EFFECT OF DEGREE OF MILLING ON PHYSICOCHEMICAL QUALITIES AND DISCRIMINATION OF THAI HOM MALI RICE BY FT-NIR SPECTROSCOPY

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ABSTRACT

The effect of degrees of milling (DOM) (0, 5, 10 and 15%) on rice varieties, i.e., Hom Mali rice, low, intermediate and high amylose rice samples, was investigated with the aim to develop the calibration models to predict the physicochemical properties of rice and classify Hom Mali rice from the aromatic and non-aromatic rice varieties by FT-NIR spectroscopy. Sixty rice samples were harvested during November 2007 and April 2008 and obtained from the rice research centers, the rice seed centers and the agriculture co-operative in Thailand. The results showed that the physicochemical properties of Hom Mali rice samples were closely similar to the low amylose rice samples, especially Pathum Thani 1 (PTT1). With increasing DOM, the apparent amylose content, alkali spreading values, and pasting properties, such as maximum (peak), breakdown, final and setback viscosity, increased whereas protein content and gel consistency were decreased. Milled rice with 15% DOM showed the highest apparent amylose content, alkali spreading value and pasting properties compared with milled rice with other DOMs. However, the DOM did not affect the alkali spreading value of rice samples.

Whole grain rice samples with different DOM were scanned in the near infrared regions (10,000-4,000 cm^{-1}) with reflectance mode using a fourier transform near infrared reflectance (FT-NIR) spectroscopy. The spectral data were pre-processed using multiplicative scatter correction (MSC), standard normal variate (SNV), second derivative, MSC + second derivative

and SNV + second derivative. The results of partial least squares modeling indicated that reasonably accurate models were attained for the moisture, protein and apparent amylose content. The original spectra showed the best model for predicting moisture content (coefficient of determination on the validation set [r^2] = 0.86, standard error of prediction [SEP] = 0.11%, bias = -0.00%), protein content (r^2 = 0.88, SEP = 0.23%, bias = -0.02%). The NIR spectra of brown rice samples transformed with SNV presented the best model for predicting apparent amylose content using five factors giving r^2 of 0.87, SEP of 1.47%, and bias of 0.23%. The spectral region at 7,142-4,012 cm^{-1} showed a good correlation to the apparent amylose content of brown rice. The NIR spectra of brown rice samples performed with SNV showed the best model for predicting alkali spreading value (r^2 = 0.86, SEP = 0.67 units on a 1-7 visual scale, bias = -0.03%). The best model for gel consistency was obtained from the NIR spectra of milled rice at 10% DOM after second derivative performed with Savitzky-Golay algorithm (r^2 = 0.88, SEP = 3.29 mm, bias = 0.08 mm). Furthermore, PLSR models for the six rice paste viscosity properties evaluated by a rapid visco analyzer (RVA) were reasonably accurate for predicting rice samples with different DOM.

Both of physicochemical properties data and spectral of NIR were used to discriminate Hom Mali rice from the aromatic and non-aromatic rice varieties by principal component analysis (PCA) and partial least square-discriminant analysis (PLS-DA). PCA could be applied to discriminate Thai rice varieties into four groups, i.e., Hom Mali rice, low, intermediate and high amylose rice groups by two principal components (PCs) according to their physicochemical properties. Rotated PC_1 and PC_2 using the varimax method were better explaining the variance of the parameters than the unrotated PCs. The rotated two PCs (PC_1+PC_2) for the five conditions of all DOM, 0, 5, 10 and 15% DOM could account for 76.83, 77.29, 80.77, 76.14 and 83.57% of total variables, respectively. PCA clearly differentiated the Rice Department 15 (RD15) variety from the PTT1 variety at the same DOM. Therefore, the stability of the DOM using PCA based on physicochemical measurements made it a preferable classification procedure for rice.

The discrimination of Hom Mali rice from the aromatic and non-aromatic rice varieties according to their spectral characteristics by PCA and PLS-DA was investigated. The best model for discrimination Hom Mali rice were obtained with PCA that developed by original spectra of milled rice samples at 10% DOM which gave the false negative and correct discriminate of 4.76

and 87.30%, respectively. Based on the different spectral NIR characteristics, including all DOM, 0, 5, 10 and 15% DOM and PLS-DA algorithm, the best calibration models established to discriminate Hom Mali rice from the other rice varieties was the NIR spectra milled rice samples at 15% DOM transformed with MSC. This discrimination model presented the false negative and correct discriminate of 3.17 and 88.89%, respectively. Therefore, the fix DOM should be recommended for discriminating Hom Mali rice by PCA and PLS-DA techniques. Overall, the results demonstrated that FT-NIR spectroscopy had potential for predicting physicochemical properties of rice and discriminating Hom Mali rice from the aromatic and non-aromatic rice varieties.

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LIST OF ABBREVIATIONS

AAM	Apparent amylose content
ASV	Alkali spreading value
BD	Rapid visco analyzer breakdown viscosity
CNT1	Chai Nat 1 rice variety
CNT2	Chai Nat 2 rice variety
DOM	Degree of milling
FT—NIR	Fourier transform near infrared
FV	Rapid visco final viscosity
GC	Gel consistency
HKLG	Hom Klong Luang rice variety
KDML105	Kao Dawk Mali 105 rice variety
LPT123	Luang Pra Tew 123 rice variety
MAX	Rapid visco analyzer maximum viscosity
MC	Moisture content
MSC	Multiplicative scatter correction
NIRS	Near infrared spectroscopy
PC	Principal component
PCA	Principal component analysis
PLS—DA	Partial least square discriminant analysis
PLSR	Partial least square regression
PSL1	Pitsanulok 1 rice variety
PSL2	Pitsanulok 2 rice variety
PTN	Protein content
PTT1	Pathum Thani 1 rice variety
PTT60	Pathum Thani 60 rice variety
PV	Rapid visco analyzer peak viscosity
RD15	Rice Department 15 variety or Kor Khor 15 variety
R^2_{cal}	Coefficient of determination for calibration set
r^2_{val}	Coefficient of determination for validation set

LIST OF ABBREVIATIONS (continued)

RPD	Relative performance determinant
Sav.Gol_2nd derv	Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order
SB	Rapid visco analyzer setback viscosity
SEC	Standard error of calibration
SEP	Standard error of prediction
SNV	Standard normal variate
SPR60	Suphanburi 60 rice variety
TV	Rapid visco analyzer trough viscosiy

CHAPTER 1

INTRODUCTION

1.1 General background

Hom Mali, Khao Dawk Mali 105 (KDML105), and Rice Department 15 (RD15) are rice varieties whose yields are of great economic value to Thailand and are all famous for their aroma, flavor, slender kernel and soft-cooking characteristics (Department of Foreign Trade, 1997). Both varieties have gained worldwide acceptance and thereby experienced rising demand because of the appreciation of their characteristics (Qiu and Zhang, 2003). In addition, the production yield of Hom Mali rice (404 kg/rai) is lower than those of other aromatic rice varieties (e.g., Pathum Thani [PTT1], Hom Klong Luang [HKLG], Pitsanulok 1 [PSL1]) (603 kg/rai), the price of the former is thus 1.3-2.5 times as high as those of other aromatic and non-aromatic rice varieties (Rice Department, 2010).

Hom Mali rice, however, possesses similar physicochemical characteristics to certain other aromatic rice varieties (e.g., PTT1, HKLG and PSL1) in that all are of long grain and slender rice varieties with a low gelatinization temperature, low apparent amylose content, and soft gel consistency (Kongseree, 2002a; Sripinyowanich, 2006). Differentiation of Hom Mali rice from the other aromatic rice varieties is not an easy task. As such, these lower priced aromatic rice varieties are often unscrupulously labeled by the sellers Hom Mali rice to obtain a higher sale price, thereby prompting customer complaints regarding the impurity of Hom Mali rice and resulting in its price being devalued (Cheaupun et al., 2005).

Besides the problem of similar inherent physicochemical characteristics, rice milling can alter or influence the physicochemical properties of rice grain. The physicochemical properties are important parameters to assess the index of milling quality, eating and cooking quality, texture of cooked rice, processing and classification of rice into many groups (e.g., four groups by apparent amylose content, three groups by gel consistency, and two types of rice varieties based on its aroma: aromatic and non-aromatic types) (Juliano, 1985; Champagne et al., 1990; Mohapatra and Bal, 2006, 2007). Moreover, these physicochemical properties correlate with the composition of rice, such as lipids, proteins, vitamins, minerals, and starch content (Juliano, 1981). In the process of rice milling, bran layers enriched with nutrients are removed, resulting in the changes in the composition of rice grain. This greatly alters the physicochemical properties as mentioned above (Wadsworth, 1994).

Extensive research has been conducted on the impact of milling on the physicochemical properties of rice, such as changes in protein content, apparent amylose content, gel consistency, and pasting properties. Increasing milling time or degree of milling results in lower lipids, proteins, ash content, and gel consistency, whereas the apparent amylose content and certain pasting properties increase (Wadsworth, 1994; Singh et al., 2000, Perdon et al., 2001; Park et al., 2001). Thus, the degree of milling affects not only the physicochemical properties but also the discrimination of rice. Therefore, the discrimination of Hom Mali rice should take into consideration the effect of degree of milling on the physicochemical properties. Discriminating Hom Mali rice from other rice varieties is of use to maintain its reputation for prime-cooking quality as well as premium price.

At present the discrimination of Hom Mali rice is a major issue of the rice industry and has received greater attention from rice producers, researchers, and consumers. The unique characteristics of Hom Mali rice are attributable to its physical and physicochemical properties whereby Hom Mali rice is classified. Various approaches have been adopted to classify Hom Mali rice, some of which are physical observation and physicochemical analysis such as the apparent amylose content (AACC, 1999), gel consistency (Cagampang et al., 1973), alkali spreading value (Little et al., 1958), DNA method (Mackill, 1995), and the pasting properties of rice performed with a rapid visco analyzer (RVA) (AACC, 2000c). Even though all the existing methods, such as physical observation, apparent amylose content, or gel consistency, are reasonably accurate in the classification of Hom Mali rice, no single method can distinguish Hom Mali rice from other rice varieties with low apparent amylose content.

