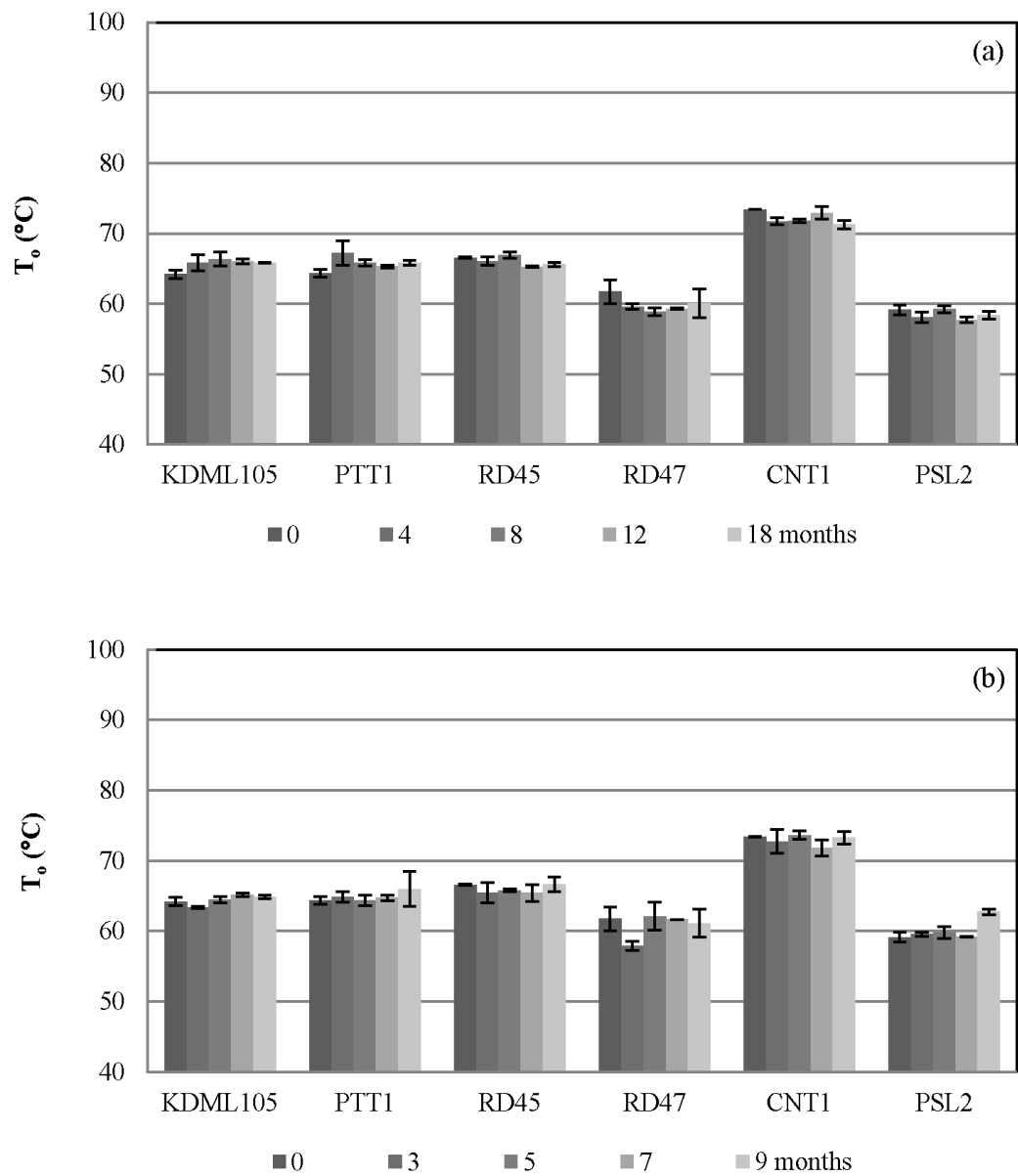


Figure 4.23 Onset temperature (T_o) of rice flour during storage at (a) 8 °C and (b) 30 °C

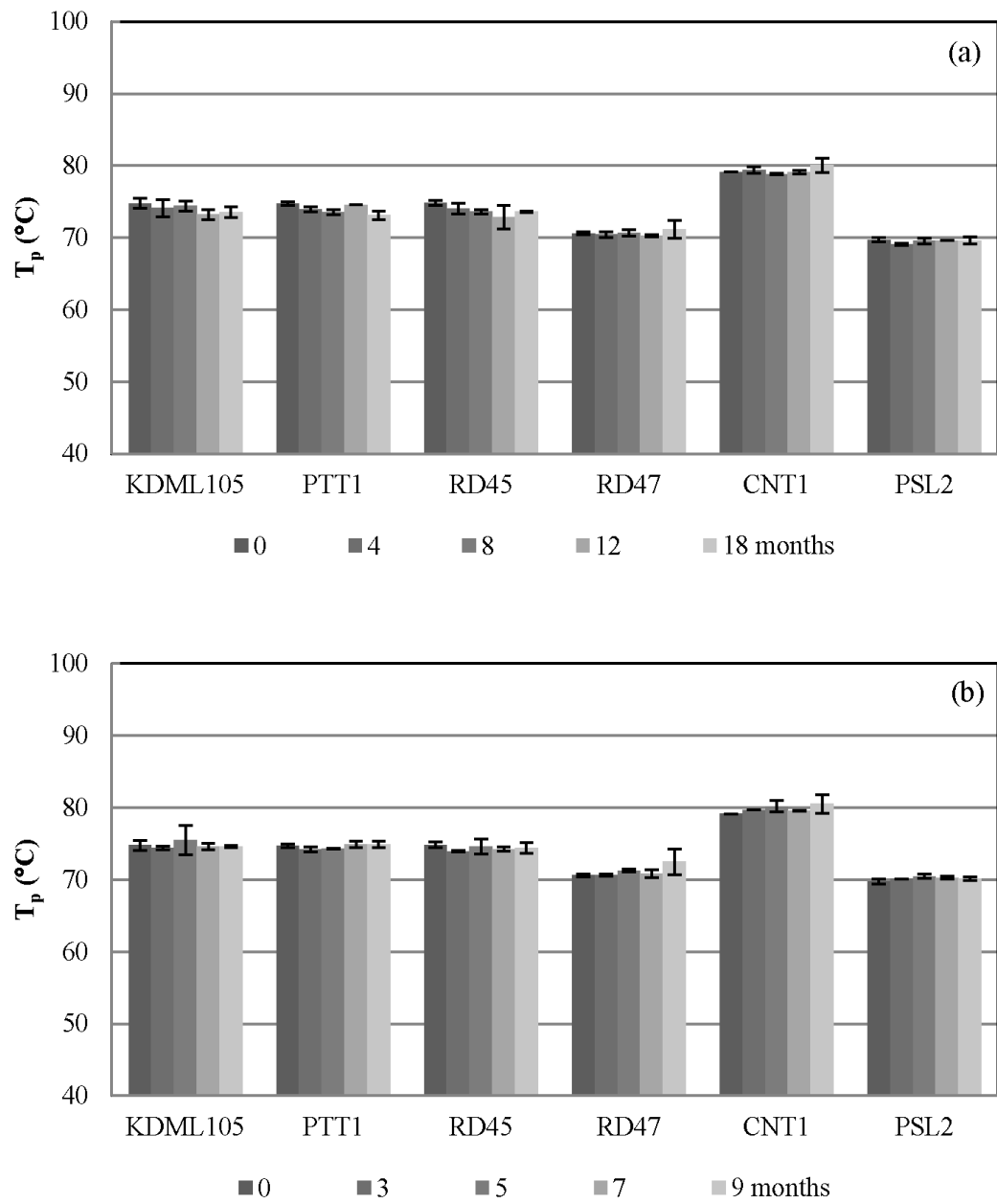


Figure 4.24 Peak temperature (T_p) of rice flour during storage at (a) 8 °C and (b) 30 °C

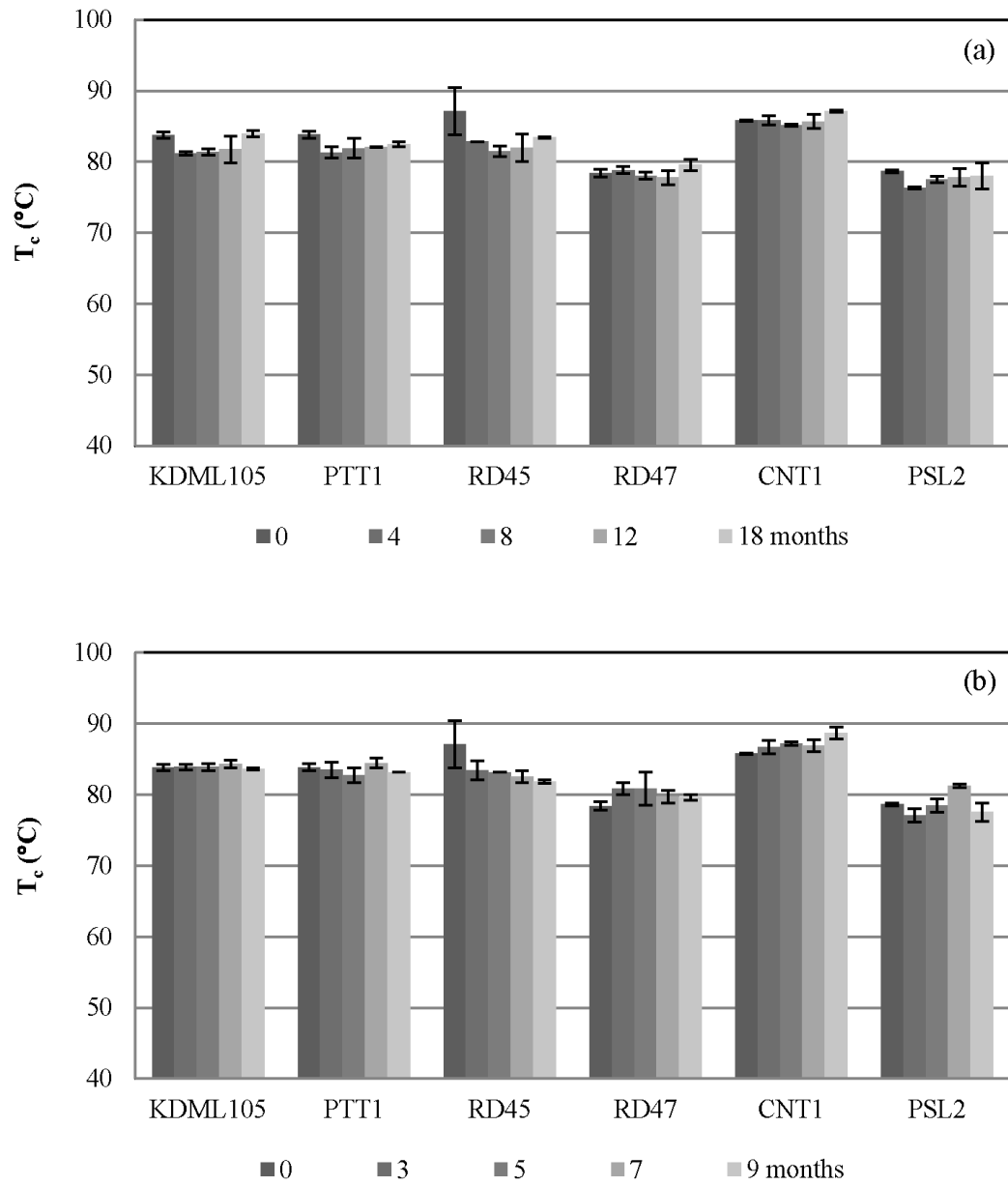


Figure 4.25 Conclusion temperature (T_c) of rice flour during storage at (a) 8 °C and (b) 30 °C

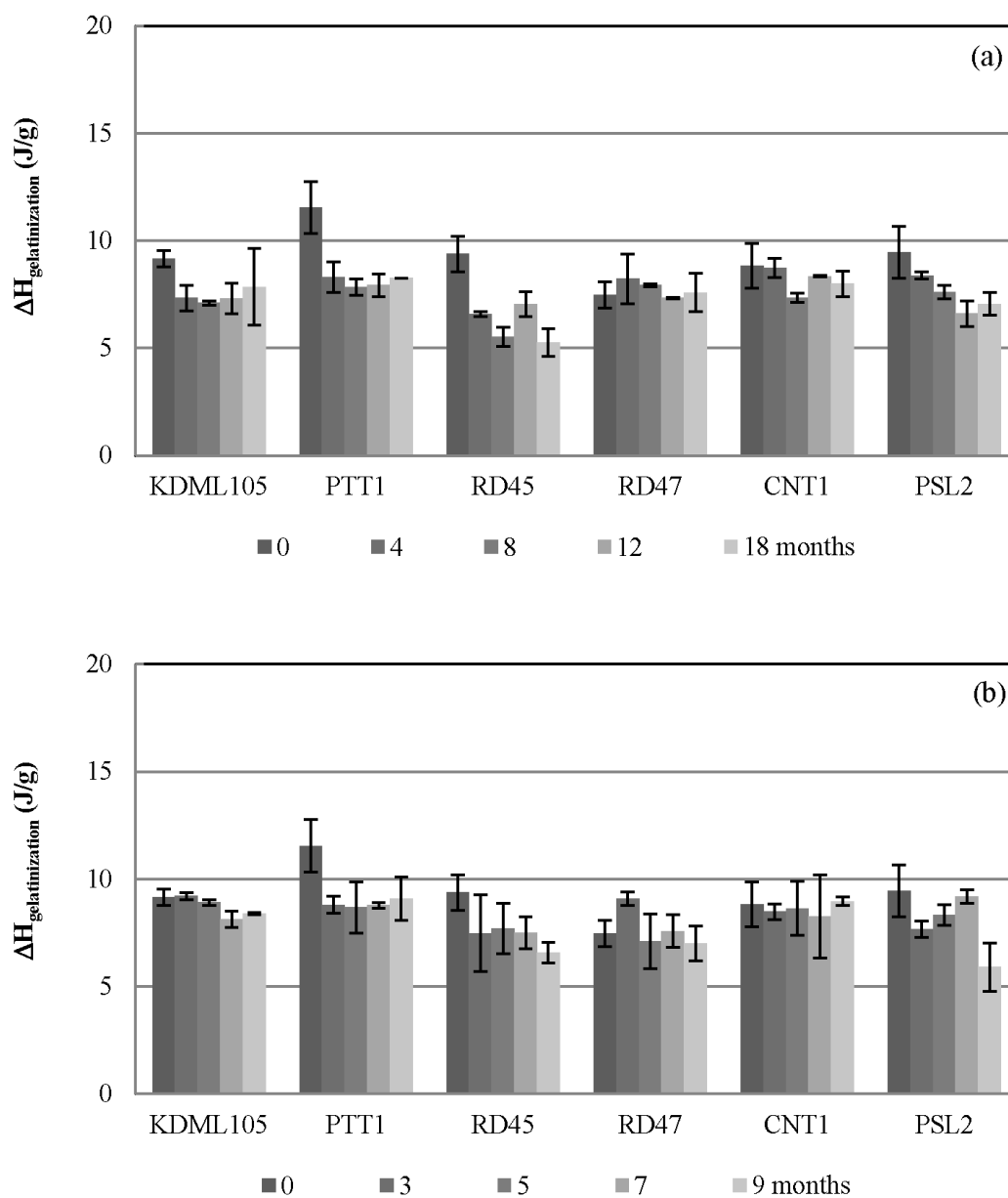


Figure 4.26 Enthalpy of gelatinization (ΔH_g) of rice flour during storage at (a) 8 °C and (b) 30 °C

4.2.7 Changes in molecular weight distribution of rice protein from rice flour during storage

Protein molecular weight distribution pattern of low and high amylose rice during storage at 8 and 30 °C are shown in Figure 4.27. Low and high amylose

rice had similar rice protein pattern and the rice protein pattern did not change after storage. This study utilized SDS-urea solution for sample preparation which could effectively dissolve protein residue in the sample and resulted in a wide range of protein molecular weight distribution as exemplified in Figure 4.27. However, rice protein molecular weight (MW) distribution in six ranges; i.e. MW over 150 kDa, MW between 100 and 120 kDa, MW between 75 and 100 kDa, MW between 40 and 55 kDa, MW between 25 and 30 kDa and MW lower than 20 kDa, slightly changed (Figures 4.28-4.33). This result showed that protein in the lower MW range (< 20 kDa) decreased for both storage temperatures, while higher MW protein in the range of 25-30, 40-55, 75-100 kDa for storage at 8 °C and 25-30, 40-55, 75-100, 100-120 kDa increased after storage at 30 °C. The result could be observed more clearly in KDML105 and PSL2 but less clear, or hardly significant, for other varieties. It is noted that rice protein contains a major proportion of 40-55 kDa polypeptides. Disulfide bonds are known to be responsible for the cross-bonding of the protein molecules resulting in a larger protein molecule and/or strengthened protein network. The aging of rice grains resulting in a large increase of disulfide intermolecular bonds and molecular weight of proteins (oryzenin) was reported earlier (Tulyathan and Leeharatanaluk, 2007). Greater changes were found at higher storage temperature.

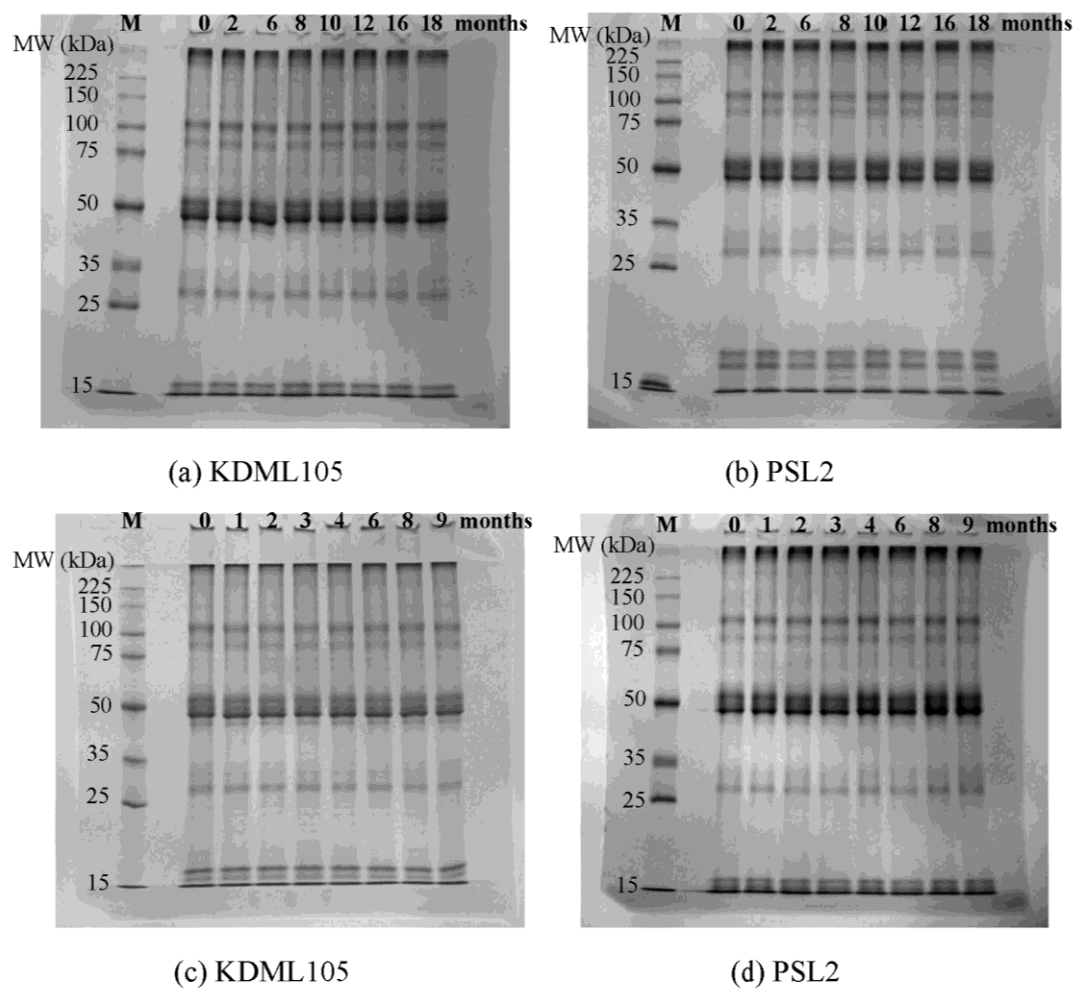


Figure 4.27 Rice protein pattern of low and high amylose rice during storage at (a, b) 8 °C and (c, d) 30 °C

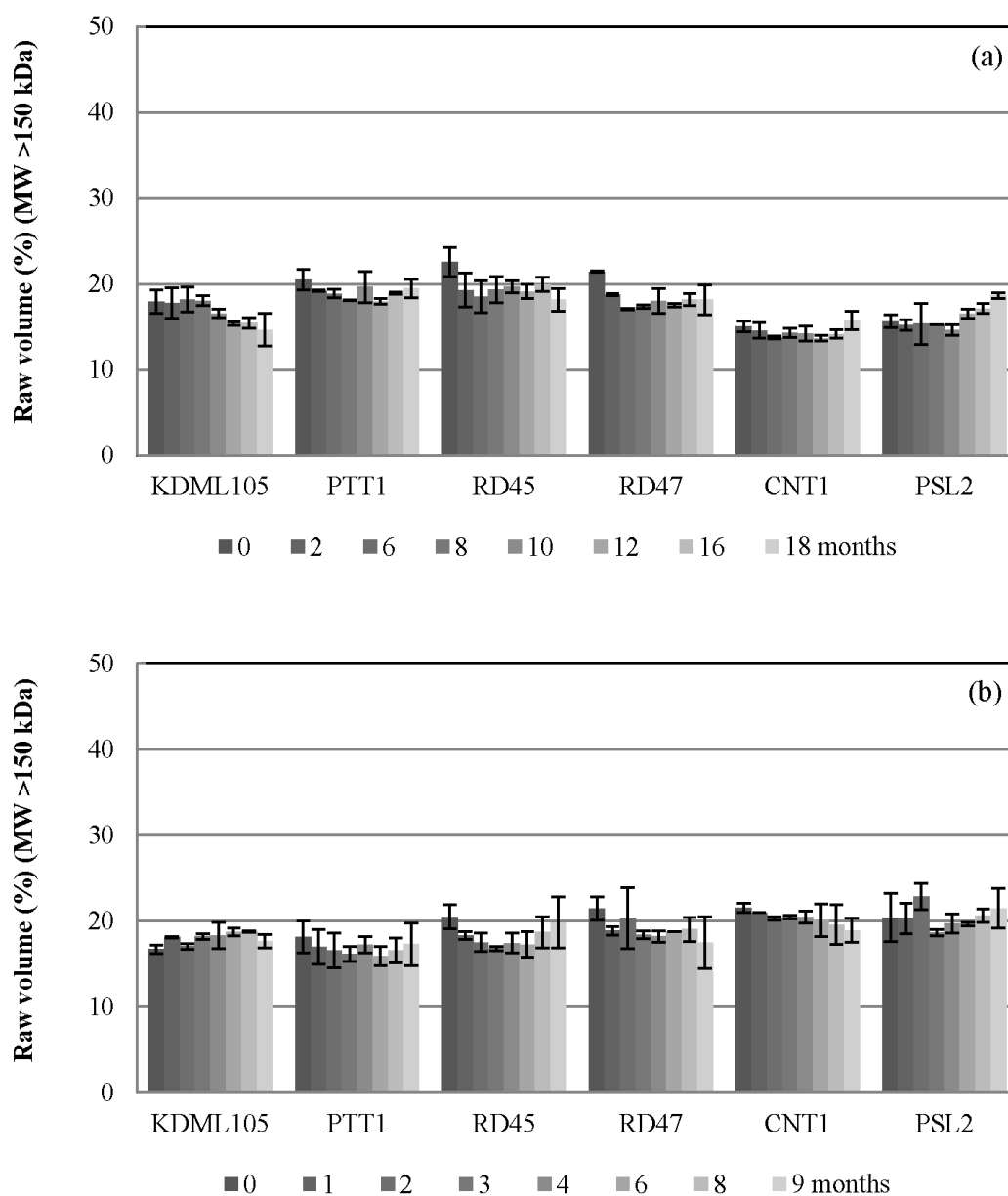


Figure 4.28 Raw volume (%) of protein molecular weight distribution (MW > 150 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C

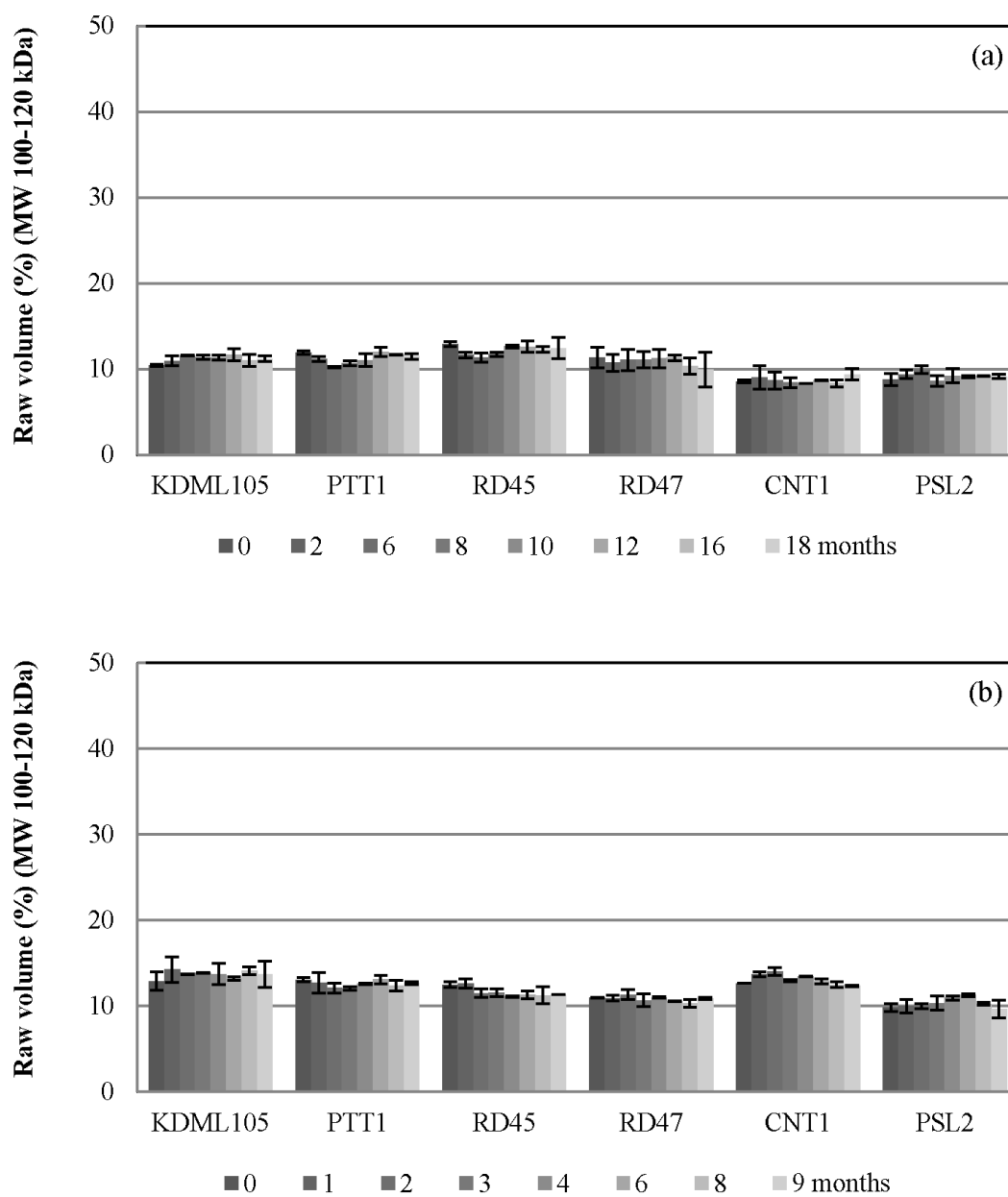


Figure 4.29 Raw volume (%) of protein molecular weight distribution (MW 100-120 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C

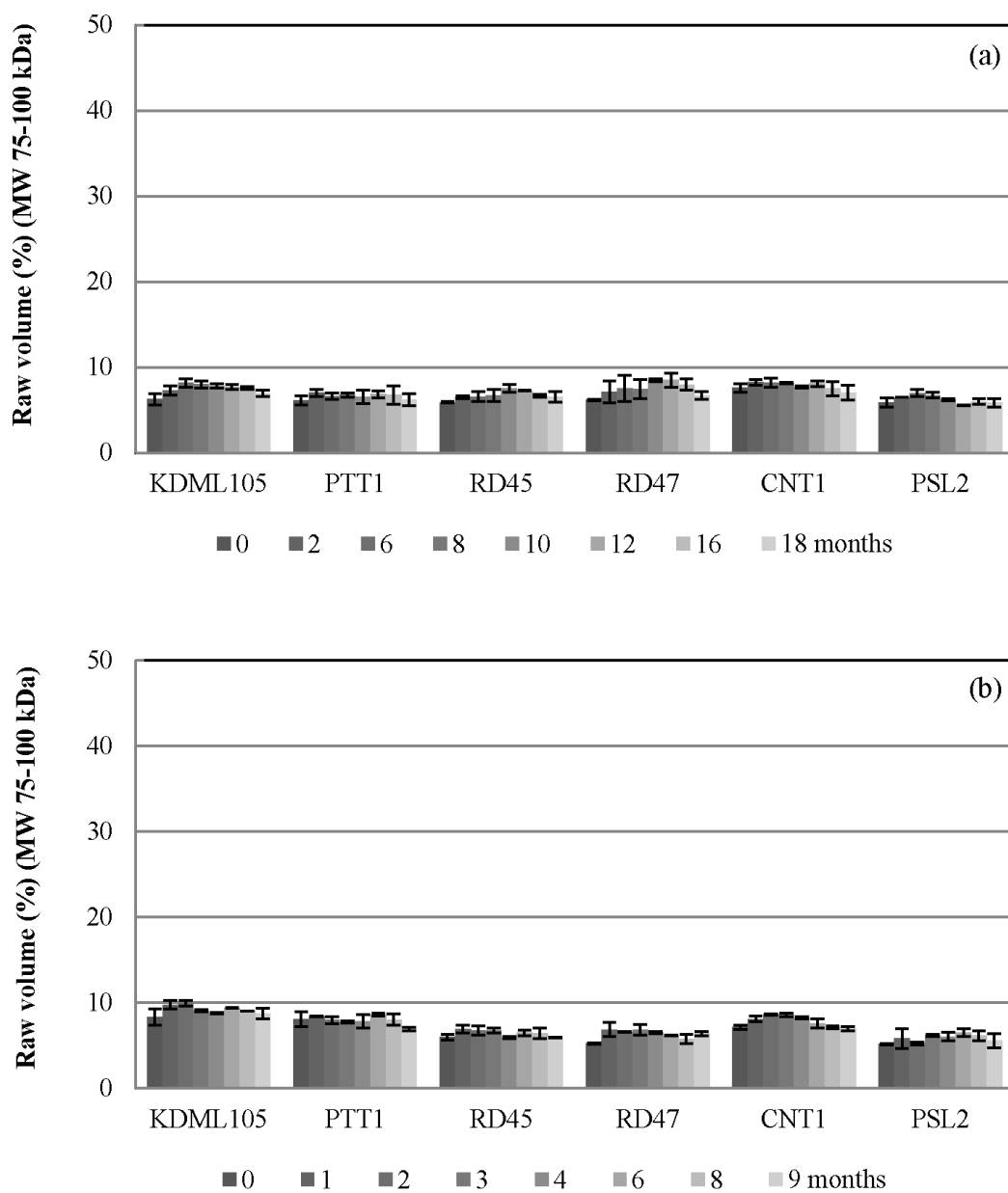


Figure 4.30 Raw volume (%) of protein molecular weight distribution (MW 75-100 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C

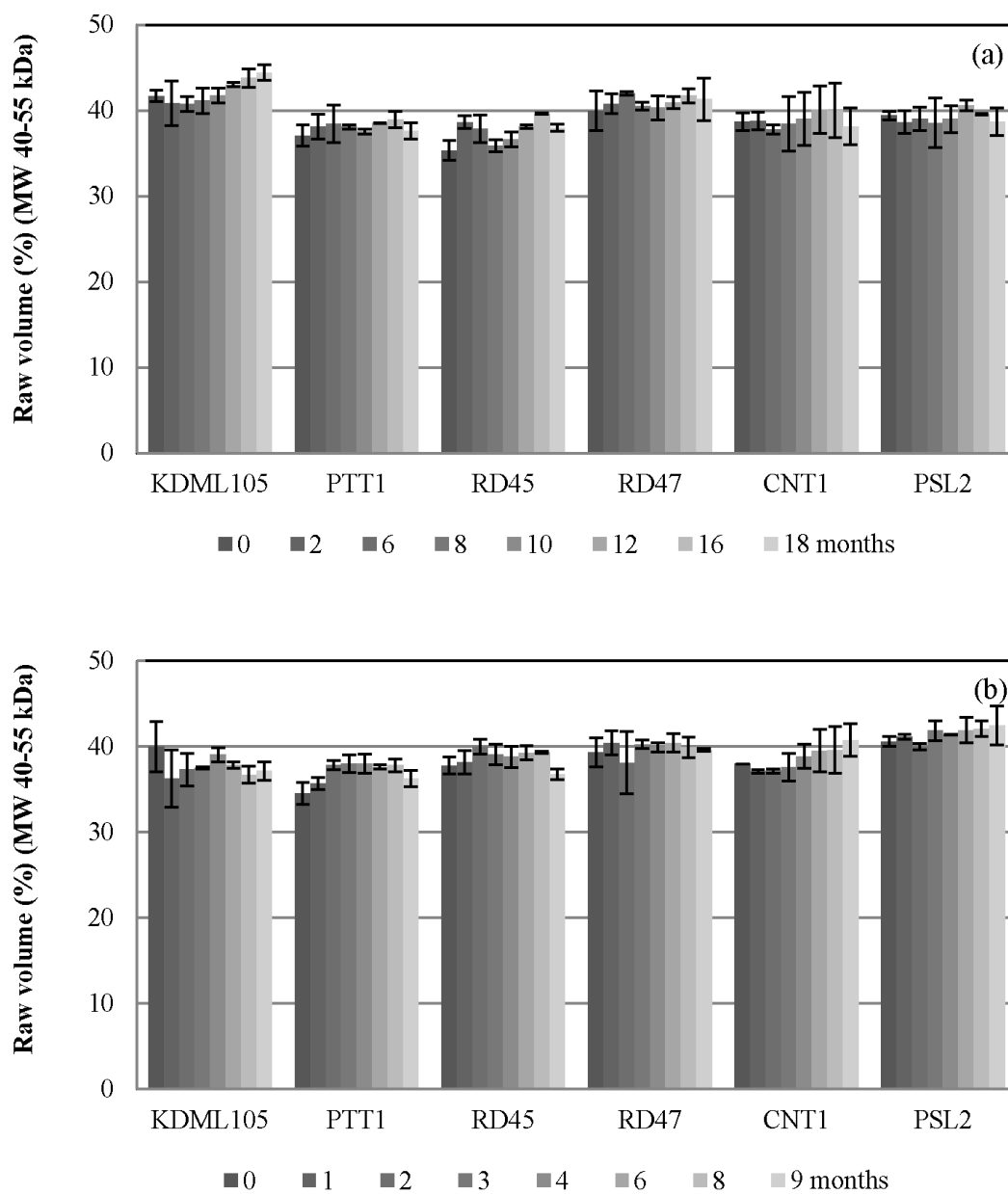


Figure 4.31 Raw volume (%) of protein molecular weight distribution (MW 40-55 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C

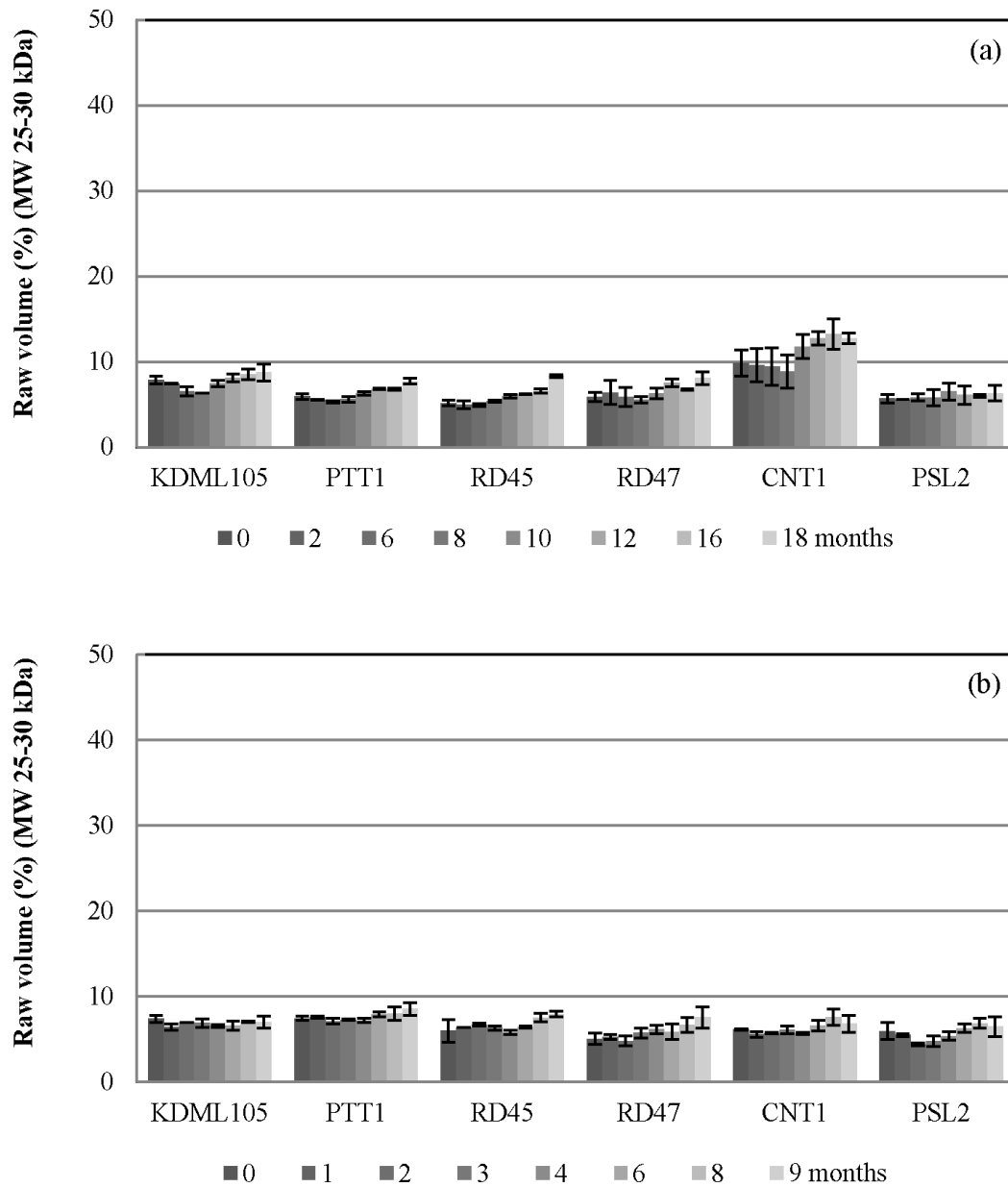


Figure 4.32 Raw volume (%) of protein molecular weight distribution (MW 25-30 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C

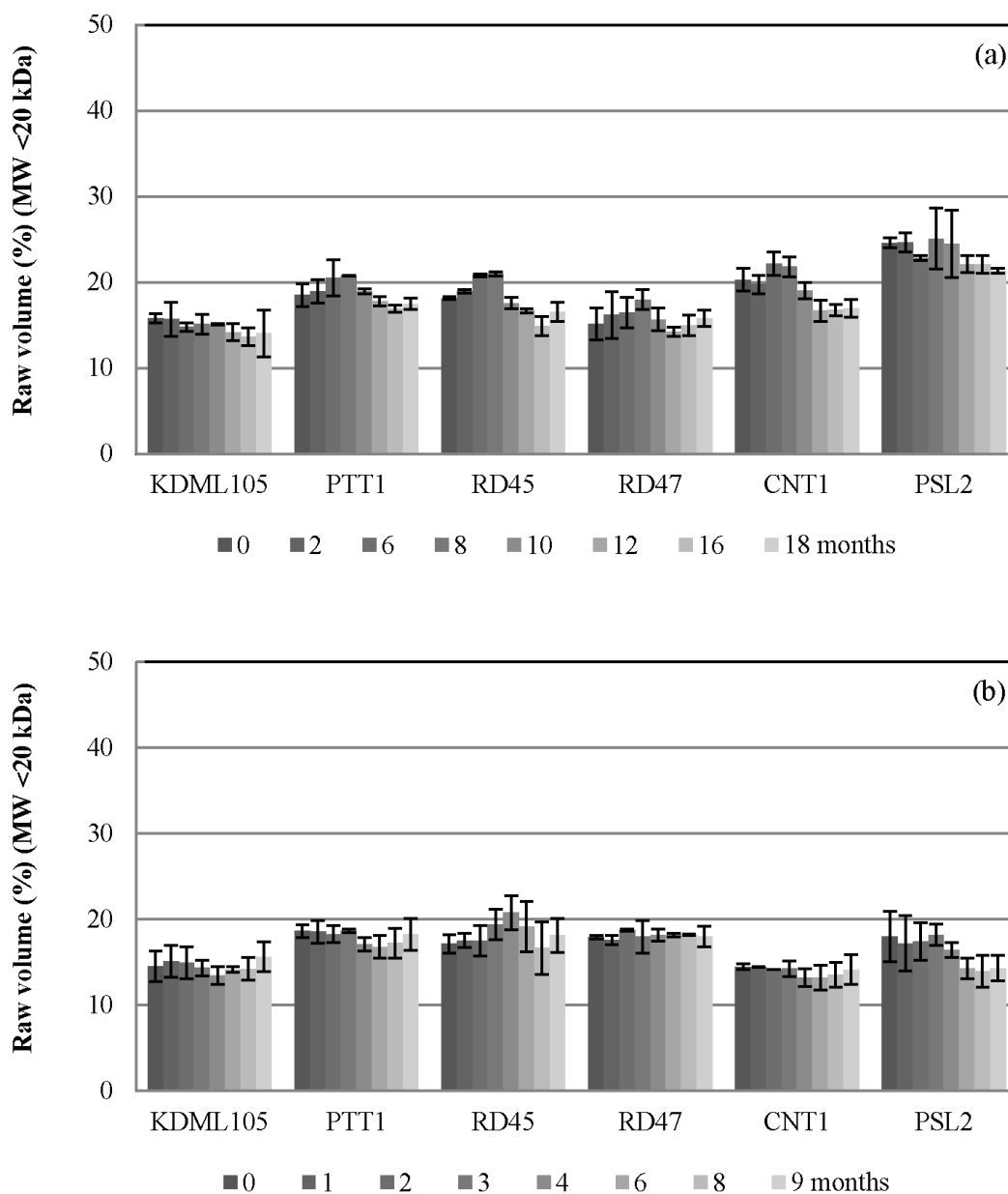


Figure 4.33 Raw volume (%) of protein molecular weight distribution (MW < 20 kDa) of rice protein from rice flour during storage at (a) 8 °C and (b) 30 °C

4.3 Principal Component Analysis

Principal Component Analysis (PCA) was performed on 36 chemical and physical properties data of fresh and aged six rice varieties. Figure 4.34 shows the score plot of all parameters of rice during aging at 8 °C and 30 °C. The score plot revealed a separation between low amylose KDML105, PTT1 and RD45, high

amylose RD47 and PSL2, and high amylose CNT1 rice samples. The exclusion of CNT1 from other high amylose rice varieties could be a result of its distinctive properties, such as head rice yield, minimum cooking time, solid loss, water uptake, volume expansion ratio, hardness, pasting temperature, peak viscosity, final viscosity, breakdown, setback, trough viscosity, onset temperature, peak temperature and conclusion temperature, as shown previously. PCA could not classify aged rice from fresh rice and unable to separate rice from different storage temperatures for all rice varieties. This could be due to the fact that properties had been recorded along aging period, where gradual changes occurred.