Additionally, the application of multivariate statistical techniques (chemometrics) or physicochemical data has gained greater acceptance as a tool to discriminate rice varieties. A number of researchers classify rice samples based on their physicochemical properties into groups through the application of Ward's cluster analysis (Bett-Garber et al., 2001), hierarchical cluster analysis (Patindol et al., 2006), discriminant analysis (DA) (Suwannaporn et al., 2007), or principal component analysis (PCA) (Pitiphunpong and Suwannaporn, 2009a). Despite valuable information provided by these analysis methods, most of them involve a time-consuming, laborious, and costly procedure (Delwiche et al., 1996). Near infrared reflectance (NIR) spectroscopy has been used to quantitatively predict the concentration of various constituents in rice grain. One advantage of NIR spectroscopy is that it can record the response of the molecular bonds of its chemical constituents to the NIR spectrum (e.g., O-H, N-H, and C-H bonds) and thereby build a characteristic spectrum that behaves as a fingerprint of the sample (Williams and Stevensen, 1990; Wang et al., 2006).

The NIR spectroscopy technique has replaced chemical analyses in rice quality to a great extent. Most existing literature on rice mainly focuses on predicting the quantity of various constituents in rice grain. Many of the models in current use have high accuracy to predict lipids, proteins, moisture, apparent amylose content, pasting and thermal properties, sensory and texture of cooked rice attributes (Villareal et al., 1994; Delwhiche et al., 1995, 1996; Bao et al., 2001; Sohn et al., 2004a, 2004b; Wu and Shi, 2004; Rittiron et al., 2004). In addition, the application of NIR spectroscopy accompanied with multivariate techniques, such as principal component analysis (PCA), discriminant analysis (DA), or partial least square discriminant analysis (PLS-DA), could classify rice varieties. Osborne et al. (1993b) discriminated Basmati rice from other rice varieties while Kwon and Cho (1998) identified Korean domestic rice from foreign rice varieties. Rittiron et al. (2005) detected the contamination of milled Japanese rice using a single kernel, and Liu et al. (2006) classified paddy rice varieties to set trading prices.

As previously mentioned, most researchers mainly focused on cultivating season, growing season, grain size (e.g., rice flour, brown rice, milled rice, or single grain), and type of spectroscopy when evaluating rice quality. There exists no report however on the effect of degree of milling on the physicochemical properties of rice using the NIR spectroscopy technology. Therefore, the development of NIR calibration models for rice with different degrees of milling might be applied to determine the physicochemical properties of Hom Mali rice and to discriminate this rice from any other rice varieties.

1.2 Objectives

1.2.1 To evaluate the effect of degree of milling on physicochemical properties of rices

1.2.2 To establish the calibration model to predict the physicochemical properties of Thai rices

1.2.3 To discriminate Thai Hom Mali rice from the other rice varieties by FT-NIR spectroscopy based on physicochemical properties at different degrees of milling

CHAPTER 2

LITERATURE REVIEW

2.1 Rice varieties

Rice (*Oryza sativa* L.) is one of the many cash crops that are of great economic value to the Kingdom. Thailand in 2010 alone exported 8.32 million tons of milled rice worth 106 billion Thai baht, increasing 5.1% in volume and 3.9% in value compared with a year earlier (Rice Department, 2011). Various rice varieties have been cultivated in Thailand, most of which can be classified based on such characteristics as cultivating season, apparent amylose content, gel consistency, texture properties, and aroma.

By cultivating season, rice can be classified into two groups: in-season rice and off-season rice. The in-season rice refers to rice cultivatable once a year, examples of which are KDML105, Luang Pra Tew 123 (LPT123), RD15, and Khao Tah Haeng 17 (KTH17). The off-season rice, on the other hand, is cultivated twice annually, examples of which are ChaiNat 1 (CNT1), ChaiNat 2 (CNT2), PTT1, PSL1, and Pitsanulok 2 (PSL2) (Naivikul, 2004).

If grouped by the apparent amylose content, rice is divided into waxy rice with 1-2% apparent amylase content (e.g., Rice Department 4 [RD4] and Rice Department 6 [RD6]); and non-waxy rice (>2%), the latter of which can be further divided into three sub-categories as: low (10-20% e.g., KDML105, RD15, PTT1, and PSL1), intermediate (20-25% e.g., Suphan Buri 2 [SPR2] and Suphan Buri 60 [SPR60]), and high apparent amylose content (>25% e.g., CNT1, CNT2, and PSL2) (Juliano, 1985; Kongseree, 2002a).

By the consistency of rice paste in 0.2 N potassium hydroxide (KOH), rice is divided into soft (61-100 mm), medium (41-60 mm), and hard gel consistency (26-40 mm) (Cagampang et al., 1973; Kongseree, 2002a).

Rice can be grouped as very soft, soft, fluffy-medium, and fluffy-hardness based on the texture characteristics of cooked rice. In addition, it is worth noting that the classification of rice according to gel consistency and texture of cooked rice correlates positively with the apparent amylose content. That is, low apparent amylose rice is identified as soft gel consistency with soft texture of cooked rice, whereas hard gel consistency with fluffy-hardness is considered as high apparent amylose rice (Bhattacharya et al., 1982; Cheaupun et al., 2005).

Rice can also be divided by its aroma into two groups: aromatic and non-aromatic rice. Aromatic rice is the rice variety with such natural chemical compounds as 2-acetyl-1-pyrroline and alk-2-enals, and alka-2, 4-dienals, giving it the dominant distinctive scent (Widjaja et al., 1996), while non-aromatic rice contains less concentration of 2-acetyl-1-pyrroline (Buttery et al.,1983). Although there exist a large number of aromatic rice varieties, only KDML105, RD15, PTT1, PSL1, Hom Klong Luang (HKLG), and Hom Suphan Buri (HSPR) KDML105 and RD15 can be identified as "Thai Hom Mali rice" while the other remaining varieties can only be referred as aromatic rice (Department of Foreign Trade, 1997). Major non-aromatic rice varieties planted in Thailand include CNT1, CNT2, SPR60, PSL2, and LPT123 (Department of Agriculture, 2003).

2.1.1 Non-aromatic rice varieties

Thai non-aromatic rice varieties play a crucial economic role domestically and globally. The Rice Department reported that 463,391 million tons of in-season and off-season non-aromatic rice varieties worth 8,016 billion baht were exported in 2011 as milled rice, brown rice, and by-products. Both in-season and off-season varieties are typically cultivated in the central plains and certain areas in the north and northeast of Thailand. Examples of the non-aromatic rice varieties are CNT1, CNT2, SPR60, PSL2, LPT123, Suphan Buri 1 (SPR1), Suphan Buri 2 (SPR2), and Pathum Thani 60 (PTN60) (Department of Agriculture, 2003). Furthermore, most non-aromatic rice varieties are non-photoperiod sensitive, thereby allowing them to be cultivated twice a year and also having higher productivity than those of aromatic varieties (Laksanalamai, 1993). Table 2.1 depicts the physicochemical properties of certain non-aromatic rice varieties.

Table 2.1 Physicochemical properties of certain non-aromatic rice varieties

Variety	Cultivated season	Physicochemical properties					Rice paste viscosity		
		MC (%)	PTN (%)	AAM (%)	GC (mm.)	ASV	GT (°C)	BD (BU)	SB (BU)
LPT123	in-season	10.0	11.1	26.0	58	4.0	70.0	270	520
KTH17	in-season	11.7	9.0	25.7	63	5.0	69.0	650	290
PTN60	off-season	10.6	6.9	28.1	31	6.1	64.0	170	660
SPR60	off-season	10.6	8.5	24.3	46	5.1	65.0	370	120
CNT1	off-season	10.9	8.9	26.6	63	5.0	72.7	790	440
PSL2	off-season	12.8	7.6	28.1	79	7.0	66.5	500	-20

Source: Kongseree (2002a)

Note: MC = Moisture content, PTN = Protein content, AAM = Apparent amylose content, GC = Gel consistency, ASV = Alkali spreading value, GT = Gelatinization temperature, BD = Breakdown viscosity, and SB = Setback viscosity

As seen in Table 2.1, LPT123 and KTH17 are in-season rice varieties while the rest are off-season varieties. The moisture and protein contents range from 10.0-12.8% and 6.97-11.1%, respectively. All of the rice varieties are characterized by high apparent amylose content contributing to high water absorption, volume expansion, and fluffy-hardness texture of cooked rice. PTT60 belongs to the hard gel consistency group while the medium gel consistency group consists of LPT123 and SPR 60 with the rest considered as possessing soft gel consistency. Although PSL2 has high apparent amylose content but its gel consistency and alkali spreading value are much similar to those of aromatic rice, resulting in lower setback viscosity compared to the other non-aromatic varieties. Therefore, it could be concluded that the non-aromatic rice varieties can be cultivated both in-season and off-season and are of high apparent amylose content.

2.1.2 Aromatic rice varieties

In Thailand the non-waxy aromatic rice, generally known as "Khao Hom," is considered to be the national pride. It is also of great economic value to the country with export volume and value in 2010 of 2.54 million tons and 68 billion baht, respectively (Rice Department, 2011). The aromatic rice has gained wide acceptance in Europe and the United States because of its aroma, flavor, and soft-cooking characteristics (Singh et al., 2000). Most aromatic rice varieties have been characterized by low apparent amylose content with 2-acetyl-1-pyrroline as the major volatile component (Weber et al., 2000). Buttery et al. (1983) isolated and identified 2-acetyl-1-pyrroline as an important compound contributing to its aromatic odor. This result suggested that 2-acetyl-1-pyrroline was a major aroma in several Asian aromatic rice varieties. Furthermore, Ahmed et al. (1996) confirmed the work of Buttery et al. (1983) that this compound was the source of the characteristic odor of aromatic rice varieties.

The available aromatic rice varieties are either “Hom Mali rice” or “Khao Hom”. Both are similar in terms of slender kernel and certain physicochemical properties such as protein content, apparent amylose content, alkali spreading value, and gel consistency. Despite the similarity between Hom Mali rice and Khao Hom, their aroma, pasting properties, and eating and cooking quality are different. In fact, only two varieties, i.e., KDML105 and RD15, are classified as “Hom Mali rice”, whereas the other aromatic rice varieties are “Khao Hom”, examples of which are HKLG, HSPR, PTT1, and PSL1 (Kongseree, 2002b; Department of Agriculture, 2003).

2.1.2.1 Hom Mali rice

Among the existing aromatic rice varieties in Thailand, Hom Mali (KDML105 and RD15) rice is of the greatest economic importance (Department of Foreign Trade, 1997). In 2010, Thailand exported 2.35 million tons of milled and brown Hom Mali rice worth 63 billion baht (Rice Department, 2011). The Office of Agricultural Economics in 2011 reported that the two rice varieties were the predominant aromatic rice exports, accounting for approximately 94% of all aromatic rice exported. Kongseree (1979) revealed that the popularity of Hom Mali rice might be attributable to its aroma rather than its low amylose content.

The KDML105 variety was discovered by a farmer in Chon Buri province in the eastern of Thailand. In 1950 the seeds of KDML105 were distributed to Cha Seong Sao province, where a district agricultural officer collected 199 panicles (Somrith, 1996). The panicle-row method was employed and pure line selection was initiated at the Kok Samrong rice research station in Lop Buri province. The outstanding line, Khao Dawk Mali 4-2-105, was then isolated and further evaluated for yield potential and adaptability for cultivation in the north, northeast, and central regions. It was later released as Khao Dawk Mali (meaning white jasmine) 105 in 1995. Nevertheless, KDML105 possesses low yield potential with approximately 450 kg/rai (Somrith, 1996; Anonymous, 1996).

In 1978, a mutant of KDML105 by radiation, RD15 was released by the Rice Department. The benefit of RD15 over KDML105 is shorter maturation of 7-15 days. Both varieties possess similar aroma and cooking and eating quality (Laksanalamai, 1993). Although there is an urgent requirement to increase production, both varieties are of low yield, non-resistant to insect, photoperiod sensitive, of in-season rice, and normally grown in the north and northeast of Thailand with infertile and drought-stricken sandy soil (Sayumpon et al., 1999). As such, new aromatic rice varieties with high yield, such as PTT1, HKLG, and PSL1, were released to the market. Nevertheless, a mixture of these new varieties and Hom Mali rice marketed under the name of "Hom Mali rice" made customers complain on its quality, thereby resulting in its devaluation. The Ministry of Agriculture and Cooperatives has therefore issued the Hom Mali rice certification to only the two varieties: KDML105 and RD15 (Department of Foreign Trade, 1997).

Hom Mali rice possesses low apparent amylose content of 12-18%, resulting in soft texture of cooked rice, low gelatinization temperature, good dispersion in alkali solution, and soft gel consistency (61-100 mm) (Cheaupun et al., 2005). However, these properties may change depending upon cultivation, especially cool temperature, light exposure duration, soil, and fertilizer (Sarkarung et al., 2000). Table 2.2 shows the physicochemical properties of Hom Mali rice cultivated in different locations. Moisture and protein contents ranged from 10.0-13.0% and 6.0-9.4%, respectively. The protein content of RD15 cultivated in the Pang Ma Pha rice research institute was the highest while that of KDML105 grown in the Chai Nat rice research institute was the lowest. The different results might be caused by the application of nitrogen fertilizer during cultivation (Somrith, 1996; Kongseree, 2002a).

As seen in the same table, apparent amylose content, gel consistency, and alkali spreading value were between 14.4-16.7%, 77-100 mm, and 6.3-7.0, respectively. Elongation ratio is the ratio of the average length of cooked rice grains to the average length of raw rice grains. Length expansion without increasing in girth is considered as a highly desirable trait in high quality rice (Dela Cruz et al., 1989). As shown in Table 2.2, the elongation ratio of RD15 cultivated in the Pang Ma Pha rice research institute was highest while those of the other plantations are normal. The cooking time is identical for the rice from all seven plantations. Gelatinization temperature, breakdown viscosity, and setback viscosity varied between 63.8-67.3°C, 440-770, and -460 to 10 BU, respectively (Kongseree, 2002a, 2004).

Table 2.2 Physicochemical properties of Hom Mali rice cultivated in different locations

Variety	Cultivated* plantations	Physicochemical properties					Cooking quality		Rice paste viscosity		
		MC (%)	PTN (%)	AAM (%)	GC (mm.)	ASV	Elongation ratio	Cooking time (min.)	GT (°C)	BD (BU)	SB (BU)
KDML105	PTT	10.5	7.7	16.1	79	7.0	1.6	15	64.5	770	-460
	CNT	13.0	6.0	14.4	80	6.7	1.6	15	66.0	660	-280
	KSR	11.9	9.0	14.6	77	6.4	1.7	15	66.0	500	-60
	PMI	10.9	7.5	16.7	100	6.6	1.7	15	67.3	440	10
	KKN	10.0	7.8	16.1	100	6.3	1.6	15	66.0	720	-400
RD15	PAN	12.6	8.2	15.6	80	7.0	1.7	15	64.5	630	-240
	PMP	10.6	9.4	15.0	100	7.0	2.0	15	63.8	630	-310

Source: Modified from Kongseree (2002a, 2004)

Note: MC = Moisture content, PTN = Protein content, AAM = Apparent amylose content, GC = Gel consistency, ASV = Alkali spreading value, GT = Gelatinization temperature, BD = Breakdown viscosity, and SB = Setback viscosity

* Cultivated locations; Pathum Thani (PTT), Chai Nat (CNT), Kok Sum Rong (KSR), Pimai (PMI), Khon Kan (KKN), Pan (PAN) and Pang Ma Pha (PMP) rice research institutes

The appearance of Hom Mali rice is of great importance to the consumers. Thus, grain size and shape are the first two criteria in the determination of Hom Mali rice quality and thereby its premium price (Adair et al., 1966). The length/width ratio of 2.5-3.0 is widely accepted as good quality (Kaul, 1970). The Ministry of Agriculture and Cooperatives has set a specification of length and length/width ratio of no less than 7 mm and 3.1:1, respectively (Department of Foreign Trade, 1997). Unfortunately, the sizes and length/width ratios of other aromatic rice varieties and those of Hom Mali rice are of little difference (Table 2.3). Therefore, it is difficult to differentiate milled Hom Mali rice from the other milled aromatic rice varieties.

Table 2.3 Size and length/width of Hom Mali and aromatic rice varieties

Variety	Size (mm)			Length-width ratio
	Length	Width	Thickness	
KDML105	7.4	2.2	1.8	3.36
RD15	7.5	2.1	1.7	3.57
HKLG	7.8	2.3	1.8	3.39
HSPR	7.5	2.2	1.8	3.54
PTT1	7.6	2.2	1.7	3.45

Source: Kongseree (2002a); Sripinyowanich (2006)

2.1.2.2 Khao Hom rice

Khao Hom rice is also aromatic rice but it is not classified as Hom Mali rice. However, many physical and physicochemical properties of Khao Hom rice are similar to those of Hom Mali rice, such as size, length/width ratio, apparent amylose content, gel consistency, and alkali spreading value (Kongseree, 2002a). Examples of Khao Hom rice are HKLG, PTT1, HSPR, and PSL1 rice varieties. Most Khao Hom rice varieties were the result of successful cross breeding, an example of HKLG, which was derived from a cross breeding between Nahng Mon S4 (traditional Thai cultivar) and IR841-85-1-1-2 (KDML105 derivative). It was named for the Klong Luang rice research station after successful breeding in 1983 (Anonymous, 1997a).

A successful selection at the Suphanburi rice research station in 1989, the HSPR variety was a multiple cross breeding of three varieties (SPR84177-8-2-2-2-1, SPR85091-13-4, and KDML105). According to the National Research Council of Thailand, PTT1 was derived from a cross breeding between BKNA6-18-3-2 and PTT85061-86-3-2-1 and developed by the Pathum Thani rice research station during 1990 and 1999. It possesses a moderate level of resistance to bacterial blight and white-backed plant hoppers (Anonymous, 1997b). The physicochemical properties and cooking quality of Hom Mali and Khao Hom rice varieties are shown in Table 2.4.

From Table 2.4, with the exception of PSL1 with 15.4% of AAM, the protein and apparent amylose contents of Khao Hom rice varieties were higher than those of Hom Mali rice varieties. Almost all of the Hom Mali and Khao Hom rice varieties are of soft gel consistency except HKLG which is of hard gel consistency due to its intermediate apparent amylose content. Scoring of alkali spreading value of all Hom Mali and Khao Hom rice varieties was very similar, varying between 6.4 and 7.0. Furthermore, the elongation ratios of both groups were almost identical; however, the cooking time of Hom Mali rice varieties appeared slightly longer than that of Khao Hom rice varieties. Rice pasting viscosity showed differences in gelatinization temperature, breakdown viscosity, and setback viscosity. Khao Hom rice with high apparent amylose content showed an increase in gelatinization temperature and setback viscosity, whereas Hom Mali rice exhibited higher breakdown viscosity. It could be concluded that the physicochemical properties of Hom Mali rice, especially rice paste viscosities that could be used to classify Hom Mali rice, are different from those of Khao Hom rice varieties.

Table 2.4 Physicochemical properties and cooking quality of Hom Mali and Khao Hom rice varieties

Variety	Physicochemical properties				Cooking quality		Rice paste viscosity		
	PTN (%)	AAM (%)	GC (mm.)	ASV	Elongation ratio	Cooking time (min)	GT (°C)	BD (BU)	SB (BU)
Hom Mali rice									
KDML105	7.7	16.1	79	7.0	1.6	15	64.5	770	-460
RD15	8.2	15.6	80	7.0	1.7	15	64.5	630	-240
Khao Hom rice									
HKLG	8.6	20.3	40	6.4	1.5	17	64.8	420	70
HSPR	9.5	18.8	69	6.7	1.6	18	66.2	600	-200
PTT1	9.5	17.1	75	7.0	1.6	16	66.1	650	-220
PSL1	8.5	15.4	78	7.0	1.7	18	65.3	630	-190

Source: Kongseree (2002a); Srisawas (2009)

Note: PTN = Protein content, AAM = Apparent amylose content, GC = Gel consistency, ASV = Alkali spreading value, GT = Gelatinization temperature, BD = Break down viscosity, and SB = Setback viscosity

Hom Mali rice of premium quality has gained wider acceptance and thereby greater demand. High-income consumers are willing to pay premium prices for quality characteristics such as aroma and desirable textural attributes (Juliano, 1993). In addition, the yield of Hom Mali rice of 404 kg/rai is much lower than that of Khao Hom rice (603 kg/rai), causing the price of Hom Mali rice to be higher than that of Khao Hom rice. The average prices of Hom Mali rice and Khao Hom rice are shown in Table 2.5.

Table 2.5 The average prices of Hom Mali rice and Khao Hom rice between 2008 and 2011

Year	Price (baht/100 kg)	
	Hom Mali rice	Khao Hom rice
2008	2,550 - 2,600	2,150 - 2,200
2009	3,400 - 3,450	2,500 - 2,550
2010	2,950 - 3,000	2,150 - 2,200
2011	2,850 - 2,900	2,200 - 2,250

Source: Thai Rice Mill Association (2011)

Because of the lower production but higher value and growing demand of Hom Mali rice, it has been subjected to mix with other aromatic rice varieties, resulting in the loss of consumer trust and market share in the world market.