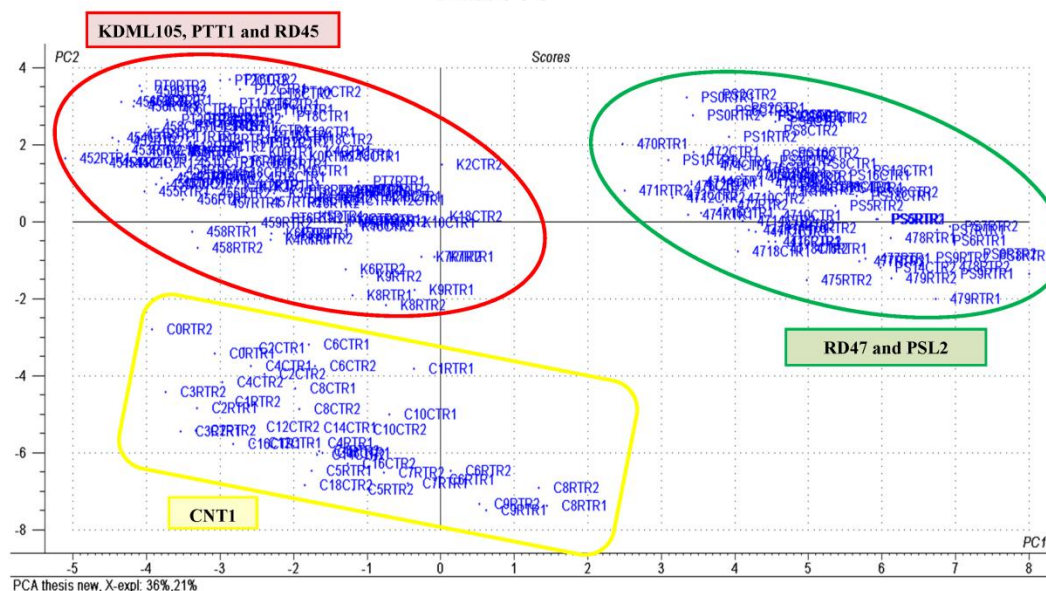


Figure 4.34 Score plot of all parameter of rice during storage at 8 °C and 30 °C

4.4 Chemometric analysis

Rice samples from the same storage conditions were analyzed using FT-NIR spectrometer in the diffuse-reflectance mode. Milling quality, color (whiteness index), cooking quality, textural properties, pasting properties, thermal properties and electrophoresis (SDS-PAGE) were used to develop the predictive model. Only 14 parameters could be used to develop good prediction models with R^2 greater than 0.7. In the stage of model development, the samples were specified to the calibration set and the validation set. Table 4.2 shows the sample data range for the calibration set

and the validation set. It is noted that the range of values for the validation set was within the range of the calibration set for all parameters. Small differences in minimum, maximum, mean and standard deviation between the calibration set and validation set indicated that both sets could represent the variations of rice. Calibration models were produced using partial least square (PLS) regression. The calibration and validation statistics are shown in Table 4.3. It was found that the treated FT-NIR spectra gave better models; higher R^2 and lower RMSEP, when compared to raw spectra. First derivatization of NIR spectra using the Savitzky-Golay method was optimal for relationship development with MCT, VER, BD, hardness, adhesiveness and T_o . Second derivatization of NIR spectra using the Savitzky-Golay method was optimal for relationship development with SB, T_p and T_c . Moving average smoothing method of NIR spectra was optimal for relationship development with only SL, while Savitzky-Golay smoothing method was optimal for relationship development with WU. In addition, standard normal variate (SNV) method was optimal for that with HRY, PT and PV. PLS regression was employed to develop a model relating treated FT-NIR data with various properties. Scatter plots for comparison of measured and predicted values for each parameter are shown in Figure 4.35. Good linearity and high R^2 indicated that the calibration equation could provide good prediction for HRY, MCT, SL, WU, VER, PT, PV, BD, SB, hardness, adhesiveness, T_o , T_p and T_c . In a recent research, Delwiche *et al.* (1996) determined milled rice quality by NIR spectroscopy in the 400-2498 nm region. They found that PLS was the most suitable technique for developing the best model. From their work, the relationship between pasting properties versus NIR spectra of breakdown and setback had the R^2 of 0.719 and 0.737, respectively. Adhesiveness gave the model with the highest R^2 of 0.9466.

Table 4.2 Range of composition variation in the samples used to develop PLS models

Parameters	Calibration set (n = 153)				Validation set (n = 75)			
	Min	Max	Mean	SD	Min	Max	Mean	SD
Head rice yield (%)	16.12	54.51	34.63	9.94	16.88	53.64	34.52	9.68
Minimum cooking time (min)	17.00	26.00	19.84	2.71	17.00	26.00	19.81	2.66
Solid loss (%)	2.55	4.55	3.47	0.53	2.58	4.48	3.47	0.52
Water uptake (%)	163.08	311.4	257.7	26.07	208.5	309.1	257.7	24.41
Volume expansion ratio	2.35	3.63	2.85	0.23	2.51	3.44	2.85	0.21
Pasting temperature (°C)	73.80	88.52	80.75	4.21	74.25	88.15	80.70	4.14
Peak viscosity (Pa.s)	0.97	3.79	2.59	1.04	1.00	3.78	2.56	0.96
Breakdown (Pa.s)	0.08	2.19	0.93	0.67	0.09	2.17	0.92	0.65
Setback (Pa.s)	0.49	2.12	1.18	0.38	0.52	2.09	1.17	0.37
Hardness (kg)	10.36	17.86	13.54	1.94	10.43	17.34	13.50	1.88
Adhesiveness (kg.s)	0.07	0.93	0.42	0.29	0.07	0.84	0.42	0.29
T _o (°C)	57.42	74.06	64.80	4.59	57.97	73.42	64.64	4.34
T _p (°C)	69.00	81.46	73.86	3.28	69.28	79.72	73.72	3.06
T _c (°C)	76.18	89.45	82.19	3.19	76.66	87.40	82.06	2.96

Note: T_o = onset temperature; T_p = peak temperature; T_c = conclusion temperature

T_o, T_p and T_c : calibration set (n = 82), validation set (n = 26)

Table 4.3 PLS model statistics for rice qualities

Parameters	Pretreatment method	Factor	Calibration set			Validation set		
			RMSEC	R ²	RMSEP	Bias	R ²	
Head rice yield (%)	Raw spectrum	8	2.8275	0.9181	3.6464	0.3391	0.8577	
	1 st derivative	7	2.8390	0.9172	3.3585	0.3385	0.8795	
	2 nd derivative	7	3.0137	0.9071	3.2716	0.1029	0.8845	
	Moving average smoothing	8	2.8446	0.9171	3.6320	0.3180	0.8586	
	Savitzky-Golay smoothing	8	2.8262	0.9182	3.6447	0.3396	0.8578	
	SNV	7	2.7229	0.9242	3.6397	0.3391	0.8582	
Minimum cooking time (min)	Raw spectrum	9	0.8468	0.9012	0.8606	-0.0242	0.8943	
	1 st derivative	7	0.7199	0.9291	0.6976	-0.1025	0.9330	
	2 nd derivative	8	0.7568	0.9215	0.8180	0.0667	0.9052	
	Moving average smoothing	9	0.8484	0.9008	0.8666	-0.0266	0.8930	
	Savitzky-Golay smoothing	9	0.8462	0.9013	0.8602	-0.0242	0.8945	
	SNV	7	0.8700	0.8956	0.8913	0.0038	0.8866	
Solid loss (%)	Raw spectrum	11	0.1930	0.8672	0.1942	0.0496	0.8681	
	1 st derivative	7	0.1969	0.8614	0.1694	0.0151	0.8932	
	2 nd derivative	7	0.2036	0.8519	0.1760	0.0211	0.8849	
	Moving average smoothing	12	0.1891	0.8723	0.1740	0.0457	0.8938	
	Savitzky-Golay smoothing	11	0.1929	0.8675	0.1941	0.0497	0.8682	
	SNV	9	0.1915	0.8693	0.1789	0.0440	0.8866	

Table 4.3 PLS model statistics for rice qualities (cont...)

Parameters	Pretreatment method	Factor	Calibration set			Validation set		
			RMSEC	R ²	RMSEP	Bias	R ²	
Water uptake (%)	Raw spectrum	10	11.5949	0.8052	8.1889	0.5984	0.8883	
	1 st derivative	7	11.6944	0.8030	6.8880	-0.8609	0.9206	
	2 nd derivative	6	12.2248	0.7839	9.5821	-0.7162	0.8473	
	Moving average smoothing	10	11.6267	0.8041	8.2178	0.5649	0.8874	
	Savitzky-Golay smoothing	10	11.5954	0.8052	8.1840	0.5933	0.8885	
	SNV	8	11.7982	0.7975	8.8263	0.0092	0.8684	
Volume expansion ratio	Raw spectrum	9	0.1105	0.7682	0.1187	0.0123	0.7157	
	1st derivative	8	0.1027	0.7992	0.1010	0.0136	0.7756	
	2 nd derivative	9	0.1155	0.7462	0.1208	0.0034	0.7042	
	Moving average smoothing	9	0.1106	0.7679	0.1182	0.0126	0.7179	
	Savitzky-Golay smoothing	9	0.1106	0.7683	0.1187	0.0122	0.7157	
	SNV	12	0.1063	0.7855	0.1142	0.0015	0.7259	
Pasting temperature (°C)	Raw spectrum	10	1.6437	0.8467	1.5773	0.1542	0.8545	
	1 st derivative	10	1.4134	0.8866	1.3638	-0.0200	0.8902	
	2 nd derivative	8	1.7318	0.8295	1.7148	-0.0710	0.8268	
	Moving average smoothing	10	1.6486	0.8458	1.5800	0.1630	0.8541	
	Savitzky-Golay smoothing	10	1.6433	0.8468	1.5775	0.1542	0.8543	
	SNV	16	1.3195	0.9003	1.3940	0.0368	0.8853	

Table 4.3 PLS model statistics for rice qualities (cont...)

Parameters	Pretreatment method	Factor	Calibration set			Validation set		
			RMSEC	R ²	RMSEP	Bias	R ²	
Peak viscosity (Pa.s)	Raw spectrum	10	0.4435	0.8240	0.3240	0.0717	0.8896	
	1 st derivative	6	0.4375	0.8291	0.3345	0.0577	0.8802	
	2 nd derivative	6	0.4467	0.8211	0.3575	0.0851	0.8675	
	Moving average smoothing	10	0.4447	0.8231	0.3220	0.0714	0.8909	
	Savitzky-Golay smoothing	10	0.4440	0.8236	0.3232	0.0712	0.8900	
	SNV	10	0.4174	0.8448	0.3270	0.0756	0.8889	
Breakdown (Pa.s)	Raw spectrum	12	0.2300	0.8804	0.2656	0.0223	0.8387	
	1 st derivative	10	0.2049	0.9049	0.2641	0.0395	0.8385	
	2 nd derivative	8	0.2648	0.8414	0.3399	0.0645	0.7375	
	Moving average smoothing	12	0.2309	0.8794	0.2661	0.0225	0.8381	
	Savitzky-Golay smoothing	12	0.2300	0.8804	0.2658	0.0225	0.8385	
	SNV	10	0.2293	0.8809	0.2753	0.0250	0.8228	
Setback (Pa.s)	Raw spectrum	10	0.1667	0.8092	0.1713	0.0119	0.7809	
	1 st derivative	6	0.1720	0.7964	0.1738	0.0045	0.7739	
	2 nd derivative	9	0.1610	0.8216	0.1593	-0.0190	0.8125	
	Moving average smoothing	10	0.1669	0.8088	0.1714	0.0126	0.7809	
	Savitzky-Golay smoothing	10	0.1666	0.8093	0.1713	0.0119	0.7811	
	SNV	8	0.1632	0.8172	0.1768	0.0150	0.7676	

Table 4.3 PLS model statistics for rice qualities (cont...)

Parameters	Pretreatment method	Factor	Calibration set			Validation set		
			RMSEC	R ²	RMSEP	Bias	R ²	
Hardness (kg)	Raw spectrum	10	0.7463	0.8490	0.6476	-0.0574	0.8866	
	1st derivative	8	0.6370	0.8907	0.5510	-0.0162	0.9136	
	2 nd derivative	7	0.7632	0.8439	0.7647	-0.0648	0.8442	
	Moving average smoothing	10	0.7505	0.8474	0.6426	-0.0557	0.8881	
	Savitzky-Golay smoothing	10	0.7517	0.8468	0.6437	-0.0562	0.8877	
	SNV	10	0.7050	0.8653	0.5966	-0.0684	0.9076	
Adhesiveness (kg.s)	Raw spectrum	12	0.0682	0.9446	0.0784	0.0046	0.9264	
	1st derivative	9	0.0654	0.9491	0.0671	0.0026	0.9465	
	2 nd derivative	9	0.0740	0.9351	0.0779	-0.0063	0.9274	
	Moving average smoothing	12	0.0686	0.9438	0.0789	0.0051	0.9258	
	Savitzky-Golay smoothing	12	0.0682	0.9446	0.0785	0.0046	0.9264	
	SNV	10	0.0681	0.9450	0.0755	-0.0026	0.9310	
T _o (°C)	Raw spectrum	9	1.6401	0.8710	1.5704	0.0492	0.8647	
	1st derivative	6	1.4896	0.8952	1.3824	0.1765	0.8962	
	2 nd derivative	7	1.4995	0.8902	1.3516	0.1396	0.9033	
	Moving average smoothing	9	1.6423	0.8707	1.5790	0.0475	0.8630	
	Savitzky-Golay smoothing	9	1.6394	0.8711	1.5681	0.0491	0.8651	
	SNV	7	1.6105	0.8754	1.6226	0.0717	0.8552	

Table 4.3 PLS model statistics for rice qualities (cont...)

Parameters	Pretreatment method	Factor	Calibration set			Validation set		
			RMSEC	R ²	RMSEP	Bias	R ²	
T _p (°C)	Raw spectrum	9	1.0271	0.8978	0.8975	0.1644	0.9158	
	1 st derivative	7	0.9829	0.9068	0.7087	0.0270	0.9450	
	2nd derivative	7	0.9739	0.9093	0.7910	0.0840	0.9314	
	Moving average smoothing	9	1.0277	0.8977	0.9020	0.1620	0.9151	
	Savitzky-Golay smoothing	9	1.0271	0.8978	0.8971	0.1646	0.9160	
	SNV	7	0.9992	0.9037	0.8697	0.1596	0.9237	
	T _c (°C)	Raw spectrum	10	1.5270	0.7643	1.2253	0.0218	0.8593
1 st derivative	7	1.4674	0.7830	1.0684	-0.0415	0.8926		
2nd derivative	7	1.4628	0.7846	1.1285	-0.1087	0.8750		
Moving average smoothing	10	1.5299	0.7634	1.2242	0.0402	0.8586		
Savitzky-Golay smoothing	10	1.5198	0.7666	1.2268	0.0532	0.8578		
SNV	6	1.5815	0.7480	1.1757	-0.0099	0.8573		

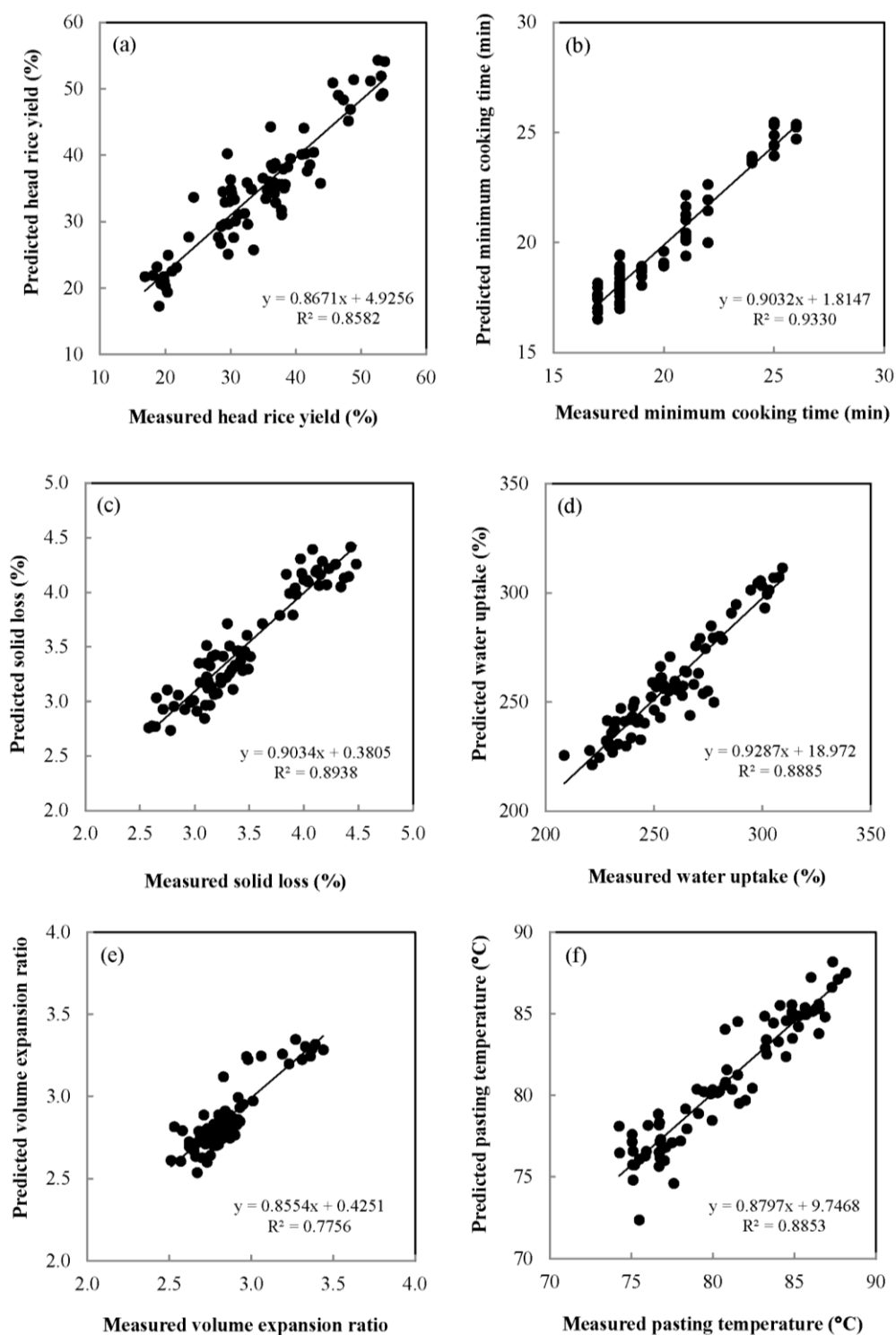


Figure 4.35 Comparison of measured and predicted values for rice qualities of validation samples for (a) head rice yield, (b) minimum cooking time, (c) solid loss, (d) water uptake, (e) volume expansion ratio, (f) pasting temperature, (g) peak viscosity, (h) breakdown, (i) setback, (j) hardness, (k) adhesiveness, (l) onset temperature, (m) peak temperature and (n) conclusion temperature

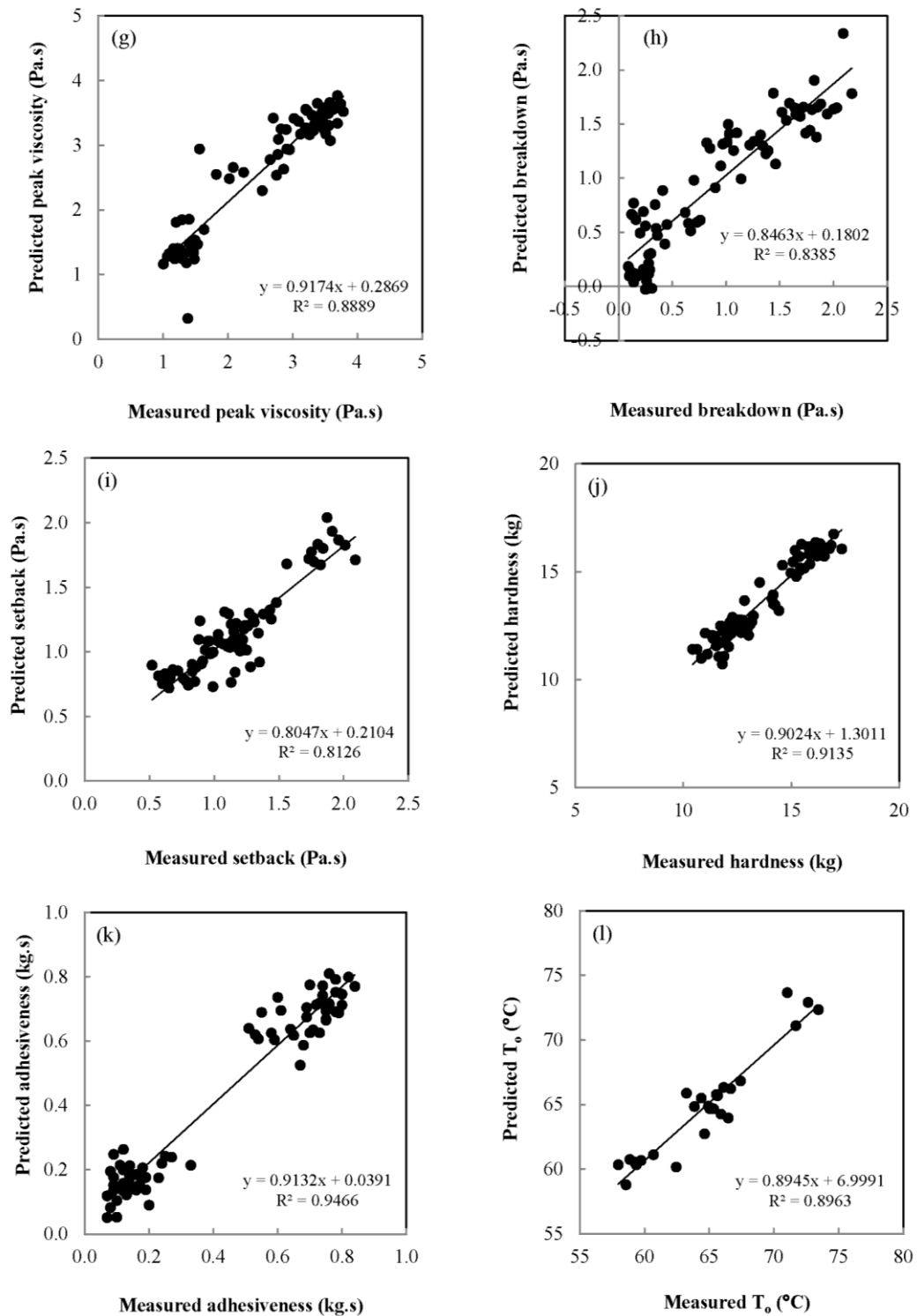


Figure 4.35 Comparison of measured and predicted values for rice qualities of validation samples for (a) head rice yield, (b) minimum cooking time, (c) solid loss, (d) water uptake, (e) volume expansion ratio, (f) pasting temperature, (g) peak viscosity, (h) breakdown, (i) setback, (j) hardness, (k) adhesiveness, (l) onset temperature, (m) peak temperature and (n) conclusion temperature (cont...)

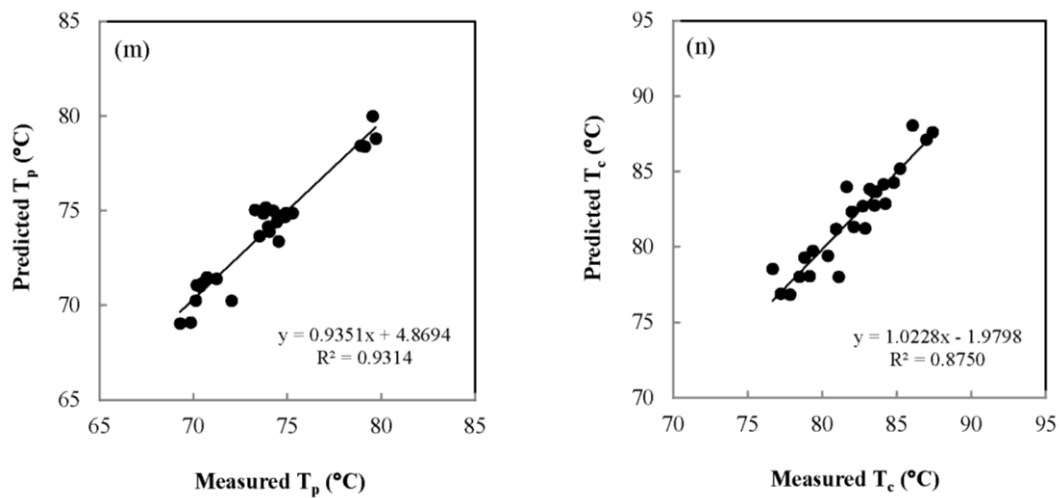


Figure 4.35 Comparison of measured and predicted values for rice qualities of validation samples for (a) head rice yield, (b) minimum cooking time, (c) solid loss, (d) water uptake, (e) volume expansion ratio, (f) pasting temperature, (g) peak viscosity, (h) breakdown, (i) setback, (j) hardness, (k) adhesiveness, (l) onset temperature, (m) peak temperature and (n) conclusion temperature (cont...)