2.2 Composition of rice

A grain of rice consists of the edible portion, called brown rice, enclosed by the hull or husk. The brown rice consisted of 8.3% protein, 74.9% carbohydrates, and small amounts of fat, fiber, and ash at 14% moisture (Table 2.6). Milled rice has 7.1% protein and 77.8% carbohydrates. These nutrients are unevenly distributed in the rice seed. The non-starchy constituents, particularly fat, fiber, minerals, and vitamins, are concentrated in the aleurone layers and germ while starch is found mainly in the endosperm (Juliano, 1981; Marshall and Wadsworht, 1993).

Table 2.6 Chemical composition of brown rice and milled rice

Chemical composition	Brown rice	Milled rice
Moisture content (%)	14.0	14.0
Protein content (g/100 g)	8.3	7.1
Fat content (g/100 g)	1.9	0.5
Total carbohydrate (g/100 g)	74.9	77.8
Fiber content (g/100 g)	0.7	0.4
Ash content (g/100 g)	1.1	0.6
Vitamin and Mineral contents		
Calcium (mg/100 g)	9.0	8.0
Phosphorus (mg/100 g)	183.0	104.0
Iron (mg/100 g)	1.6	1.2
Thiamine (mg/100 g)	0.3	0.1
Riboflavin (mg/100 g)	0.1	0.1
Niacin (mg/100 g)	3.9	2.3

Source: Modified from Juliano (1981); Marshall and Wadsworth (1993)

2.2.1 Moisture content

Moisture content influences rice quality. The optimum moisture contents for storage paddy and long term storage rice are respectively 13% and 9% (Juliano, 1972). The moisture content affects not only the milling yield and storability but also the taste and flavor. The flavor of cooked rice is affected by such physical properties as moisture content, cohesion, elasticity, and hardness. Of all the physical properties, the moisture content of rice is the major factor influencing the flavor of cooked rice (Lin et al., 2006).

The methodology for measuring moisture content is classified as direct and indirect methods. The direct method commonly involves removal of the water by oven heating. The moisture content ratio is then calculated from the weight loss. Although the traditional oven measurement has high accuracy, this approach is time-consuming. The indirect method measures the relationship between physical properties and the moisture content of the rice (ASAE Standards, 1997).

2.2.2 Starch

Starch presents in the form of compound granules 3-10 μm in size. These starch granules are polyhedral due to their close packing in the endosperm cell of the mature grain. One particular physicochemical characteristic of the starch is gelatinization temperature, the temperature range in which the starch granules start to swell irreversibly in hot water with loss of crystallinity (Singh et al., 2006). Starch properties depend upon such physical and chemical characteristics as granule size, granule size distribution, amylose/amylopectin ratio, and mineral content (Singh et al., 2003).

Starch which is typically made up of glucose units occurs as two distinct fractions: a branched fraction called "amylopectin" and a linear fraction called "amylose". Starch is classified as waxy (<2% amylose) and non-waxy rice (>5% amylose). Waxy starch stains reddish brown with iodine solution while purple blue is presented in non-waxy starch. This amylose iodine blue complex is the basis for the amylose determination of non-waxy starch. The amylose and amylopectin contents of non-waxy milled rice generally range from 7 to 33% and from 63 to 91%, respectively (Juliano, 1981; Marshall and Wadsworht, 1993).

2.2.3 Protein content

Protein which is non-uniformly distributed in the rice grain is highly concentrated in the bran and periphery of the endosperm but is of smaller quantity toward the center of the grain (Little and Dawson, 1960). Three types of protein bodies have been identified, i.e., crystalline, small spherical, and large spherical. Bechtel and Pomeranz (1978) reported that the central region of rice grain contains only large spherical protein bodies which remain intact during the cooking process. The large spherical protein bodies however become more resistant to digestive enzymes, thus decreasing protein digestibility.

Rice proteins are mainly water-insoluble. Cagampang et al. (1966) found out of the total protein 3.8-8.8% albumins (water-soluble proteins), 9.6-10.8% globulins (salt-soluble proteins), 2.6-3.3% prolamins (alcohol-soluble proteins), and 66.1-78.0% glutelins (alkali-soluble proteins). Hamada (2000) concluded that glutelins constitute the main fraction of rice proteins, and their polypeptide composition is similar to that of the legumins but glutelins are of poor solubility. In addition, rice proteins are considered valuable because of their colorlessness, bland taste, hypoallergenic and hypocholesterolemic properties (Ju et al., 2001).

The protein content is usually calculated from Kjeldahl nitrogen multiplied by the factor of 5.95. This factor is based on the total nitrogen content of the major rice protein (glutelin) of 16.8% (Juliano, 1972). Nowadays, the substitution of combustion analysis for the Kjeldahl method in the nitrogen determination has reduced some of the environmentally unfavorable aspects of protein determination. Nevertheless, the combustion analysis is still time-consuming and suffers from a small bias relative to the Kjeldahl method (Himmelsbach et al., 2001).

The chemical composition of aromatic rice, such as protein and starch contents, differs from that of non-aromatic rice varieties, depending on growth condition, cultivated location, and season (Table 2.7). Navasearttavisootr (2004) found that the starch content of aromatic rice was slightly lower than that of non-aromatic rice, and so was the protein content. Yadav and Jindal (2008) also demonstrated that, except for HKLG variety which could be attributed to nitrogen fertilizer application, the protein content of aromatic rice was lower than that of other rice varieties.

Protein content also influences cooking quality such as cooking time, water penetration, and texture of cooked rice. Hamaker (1993) found protein content in rice affected texture of cooked rice, especially tenderness and cohesiveness of cooked rice. The texture of cooked rice with high protein tended to be tougher and chewier than that of cooked rice with low protein. These results were consistent with the work of Delwiche et al. (1996) who reported that cooked rice with higher protein levels was significantly less tender than rice with low protein content.

Furthermore, protein content positively correlated with cooking time. High protein rice also showed lower water absorption than low protein rice, thereby resulting in higher in cooking time. This result is attributable to the fact that protein content form a thicker barrier around the starch granule, hindering water penetration into rice grain (Hamaker, 1993).

Table 2.7 Starch and protein contents of aromatic and non-aromatic rice varieties

Variety	Starch content (% d.b.)	Protein content (% d.b.)
Aromatic rices		
KDML105	85.9	8.0
HKLG	No data	7.5
HSPR	No data	9.1
PTT1	89.6	7.8
Non-aromatic rices		
SPR1	87.8	7.8
SPR60	90.8	8.0
SPR90	90.7	9.1
CNT1	No data	8.1
LPT123	No data	8.2

Source: Modified from Navasearttavisootr (2004); Yadav and Jindal (2008)

2.2.4 Fat content

Rice fat content is genetically controlled by multiple genes and has a relatively higher heritability. About 80% of the lipids of brown rice are located in the bran, and about one-third of this fraction is in the embryo (Hu et al., 2004). Fat content has great influence on rice appearance and eating quality although it is of relatively low content (Chen and Zhu, 1998). Soxhlet, Goldfisch, and Soxtec techniques have been widely used to determine the fat content in rice. However, with the employment of these conventional methods, the sample needs to be pulverized and a long period of time is required for solubilizing and extracting the fat (Matsler and Siebenmorgen, 2005).

Fat occurs in both free and starch bound forms. Lipid oxidation is the major deterioration process during rice storage and releases free fatty acids and carbonyl compounds. Both compounds affect rice quality, especially a decrease in aroma of cooked rice. The American Official Association of Chemistry (AOAC) method is used to determine lipid content and recently NIR spectroscopy has also been applied (Wang et al., 2006).

2.2.5 Vitamins content

Higher levels of vitamins are generally present in brown than in milled rice. A major proportion of these vitamins are located in aleurone layers and embryo. Rice nonetheless contains little or no vitamin A, ascorbic acid, and vitamin D (Juliano, 1972). Hinton (1948) reported that 34.5% of thiamine was found in the pericarp, tegmen, and aleurone layers, 47% in the scutellum, 10.8% in the embryo, and 8.0% in the endosperm.

2.2.6 Minerals content

The mineral composition of rice varies considerably as a result of differing soil composition in which rice is grown and differing analytical methods used by various investigators. The ash distribution in brown rice was reported to be 51% in bran, 10% in germ, 11% in polish, and 28% in milled rice. Iron, phosphorus, and potassium show a distribution similar to total ash. However, some minerals are relatively more evenly distributed in the grain (Juliano, 1972).

2.2.7 Aroma

Among different quality traits, aroma is considered the most important quality for aromatic rice. A popcorn-like aroma, 2-acetyl-1-pyrroline, has been reported as the major compound that gives aromatic rice varieties their characteristic aroma and flavor. Although this compound presents in all rice varieties, the concentration is much greater in aromatic varieties (Wilkinson and Champagne, 2004). Widjaja et al. (1996) found that the major components of aromatic rice were alkanals, alk-2-enals, alka-2,4-dienals, 2-acetyl-1-pyrroline and 2-

phenylethanol and that non-aromatic rice contained more n-hexanal, 1-coten-3-ol, n-nonanal, 2-pentlylfuran, 4-vinylguaiacol and 4-vinylphenol than aromatic rice.

However, the potential volatile aromatic compound in the aromatic rice was identified as 2-acetyl-1-pyrroline (Yoshihashi et al., 1998). Weber et al. (2000) and Sripinyowanich (2006) evaluated the volatile compound, 2-acetly-1-pyrroline, in cooked aromatic and non-aromatic rice varieties. The result showed the higher concentration of this compound in the aromatic rice compared to non-aromatic rice varieties (Table 2.8). The 2-acetyl-1-pyrroline concentration in KDML105 (2,200 *ng/g*) was the highest and twice concentrated as PTT1 (1,100 *ng/g*). Moreover, Sripinyowanich (2006) noted that although HKLG (1,650 *ng/g*) was lower in 2-acetyl-1-pyrroline content than KDML105, the panelists were unable to distinguish between the aroma quality of KDML105 and HKLG.

Table 2.8 Concentration of 2-acetyl-1-pyrroline in cooked rice varieties

Variety	2-acetyl-1-pyrroline concentration (*ng/g**)
Aromatic rice	
KDML105	2,200
RD15	2,100
Non-aromatic rice	
PTT1	1,100
HKLG	1,650
HSPR	1,240

* calculated in terms of dry weight of rice

Source: Modified from Weber et al. (2000); Sripinyowanich (2006)

Moreover, Somrith (1996) reported that the aroma content of KDML105 rice grain varied according to the planting area. Milled rice from the northeast region has strong and stable aroma while samples from some areas in the central and north regions have very weak or no aroma. It is believed that the aroma in KDML105 varies, depending upon the planting area, soil type, and soil fertility.

2.3 Physicochemical properties of rice

Physicochemical properties of rice grains are an important factor to evaluate their cooking and processing characteristics. Nowadays, they are widely used in conjunction with the multivariate method in the classification of rice varieties (Nakamura et al., 2002; Suwannaporn et al., 2007; Patindol et al., 2009; Pitiphonpong and Suwannaporn, 2009b). These properties include moisture content, protein content, apparent amylose content, gel consistency, alkali spreading value in terms of the extent of disintegration of whole kernel milled rice in contact with alkali solution which is an indicator of gelatinization temperature, rice paste viscosity, and gelatinization temperature (Juliano, 1985).

2.3.1 Apparent amylose content

Apparent amylose content (AAM) is now used to clarify the distinction between amylose content that exists and amylose content that is actually measured by the colorimetric method (Takeda et al., 1987). The apparent amylose content in milled rice and its starch influences cooked rice texture and correlates positively with water absorption and volume expansion, hardness, and whiteness of cooked rice whereas it correlates negatively with stickiness of cooked rice (Villareal et al., 1994). Besides these properties, the apparent amylose content led to the retrogradation of gelatinized starch, which induced the formation and subsequent aggregation of double helices of both amylose and amylopectin chains during the long term storage. It also influences the firmness, viscosity, and textural staling of starch-containing systems. Retrogradation of gelatinized starch refers to setback viscosity of starch when measured by RVA or brabender visco-amylograph (Lii et al., 2004).

The universal method for determination of apparent amylose content has been a colorimetric assay in which iodine binds with amylose to produce a blue amylose-iodine complex measured at 620 nm (AACC, 1999). Amylopectin also produces a colored reaction with iodine, interfering the direct measurement of blue amylose-iodine complex. Attempts have been made to reduce the interference of the amylopectin-iodine complex with the use of amylose-amylopectin mixtures as standard curve (Landers et al., 1991). In general, chemical methods for apparent amylose content determination in rice have the drawbacks of being time-consuming, slow, and somewhat imprecise due to various factors, including difficulty in developing suitable reference curves from starch mixtures of amylose-to-amylopectin ratios and problems encountered in solubilization of the milled rice flours (Himmelsbach et al., 2001).

2.3.2 Gel consistency

Gel consistency refers to the consistency of a cold 4.4% milled rice paste in 0.2 N KOH. It is measured by the length in a test tube of the cold gel held horizontally for 0.5 or 1 hour. The gel consistency test is developed to be an index of cooked rice hardness among high apparent amylose rice varieties. The test is based on the consistency of milled rice paste that has been gelatinized under diluted alkali at boiling temperature and then cooled to room temperature (Cagampang et al., 1973). The test classifies rice into three categories: soft, medium and hard gel consistency (Table 2.9).

Table 2.9 Numerical scale for length of gel consistency

Length of gel (mm)	Gel characteristics
<40	hard gel consistency
41 - 60	medium gel consistency
61 - 100	soft gel consistency

Source: Cagampang et al. (1973)

Gel consistency negatively correlates with texture of cooked rice. Rice with apparent amylose content below 20% is of soft gel consistency, giving rise to soft and sticky cooked rice. On the other hand, rice with hard gel consistency usually contains 25% apparent amylose content, causing cooked rice to be dry, fluffy and firm (Juliano, 1993). It was explained that hard gel consistency types are mainly found in high apparent amylose rice (Juliano and Pascual, 1981). Furthermore, the gel consistency negatively correlates with setback viscosity because high apparent amylose rice has higher cooling curve, resulting in an increase in setback viscosity during cooling. In contrast, low apparent amylose rice does not exhibit this property in this stage (Sowbhagya et al., 1987).

2.3.3 Gelatinization temperature

The gelatinization temperature of the endosperm starch refers to the cooking temperature at which water is absorbed and the starch granules swell irreversibly in hot water with a simultaneous loss of crystallinity and birefringence (Juliano, 1993). The gelatinization

2.3.3 Gelatinization temperature

The gelatinization temperature of the endosperm starch refers to the cooking temperature at which water is absorbed and the starch granules swell irreversibly in hot water with a simultaneous loss of crystallinity and birefringence (Juliano, 1993). The gelatinization temperatures of rice varieties could be classified as low (55-70°C), intermediate (70-74°C), and high (75-79°C) (Dela Cruz and Khush, 2000). An estimate of the gelatinization temperature is indexed by the alkali spreading value (Little et al., 1958). The degree of spreading value of individual milled rice kernels in a weak solution (1.7% KOH) closely correlated with gelatinization temperature. Rice with a low gelatinization temperature disintegrates completely, whereas rice with an intermediate gelatinization temperature shows only partial disintegration (Delwiche et al., 1996). Rice with a high gelatinization temperature remains largely unaffected in the alkali solution as shown in Table 2.10. In a breeding program, the alkali spreading value is extensively useful for estimating gelatinization temperature.

An important property of rice, gelatinization temperature is closely related to the overall rice cooking behavior and to the texture of cooked products. During rice cooking, starch granules lose birefringence and undergo gelatinization. Thus, gelatinization temperature positively correlates with cooking time of milled rice but does not correlate with the texture of cooked rice. Rice varieties with high gelatinization temperature generally have high apparent amylose content (Juliano, 1985).

2.3.4 Alkali spreading value

Alkali spreading value is used as an inverse indicator of gelatinization temperature of milled rice starch granules (Delwiche et al., 1996). The alkali spreading value relies on visual observation of the degree of dispersion of six grains after immersing overnight in 1.7% KOH for waxy and non-waxy rice, respectively. The alkali spreading value score is inversely correlated to gelatinization temperature. Rice with low gelatinization temperature completely disintegrates in 1.7% KOH solution, whereas rice with intermediate gelatinization temperature shows partial disintegration. Rice with high gelatinization remains largely unaffected in alkali solution. Alkali spreading value can be classified into 3 groups according to their gelatinization temperature: low (55-70°C), intermediate (70-74°C), and high gelatinization temperature (75-80°C) (Table 2.10) (Juliano et al., 1964).

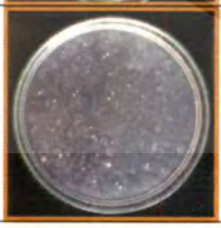
Prathepha et al. (2005) found that starch granules of glutinous rice varieties showed high levels of disintegration in alkali solution while those of non-glutinous rice varieties were significantly more resistant to alkali digestibility. In addition, the disintegration of rice starch granules was affected by the fine structure of amylopectin. Umemoto et al. (2002) reported that the amylopectin chain-length profiles of disintegrated-starch granule cultivars were clearly different from those of the unaffected-starch granule cultivars. Starch granules that had amylopectin enriched in short chains (degree of polymerization or DP 7 to 10) were more easily disintegrated in alkali solution than those in long chains (DP 12 to 21).

As previously mentioned, the physicochemical properties of aromatic rice clearly differ from non-aromatic rice varieties. As seen in Table 2.11, aromatic rice varieties are of low apparent amylose content (15.95-18.90%), soft gel consistency (74.5-89.5 mm), and alkali spreading value of 7.0 which indicates high gelatinization temperature. On the other hand, non-aromatic rice varieties are of intermediate and high apparent amylose content. The SPR60, Rice Department 7 (RD7), and Rice Department 23 (RD23) varieties are of intermediate apparent amylose content (22.30-23.41%) and intermediate gel consistency (48.0-53.0 mm). Suphan Buri 90 (SPR90), Suphan Buri 1 (SPR1), CNT1, and LPT123 are of high apparent amylose content (26.91-28.16%) and hard gel consistency. Almost all alkali spreading values of the non-aromatic rice varieties imply high gelatinization temperature except SPR 90 and LPT123 (Kongseree, 2002a).

2.3.5 Pasting properties of rice

Pasting properties of rice are key determinants of quality which affect the final product texture (Vongsawasdi et al., 2009). Limpisut and Jindal (2002) reported that pasting temperature, peak and setback viscosities were the most significant variables in the development of predictive models for evaluating the hardness and adhesiveness of cooked rice. This finding was similar to that reported by Juliano and Pascual (1980) who found that the peak viscosity correlated with hardness and stickiness of cooked rice.

Table 2.10 Numerical scale for scoring gelatinization temperature of rice

Score	Spreading characteristics	Spreading description	Gelatinization temperature
1		Grain not affected	High
2		Grain swollen	High
3		Grain swollen; collar incomplete or narrow	High
4		Grain swollen; collar complete and wide	Intermediate
5		Grain split or segmented; collar complete and wide	Intermediate
6		Grain dispersed merging with collar	Low
7		Grain completely dispersed and intermingled	Low

Source: Modified from Dela Cruz and Khush (2000)

Table 2.11 Physicochemical properties of aromatic and non-aromatic rice varieties

Variety	Apparent amylose content (% d.b.)	Gel consistency (mm)	Alkali spreading value
Aromatic rices			
KDML105	15.95	79.0	7.0
HKLG	17.34	89.5	7.0
HSPR	18.90	74.5	7.0
Non-aromatic rices			
SPR60	22.30	49.0	6.7
RD7	23.13	48.0	4.8
RD23	23.41	53.0	5.0
SPR90	26.91	33.5	7.0
SPR1	27.34	38.0	5.0
CNT1	28.05	34.0	5.4
LPT123	28.16	36.0	6.0

Source: Yadav and Jindal (2008)

Furthermore, pasting properties of rice during heating and cooling are often measured as an indicator of the processing characteristics of milled rice and rice flour (Perdon et al., 2001). These properties are primarily concerned with the gelatinization and retrogradation of starch granules. During heating in water, starch granules swell several times, depending on their initial size and resulting from the loss of crystalline order and water absorption. Finally, the granules are partially ruptured, releasing amylose, and aggregate a three-dimensional network with the swollen granules embedded into the matrix. The swollen granules mainly contribute to the increase in viscosity in RVA and the breakdown viscosity is caused by the breakdown of the gelatinized starch granules. This phenomenon is generally known as “gelatinization of starch” (Han and Hamaker, 2001; Mariotti et al., 2009).

Afterward, the swollen starch granules form a strong packed gel structure with high shear resistance during cooling due to “starch retrogradation”. Retrogradation of gelatinized starch involves the reordering of the amylose chains in short-term period and a slower reorganization of amylopectin after longer periods. Retrogradation is the main phenomenon that influences the texture of cooked rice. The rate of retrogradation is affected by several factors, including amylose and amylopectin ratios, protein, and fiber (Mariotti et al., 2009).