4.5 Aging kinetics modeling

To obtain aging kinetics model parameters, all observed data were fitted and the regression coefficients were compared. Both the zeroth order and the fractional conversion first order kinetics models were applied to explain changes of rice properties. The models parameters are shown in Appendix C.4 (Table C.4). For the first-order fractional conversion kinetic model, the progress of process directly proportioned to the reactant concentration and the changes start from an initial value (A_0) that tends to increase or decrease to an equilibrium value (A_∞). In the process of model fitting, the first-order fractional conversion kinetic model was applied to fit the experimental data at 30 °C to obtain A_0 and A_∞ that is the projected parameter at the beginning of storage and that projected at equilibrium, respectively. A_0 and A_∞ were then applied in the fitting of the observation data at 8 °C to obtain the rate constant (k). The same set of observation data was also fitted using the zeroth order kinetics model. As zeroth order kinetics model is basically a linear model, in which the process takes place at a constant rate independent of concentration involve in process and the value tends to decrease or increase to an unlimited value, no A_∞ was necessary for the model fitting.

It was found that only nine attributes could be fitted using both the Zeroth order kinetics model and the first-order fractional conversion kinetic model which gave a reasonably high R-squared ($R^2 \geq 0.7$). However, better model fitting was resulted from the first-order fractional conversion kinetic model for the majority of rice data and, thus shown in Table 4.4. The first-order fractional conversion kinetic model could explain the changes in all rice varieties (KDML105, PTT1, RD45, RD47, CNT1, PSL2) after rice storage at 30 °C for 9 parameters ($R^2 \geq 0.7$); SL, WU, VER (except RD47), PT, PV, BD, SB, hardness and adhesiveness. It was observed that low amylose rice had higher A_0 and k for changes in PV and BD for storage at 30 °C than high amylose rice, but gave lower A_0 and k than high amylose rice for SL, PT and SB. It could be seen that the rate constant for changes in adhesiveness of rice stored at 8 °C was about one-third for PSL2 and about a quarter for CNT1 of that stored at 30 °C. Figure 4.36 shows the observed rice properties compared to the predictive values using the first-order fractional conversion kinetic model prediction using equation below and the kinetics parameters in Table 4.4.

$$A_t = A_\infty + (A_0 - A_\infty) \cdot e^{-kt}$$

For the properties obtained from rice stored at 8 °C, the first-order fractional conversion kinetic model could only be used to explain some changes in 7 rice properties ($R^2 \geq 0.7$); SL (PTT1 and RD45), WU (except RD45), VER (RD45, CNT1 and PSL2), PV (KDML105 and RD45), BD (KDML105), hardness (PTT1, RD45 and PSL2) and adhesiveness (CNT1 and PSL2). Most changes in rice stored at 8 °C could not be explained very well by any of the proposed model because the increase or decrease of each attributes was marginal, if not constant.

Finally, proposed steps to be carried out for age prediction of any of the six rice varieties studied are presented in Figure 4.37. An NIR spectrum for milled rice can be collected and the modeled parameters can be obtained for subsequent input in the kinetic model for prediction of temperature and time of storage. However, future work needs to be carried out so that more data on rice quality can be collected at different temperatures and the accuracy of the model can be improved.

Table 4.4 Kinetics model parameters (First order) for changes in rice and flour properties during storage at 8 °C and 30 °C.

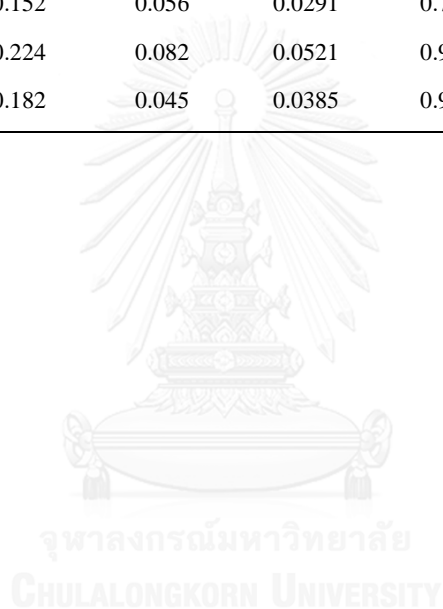
Rice varieties	First order fractional conversion kinetics model parameters					
	A ₀	A _∞	30 °C		8 °C	
			k (week ⁻¹)	R ²	k (week ⁻¹)	R ²
Solid loss (%)						
KDML105	3.3150	2.2200	0.0238	0.90	0.0034	0.26
PTT1	3.5059	1.3806	0.0072	0.88	0.0032	0.72
RD45	3.6532	2.8364	0.0297	0.90	0.0114	0.83
RD47	4.1790	3.8795	0.2049	0.81	-0.0018	0.05
CNT1	3.3211	2.6380	0.3318	0.93	0.0093	0.27
PSL2	4.5392	4.0698	0.5396	0.94	0.0231	0.18
Water uptake (%)						
KDML105	243.0512	275.1864	0.0384	0.78	0.0150	0.92
PTT1	240.4357	260.1205	0.1708	0.82	0.0278	0.72
RD45	242.2802	278.777	0.4822	0.93	0.0660	0.69
RD47	207.1828	244.3575	0.1416	0.88	0.0444	0.81
CNT1	270.4389	303.0424	0.4774	0.91	0.0624	0.92
PSL2	219.1664	247.3296	0.0384	0.79	0.0106	0.91
Volume expansion ratio						
KDML105	2.6335	3.0633	0.0331	0.95	0.0092	0.55
PTT1	2.6268	2.8711	0.2016	0.78	0.0094	0.24
RD45	2.5748	2.9207	0.1711	0.98	0.0163	0.74
RD47	2.6019	2.9201	0.0846	0.61	0.0258	0.55
CNT1	2.8464	3.3554	0.2616	0.97	0.0374	0.82
PSL2	2.4245	2.7803	0.1965	0.88	0.0334	0.91
Pasting temp (°C)						
KDML105	74.3	84.4	0.017	0.98	0.0022	0.66
PTT1	75.6	85.4	0.031	0.95	0.0034	0.60
RD45	74.9	85.2	0.033	0.96	0.0039	0.65
RD47	81.97	91.43	0.03	0.96	0.0061	0.33
CNT1	79.27	90.02	0.029	0.97	0.0029	0.47
PSL2	83.83	91.39	0.023	0.96	0.0043	0.38

Table 4.4 Kinetics model parameters (First order) for changes in rice and flour properties during storage at 8 °C and 30 °C (cont...)

Rice varieties	First order fractional conversion kinetics model parameters					
	A ₀	A _∞	30 °C		8 °C	
			k (week ⁻¹)	R ²	k (week ⁻¹)	R ²
Peak viscosity (Pa.s)						
KDML105	3.721	2.563	0.028	0.84	0.0070	0.75
PTT1	3.672	2.681	0.032	0.87	0.0080	0.54
RD45	3.835	2.896	0.040	0.77	0.0087	0.74
RD47	1.745	0.928	0.047	0.97	0.0088	0.61
CNT1	2.923	1.450	0.031	0.93	0.0023	0.45
PSL2	1.397	0.698	0.019	0.80	0.0027	0.34
Breakdown (Pa.s)						
KDML105	2.227	0.053	0.0275	0.92	0.0047	0.78
PTT1	1.964	0.378	0.0397	0.86	0.0099	0.57
RD45	2.231	0.623	0.0455	0.90	0.0097	0.57
RD47	0.4920	0.0357	0.0670	0.93	0.0130	0.32
CNT1	1.028	0	0.0620	0.93	0.0079	0.31
PSL2	0.346	0	0.0370	0.92	0.0064	0.18
Setback (Pa.s)						
KDML105	0.9179	1.3916	0.0375	0.95	0.0046	0.03
PTT1	1.1147	1.7646	0.0241	0.92	0.0037	0.01
RD45	1.0722	1.6113	0.0256	0.94	0.0028	0.00
RD47	1.4942	0.5014	0.0814	0.93	0.0192	0.59
CNT1	2.1439	0.8043	0.0140	0.90	0.0068	0.39
PSL2	1.2340	0.3188	0.0431	0.93	0.0124	0.50
Hardness (kg)						
KDML105	11.43	13.20	0.038	0.90	0.0128	0.43
PTT1	11.38	13.50	0.039	0.87	0.0193	0.90
RD45	10.54	13.00	0.032	0.95	0.0110	0.82
RD47	14.869	19.394	0.011	0.83	0.0051	0.62
CNT1	11.673	20.576	0.013	0.93	0.0054	0.60
PSL2	13.900	18.150	0.047	0.94	0.0188	0.83

Table 4.4 Kinetics model parameters (First order) for changes in rice and flour properties during storage at 8 °C and 30 °C (cont...)

Rice varieties	First order fractional conversion kinetics model parameters					
	A_0	A_∞	30 °C		8 °C	
			k (week ⁻¹)	R^2	k (week ⁻¹)	R^2
Adhesiveness (kg.s)						
KDML105	0.723	0.413	0.0261	0.81	0.0005	0.16
PTT1	0.759	0.000	0.0088	0.80	0.0006	0.16
RD45	0.784	0.504	0.0296	0.87	0.0006	0.35
RD47	0.152	0.056	0.0291	0.75	0.0047	0.40
CNT1	0.224	0.082	0.0521	0.94	0.0124	0.80
PSL2	0.182	0.045	0.0385	0.97	0.0109	0.87



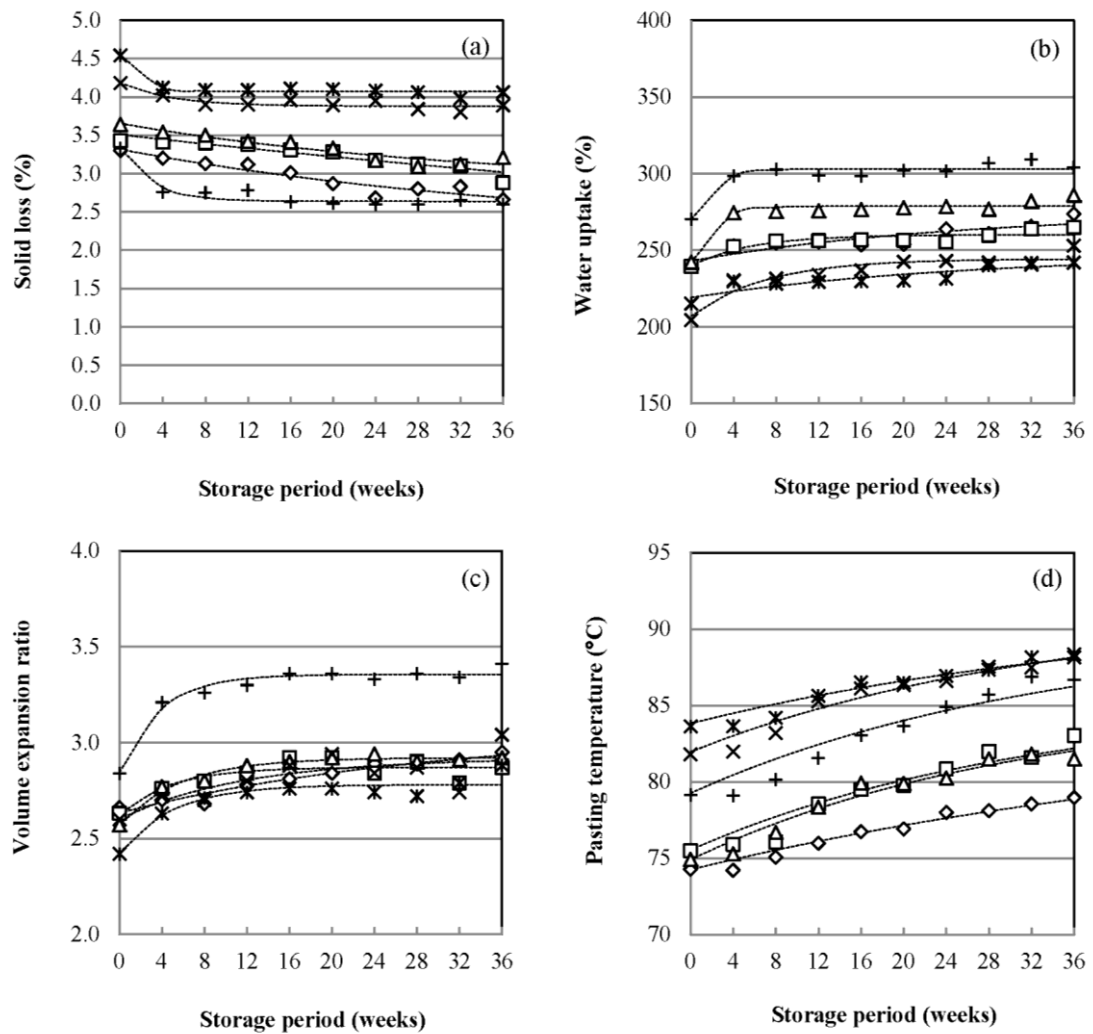


Figure 4.36 Comparison of measured (\diamond = KDML105, \square = PTT1, Δ = RD45, \times = RD47, $+$ = CNT1 and $*$ = PSL2) and predicted (---) values for rice qualities (30 °C storage) of the first-order fractional conversion kinetic model for (a) solid loss, (b) water uptake, (c) volume expansion ratio, (d) pasting temperature, (e) peak viscosity, (f) breakdown, (g) setback, (h) hardness and (i) adhesiveness

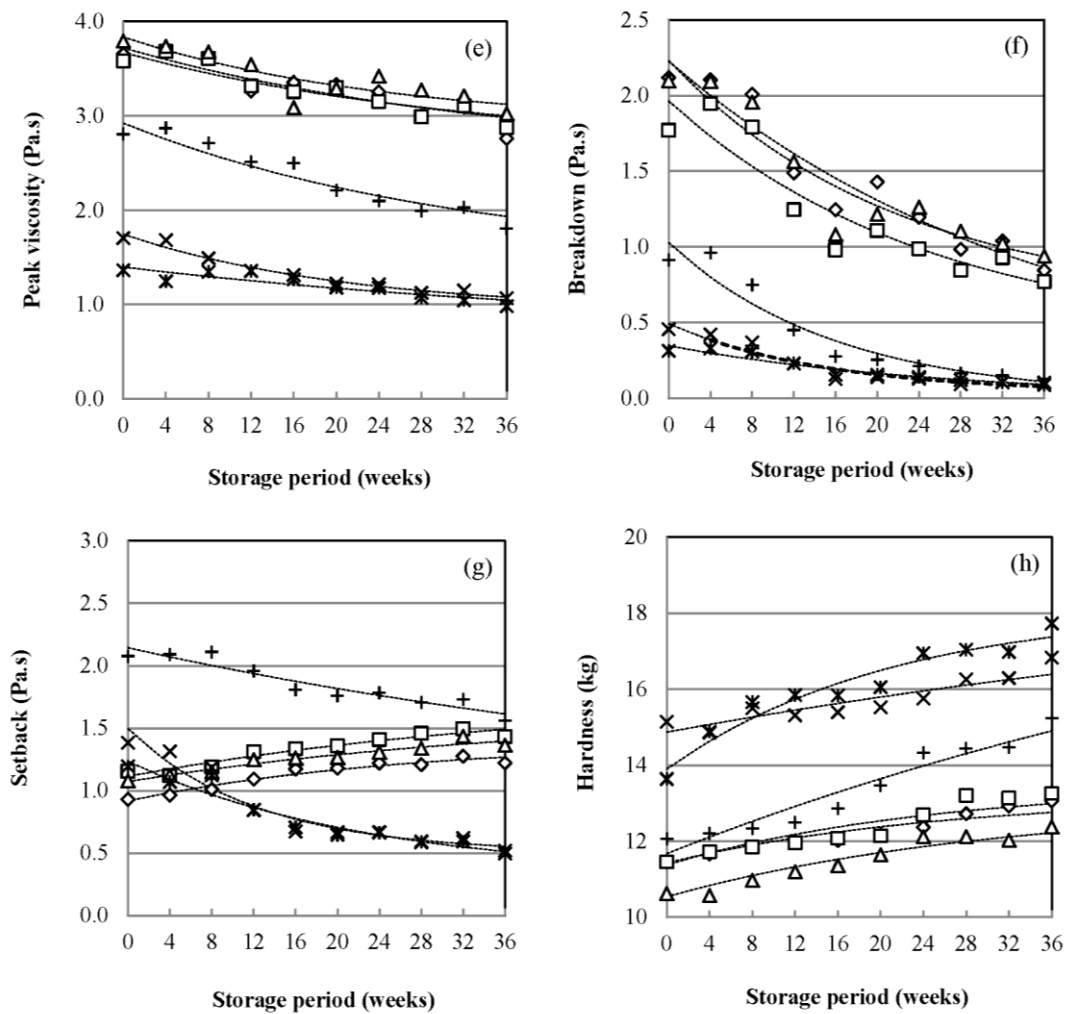


Figure 4.36 Comparison of measured (\diamond = KDML105, \square = PTT1, Δ = RD45, x = RD47, $+$ = CNT1 and $*$ = PSL2) and predicted (---) values for rice qualities (30 °C storage) of the first-order fractional conversion kinetic model for (a) solid loss, (b) water uptake, (c) volume expansion ratio, (d) pasting temperature, (e) peak viscosity, (f) breakdown, (g) setback, (h) hardness and (i) adhesiveness (cont...)

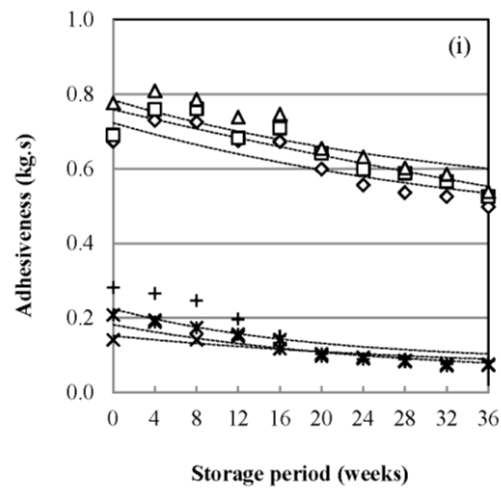


Figure 4.36 Comparison of measured ($\diamond =$ KDML105, $\square =$ PTT1, $\Delta =$ RD45, $x =$ RD47, $+$ = CNT1 and $*$ = PSL2) and predicted (---) values for rice qualities (30 °C storage) of the first-order fractional conversion kinetic model for (a) solid loss, (b) water uptake, (c) volume expansion ratio, (d) pasting temperature, (e) peak viscosity, (f) breakdown, (g) setback, (h) hardness and (i) adhesiveness (cont...)

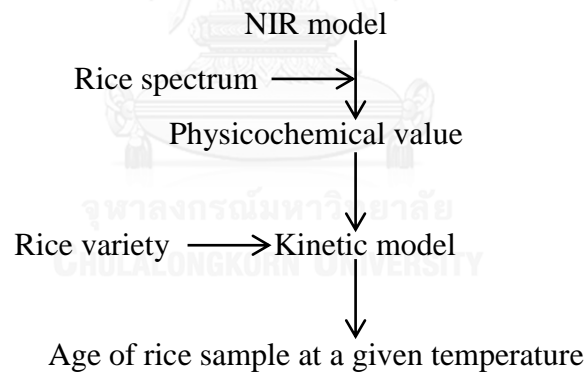


Figure 4.37 Steps to obtain age of rice by NIR models and kinetic models

CHAPTER V

CONCLUSIONS

In summary, low and high amylose rice varieties differed greatly in milling quality (head rice yield), cooking quality (solid loss and water uptake), cooked rice texture (hardness, adhesiveness, gumminess and chewiness) and pasting property of rice flour (pasting temperature, peak viscosity and breakdown). During storage, these properties changed continuously and more extensively at 30 °C. The properties that showed an obvious increasing trend include head rice yield, minimum cooking time, water uptake, volume expansion ratio, cooked length/breadth ratio, pasting temperature, hardness, cohesiveness, springiness, gumminess and chewiness. The properties that reduced with aging include whiteness index, solid loss, peak viscosity, breakdown and adhesiveness. Low amylose rice varieties showed distinctive lower pasting temperature, hardness, gumminess and chewiness and higher peak viscosity, breakdown and adhesiveness than high amylose rice varieties. It was observed that CNT1, which is high amylose rice, had solid loss, water uptake and hardness that were in the same range of low amylose rice. The reduction in enthalpy of gelatinization was more dramatic during the first part of storage; 3 and 4 months of storage at 30 °C and 8 °C, respectively. The value tended to change slightly thereafter.

From Principal Component Analysis (PCA) of all observed parameters, rice varieties in this study could be classified into 3 groups; (1) low amylose rice including KDML105, PTT1 and RD45, (2) high amylose RD47 and PSL2 and (3) high amylose CNT1. Differences in aged versus fresh rice stored at different temperatures were not detected using PCA, except for high amylose PSL2.

From partial least square (PLS) regression between FT-NIR spectra and rice properties, predictive models for 14 parameters were developed ($R^2 > 0.7$). These include head rice yield, minimum cooking time, solid loss, water uptake, volume expansion ratio, pasting temperature, peak viscosity, breakdown, setback, hardness, adhesiveness, T_o , T_p and T_c . It was found that the treated NIR spectra gave better models when compared to raw spectra (high R^2 and low RMSEP).

Changes in solid loss, water uptake, volume expansion ratio, pasting temperature, peak viscosity, breakdown, setback, hardness and adhesiveness during storage at 30 °C were reasonably explained ($R^2 \geq 0.7$) using the first-order fractional conversion kinetic model. The same kinetic model could be used to explain only a few properties of some rice varieties that were stored at 8 °C.

Suggestion

1. Since the samples in this study came from one crop year and specific cultivation area, the application of the model can possibly be limited. More samples from other cultivation area and crop year can be collected and studied to improve the applicability of the proposed models.
2. To be able to utilize the Arrhenius relationship for temperature and time prediction, data needs to be collected from samples stored at different temperatures and the activation energy needs to be re-calculated.