The pasting properties of rice can be determined by Brabender visco/amylograph and RVA. RVA measures viscosity changes during a set temperature profile. These changes have been demonstrated in the RVA amylograph as shown in Figure 2.1. The values of viscosity were reported in units termed "rapid visco units (RVU)" (Blankeney et al., 1991). The formation of RVA curve involves a transition from a powder of semicrystalline polymers and complexed lipids to a paste of gelatinized and denatured polymers and lipid. The viscosity begins in excess water of hydrated starch at 65°C. As the same sample is heated further, viscosity rapidly increases as starch granules swell, amylose leaches, and some amylose complexes with lipids and protein presumably denature. Peak viscosity occurs when swelling and shear are balanced. During breakdown, the rice gel displays thixotropic behavior, either due to alignment or mechanical breakdown of polymers. The third region of the curve, from the trough to final viscosity, occurs as the system cools to 50°C. The composition of the paste at the trough also influences lift-off, during which amylose molecules aggregate into a network, embedding remnants of protein within starch granules (Fitzgerald et al., 2003).

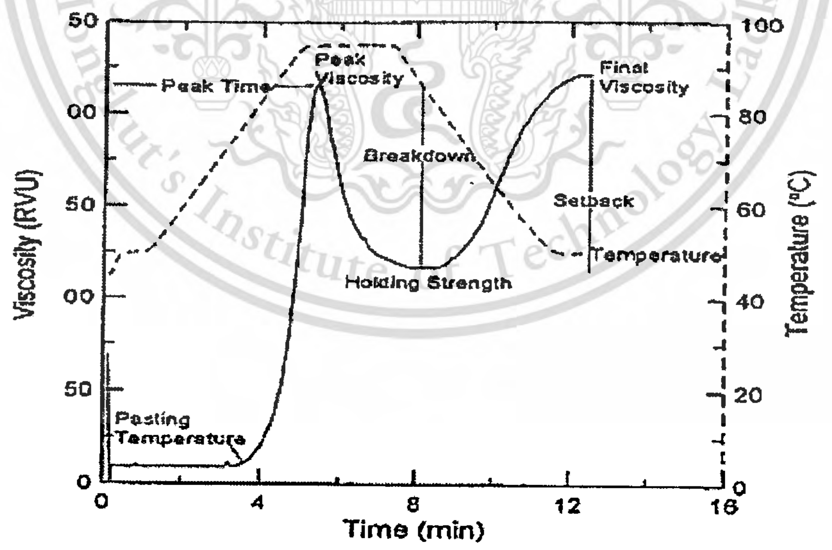


Figure 2.1 Rapid visco amylograph analysis

Source: Blankeney et al. (1991)

RVA parameters comprise peak, breakdown, setback, final, trough viscosities, peak time and pasting temperature. From Figure 2.1, the definitions of these properties are as follows: *Peak viscosity* represents the maximum viscosity recorded during the heating and occurs after the heating cycle reaches 95°C. *Breakdown viscosity* is the viscosity of the paste during the 95°C holding period. *Setback* is an indicator of retrogradation of the paste. *Final viscosity* is the viscosity at the finish of the test, and *trough* (no analogous amylograph term) means the maximum viscosity occurs during the cooling period (Delwiche et al., 1996).

Viscosity is measured as resistance to stir as the slurry of flour water is heated. The processes and interactions that occur during heating and stirring likely depend on the physical characteristics of the different components of the flour (Fitzgerald et al., 2003). Several factors affect RVA amylograph, such as rice composition, amylose and amylopectin ratios, molecular structure, particle size, shear, gelling rates, and others. Among these factors, the amylose and amylopectin ratio is the major factors that influence the pasting properties of rice. Starch swelling is a property of amylopectin whereas amylose has been known to restrict it. Restricted starch granule swelling results in a lower peak viscosity based on measurement with a Brabender viscoamylograph and RVA. Breakdown viscosity positively correlates with the proportion of short amylopectin chains, negatively with long chains, and also negatively with amylose content (Meadows and Barton-II, 2002; Patindol et al., 2009). In addition, protein and fat contents are crucial for the melting point in rice and the rate of retrogradation of starch (Singh et al., 2000).

Furthermore, pasting characteristics are related to the classification of rice. Noosuk et al. (2003) reported that peak viscosity and swelling power could classify rice varieties as waxy and non-waxy rice. It was found that the waxy rice had a higher peak viscosity and swelling volume than the non-waxy rice. Pitiphonpong and Suwannaporn (2009a) suggested that peak viscosity, setback viscosity, and principal component analysis (PCA) could be used as variables to classify cultivated locations of KDML105 into four groups: the upper central region, the lower central region, the lower northeast region, and the upper northeast region of Thailand.

Therefore, it is possible to discriminate rice varieties according to their physicochemical properties such as apparent amylose content, gel consistency, alkali spreading value, and some pasting properties of rice such as peak, breakdown, and setback viscosity.

Furthermore, volatile compounds also can be used to classify rice varieties into two groups: aromatic and non-aromatic rice varieties (Juliano, 1993; Dela Cruz and Khush, 2000).

2.4 Factor affecting rice composition

The composition of rice is influenced by rice varieties, growth conditions, and processing technology. Rice varieties relate to the grain quality characteristics. Furthermore, growth conditions strongly affect composition and functionalities of rice. Lastly, processing technology, such as handling, drying, storage, rice mill processing, especially the control of degree of milling during rice milling, also affects the composition of rice (Bahmaniar and Ranjbar, 2007).

2.4.1 Rice varieties and environment

Rice varieties and environment impact influence the composition of rice. Many rice varieties differ in hardness distribution of the endosperm. Nagato and Kono (1963) classified 380 rice varieties on the basis of hardness distribution, length to width ratio, and cross-section structure of the endosperm tissue. The results showed that *indica* varieties tended to have a hardness ratio of less than 1.0 whereas a hardness ratio more than 1.0 was observed in *japonica* varieties.

Environment affects the composition of rice in terms of aroma, apparent amylose content, gel consistency, and elongation ratio. Aroma development is influenced by both genetic factors and environment. It is known that aroma is best developing where growing temperature is cooler during maturity (Somrith, 1996). Basmati rice varieties require relatively cooler temperature (25°C/21°C-day/night) during crop maturity (Singh et al., 2000). In general, temperature negatively correlates with apparent amylose content and positively with gelatinization temperature (Lee et al., 1996). In addition, Asaoka et al. (1985) reported that ambient temperature during ripening influenced the fine structure of amylopectin and amylose of rice. Dela Cruz et al. (1989) stated that apparent amylose content decreased with increase in temperature whereas gel consistency and gelatinzation temperature did not show any interaction with temperature.

Grain elongation is also influenced by environmental factors, especially temperature at the time of ripening. Maximum grain elongation was observed at 25/21°C-day/night temperature during the ripening. This explained differences in elongation between basmati rice grown in Punjab which elongated more than the one grown at Dokri due to high temperature (Dela Cruz, 1991).

2.4.2 Growth conditions and geological cultivations

Growth conditions of rice also influence the composition of rice. Fertilizer-nitrogen application showed to be effective for increasing rice grain protein content when applied up to panicle initiation stage (Patrick and Hoskins, 1974). Bahmaniar and Ranjbar (2007) evaluated the effects of various levels of nitrogen and potassium application on physicochemical properties. The results showed that the application of nitrogen increased gel consistency but decreased apparent amylose content of rice grain. However, nitrogen fertilizer insignificantly affected the gelatinization temperature. Application of potassium increased gel consistency and protein content but did not significantly affect the gelatinization temperature and apparent amylose content.

In addition, geological cultivation affects the chemical composition of rice. Gomez and Veskosit (1973) found that the composition, such as protein, lipid, fiber, ash, moisture, and carbohydrate, of rice varieties which were grown in the Philippines and Thailand was greatly different. Singh et al. (2005) later reported that geological cultivation affected variation in composition and cooking quality of rice grain. The results were in accordance with the work of Cameron et al. (2007) which showed that medium-grain rice cultivars from Arkansas and California differed in physical attributes, chemical composition, and functionality. However, when the cultivars were grown in Arkansas, their differences were significantly reduced, suggesting that the unique environments of both states have a considerable impact on the rice composition and properties.

The cultivated location affected the aroma content of KDML105. Somrith (1996) reported that Hom Mali rice harvested from the northeast region of Thailand had stronger and more intense aroma than that cultivated from the central and other regions. It is believed that the aroma in KDML105 varies, depending upon the locations, soil types, and soil fertility. Furthermore, the locations also affect minerals in rice grain. Ahn et al. (2010) studied the influence of variety, location, growing year, and storage on the total phosphorus in Korean rice varieties. The results showed that locations and varieties had a significant effect on the total phosphorus content in rice.

2.4.3 Degree of milling

Degree of milling is a measure of the bran layers and germs that have been removed from the rice endosperm. The degree of milling is expressed as the weight percentage of bran removed from brown rice (Wadsworth, 1994). It is extremely important to both the rice industry and consumers. The amount of bran remaining affects the stability, quality, and value of product, with respect to appearance and end-use functionality (Chen et al., 1997). Moreover, it is important in determining the grade of milled rice as it affects head rice yield, insect infestation, and the economic return of the milled rice (Yadav and Jindal, 2008).

The methods including visual examination, chemical composition analysis, and optical measurements have been developed to indicate the degree of milling of milled rice. Additionally, the weight percentage of bran removed from brown rice is a basic technique to express the degree of milling (Wadsworth, 1994). The USDA Federal Grain Inspection Service (FGIS) standards specify that the degree of milling is classified by visual observation into four grades: well-milled (removed outermost cells from starchy endosperm), reasonably well-milled (7-8% weight of brown rice), lightly milled (5-6% weight of brown rice), and under-milled (3-4% weight of brown rice) (Archer and Siebenmorgen, 1995). Chemical composition analysis typically consists of a measure of surface fat although total fat or thiamin and phosphorus contents of the milled rice have been used (Wadsworth et al., 1991). Optical measurements determine the intensity of the visible light reflected from or transmitted through milled rice. At present, there exist a number of commercial measurement systems of the optical degree of milling, an example of which is the Satake milling meter which uses the amounts of both reflected and transmitted light to calculate the degree of milling on a scale of 0 to 199 (Siebenmorgen and Sun, 1994).

Milling time affects both head rice yield and degree of milling. Andrews et al. (1992) showed that as milling time increased, head rice yield decreased and degree of milling increased. Yadav and Jindal (2008) reported that head rice yield reduced in the range of 18.9-5.5% in all rice varieties after 2.5 minutes of milling from the initial head rice yield range of 68.2-92.6%. Siebenmorgen and Sun (1994) also showed high correlations between the degree of milling readings taken by the Satake milling meter and surface fat concentration measurements. Furthermore, Park et al. (2001) reported that whiteness increased significantly with increased removal of the bran layer during milling.