REFERENCES

- Agricultural Research and Development Agency (2016). *Rice histories* [Online]. Available from: <http://www.arda.or.th/kasetinfo/rice/rice-histories.html> [2016, Sep 15].
- Ahmed, J., Dolan, K., and Mishra, D. (2012). Chemical reaction kinetics pertaining to foods. In "Handbook of Food Process Design" (J. Ahmed and M. S. Rahman, eds.), pp. 113-166. Blackwell Publishing Ltd.
- Alexandrakis, D., Downey, G., and Scannell, A. G. (2012). Rapid non-destructive detection of spoilage of intact chicken breast muscle using near-infrared and Fourier transform mid-infrared spectroscopy and multivariate statistics. *Food and Bioprocess Technology* **5**, 338-347.
- AOAC (2012). "Official Methods of Analysis," 19th/Ed. The Association of the Official Analytical Chemists, Maryland.
- Arendt, E. K., and Zannini, E. (2013). "Cereal Grains for the Food and Beverage Industries," Woodhead Publishing Limited, Cambridge.
- Armstrong, P., Maghirang, E., Xie, F., and Dowell, F. (2006). Comparison of dispersive and Fourier-transform NIR instruments for measuring grain and flour attributes. *Applied engineering in agriculture* **22**, 453-457.
- Bagchi, T. B., Sharma, S., and Chattopadhyay, K. (2016). Development of NIRS models to predict protein and amylose content of brown rice and proximate compositions of rice bran. *Food chemistry* **191**, 21-27.
- Ball, S., Guan, H.-P., James, M., Myers, A., Keeling, P., Mouille, G., Buléon, A., Colonna, P., and Preiss, J. (1996). From glycogen to amylopectin: a model for the biogenesis of the plant starch granule. *Cell* **86**, 349-352.
- Bao, J., Shen, Y., and Jin, L. (2007). Determination of thermal and retrogradation properties of rice starch using near-infrared spectroscopy. *Journal of Cereal Science* **46**, 75-81.
- Basak, S., Tyagi, R., and Srivastava, K. (2002). Biochemical characterization of aromatic and non-aromatic rice cultivars. *Journal of food science and technology* **39**, 55-58.
- Batten, G. (1998). Plant analysis using near infrared reflectance spectroscopy: the potential and the limitations. *Animal Production Science* **38**, 697-706.
- Bechtel, D. B., and Pomeranz, Y. (1978). Ultrastructure of the mature ungerminated rice (*Oryza sativa*) caryopsis. The starchy endosperm. *American Journal of Botany*, 684-691.
- Bhattacharya, K. R. (2011a). Ageing of rice. In "Rice Quality: A Guide to Rice Properties and Analysis" (K. R. Bhattacharya, ed.), pp. 116-163. Woodhead Publishing.
- Bhattacharya, K. R. (2011b). Physical properties of rice. In "Rice Quality: A Guide to Rice Properties and Analysis" (K. R. Bhattacharya, ed.), pp. 26-60. Woodhead Publishing.
- Buléon, A., Colonna, P., Planchot, V., and Ball, S. (1998). Starch granules: structure and biosynthesis. *International journal of biological macromolecules* **23**, 85-112.

- Cao, W., Nishiyama, Y., and Koide, S. (2004). Physicochemical, mechanical and thermal properties of brown rice grain with various moisture contents. *International journal of food science & technology* **39**, 899-906.
- Cen, H., and He, Y. (2007). Theory and application of near infrared reflectance spectroscopy in determination of food quality. *Trends in Food Science & Technology* **18**, 72-83.
- Chalmers, J. M., and Griffiths, P. R. (2002). "Handbook of Vibrational Spectroscopy," Wiley-VCH, Weinheim, Germany.
- Champagne, E. T., Lyon, B. G., Min, B. K., Vinyard, B. T., Bett, K. L., Barton, F. E., Webb, B. D., McClung, A. M., Moldenhauer, K. A., and Linscombe, S. (1998). Effects of postharvest processing on texture profile analysis of cooked rice. *Cereal Chemistry* **75**, 181-186.
- Champagne, E. T., Wood, D. F., Juliano, B. O., and Bechtel, D. B. (2004). The rice grain and its gross composition. In "Rice: Chemistry and technology " (E. T. Champagne, ed.), pp. 77-107. AACC International, Inc, St Paul, MN.
- Cheapun, K., Wongpiyachon, S., and Kongseree, N. (2005). Improving rice grain quality in Thailand. In "Proceeding of the World Rice Research Conference" (K. Toriyama, K. L. Heong and B. Hardy, eds.), pp. 248-250. International Rice Research Institute and Japan International Research Center for Agricultural Science, Tokyo and Tsukuba, Japan.
- Chen, K., and Huang, M. (2010). Prediction of milled rice grades using Fourier transform near-infrared spectroscopy and artificial neural networks. *Journal of cereal science* **52**, 221-226.
- Childs, N. W. (2004). Production and utilization of rice. In "Rice: Chemistry and Technology" (E. T. Champagne, ed.), pp. 1-24. AACC International, Inc., St. Paul, MN.
- Choudhury, N. H., and Juliano, B. O. (1980). Effect of amylose content on the lipids of mature rice grain. *Phytochemistry* **19**, 1385-1389.
- Chrastil, J. (1990). Protein-starch interactions in rice grains. Influence of storage on oryzenin and starch. *Journal of Agricultural and Food Chemistry* **38**, 1804-1809.
- Cozzolino, D., Roumeliotis, S., and Eglinton, J. (2013). Relationships between swelling power, water solubility and near-infrared spectra in whole grain barley: a feasibility study. *Food and Bioprocess Technology* **6**, 2732-2738.
- Del Rosario, A. R., Briones, V. P., Vidal, A. J., and Juliano, B. O. (1968). Composition and endosperm structure of developing and mature rice kernel. *Cereal Chemistry* **45**, 225-235.
- Delcour, J. A., and Hosney, C. R. (2010). Structure of cereals. In "Principles of Cereal Science and Technology" (J. A. Delcour and C. R. Hosney, eds.), pp. 1-22. AACC International, Inc., St Paul, MN.
- Delwiche, S. R., McKENZIE, K. S., and Webb, B. D. (1996). Quality characteristics in rice by near-infrared reflectance analysis of whole-grain milled samples. *Cereal Chemistry* **73**, 257-263.
- Department of Foreign Trade (2016). *Rice industry of Thailand in 2015-2016* [Online]. Available from: http://www.dft.go.th/LinkClick.aspx?fileticket=p6iLTgSSD_4%3D&tabid=401 [2016, Sep 26].

- Faruq, G., Prodhan, Z. H., and Nezhadahmadi, A. (2015). Effects of ageing on selected cooking quality parameters of rice. *International Journal of Food Properties* **18**, 922-933.
- Gibson, T., Solah, V., and McCleary, B. (1997). A procedure to measure amylose in cereal starches and flours with concanavalin A. *Journal of Cereal Science* **25**, 111-119.
- Gomez, K. A. (1979). Effect of environment on protein and amylose content of rice. In "Chemical Aspects of Rice Grain Quality" (IRRI, ed.), pp. 56-68. IRRI, Los Banos, Laguna.
- Gujral, H. S., and Kumar, V. (2003). Effect of accelerated aging on the physicochemical and textural properties of brown and milled rice. *Journal of Food Engineering* **59**, 117-121.
- Haughey, S. A., Graham, S. F., Cancouët, E., and Elliott, C. T. (2013). The application of near-infrared reflectance spectroscopy (NIRS) to detect melamine adulteration of soya bean meal. *Food Chemistry* **136**, 1557-1561.
- Hayakawa, T., Seo, S. W., and Igaue, I. (1980). Electron Microscopic Observation of Rice Grain. *Journal of the Japanese Society of Starch Science* **27**, 173-179.
- Himmelsbach, D., Barton, F., McClung, A., and Champagne, E. (2001). Protein and apparent amylose contents of milled rice by NIR-FT/Raman spectroscopy. *Cereal chemistry* **78**, 488-492.
- Hinton, J., and Shaw, B. (1954). The distribution of nicotinic acid in the rice grain. *British Journal of Nutrition* **8**, 65-71.
- Hódsági, M., Gergely, S., Gelencsér, T., and Salgó, A. (2012). Investigations of native and resistant starches and their mixtures using near-infrared spectroscopy. *Food and bioprocess technology* **5**, 401-407.
- Iida, S., Amano, E., and Nishio, T. (1993). A rice (*Oryza sativa* L.) mutant having a low content of glutelin and a high content of prolamine. *Theoretical and Applied Genetics* **87**, 374-378.
- Ito, S., Sato, S., and Fujino, Y. (1979). Internal lipid in rice starch. *Starch-Stärke* **31**, 217-221.
- Jaisut, D., Prachayawarakorn, S., Varanyanond, W., Tungtrakul, P., and Soponronnarit, S. (2009). Accelerated aging of jasmine brown rice by high-temperature fluidization technique. *Food Research International* **42**, 674-681.
- Jha, S. N. (2010). Near Infrared Spectroscopy. In "Nondestructive Evaluation of Food Quality" (S. N. Jha, ed.), pp. 141-212. Springer, Berlin, Heidelberg.
- Juliano, B. O. (1972). Rice quality. In "Australian Rice Research Conference", pp. 6(a) 1-7, Australia.
- Juliano, B. O. (1985). Criteria and tests for rice grain qualities. In "Rice: Chemistry and Technology" (B. O. Juliano, ed.), pp. 443-524. American association of cereal chemists, St. Paul, MN, USA.
- Juliano, B. O. (2003). Rice. In "Encyclopedia of Food Sciences and Nutrition" (B. Caballero, C. Trvgo and P. M. Fingcas, eds.). Academic Press, Oxford.
- Juliano, B. O. (2005). Overview of rice. In "Proceeding of the World Rice Research Conference" (K. Toriyama, K. L. Heong and B. Hardy, eds.), pp. 268-270. International Rice Research Institute and Japan International Research Center for Agricultural Science, Tokyo and Tsukuba, Japan.

- Kaminski, T. A., Brackmann, A., da Silva, L. P., Nicoletti, A. M., and Roberto, B. S. (2013). Changes in culinary, viscoamylographic and sensory characteristics during rice storage at different temperatures. *Journal of stored products research* **53**, 37-42.
- Katekhong, W., and Charoenrein, S. (2014). Effect of rice ageing and freeze-thaw cycle on textural properties of cooked rice (*Oryza sativa* L.) cv. Khao Dawk Mali 105. *International Journal of Food Science & Technology* **49**, 2283-2289.
- Kaur, K., and Singh, N. (2000). Amylose-lipid complex formation during cooking of rice flour. *Food Chemistry* **71**, 511-517.
- Kennedy, G., and Burlingame, B. (2003). Analysis of food composition data on rice from a plant genetic resources perspective. *Food Chemistry* **80**, 589-596.
- Kim, J. M., Song, J. Y., and Shin, M. (2010). Physicochemical properties of high amylose rice starches purified from Korean cultivars. *Starch-Stärke* **62**, 262-268.
- Kim, K.-M., Jang, I.-S., Ha, S.-D., and Bae, D.-H. (2004). Improved storage stability of brown rice by coating with rice bran protein. *Korean Journal of Food Science and Technology* **36**, 490-500.
- Kim, S.-K., and Cho, E.-J. (1993). Effects of storage temperatures on the physicochemical properties of milled rice. *Journal of the Korean Society for Applied Biological Chemistry* **36**, 146-153.
- Kitahara, K., Tanaka, T., Suganuma, T., and Nagahama, T. (1997). Release of bound lipids in cereal starches upon hydrolysis by glucoamylase. *Cereal chemistry* **74**, 1-6.
- Laemmli, U. K. (1970). Cleavage of structural proteins during the assembly of the head of bacteriophage T4. *nature* **227**, 680-685.
- Li, L., Zhao, C., Zhang, Y., Yao, J., Yang, W., Hu, Q., Wang, C., and Cao, C. (2017). Effect of stable antimicrobial nano-silver packaging on inhibiting mildew and in storage of rice. *Food Chemistry* **215**, 477-482.
- Likitwattanasade, T., and Hongsprabhas, P. (2010). Effect of storage proteins on pasting properties and microstructure of Thai rice. *Food Research International* **43**, 1402-1409.
- Liu, F., Jin, Z. L., Naem, M. S., Tian, T., Zhang, F., He, Y., Fang, H., Qingfu, F. Y., and Zhou, W. J. (2011). Applying near-infrared spectroscopy and chemometrics to determine total amino acids in herbicide-stressed oilseed rape leaves. *Food and Bioprocess Technology* **4**, 1314-1321.
- Lu, Z. H., and Collado, L. S. (2010). Rice and starch-based noodles. In "Asian Noodles" (G. G. Hou, ed.), pp. 393-431. John Wiley & Sons, Inc.
- Lund, D. B. (1986). Kinetics of Physical Changes in Foods. In "Physical and Chemical Properties of Food", pp. 367. American Society of Agricultural Engineers, Michigan, USA.
- Mark, H. (2001). Fundamental of Near-Infrared Spectroscopy. In "Near-Infrared Applications in Biotechnology" (R. Raghavachari, ed.), pp. 293-321. Marcel Dekker, Inc., USA.
- Marshall, W. E., and Wadsworth, J. I. (1994). Introduction. In "Rice Science and Technology" (W. E. Marshall and J. I. Wadsworth, eds.). Marcel Dekker, New York, USA.

- Matsuzaki, A. (1995). Trends of breeding and varieties. In "Rice Post Harvest Technology" (A. Hosokawa, ed.), pp. 108. The Food Agency, Ministry of Agricultural, Forestry and Fisheries, Japan.
- McClure, W. F. (2007). Introduction. In "Near-Infrared Spectroscopy in Food Science and Technology" (Y. Ozaki, W. F. McClure and A. A. Christy, eds.), pp. 1-10. John Wiley & Sons, Inc., USA.
- Mutters, R. G., and Thompson, J. F. (2009). Rice quality in the global market. In "Rice Quality Handbook" (R. G. Mutters and J. F. Thompson, eds.). University of California, Agriculture and Natural Resources, California, USA.
- Naes, T., Isaksson, T., Fearn, T., and Davies, T. (2002). "Multivariate Calibration and Classification," NIR Publication, Chichester.
- National Bureau of Agricultural Commodity and Food Standards (2012). *Thai Agricultural Standard (TAS) 4004-2012 Rice* [Online]. Available from: <http://www.acfs.go.th/standard/download/RICE-1.pdf> [2013, January 28].
- Noomhorm, A., Kongseree, N., and Apintanapong, M. (1997). Effect of aging on the quality of glutinous rice crackers. *Cereal chemistry* **74**, 12-15.
- Norkaew, O., Boontakham, P., Dumri, K., Noenplab, A. N. L., Sookwong, P., and Mahatheeranont, S. (2017). Effect of post-harvest treatment on bioactive phytochemicals of Thai black rice. *Food Chemistry* **217**, 98-105.
- Osborne, B. G. (2000). Near-infrared spectroscopy in food analysis. *Encyclopedia of analytical Chemistry*.
- Osborne, B. G. (2006). Applications of near infrared spectroscopy in quality screening of early-generation material in cereal breeding programmes. *Journal of near infrared spectroscopy* **14**, 93-101.
- Osborne, B. G., Fearn, T., and Hindle, P. H. (1993a). Introduction. In "Practical NIR Spectroscopy with Applications in Food and Beverage Analysis", pp. 1-12. Longman Singapore Publishers (Pte) Ltd., Singapore.
- Osborne, B. G., Mertens, B., Thompson, M., and Fearn, T. (1993b). The authentication of Basmati rice using near infrared spectroscopy. *J. Near Infrared Spectrosc* **1**, 77-84.
- Ozaki, Y., Morita, S., and Du, Y. (2007). Spectral analysis. In "Near-Infrared Spectroscopy in Food Science and Technology" (Y. Ozaki, W. F. McClure and A. A. Christy, eds.), pp. 47-72. John Wiley & Sons, Inc., USA.
- Pal, V., Pandey, J., and Sah, P. (1999). Effect of degree of polish on proximate composition of milled rice. *Journal of food science and technology* **36**, 160-162.
- Paraginski, R. T., Vanier, N. L., Berrios, J. D. J., de Oliveira, M., and Elias, M. C. (2014). Physicochemical and pasting properties of maize as affected by storage temperature. *Journal of Stored Products Research* **59**, 209-214.
- Park, C. E., Kim, Y. S., Park, K. J., and Kim, B. K. (2012). Changes in physicochemical characteristics of rice during storage at different temperatures. *Journal of stored products research* **48**, 25-29.
- Park, I., Kim, S. H., Chung, I. M., and Shoemaker, C. F. (2013). Effect of amylopectin long chains on measured amylose content and their correlation with pasting properties. *Starch-Stärke* **65**, 227-235.
- Perez, C. M., and Juliano, B. O. (1981). Texture changes and storage of rice. *Journal of Texture Studies* **12**, 321-333.

- Posom, J., and Sirisomboon, P. (2014). Evaluation of the thermal properties of *Jatropha curcas* L. kernels using near-infrared spectroscopy. *Biosystems Engineering* **125**, 45-53.
- Ramesh, M., Bhattacharya, K., and Mitchell, J. (2000). Developments in understanding the basis of cooked-rice texture. *Critical Reviews in Food Science and Nutrition* **40**, 449-460.
- Rice Department (2016). *Rice variety* [Online]. Available from: <http://www.brrd.in.th/rkb/varieties/index.php.htm> [2016, Sep 14].
- Ricepedia (2016). *Cultivated rice species* [Online]. Available from: <http://www.ricepedia.org/rice-as-a-plant/rice-species/cultivated-rice-species> [2016, Sep 14].
- Ritthiruangdej, P. (2006). Evaluation of Thai fish sauce qualities by Near-Infrared Spectroscopy, Kasetsart University.
- Rizvi, A., and Tong, C. (1997). Fractional conversion for determining texture degradation kinetics of vegetables. *Journal of Food Science* **62**, 1-7.
- Rosell, C. M., and Gómez, M. (2014). Rice. In "Bakery Products Science and Technology" (W. Zhou, Y. H. Hui, I. D. Leyn, M. A. Pagani, C. M. Rosell, J. D. Selman and N. Therdthai, eds.), pp. 89-106. John Wiley & Sons, Ltd.
- Shahin, M. A., Symons, S. J., and Hatcher, D. W. (2014). Quantification of mildew damage in soft red winter wheat based on spectral characteristics of bulk samples: a comparison of visible-near-infrared imaging and near-infrared spectroscopy. *Food and Bioprocess Technology* **7**, 224-234.
- Shao, Y., Cen, Y., He, Y., and Liu, F. (2011). Infrared spectroscopy and chemometrics for the starch and protein prediction in irradiated rice. *Food chemistry* **126**, 1856-1861.
- Shao, Y., and He, Y. (2009). Measurement of soluble solids content and pH of yogurt using visible/near infrared spectroscopy and chemometrics. *Food and Bioprocess Technology* **2**, 229-233.
- Shih, F. F. (2004). Rice proteins. In "Rice Chemistry and Technology" (E. T. Champagne, ed.). AACC International, Inc., St Paul, MN.
- Singh, N., Kaur, L., Sodhi, N. S., and Sekhon, K. S. (2005). Physicochemical, cooking and textural properties of milled rice from different Indian rice cultivars. *Food Chemistry* **89**, 253-259.
- Singh, V. (1998). Rice research finds no takers in the developed world. In "The Economic Times", India.
- Sirisomboon, C. D., Putthang, R., and Sirisomboon, P. (2013). Application of near infrared spectroscopy to detect aflatoxigenic fungal contamination in rice. *Food Control* **33**, 207-214.
- Sirisontaralak, P., and Noomhorm, A. (2007). Changes in physicochemical and sensory-properties of irradiated rice during storage. *Journal of stored products research* **43**, 282-289.
- Skoog, D. A., Holler, F. J., and Nieman, T. A. (1998). "Principles of Instrumental Analysis," Harcourt Brace College Publishers, Chicago.
- Smanalieva, J., Salieva, K., Borkoev, B., Windhab, E. J., and Fischer, P. (2015). Investigation of changes in chemical composition and rheological properties of Kyrgyz rice cultivars (Ozgon rice) depending on long-term stack-storage after harvesting. *LWT-Food Science and Technology* **63**, 626-632.

- Sodhi, N. S., Singh, N., Arora, M., and Singh, J. (2003). Changes in physico-chemical, thermal, cooking and textural properties of rice during aging. *Journal of food processing and preservation* **27**, 387-400.
- Soponronnarit, S., Chiawwet, M., Prachayawarakorn, S., Tungtrakul, P., and Taechapiroj, C. (2008). Comparative study of physicochemical properties of accelerated and naturally aged rice. *Journal of Food Engineering* **85**, 268-276.
- Szigedi, T., Lénárt, J., Dernovics, M., Turza, S., and Fodor, M. (2012). Protein content determination in Brassica oleracea species using FT-NIR technique and PLS regression. *International Journal of Food Science & Technology* **47**, 436-440.
- Takeda, Y., Hizukuri, S., and Juliano, B. O. (1987). Structures of rice amylopectins with low and high affinities for iodine. *Carbohydrate Research* **168**, 79-88.
- Tananuwong, K., and Malila, Y. (2011). Changes in physicochemical properties of organic hulled rice during storage under different conditions. *Food Chemistry* **125**, 179-185.
- Tavakolian, M. S., Silaghi, F. A., Fabbri, A., Molari, G., Giunchi, A., and Guarnieri, A. (2013). Differentiation of post harvest date fruit varieties non-destructively using FT-NIR spectroscopy. *International Journal of Food Science & Technology* **48**, 1282-1288.
- Teo, C., Karim, A. A., Cheah, P., Norziah, M., and Seow, C. (2000). On the roles of protein and starch in the aging of non-waxy rice flour. *Food Chemistry* **69**, 229-236.
- Thai Rice Foundation under Royal Patronage (2006). *About rice* [Online]. Available from: http://www.thairice.org/html/aboutrice/about_rice2.htm [2016, Sep 14].
- Thanathornvarakul, N., Anuntagool, J., and Tananuwong, K. (2016). Aging of low and high amylose rice at elevated temperature: Mechanism and predictive modeling. *Journal of Cereal Science* **70**, 155-163.
- Tsuchikawa, S. (2007). Sampling Techniques. In "Near-Infrared Spectroscopy in Food Science and Technology" (Y. Ozaki, W. F. McClure and A. A. Christy, eds.), pp. 133-143. John Wiley & Sons, Inc., USA.
- Tsuchikawa, S., and McClure, W. F. (2007). Time-of-Flight Spectroscopy. In "Near-Infrared Spectroscopy in Food Science and Technology" (Y. Ozaki, W. F. McClure and A. A. Christy, eds.), pp. 109-119. John Wiley & Sons, Inc., USA.
- Tulyathan, V., and Leeharatanaluk, B. (2007). Changes in quality of rice (*Oryza sativa* L.) cv. Khao Dawk Mali 105 during storage. *Journal of food biochemistry* **31**, 415-425.
- Varavinit, S., Shobsngob, S., Varayanond, W., Chinachoti, P., and Naivikul, O. (2003). Effect of amylose content on gelatinization, retrogradation and pasting properties of flours from different cultivars of Thai rice. *Starch-Stärke* **55**, 410-415.
- Villareal, C. P., De La Cruz, N. M., and Juliano, B. O. (1994). Rice amylose analysis by near-infrared transmittance spectroscopy. *Cereal Chemistry* **71**, 292-296.
- Woo, H. D., We, G. J., Kang, T. Y., Shon, K. H., Chung, H. W., Yoon, M. R., Lee, J. S., and Ko, S. (2015). Physicochemical and Gelatinization Properties of Starches Separated from Various Rice Cultivars. *Journal of food science* **80**, E2208-E2216.

- Workman, J. (2001). NIR spectroscopy calibration basics. In "Handbook of Near-Infrared Analysis" (D. A. Burns and E. W. Ciurczak, eds.), pp. 91-128. Marcel Dekker, New York.
- Workman, J. J., and Weyer, L. (2008). Introduction to Near-Infrared Spectra. In "Practical Guide to Interpretive Near-Infrared Spectroscopy", pp. 1-21. CRC Press, USA.
- Wu, D., Nie, P., He, Y., and Bao, Y. (2012). Determination of calcium content in powdered milk using near and mid-infrared spectroscopy with variable selection and chemometrics. *Food and Bioprocess Technology* **5**, 1402-1410.
- Wu, J., and Shi, C. (2004). Prediction of grain weight, brown rice weight and amylose content in single rice grains using near-infrared reflectance spectroscopy. *Field Crops Research* **87**, 13-21.
- Wu, J., and Shi, C. (2007). Calibration model optimization for rice cooking characteristics by near infrared reflectance spectroscopy (NIRS). *Food chemistry* **103**, 1054-1061.
- Xie, L., Tang, S., Chen, N., Luo, J., Jiao, G., Shao, G., Wei, X., and Hu, P. (2014). Optimisation of near-infrared reflectance model in measuring protein and amylose content of rice flour. *Food chemistry* **142**, 92-100.
- Yu, Y., Wing, R. A., and Li, J. (2013). Grain quality. In "Genetics and Genomics of Rice" (Q. Zhang and R. A. Wing, eds.), pp. 237-254. Springer Science+Business Media, New York, USA.
- Zhang, B., Rong, Z., Shi, Y., Wu, J., and Shi, C. (2011). Prediction of the amino acid composition in brown rice using different sample status by near-infrared reflectance spectroscopy. *Food Chemistry* **127**, 275-281.
- Zhou, Z., Robards, K., Helliwell, S., and Blanchard, C. (2002a). Ageing of stored rice: changes in chemical and physical attributes. *Journal of Cereal Science* **35**, 65-78.
- Zhou, Z., Robards, K., Helliwell, S., and Blanchard, C. (2002b). Composition and functional properties of rice. *International journal of food science & technology* **37**, 849-868.
- Zhou, Z., Robards, K., Helliwell, S., and Blanchard, C. (2003). Effect of rice storage on pasting properties of rice flour. *Food Research International* **36**, 625-634.
- Zhou, Z., Robards, K., Helliwell, S., and Blanchard, C. (2007). Effect of storage temperature on cooking behaviour of rice. *Food Chemistry* **105**, 491-497.
- Zhou, Z., Robards, K., Helliwell, S., and Blanchard, C. (2010). Effect of storage temperature on rice thermal properties. *Food Research International* **43**, 709-715.
- Zhou, Z., Wang, X., Si, X., Blanchard, C., and Strappe, P. (2015). The ageing mechanism of stored rice: A concept model from the past to the present. *Journal of Stored Products Research* **64**, 80-87.
- Zhu, L.-J., Liu, Q.-Q., Wilson, J. D., Gu, M.-H., and Shi, Y.-C. (2011). Digestibility and physicochemical properties of rice (*Oryza sativa* L.) flours and starches differing in amylose content. *Carbohydrate Polymers* **86**, 1751-1759.

APPENDIX



จุฬาลงกรณ์มหาวิทยาลัย
CHULALONGKORN UNIVERSITY

APPENDIX A

CHEMICAL ANALYSIS PROCEDURES

A.1 Moisture content (AOAC, 2012)

Apparatus

1. Aluminum pan
2. Hot air oven (Binder, model ED/FD, Germany)
3. Weighing machine (4 digits) (Sartorius, BSA224S, Germany)
4. Desiccator

Procedures

1. The empty aluminum pans was heated at 105 °C until weight constant and cooled down in desiccator.
2. Three gram of the sample was weighed into pre-weighed aluminum pan and dried at 105 °C for 8 hours in a hot air oven.
3. The heated aluminum pan and sample was removed to desiccator for cooling.
4. The aluminum pan and sample was weighed after cooling.
5. Drying is repeated until constant weight is achieved.
6. Moisture content could calculate from equation A.1.

$$\text{Moisture content (\% wet basis)} = \frac{W_2 - W_3}{W_2 - W_1} \times 100 \quad (\text{A.1})$$

W_1 : Constant weight (g) of aluminum pan

W_2 : Weight (g) of sample with aluminum pan before drying

W_3 : Weight (g) of sample with aluminum pan after drying

A.2 Protein content using Kjeldahl method (AOAC, 2012)

Apparatus

1. Filter paper (Whatman No.41)
2. Weighing machine (4 digits) (Sartorius, BSA224S, Germany)
3. Kjeldahl tube (Buchi, Switzerland)
4. Buchi digestion unit (Buchi, model K-424, Switzerland)
5. Buchi scrubber (Buchi, model B-414, Switzerland)
6. Distillation apparatus (Buchi, model B-324, Switzerland)

Reagent

1. Selenium mixture (Merck, Germany)
2. Sulphuric acid 98% (QRëC®, New Zealand)
3. Sodium hydroxide (QRëC®, New Zealand)
4. Boric acid (Univar, Ajax Finechem, Australia)
5. Hydrochloric acid 37% (QRëC®, New Zealand)
6. Mixed indicator solution: methyl red- methylene blue

Procedures

1. One gram of the sample was weighed into filter paper (Whatman No.41) and moved to Kjeldahl tube.
2. Add 5 gram of selenium mixture and 20 mL of sulphuric acid
3. Manage a blank test following the method but used 1 mL of distilled water substitute for the sample
4. Place the tube on the Buchi digestion unit with Buchi scrubber and heat until to obtain clear red-brown solution
5. Cooled the sample to room temperature
6. Add 50 mL of 4% (w/v) boric acid solution into 250 mL flask, add 2 drops of the indicator solution, mix and place flask under the condenser of the distillation apparatus with the distillation mode such as
 - Distilled water: 50 mL
 - 50% NaOH: 60 mL
 - Distillation time: 5 min
 - Steam: 100%
7. Titrate the solution in the flask with 0.1 N HCl until obtained claret solution
8. Record the volume of 0.1 N HCl
9. Protein content could calculate from equation A.2.1 and A.2.2, respectively

$$\text{Total nitrogen (\% wet basis)} = \frac{(V - B) \times N \times 1.4}{W} \quad (\text{A.2.1})$$

V: Volume (mL) of 0.1 N HCl required for the sample titration

B: Volume (mL) of 0.1 N HCl required for the blank test

N: Normality factor of HCl solution

W: weight of sample (g)

$$\text{Protein content (\% wet basis)} = \text{Total nitrogen (\%)} \times 5.95 \quad (\text{A.2.2})$$

5.95: Multiply factor for used to obtain rice protein (%)

A.3 Lipid content (AOAC, 2012)

Apparatus

1. Filter paper (Whatman No.1)
2. Weighing machine (4 digits)
3. Extraction thimbles
4. Soxhlet
5. Rotary evaporator
6. Hot air oven
7. Desiccator

Reagent

1. Petroleum ether (QRëC®, New Zealand)

Procedures

1. Dried flat bottom flask at 105 °C in hot air oven for 1 hour or until constant weight and cooled down in desiccator
2. Weigh 4 gram of sample (without moisture) on filter paper and wrap
3. Move the filter paper (Whatman No.1) with sample into extraction thimble
4. Place the extraction thimble in the Soxhlet extraction and connected a weighed flat bottom flask containing 250 mL petroleum ether
5. Connect the extractor to a reflux condenser
6. Extract fat for 4 hours at condensation rate of 5-6 drops/second
7. Evaporated the petroleum ether by rotary evaporator
8. Dried flat bottom flask at 100 °C in hot air oven until constant weight, cooled down in desiccator and weigh
9. Lipid content could calculate from equation A.3

$$\text{Lipid content (\% dry basis)} = \frac{W_2 - W_3}{W_1} \times 100 \quad (\text{A.3})$$

W₁: Weight (g) of sample

W_2 : Weight (g) of flat bottom flask with lipid

W_3 : Weight (g) of flat bottom flask without lipid

A.4 Crude fiber content (AOAC, 2012)

Apparatus

1. Büchner funnel
2. Crucible
3. Desiccator
4. Hot air oven
5. Muffle furnace
6. Weighing machine (4 digits)
7. Filter paper (Whatman No. 1 and 42)

Reagent

1. 98% Sulphuric acid
2. Sodium hydroxide
3. 95% Ethanol

Procedures

1. Weigh 3 gram of sample (without lipid) obtained from the determination of lipid content (W_1) into 600 mL beaker
2. Add 200 mL of 1.25% sulphuric acid in the beaker
3. Heat at Boiling point for 30 minute (control volume of solution with boiling water)
4. Filter the content from 3. Through a Büchner funnel with a filter paper (Whatman No. 1)
5. Wash with boiling water until acid-free
6. Remove the content from 5. into the original beaker and add 200 mL of 1.25% Sodium hydroxide
7. Heat at Boiling point for 30 minute (control volume of solution with boiling water)
8. Filter the content from 3. Through a Büchner funnel with a filter paper (Whatman No. 42)
9. Wash with boiling water until base-free

10. Wash twice with 25 mL of 95% ethanol
11. Dried the filter paper with content (from 10.) at 105 °C until constant weigh (W_2)
12. Transfer the dried sample into crucible (pre-weigh)
13. Ashing in muffle furnace at 550 °C until obtain the white ash
14. Cool down the crucible in a desiccator and weight (W_3)
15. Crude fiber content could calculate from equation A.4

$$\text{Crude fiber content (\% dry basis)} = \frac{W_2 - W_3}{W_1} \times 100 \quad (\text{A.4})$$

W_1 : Weight (g) of sample

W_2 : Weight (g) of insoluble matter

W_3 : Weight (g) of ash

A.5 Ash content (AOAC, 2012)

Apparatus

1. Crucible
2. Muffle furnace (Fisher Scientific, Isotemp, USA)
3. Hot plate
4. Desiccator
5. Weighing machine (4 digits) (Sartorius, BSA224S, Germany)

Procedures

1. Ashing the crucible by muffle furnace at 550 °C for 1 hour or until constant weight and cooled down in desiccator (W_1)
2. Two gram of the sample (W_2) was weighed into pre-weighed crucible
3. Ashing the crucible with sample from 2. by hot plate in fume-hood until the sample become thoroughly charred and without smoke
4. Ashing the crucible with sample from 3. By muffle furnace at 550 °C until obtain the white ash with constant weight and cooled down in desiccator (W_3)
5. Ash content could calculate from equation A.5

$$\text{Ash content (\% wet basis)} = \frac{W_3 - W_1}{W_2 - W_1} \times 100 \quad (\text{A.5})$$

W_1 : Weight (g) of crucible

W_2 : Weight (g) of sample with crucible before ashing

W_3 : Weight (g) of sample with crucible after ashing

A.6 Carbohydrate content (AOAC, 2012)

Calculation

$$\text{Carbohydrate content (\% dry basis)} = 100 - \%(\text{Protein} + \text{Lipid} + \text{Crude fiber} + \text{Ash}) \quad (\text{A.6})$$

A.7 Amylose content

Defatted sample preparation (Gibson *et al.*, 1997)

1. 20-25 mg rice flour were weighed into a 10 mL screw capped Kimax tube
2. The sample was dispersed in 1 mL DMSO
3. Mix at low speed on a vortex mixer
4. Place the tube in a boiling water bath for 1 minute
5. Remove the tube and vortex at high speed
6. Return the tube to the boiling water bath for 15 minute with intermittent stirring
7. Remove the tube from the boiling water bath and mix at high speed on a vortex mixer
8. Add 4 mL of 95%(v/v) ethanol to precipitate the sample
9. Add 2 mL of 95%(v/v) ethanol and mix by inversion
10. Stand at room temperature for 15 minute
11. Centrifuge at 2000g for 5 minute
12. Discard the supernatant
13. Drain on tissue paper for 10 min
14. Collect the precipitate (defatted sample)

Amylose content by amperometric titration (Takeda *et al.*, 1987)

1. Dissolve 100-120 mg of defatted sample in 5 mL of M KOH
2. Add 80 mL of water, 10 mL of M HCl and 5 mL of 0.4M KI
3. Stir at 25 °C
4. Titrate continuously (~0.1 mL/min) with 1.67 mM of KIO₃ by a micro-tube pump and monitor by measurement of the electric current with Pt electrodes

5. Determine the blue value
6. Calculate amylose content from equation A.7

$$\text{Amylose content (\%)} = \frac{\text{Iodine affinity of starch}}{\text{Iodine affinity of amylose}} \times 20 \times 100 \quad (\text{A.7})$$

A.8 Electrophoresis of rice protein (modified from Laemmli (1970) and Iida *et al.* (1993))

Apparatus

1. OmniPAGE Electrophoresis equipment (Cleaver Scientific Ltd, CVS10DSYS, UK)
2. Power supply (Major Science, MS300V, USA)
3. Centrifuge (Eppendorf, MiniSpin plus, Germany)
4. Gel documentation (Syngene, InGeniusL, UK)
5. Weighing machine (4 digits) (Sartorius, BSA224S, Germany)

Reagent

1. Perfect Protein™ Markers, 10-225 kDa (Navogen®, Merck Millipore, USA)
2. Acrylamide (Fluka, Sigma-Aldrich Co. LLC., Switzerland)
3. N,N'-Methylenebisacrylamide (Fluka, Sigma-Aldrich Co. LLC., Switzerland)
4. Tris (Hydroxymethyl) aminomethane (Tris-base) (CARLO ERBA Reagents, France)
5. Sodium dodecyl sulfate (SDS) (APS, Ajax Finechem, Australia)
6. Ammonium persulfate (APS) (OmniPur®, Merck Millipore, USA)
7. N,N,N',N'-Tetramethyl ethylenediamine (TEMED) (OmniPur®, Merck Millipore, USA)
8. Hydrochloric acid 37%(QRëC®, New Zealand)
9. Urea(Unilab, Ajax Finechem, Australia)
10. Glycerol (Univar, Ajax Finechem, Australia)
11. Glycine (Research Organics, USA)

12. Glacial Acetic acid (QRëC®, New Zealand)
13. 95% Ethanol
14. 1-Butanol (AnalR®, VWR International Ltd., UK)
15. Coomassie brilliant blue R-250 (Imperial Chemical Industries PLC, Merck Millipore, Germany)
16. Bromophenol Blue sodium salt (OmniPur®, Merck Millipore, USA)

Gel preparation

1. Set the gel preparation equipment
2. Prepare separating gel solution (Table A.8.1) by mix all reagent except APS and TEMED
3. Add APS and TEMED and mix together
4. Add the solution into empty space between 2 glasses (5.6 mL solution/gel)
5. Add 1-butanol to cover the surface of gel
6. Set to gel polymerization for 40 minute
7. Remove 1-butanol from the gel surface and rinse the gel surface with distilled water
8. Prepare stacking gel solution (Table A.8.1) by mix all reagent except APS and TEMED
9. Add APS and TEMED and mix together
10. Add the solution into empty space between 2 glasses over the separating gel (1 mL solution/gel)
11. Set the comb
12. Set to gel polymerization for 2 hour and 20 minute
13. Move the gel preparation equipment into the tank
14. Add electrode running gel buffer (Table A.8.2) to submerge the gel

Table A.8.1 Composition of separating gel and stacking gel

Composition	Separating gel	Stacking gel
Distilled water	8.02 mL	6.10 mL
1.5 M Tris-base, pH 8.8	5.00 mL	-
0.5 M Tris-base, pH 6.8	-	2.50 mL
10% Sodium dodecyl sulfate	200 μ L	100 μ L
Acrylamide solution (30% T, 2.67% C)	6.67 mL	1.33 mL
10% Ammonium persulfate	100 μ L	50 μ L
Tetramethyl ethylenediamine (TEMED)	10 μ L	5 μ L
Total volume	20 mL	10 mL

Note: % T means that the total solids content, % C means that the cross-linker acrylamide monomer.

Table A.8.2 Composition of electrode running gel buffer

Composition	Quantity
Distilled water	1 L
Tris-base	3.02 g
SDS	1.00 g
Glycine	14.40 g

APPENDIX B
PHYSICAL ANALYSIS PROCEDURES

B.1 Pasting properties

Table B.1 Temperature profile (standard profile 1)

Procedures	Temperature (°C)	Speed (rpm)	Time (min:sec)
1	50	960	0:00
2	50	160	0:10
3	50	160	1:00
4	95	160	4:42
5	95	160	7:12
6	50	160	11:00
End of measurement			13:00

APPENDIX C
SUPPLEMENTARY DATA

C.1 Gelatinization temperature range and enthalpy of amylose/lipid complexes of rice flour during storage at 8 °C and 30 °C.

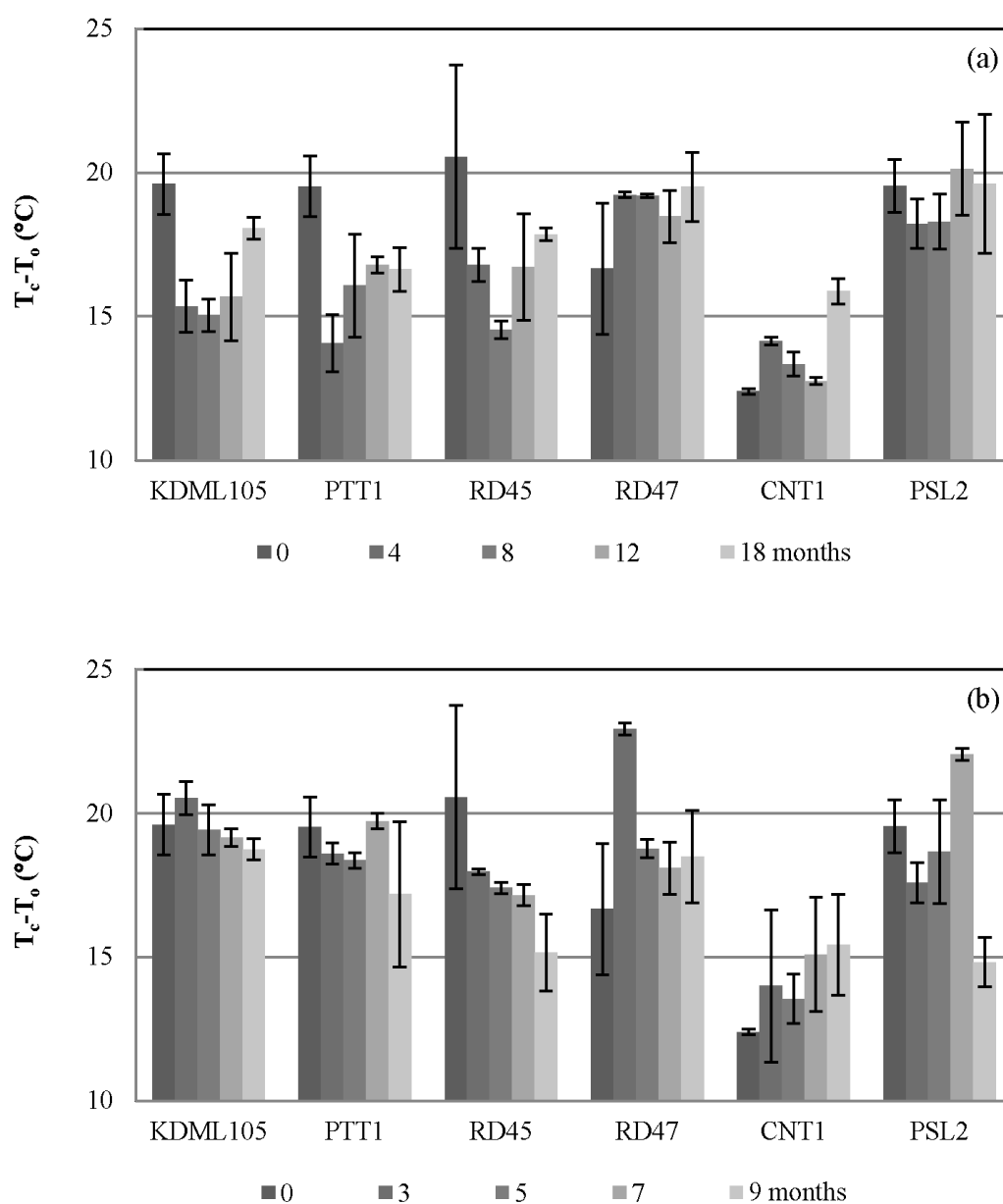


Figure C.1.1 Gelatinization temperature range (T_c-T_0) of rice flour during storage at (a) 8 °C and (b) 30 °C

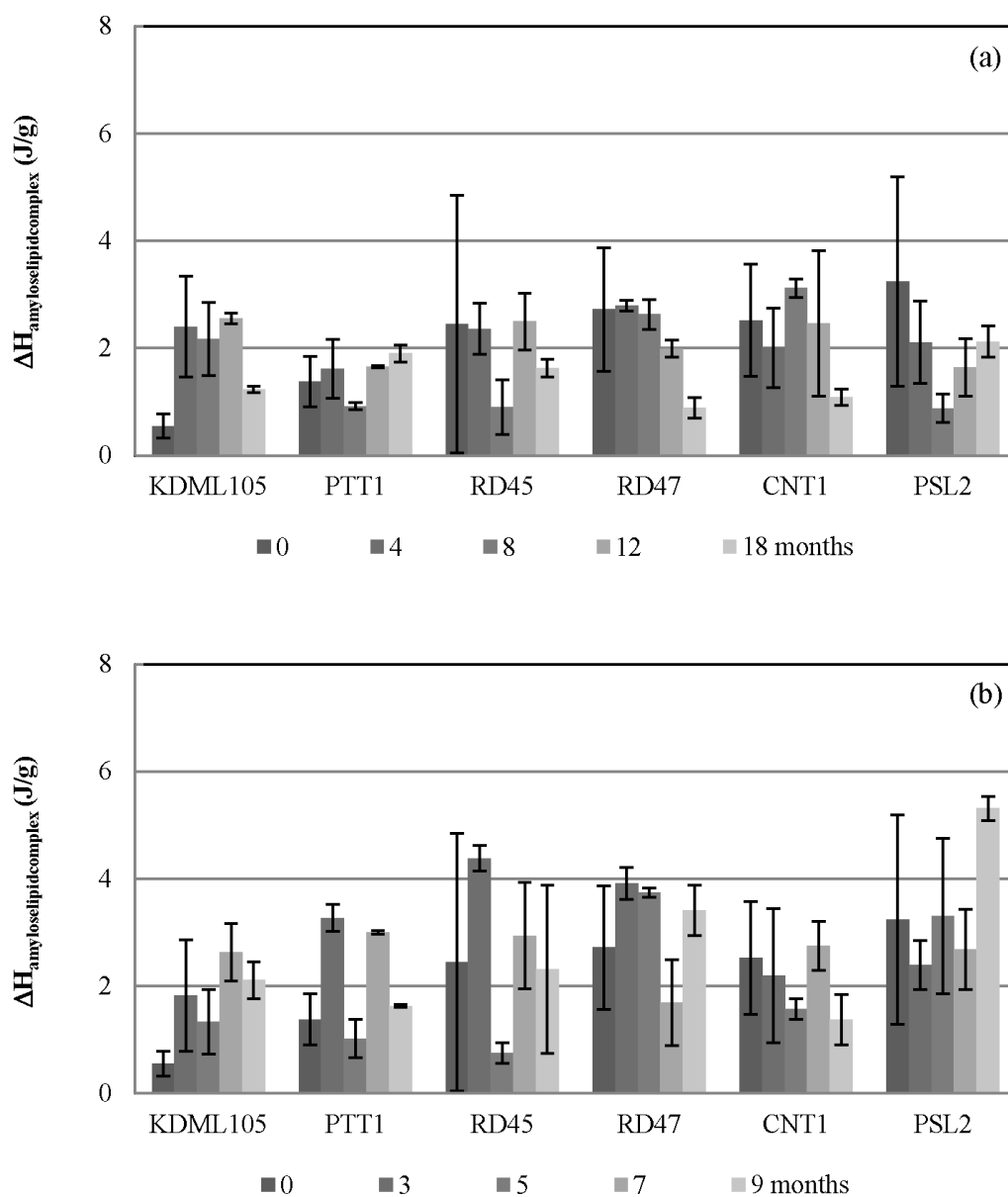


Figure C.1.2 Enthalpy of amylose/lipid complexes (ΔH_{al}) of rice flour during storage at (a) 8 °C and (b) 30 °C