2.4.3.1 Effect of degree of milling on composition and physiochemical properties of rice

Degree of milling not only influences the milling quality but also affects the composition and physicochemical properties of rice. Brown rice consists of bran layer (6-7% of its total weight), embryo (2-3%) and endosperm (about 90%), and contains more nutrients, such as proteins, lipids, vitamins and minerals, than milled rice. These nutrients exist mainly in the germ and bran layers of the rice grains. However, they are almost entirely removed during the milling process from brown rice to milled rice (Chen et al., 1998; Park et al., 2001; Lamberts et al., 2007).

A) Moisture content

Moisture content, head rice yield, and degree of milling are closely correlated. Webb and Calderwood (1978) investigated the effect of rice moisture content on the degree of milling and head rice yields obtained under the standard milling conditions. Rice samples with different moisture contents were milled to the same degree of milling by adjusting milling conditions. The results showed that the degree of milling with low moisture rice (6-10%) was considerably more resistant to milling at each mill setting than samples of high moisture rice (14-16%). Thus, head rice yield from the low moisture rice milled at standard mill settings was higher than that from high moisture rice. Park et al. (2001) later found that degree of milling affected moisture content (Table 2.12). Moisture content tended to decrease with an increase in the degree of milling up to 14%. This result might be attributable to the increased temperature of rice grain during rice mill processing.

Table 2.12 Effect of degree of milling on the proximate composition of rice

Degree of milling (%)	Moisture content (%)	Protein content (%)	Fat content (%)	Ash content (%)
8.0	15.4	6.65	0.55	0.42
9.5	14.8	6.29	0.37	0.41
11.0	15.0	6.27	0.24	0.32
12.5	14.4	6.09	0.20	0.26
14.0	14.2	5.92	0.19	0.26

Source: Park et al. (2001)

B) Protein content

During the milling process from brown rice to milled rice, the loss of protein content reached 28.6%. The protein content decreased as a function of degree of milling and reduced from the outer to the core endosperm (Lamberts et al., 2007). The phenomenon is explained in Table 2.12 and Figure 2.2. This corresponds with Lyon et al.'s work (1999) which found that deep-milled samples generally had lower protein content than regular-milled samples.

C) Fat content

The effect of degree of milling on fat content is similar to that on the moisture and protein contents (Table 2.12). Fat content decreased as the degree of milling increased. This could be explained by the removal of the caryopsis coat, aleurone, and subaleurone layers which contain high fat content (Park et al., 2001).

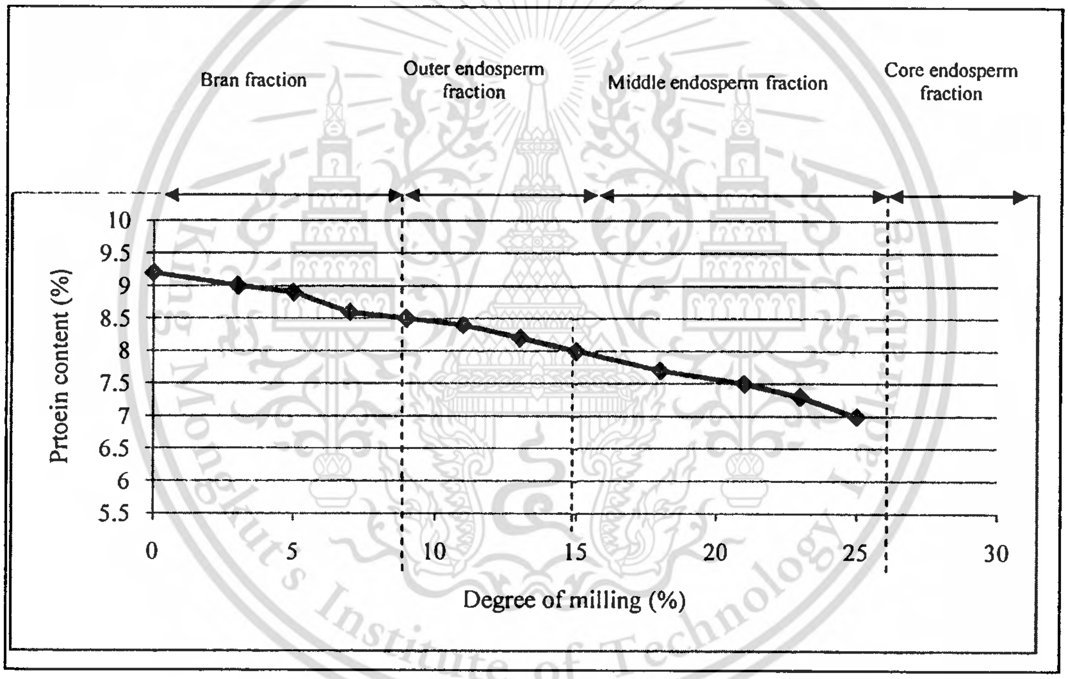


Figure 2.2 Protein content of rice as a function of degree of milling

Source: Lamberts et al. (2007)

D) Vitamin and mineral contents

Vitamins and minerals, concentrated in the germ and outer layer of the starchy endosperm, are removed in the course of milling, thus reducing the nutritive value of the rice (Mohpatra and Bal, 2007). Villareal et al. (1991) reported the amounts of various minerals and vitamins removed from brown rice during milling to produce well-milled rice. The results showed that thiamine content dramatically decreased up to 87%. This corresponds with the work of Bryant et al. (2005) who studied the effect of degree of milling on phytic acid and zinc in Bijing 37 and Zhongyou 752 varieties. Phytic acid and zinc of both varieties tended to decrease as the milling time increased (Table 2.13).

Lamberts et al. (2007) also found that the mineral content decreased as a function of degree of milling. Its average level in brown rice (0% degree of milling) was 1.6%, and mineral concentrations decreased from the outer bran layers toward the middle endosperm.

Table 2.13 Effect of milling time on phytic acid and zinc contents in milled rice

Milling time (seconds)	Rice variety			
	Bijing 37		Zhongyou 752	
	PA (gkg^{-1})	Zn ($mgkg^{-1}$)	PA (gkg^{-1})	Zn ($mgkg^{-1}$)
0	8.9	22.1	7.8	22.8
6	9.0	20.8	7.6	20.7
10	8.9	20.0	7.9	22.6
20	6.9	19.8	8.7	22.6
30	6.5	21.7	6.8	21.5
45	6.3	22.3	6.5	18.1
60	4.8	21.2	6.3	17.7
90	3.1	20.1	4.7	16.3
120	2.1	15.0	3.2	16.4
180	0.7	14.8	0.9	15.9
300	0.2	13.7	0.1	16.7

Source: Bryant et al. (2005)

E) Apparent amylose content

Apparent amylose content is one of the major criteria in evaluating rice quality because of its very close relationship with cooking and eating qualities (Juliano, 1993). Degree of milling increases the apparent amylose content while reducing the moisture, protein, fat, vitamin and mineral contents. Apparent amylose content was positively correlated with degree of milling in that it increased as the degree of milling increased (Perdon et al., 2001). In 2003, Zhang et al. also pronounced the corresponding correlation in *japonica* and *indica* rice varieties. The apparent amylose content of *japonica* and *indica* rice respectively increased 1.36 and 1.95% when the degree of milling increased by 10%. Both results indicated that the apparent amylose content of outer layer in rice grain is lower than that of inner layer. In addition, the increase in the apparent amylose content of the rice starch from outer to inner layers reflects a significant difference in rice starch composition (Wadsworth, 1994).

F) Gel consistency

As mentioned in 2.3.5, gel consistency determination, based on the consistency of milled rice paste, is performed by boiling rice flour in alkali solution and then cooling to room temperature. Thus, this procedure is concerned with the gelatinization and retrogradation of rice starch which are influenced by particle size, protein, lipid, apparent amylose content, and degree of milling (Cagampang et al., 1973; Marshall et al., 1990; Marshall, 1992).

The degree of milling is a very important factor affecting gel consistency which decreased as the degree of milling increased. This phenomenon is caused by lipid content in the outer layer of rice grain that is removed during the milling process from brown rice to milled rice. Perez (1979) found that the lipid in rice grain is a major constituent that affects gel consistency. This effect of lipid on gel consistency is probably caused by the formation of an amylose-fatty acid-complex, resulting in the flow of gel paste being inhibited. Furthermore, Mariotti et al. (2009) reported that gel consistency value decreased accordingly with increase in the degree of milling, resulting in a higher proportion of the apparent amylose content and degree of retrogradation of rice starch.

G) Alkali spreading value

Alkali spreading value is used as an inverse indicator of the gelatinization temperature of milled rice (Delwiche et al., 1996). In 1975, Sidhu et al. investigated the effect of extended milling of three coarse (IR8, Jaya and HM95), two medium-fine (Palman 579 and RP5-3), and fine-grained (Basmati 370) Indian varieties of paddy rice. The results showed that all varieties tended to increase alkali spreading value with increase in degree of milling. However, the effect of degree of milling on alkali spreading value of rice grain is inconclusive because of the limited data.

H) Pasting properties of rice

Pasting properties of rice are related to gelatinization of rice starch which is influenced by the composition of rice grain, such as apparent amylose content, amylopectin content, proteins and lipids (Fitzgerald et al., 2003; Mariotti et al., 2009). The components, especially lipid and protein contents located in the outer layers of the rice grain, may act as a diffusion barrier for water retarding its penetration to the starch granules, thereby delaying the gelatinization process. During rice mill processing, these constituents and a part of the starchy endosperm are removed, resulting in the lower gelatinization temperature (Desikachar et al., 1965; Champagne et al., 1990). These results were consistent with that by Marshall et al. (1990) who observed the significantly reduced pasting temperatures with the removal of the outer layers of the kernel.

Furthermore, Biliaderis and Juliano (1993) reported that lipid in rice grain can form with both amylose and amylopectin molecules in three-dimensional conformation affecting the thermal and mechanical properties of the gel. Whistler and BeMiller (1997) later found the effect of lipid and protein concentrations on starch pasting properties, either facilitating or hindering junction zone formation, thus affecting the firmness of the gel during pasting.

From literatures, the degree of milling significantly positively correlates with the pasting properties of rice. Peak viscosity, trough, breakdown, final and setback viscosities tended to increase with the increased degree of milling (Perdon et al., 2001). Peak viscosity, reflecting the swelling extent of the starch granules, was higher for milled rice in relation to its higher starch and lower protein content. The amylase activity of brown rice played a major role in the reduction of peak viscosity. The amylase activity decreased with the increased degree of milling, resulting in the increased peak viscosity (Perdon et al., 2001; Mariotti et al., 2005).