C.2 NIR spectra

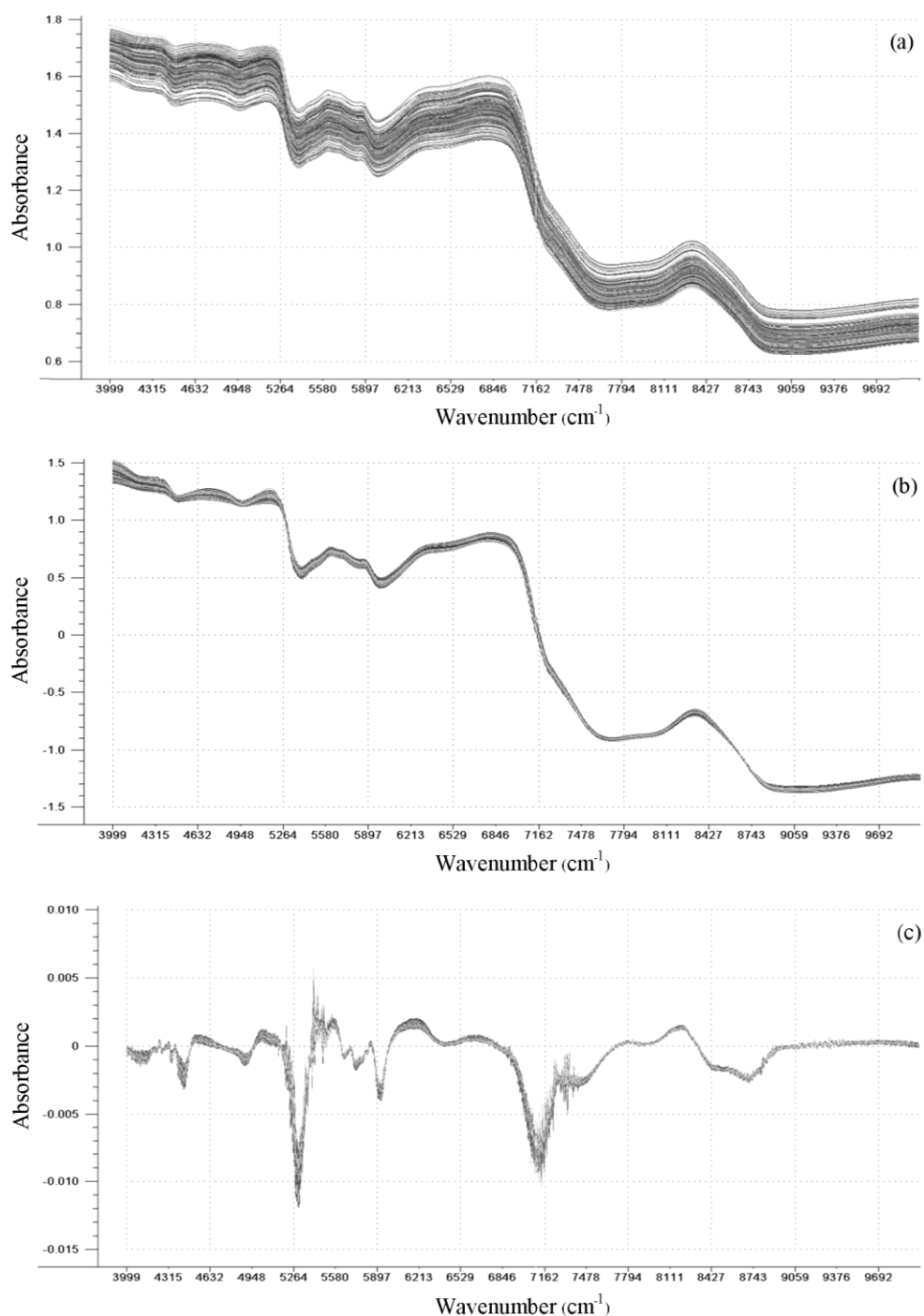


Figure C.2.1 NIR spectra of rice grains during storage at 8 °C and 30 °C (a) Raw spectra (b) SNV preprocessing spectra for HRY (c) 1st derivative preprocessing spectra for MCT (d) Moving average smoothing preprocessing spectra for SL (e) Savitzky-Golay smoothing preprocessing spectra for WU (f) 1st derivative preprocessing spectra for VER (g) SNV preprocessing spectra for PT (h) SNV preprocessing spectra for PV (i) 1st derivative preprocessing spectra for BD (j) 2nd derivative preprocessing spectra for SB (k) 1st derivative preprocessing spectra for H (l) 1st derivative preprocessing spectra for Ad (m) 1st derivative preprocessing spectra for T_o (n) 2nd derivative preprocessing spectra for T_p (o) 2nd derivative preprocessing spectra for T_c

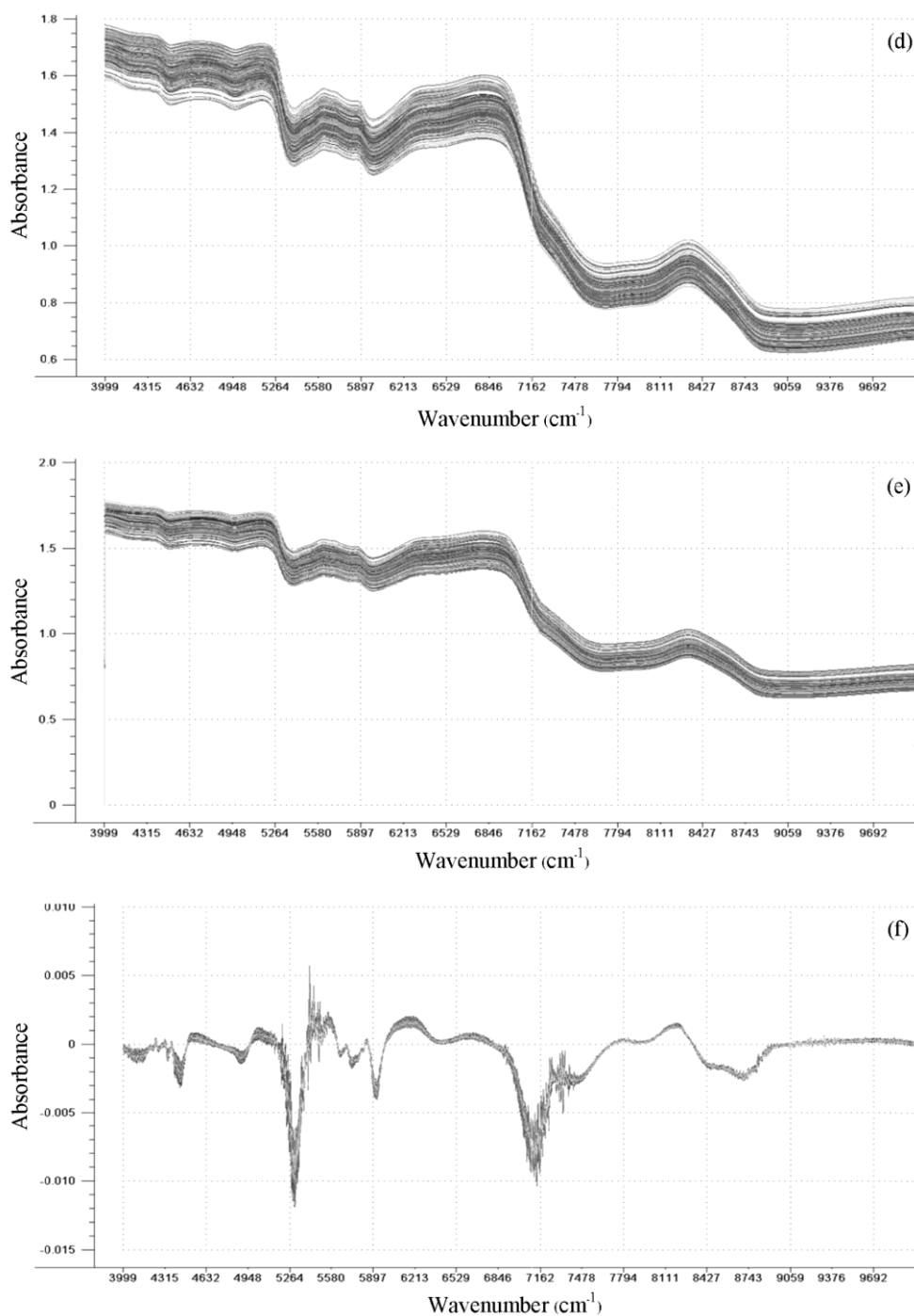


Figure C.2.1 NIR spectra of rice grains during storage at 8 °C and 30 °C (a) Raw spectra (b) SNV preprocessing spectra for HRY (c) 1st derivative preprocessing spectra for MCT (d) Moving average smoothing preprocessing spectra for SL (e) Savitzky-Golay smoothing preprocessing spectra for WU (f) 1st derivative preprocessing spectra for VER (g) SNV preprocessing spectra for PT (h) SNV preprocessing spectra for PV (i) 1st derivative preprocessing spectra for BD (j) 2nd derivative preprocessing spectra for SB (k) 1st derivative preprocessing spectra for H (l) 1st derivative preprocessing spectra for Ad (m) 1st derivative preprocessing spectra for T_o (n) 2nd derivative preprocessing spectra for T_p (o) 2nd derivative preprocessing spectra for T_c (cont...)

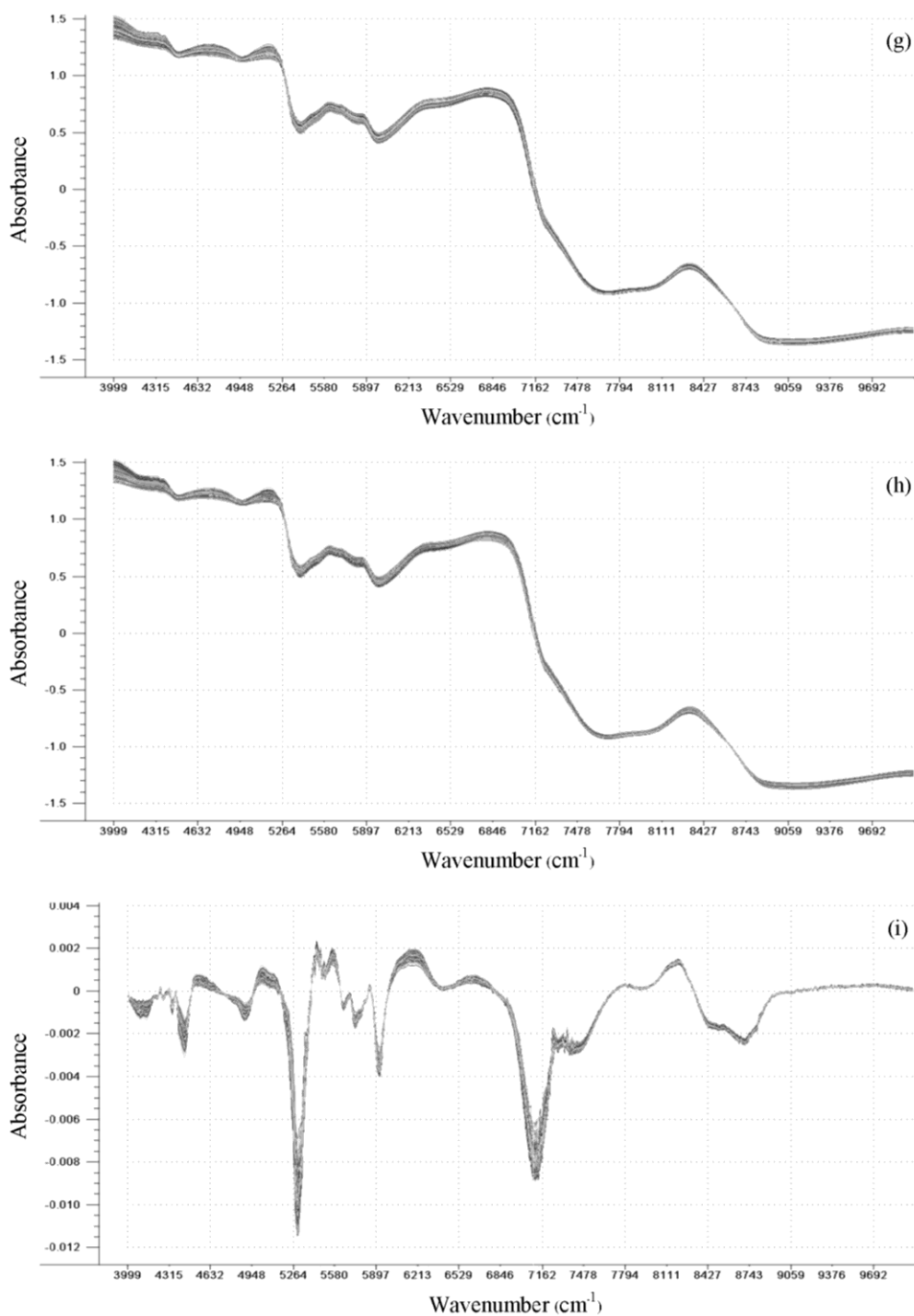


Figure C.2.1 NIR spectra of rice grains during storage at 8 °C and 30 °C (a) Raw spectra (b) SNV preprocessing spectra for HRY (c) 1st derivative preprocessing spectra for MCT (d) Moving average smoothing preprocessing spectra for SL (e) Savitzky-Golay smoothing preprocessing spectra for WU (f) 1st derivative preprocessing spectra for VER (g) SNV preprocessing spectra for PT (h) SNV preprocessing spectra for PV (i) 1st derivative preprocessing spectra for BD (j) 2nd derivative preprocessing spectra for SB (k) 1st derivative preprocessing spectra for H (l) 1st derivative preprocessing spectra for Ad (m) 1st derivative preprocessing spectra for T_o (n) 2nd derivative preprocessing spectra for T_p (o) 2nd derivative preprocessing spectra for T_c (cont...)

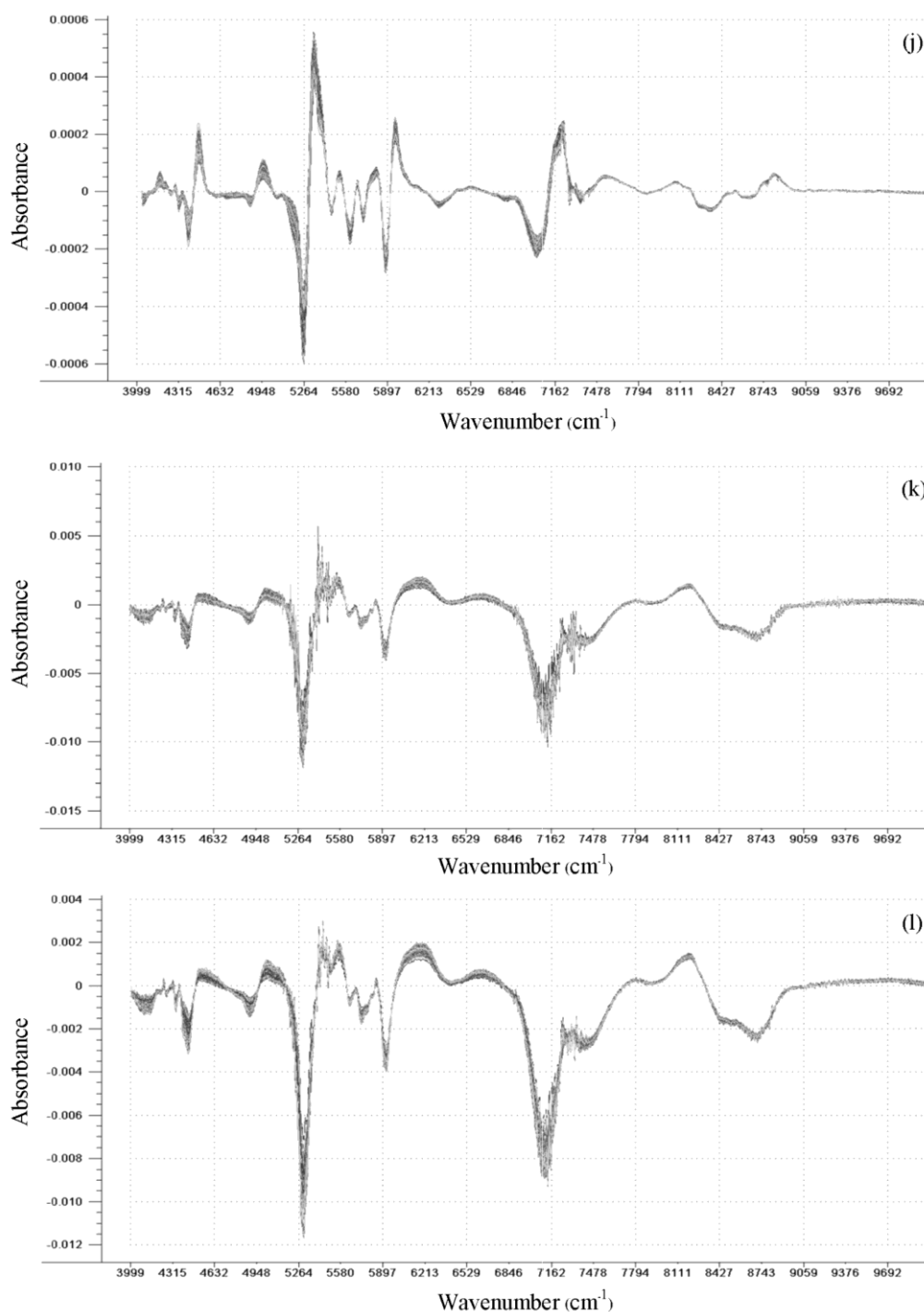


Figure C.2.1 NIR spectra of rice grains during storage at 8 °C and 30 °C (a) Raw spectra (b) SNV preprocessing spectra for HRY (c) 1st derivative preprocessing spectra for MCT (d) Moving average smoothing preprocessing spectra for SL (e) Savitzky-Golay smoothing preprocessing spectra for WU (f) 1st derivative preprocessing spectra for VER (g) SNV preprocessing spectra for PT (h) SNV preprocessing spectra for PV (i) 1st derivative preprocessing spectra for BD (j) 2nd derivative preprocessing spectra for SB (k) 1st derivative preprocessing spectra for H (l) 1st derivative preprocessing spectra for Ad (m) 1st derivative preprocessing spectra for T_o (n) 2nd derivative preprocessing spectra for T_p (o) 2nd derivative preprocessing spectra for T_c (cont...)

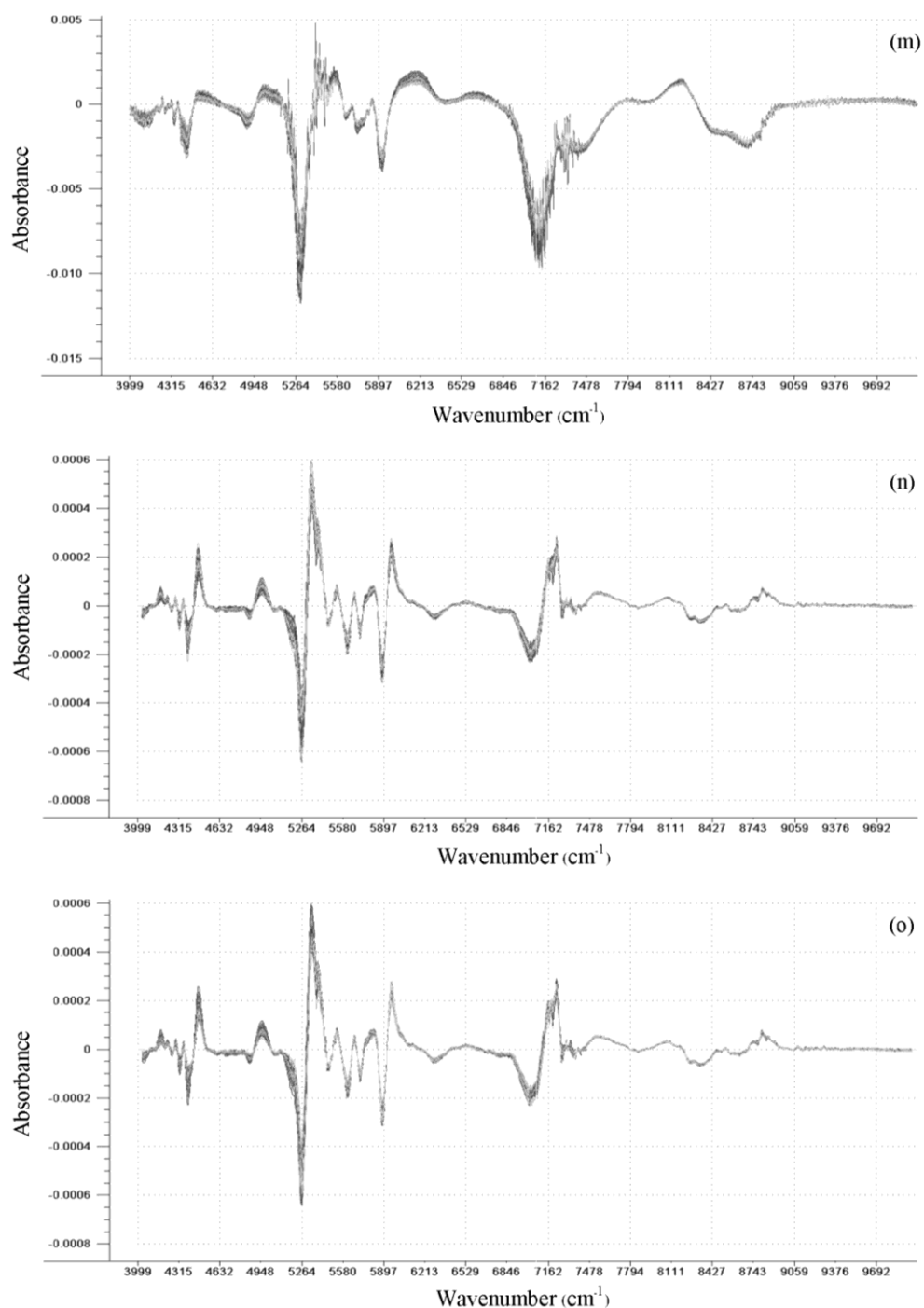


Figure C.2.1 NIR spectra of rice grains during storage at 8 °C and 30 °C (a) Raw spectra (b) SNV preprocessing spectra for HRY (c) 1st derivative preprocessing spectra for MCT (d) Moving average smoothing preprocessing spectra for SL (e) Savitzky-Golay smoothing preprocessing spectra for WU (f) 1st derivative preprocessing spectra for VER (g) SNV preprocessing spectra for PT (h) SNV preprocessing spectra for PV (i) 1st derivative preprocessing spectra for BD (j) 2nd derivative preprocessing spectra for SB (k) 1st derivative preprocessing spectra for H (l) 1st derivative preprocessing spectra for Ad (m) 1st derivative preprocessing spectra for T_o (n) 2nd derivative preprocessing spectra for T_p (o) 2nd derivative preprocessing spectra for T_c (cont...)

C.3 NIR model pattern

$$\text{Value} = a + \sum_{i=10000}^{4000} b_{\lambda} x_i$$

Note: a means constant at X intercept

b_{λ} means loading factor from spectra region of $10000 - 4000 \text{ cm}^{-1}$

x_i means new factor function from initial factor



C.4 Kinetics model parameters for changes in rice and flour properties during storage at 8 °C and 30 °C

Table C.4.1 Kinetics model parameters for changes in rice and flour properties during storage at 8 °C and 30 °C

Rice varieties	First order fractional conversion kinetics model parameters						Zero th order kinetics model parameters					
	30 °C			8 °C			30 °C			8 °C		
	A ₀	A _∞	k (week ⁻¹)	R ²	k (week ⁻¹)	R ²	A ₀	k (week ⁻¹)	R ²	k (week ⁻¹)	R ²	R ²
Solid loss (%)												
KDML105	3.3150	2.2200	0.0238	0.90	0.0034	0.26	3.2725	-0.0174	0.89	-0.0025	0.23	
PTT1	3.5059	1.3806	0.0072	0.88	0.0032	0.72	3.4984	-0.0139	0.90	-0.0061	0.73	
RD45	3.6532	2.8364	0.0297	0.90	0.0114	0.83	3.6073	-0.0147	0.88	-0.0058	0.75	
RD47	4.1790	3.8795	0.2049	0.81	-0.0018	0.05	4.0522	-0.0066	0.57	0.0031	-0.20	
CNT1	3.3211	2.6380	0.3318	0.93	0.0093	0.27	2.9669	-0.0131	0.51	0.0023	-1.44	
PSL2	4.5392	4.0698	0.5396	0.94	0.0231	0.18	4.2727	-0.0083	0.44	-7*10 ⁻⁷	-0.04	
Water uptake (%)												
KDML105	243.0512	275.1864	0.0384	0.78	0.0150	0.92	245.18	0.6793	0.81	0.2927	0.86	
PTT1	240.4357	260.1205	0.1708	0.82	0.0278	0.72	247.26	0.4925	0.72	0.1317	0.57	
RD45	242.2802	278.777	0.4822	0.93	0.0660	0.69	261.87	0.7009	0.51	0.2054	0.41	
RD47	207.1828	244.3575	0.1416	0.88	0.0444	0.81	219.67	0.8959	0.71	0.3908	0.77	
CNT1	270.4389	303.0424	0.4774	0.91	0.0624	0.92	288.01	0.6227	0.49	0.2977	0.71	
PSL2	219.1664	247.3296	0.0384	0.79	0.0106	0.91	221.14	0.5896	0.80	0.1895	0.79	

Table C.4.1 Kinetics model parameters for changes in rice and flour properties during storage at 8 °C and 30 °C (cont...)

Rice varieties	First order fractional conversion kinetics model parameters						Zero th order kinetics model parameters					
	30 °C			8 °C			30 °C			8 °C		
	A ₀	k (week ⁻¹)	R ²	A _∞	k (week ⁻¹)	R ²	A ₀	k (week ⁻¹)	R ²	k (week ⁻¹)	R ²	R ²
Volume expansion ratio												
KDML105	2.6335	0.0331	0.95	3.0633	0.0092	0.55	2.6613	0.0083	0.95	0.0025	0.55	0.55
PTT1	2.6268	0.2016	0.78	2.8711	0.0094	0.24	2.7487	0.0043	0.36	-0.0006	-0.70	-0.70
RD45	2.5748	0.1711	0.98	2.9207	0.0163	0.74	2.7193	0.0073	0.62	0.0007	0.17	0.17
RD47	2.6019	0.0846	0.61	2.9201	0.0258	0.55	2.6731	0.0078	0.54	0.0031	0.60	0.60
CNT1	2.8464	0.2616	0.97	3.3554	0.0374	0.82	3.0962	0.01	0.55	0.0049	0.59	0.59
PSL2	2.4245	0.1965	0.88	2.7803	0.0334	0.91	2.5702	0.008	0.64	0.0029	0.71	0.71
Pasting temp (°C)												
KDML105	74.3	0.017	0.98	84.4	0.0022	0.66	74.105	0.1429	0.97	0.024	0.48	0.48
PTT1	75.6	0.031	0.95	85.4	0.0034	0.60	75.321	0.2194	0.96	0.0346	0.38	0.38
RD45	74.9	0.033	0.96	85.2	0.0039	0.65	75.328	0.2044	0.92	0.027	0.60	0.60
RD47	81.97	0.03	0.96	91.43	0.0061	0.33	82.131	0.1841	0.92	0.0436	-0.20	-0.20
CNT1	79.27	0.029	0.97	90.02	0.0029	0.47	78.677	0.2446	0.98	0.0397	-0.35	-0.35
PSL2	83.83	0.023	0.96	91.39	0.0043	0.38	83.537	0.1418	0.96	0.0341	-0.03	-0.03
Peak viscosity (Pa.s)												
KDML105	3.721	0.028	0.84	2.563	0.0070	0.75	3.7203	-0.0233	0.88	-0.0067	0.63	0.63
PTT1	3.672	0.032	0.87	2.681	0.0080	0.54	3.6672	-0.0211	0.90	-0.0063	0.49	0.49
RD45	3.835	0.040	0.77	2.896	0.0087	0.74	3.7548	-0.0194	0.74	-0.0048	0.73	0.73
RD47	1.745	0.047	0.97	0.928	0.0088	0.61	1.6545	-0.0179	0.92	-0.0037	0.53	0.53
CNT1	2.923	0.031	0.93	1.450	0.0023	0.45	2.8983	-0.0303	0.96	-0.0027	0.46	0.46
PSL2	1.397	0.019	0.80	0.698	0.0027	0.34	1.3899	-0.0104	0.85	-0.0017	0.35	0.35

Table C.4.1 Kinetics model parameters for changes in rice and flour properties during storage at 8 °C and 30 °C (cont....)

Rice varieties	First order fractional conversion kinetics model parameters					Zero th order kinetics model parameters						
	A ₀	30 °C			8 °C		A ₀	30 °C			8 °C	
		k (week ⁻¹)	R ²	k (week ⁻¹)	R ²	k (week ⁻¹)		R ²	k (week ⁻¹)	R ²	k (week ⁻¹)	R ²
Breakdown (Pa.s)												
KDML105	2.227	0.053	0.0275	0.92	0.0047	0.78	2.1202	-0.0375	0.91	-0.0067	0.60	
PTT1	1.964	0.378	0.0397	0.86	0.0099	0.57	1.8237	-0.0326	0.82	-0.0088	0.20	
RD45	2.231	0.623	0.0455	0.90	0.0097	0.57	2.0598	-0.0348	0.85	-0.0082	0.37	
RD47	0.4920	0.0357	0.067	0.93	0.0130	0.32	0.4095	-0.0107	0.82	-0.0023	0.11	
CNT1	1.028	0	0.062	0.93	0.0079	0.31	0.8739	-0.0249	0.85	-0.0032	0.25	
PSL2	0.346	0	0.037	0.92	0.0064	0.18	0.3258	-0.0073	0.90	-0.0014	0.00	
Setback (Pa.s)												
KDML105	0.9179	1.3916	0.0375	0.95	0.0046	0.03	0.9589	0.0094	0.88	0.0006	-0.01	
PTT1	1.1147	1.7646	0.0241	0.92	0.0037	0.01	1.1414	0.0103	0.89	0.0011	-0.27	
RD45	1.0722	1.6113	0.0256	0.94	0.0028	0.00	1.0957	0.0089	0.92	0.0006	-0.16	
RD47	1.4942	0.5014	0.0814	0.93	0.0192	0.59	1.2863	-0.0245	0.84	-0.0078	0.19	
CNT1	2.1439	0.8043	0.0140	0.90	0.0068	0.39	2.1267	-0.0148	0.90	-0.0051	-0.33	
PSL2	1.2340	0.3188	0.0431	0.93	0.0124	0.50	1.1448	-0.0195	0.89	-0.0062	0.25	

Table C.4.1 Kinetics model parameters for changes in rice and flour properties during storage at 8 °C and 30 °C (cont...)

Rice varieties	First order fractional conversion kinetics model parameters				Zero th order kinetics model parameters			
	30 °C		8 °C		30 °C		8 °C	
	A ₀	k (week ⁻¹)	R ²	k (week ⁻¹)	R ²	A ₀	k (week ⁻¹)	R ²
Hardness (kg)								
KDML105	11.43	0.038	0.90	0.0128	0.43	11.433	0.0437	0.97
PTT1	11.38	0.039	0.87	0.0193	0.90	11.386	0.0533	0.94
RD45	10.54	0.032	0.95	0.0110	0.82	10.545	0.0528	0.95
RD47	14.869	0.011	0.83	0.0051	0.62	14.854	0.0462	0.86
CNT1	11.673	0.013	0.93	0.0054	0.60	11.718	0.0926	0.95
PSL2	13.900	0.047	0.94	0.0188	0.83	14.37	0.0938	0.90
Adhesiveness (kg.s)								
KDML105	0.723	0.0261	0.81	0.0005	0.16	0.7438	-0.0068	0.87
PTT1	0.759	0.0088	0.80	0.0006	0.16	0.7734	-0.0065	0.82
RD45	0.784	0.0296	0.87	0.0006	0.35	0.8303	-0.0079	0.93
RD47	0.152	0.0291	0.75	0.0047	0.40	0.1656	-0.0026	0.78
CNT1	0.224	0.0521	0.94	0.0124	0.80	0.2778	-0.0066	0.90
PSL2	0.182	0.0385	0.97	0.0109	0.87	0.1948	-0.0039	0.94

C.5 Conference proceeding

Chemical and Physical Changes of High and Low Amylose Rice during Storage

Sunee Jungtheerapanich and Jirarat Anuntagool *

Department of Food Technology, Faculty of Science, Chulalongkorn University,
254 Phayathai, Bangkok, 10330, Tel: +66 2218 5515-6, Fax: +66 2254 4314,
E-mail address: Jirarat.t@chula.ac.th

Written for presentation at the
2013 CIGR Section VII International Technical Symposium on

“Advanced food processing and quality management”

Guangzhou, China, 3-7 November, 2013

Abstract. *During rice storage, a number of chemical and physical changes occur. These changes include textural properties, pasting properties, thermal properties and others. Rice aging mechanisms involve starch, protein and lipids. External factors, e.g. temperature, moisture content, storage time and packaging, play an important role in either slowing down or accelerating aging of rice during storage. The aim of this research was to study aging of high and low amylose rice. Effects of storage temperatures and times on chemical and physical properties of high (CNT1) and low (PTT1) amylose rice were investigated. The samples were vacuum-packed in laminated aluminum bags and stored at 30°C for 6 months and 8°C for 12 months. Higher storage temperature and longer storage time led to a decrease in solid loss and breakdown, and an increase in water uptake, elongation ratio, cooked length-breadth ratio, volume expansion, pasting temperature and through viscosity at a greater extent when compared to lower storage temperature and shorter storage time. However, minimum cooking time, rice grain moisture content and protein content did not change.*

Keywords: High and low amylose rice, aging of rice, chemical and physical properties, storage temperature

Introduction

It has been known that aging causes various changes to rice. These changes include textural properties, pasting properties, thermal properties and others, e.g. increase in water uptake, volume expansion, hardness of cooked rice, cohesiveness of cooked rice, pasting temperature and setback, while solid loss, adhesiveness of cooked rice, peak viscosity and breakdown decreased (Jirathumkitkul, 1998; Zhou, Robards, Helliwell, & Blanchard, 2007; Soponronnarit, Chiawwet, Prachayawarakorn, Tungtrakul, & Taechapairoj, 2008; Likitwattanasade, 2009; Park, Kim, Park, & Kim, 2012). External factors, e.g. temperature, moisture content, storage time and packaging, play an important role in either slowing down or accelerating aging of rice during storage. Internal factors, such as protein, lipids and amylose are also responsible for the extent of rice aging. The aim of this research is to study aging of high and low amylose rice.

Materials and methods

1. Sample preparation

The paddy of Pathum Thani 1 (PTT1) from Khlong Luang Rice Research Center and Chai Nat 1 (CNT1) from Ratchaburi Rice Research Center) were vacuum-packed in laminated aluminum bags and stored at 8 °C for 12 months and 30 °C for 6 months.

2. Determination of chemical and physical properties

2 cultivars of rice were analyzed for chemical and physical properties. Moisture content and protein content were analyzed according to AOAC method section 32 (AOAC, 2005). Physical properties including cooking quality (minimum cooking time, solid loss, water uptake, elongation ratio, cooked length-breadth ratio and volume expansion) were determined following the method of Gujral & Kumar (2003) and Zhou et al. (2007) and pasting properties were determined using an RVA (standard profile 1; New Port Scientific Instrument and Engineer, Warriewater, Australia). Minimum cooking time that was needed to fully cook rice was determined by cooking 1 g of head rice grain in 10 ml of distilled water in test tube. Solid loss (%) and water uptake (%) were analyzed following the method that was modified from Gujral & Kumar (2003). Elongation ratio was calculated from length of 10 cooked rice grains divided by length of 10 uncooked rice grains. Cooked length-breadth ratio was calculated from length of 10 cooked rice grains divided by breadth of 10 cooked rice grains. Volume expansion ratio was calculated as the ratio of the volume of the cooked rice to the initial volume of the raw rice.

Results and discussion

Moisture content and protein content of rice during storage were slightly changed. It was found that minimum cooking time of PTT1 did not change during storage but minimum cooking time of CNT1 increased after storage for 3 months and 8 months at 30°C and 8°C, respectively. Solid loss of PTT1 and CNT1 decreased during storage. High amylose rice (CNT1) showed lower solid loss at the beginning and it continued to decrease over 4 months. High storage temperature had a greater influence on solid loss. Water uptake, elongation ratio, cooked length-breadth ratio and volume expansion of CNT1 were higher than those of PTT1 and the values continued to increase during storage. It was observed that pasting temperature and through viscosity of PTT1 and CNT1 increased during storage whereas breakdown decreased. Storage at higher temperature caused pasting temperature and through viscosity to increase and breakdown viscosity to decrease and it imposed more effect on high amylose rice than low amylose rice.

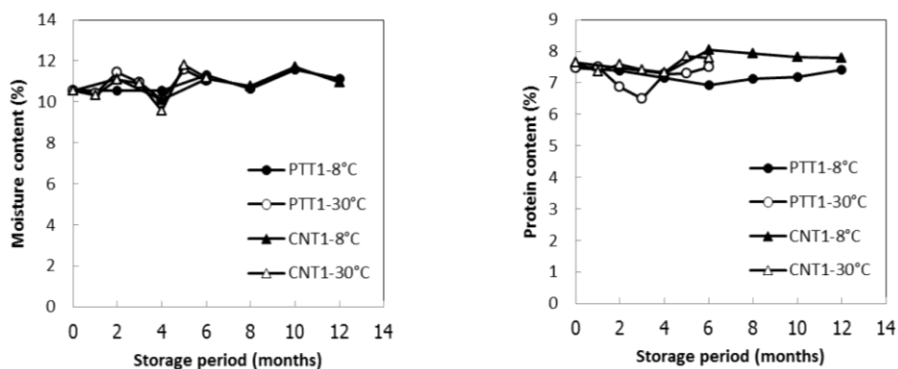


Figure 1. Moisture content and protein content of rice during storage at 8°C and 30°C

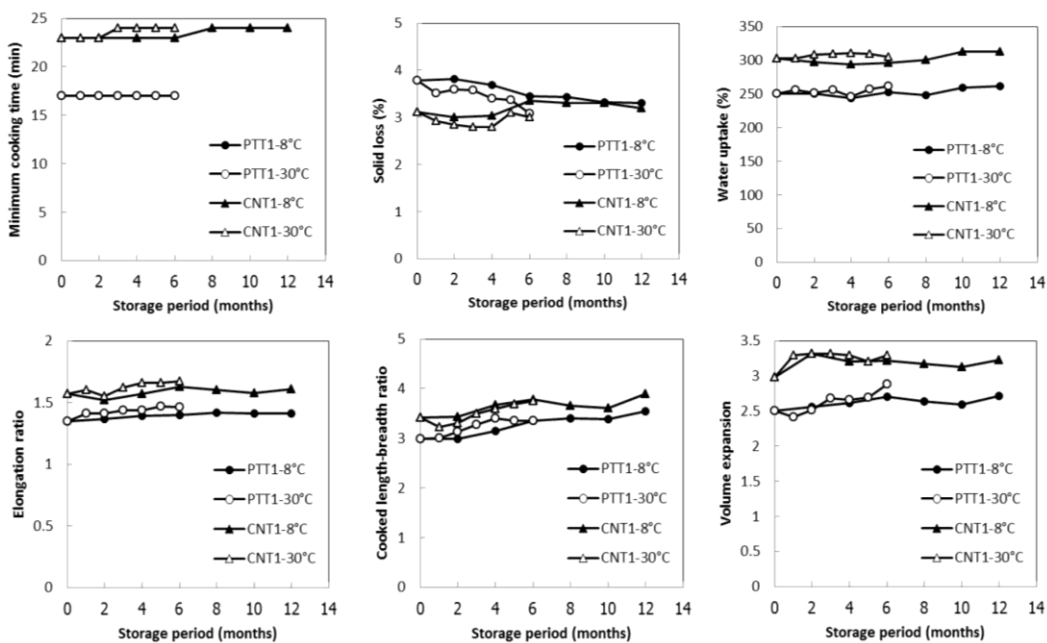


Figure 2. Cooking quality of rice during storage at 8°C and 30°C

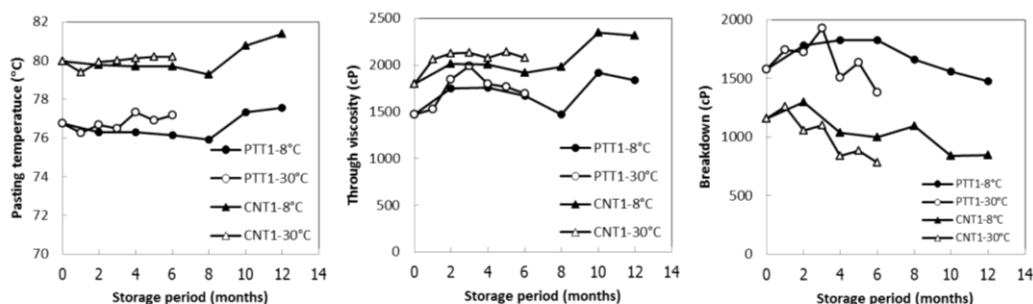


Figure 3. Pasting properties of rice during storage at 8°C and 30°C

Conclusions

Amylose content, storage time and storage temperature had an effect on rice quality. During storage, higher amylose content, longer storage time and higher storage temperature led to a greater decrease in solid loss and breakdown, and an increase in water uptake, elongation ratio, cooked length-breadth ratio, volume expansion, pasting temperature and through viscosity at a greater extent when compared to lower amylose content, shorter storage time and lower storage temperature. However, minimum cooking time, rice grain moisture content and protein content did not change.

Acknowledgements

Raw material support from Khlong Luang Rice Research Center and Ratchaburi Rice Research Center are gratefully acknowledged. The research is funded by under the project "Predictive Modeling for Rice Aging" project number 2555NRCT716, National Research Council of Thailand (NRCT) under the management of Agricultural Research and Development Agency (ARDA).

References

- AOAC. 2005. *Official Methods of Analysis*. 18th ed. Maryland: The Association of Official Analytical Chemists.
- Gujral, H.S., & Kumar, V. 2003. Effect of accelerated aging on the physicochemical and textural properties of brown and milled rice. *Journal of Food Engineering* **59**: 117-121.
- Jirathumkitkul, P. 1998. Effect of storage conditions on quality of brown rice. MS thesis. Bangkok, Thailand: Kasetsart University, Department of Food Science and Technology.
- Likitwattanasade, T. 2009. Effect of accelerated aging on functional properties of rice grain and flour. MS thesis. Bangkok, Thailand: Kasetsart University, Department of Food Science and Technology.
- Park, C.E., Kim, Y.S., Park, K.J., & Kim, B.K. 2012. Changes in physicochemical characteristics of rice during storage at different temperatures. *Journal of Stored Products Research* **48**: 25-29.
- Soponronnarit, S., Chiawwet, M., Prachayawarakorn, S., Tungtrakul, P., & Taechapairoj, C. 2008. Comparative study of physicochemical properties of accelerated and naturally aged rice. *Journal of Food Engineering* **85**: 268-276.
- Zhou, Z., Robards, K., Helliwell, S., & Blanchard, C. 2007. Effect of storage temperature on cooking behaviour of rice. *Food Chemistry* **105**: 491-497.

VITA

Miss Sunee Jungtheerapanich was born on August 22, 1982, in Saraburi, Thailand. She obtained the Bachelor of Science degree (Agro – Industrial Product Development) with First Class Honours in Agro – Industrial Product Development from Faculty of Agro – Industry, Kasetsart University in 2005 and the Master of Science degree (Agro – Industrial Product Development) majoring in Agro – Industrial Product Development from Faculty of Graduate School, Kasetsart University in 2008. She entered a Ph.D. program in Food Technology at Chulalongkorn University in 2011 and earned the degree in 2016. Over the course of her study, she had served as a research assistant in the project entitled “Predictive modeling for rice aging” that was funded by the Agricultural Research and Development Agency (ARDA) and the National Research Council of Thailand (NRCT) (grant number 2555NRCT716 and PRP5705021150).

List of publication

Jungtheerapanich, S., Tananuwong, K., and Anuntagool, J. 2016. Aging kinetics of low amylose rice during storage at ambient and chilled temperatures. *International Journal of Food Properties* (In Press).

List of conference proceeding

Jungtheerapanich, S. and Anuntagool, J. 2013. Chemical and Physical Changes of High and Low Amylose Rice during Storage. *Proceeding of the 8th CIGR Section VI International Technical Symposium on “Advanced food processing and quality management”*, 3-7 November 2013. Guangzhou, China.