Setback viscosity is also affected by the degree of milling. The setback value of brown rice was lower than that of milled rice due to the increases in the latter's apparent amylose content and retrogradation (Mohapatra and Bal, 2006; Patindol et al., 2009). The pasting properties of rice flour at different degrees of milling are shown in Table 2.14.

Table 2.14 Pasting properties of rice flour at different milling degrees

Degree of milling (%)	Pasting temperature (°C)	Maximum viscosity (BU)	Consistency (BU)	Breakdown viscosity (BU)	Setback viscosity (BU)
8.0	63.65	469.5	166.5	216.0	-100.5
9.5	63.45	488.5	209.5	286.5	-77.0
11.0	63.35	530.0	240.0	294.5	-54.5
12.5	63.20	580.0	260.0	308.5	-48.5
14.0	63.15	586.5	260.5	312.0	-51.5

Source: Park et al. (2001)

2.4.3.2 Effect of degree of milling on sensory and cooking quality

Park et al. (2001) reported that the degree of milling did not affect the physicochemical properties, but sensory and cooking quality of rice. They found that removing the outer 1% of brown rice kernel increased the water absorption during cooking, thereby giving rise to the increased volume of cooked rice. Additionally, Mohapatra and Bal (2006) reported that the degree of milling positively affected water uptake ratio, volume expansion ratio, length expansion ratio, cohesiveness, and adhesiveness; but negatively affected the optimum cooking time and hardness.

2.5 Near infrared reflectance spectroscopy and its application in rice grains

Nowadays the near infrared reflectance (NIR) spectroscopy is one of the best techniques for examining rice quality. This technique gives the absorption in the near infrared region that can be related to the main chemical components of rice grain, such as carbohydrates, proteins, fats and waters (Williams and Norris, 2001). Several studies have been reported on the use of NIR spectroscopy as a rapid and cost-effective analytical tool to determine the food structure and properties in the fundamental research and to monitor process as on-line sensors (Ozaki et al., 2006; Nicolaï, et al., 2007).

2.5.1 Fundamentals of near infrared spectroscopy

Near infrared radiation was discovered by Friedrich Wilhelm Herschel in 1800 and by definition covers the wavelength range from 780 to 2500 nm. When radiation passes through the sample, the incident radiation may be reflected, absorbed, or transmitted. The relative contribution of each phenomenon depends on a specific frequency of molecular bond of the chemical constitutions and physical parameters of the sample and thereby builds a unique characteristic spectrum that behaves as a fingerprint of the sample. Advanced multivariate statistical techniques, such as partial least squares regression (PLSR) and multiple linear regressions (MLR), are applied to extract the required information from the usually original spectra (Nicolaï et al., 2007).

The intensity of one wavelength transmitted through the sample (I) is related to the intensity incident on this sample (I_o) to the path length in the sample (b) and to the concentration of the desired component (c) by the equation of Beer-Lambert (Osborne et al., 1993a).

$$\log (I_o/I) = abc$$

where:

a	=	absorptivity of the component at a particular wavelength
$\log (I_o/I)$	=	absorbance (A)

Molecules that absorb near infrared energy vibrate primarily in two fundamental modes: (1) stretching and (2) bending. Stretching is defined as a continuous change in the interatomic distance along the axis between two atoms, while bending is defined as a change in the bond angle between two atoms. Stretching vibrations occur at higher frequencies (lower wavelength) than bending vibrations. Most absorption bands in the near infrared region are overtone or combination bands of the fundamental absorption bands in the infrared region of the electromagnetic spectrum due to vibrational and rotational transitions (Nicolaï et al., 2007, Workmand and Weyer, 2008).

Combination bands are the summation of fundamental bands. Most near infrared absorptions result from the harmonics and overtones of X-H fundamental stretching and bending vibrational modes. Other functional groups relative to NIR spectroscopy can include hydrogen bonding, carbonyl carbon to oxygen stretch, carbon to nitrogen stretch, carbon to carbon stretch, and metal halides. Specific molecular bonds, most active in the NIR spectroscopy, are listed in Table 2.15, with X-H bonds being the more active and intense (Workmand and Weyer, 2008).

Mostly observed bands in the NIR spectroscopy include the combination bands and first, second, or third overtones of O-H, N-H, and C-H fundamentals (Williams and Norris, 2001; Workmand and Weyer, 2008).

Table 2.15 Specific molecular bonds active in NIR

Molecular bonds	Molecular bonds
C = O from aldehydes	C – N from amines, alkyl
C = O from amides	C – N from amines, aromatic
C = O from carboxylic acids	C – O from alcohols, ethers, and esters
C = O from esters	N – H from amides
C = O from ketones	N – H from amines
C – H from aldehydes	NO_2 from nitro groups
C – H from alkanes	O – H from alcohols (no hydrogen bonding)
C – H from alkenes	O – H from alcohols (with hydrogen bonding)
C – H from alkynes	O – H from carboxylic acids
C – H from aromatic compounds	

Source: Workmand and Weyer (2008)

2.5.2 Pre-processing of spectral data

Near infrared radiation interacts with the sample as reflection, refraction, and transmission. Thus, its spectra contain information relating to differences in bond strengths, chemical species, electronegativity, and hydrogen bonding. During measurement of a sample, original spectrum can cause an offset error or multiplicative errors due to coloration of the sample and variable particle sizes which caused scattering effect appearance, and to pathlength differences (Nicolaï et al., 2007, Workmand and Weyer, 2008).

These effects cause the spectral variations and baseline shifts that subsequently directly affect the calibration model. Therefore, pre-processing of spectral data is often of importance. The main goal of pre-processing of spectral data is to reduce the undesired effects that cause the calibration problems. Several methods are used for pre-processing spectral data, such as derivative, multiplicative scatter correction (MSC), standard normal variate (SNV), normalization, and baseline correction (Rinnan et al., 2009). However, in this literature review, only derivative, MSC and SNV employed in this work will be discussed.

2.5.2.1 Derivatives (Rinnan et al., 2009)

Derivatives are usually used to remove background signals or to enhance visual resolution. Generally, second derivative is the most popular method for processing near infrared spectra. A simple formula for calculating second derivative which employs three point second central differences is given by:

$$\left\{[d^2\log(1/R)] / d^2\lambda\right\}_{\lambda-\lambda_i} = c[\log(1/R_{\lambda-\lambda_i}) - 2\log(1/R_{\lambda_i}) + \log(1/R_{\lambda_{i+j}})]$$

where:

c = scaling constant

i = wavelength index where the second derivative is computed

j = finite difference gap

2.5.2.2 Multiplicative scatter correction (MSC)

Scattering results from multiple refractions at phase changes inside the material. The main scattering effects in cereals are different sizes of starch granules caused by diffraction at the particle surface where the refractive index is different from that of the surroundings. The scattering is also dependent on the size, shape, and microstructure (Nicolaï et al., 2007). Moreover, the log $1/R$ values of reflectance spectra of ground grain samples are affected by particle size, with coarser samples having higher absorption and higher log $1/R$ values. Therefore, the particle size effect is also greater at longer wavelength (Norris and Williams, 1984).

This effect can be removed by applying MSC which rotates each spectrum so that it fits as closely as possible to the mean of reference spectrum or the average spectra over a set of samples (Rinnan et al., 2009). MSC is used to minimize the additive and multiplicative effects of scatter arising mainly from differences in particle size between samples. It is performed by calculating the slope, *a*, and offset, *b*, of the regression between each individual spectrum and a reference spectrum (usually the average spectrum for the calibration set) (Romía and Bernàrdez, 2009).

$$X = aX_{ref} + b$$

Coefficients a and b are used to correct each spectrum by using the expression below:

$$X_{corr} = \frac{X-b}{a}$$

Where X_{ref} and X_{corr} are a reference and corrected spectra, respectively.

2.5.2.3 Standard normal variate (SNV)

SNV treatment is done by autoscaling each spectrum by calculating the mean and standard deviation between the absorbances for the spectrum:

$$X_{SNV} = \frac{X - X_{avg}}{X_{sd}}$$

Where X is the spectrum of NIR, X_{avg} is the average spectrum of NIR and X_{sd} is the standard deviation spectrum of NIR. This pre-processing also reduces the additive and multiplicative effects of scattering (Romía and Bernàrdez, 2009). In comparison with MSC, the SNV technique does not require a reference spectrum. In general, SNV and the original MSC lead to very similar results (Rinnan et al., 2009).

2.5.3 Partial least square regression (PLSR) for calibration model

The calibration model is constructed on the relationship between the dependent "Y variables" (protein, apparent amylose content, gel consistency, etc.) and the independent "X variables" (optical data; log 1/R). The calibration model is usually constructed from two samples sets: calibration and validation set. Calibration set, obtained from spectral data, is mainly used for predicting the data, while validation set is for evaluating calibration equation (Williams, 2007). As previously stated, a variety of mathematical algorithms, such as multiple linear regression (MLR), principal component regression (PCR), PLSR, and artificial neural networks (ANN), are available for constructing models and a wide range of statistical techniques existed for their assessment and optimization (Romía and Bernàrdez, 2009).

PLSR analysis is widely used in Vis/NIR spectroscopy analysis. The PLSR analysis can establish a regression model to predict the content of chemical components or be responsive to the Y-value. PLSR considers simultaneously the variable matrix Y and the variable matrix X (Liu and He, 2008). The formula of PLSR is:

$$Y = k_0 + k_1F_1 + k_2F_2$$

The Y-variables are related to the variables x via auxiliary variables called latent variables, or PLSR factors or components, which are linear combinations of the variables X_1, X_2,....,X_k and highly similar to the PCs calculated by PCA and used for PCR. In PLSR, each component is obtained by maximizing the covariance between Y and every possible linear function of X. For the interpretation of the PLSR model, the x-loadings show how well the x-variable is taken into account by the model components. It can be used to understand how much each x-variable contributes to the meaningful variety variation in the data, and to interpret variable relationships. It is also useful to interpret the meaning of each model component. The loading weights show how much each wavelength (x-variable) contributes to explain the response variation along each model component. The loading weights are normalized so that their lengths could be interpreted as well as their directions (Wold et al., 2001; Liu and He, 2008; Romía and Bernàrdez, 2009).

To evaluate the prediction ability of the calibration model in PLS analysis, the cross validation technique is used. Prediction ability is then tested by predicting samples with known dependent variables. Samples in the calibration set are grouped into smaller sets, and the dependent variables of these sets can be predicted from the calibration models of the remaining samples. Cross validation of a calibration model makes it possible to select the optimum number of latent variables or factors. When the number of latent variables exceeds the optimum number, the error of prediction increases again. By including too many latent variables, over-fitting of the calibration model is determined. The standard error of prediction (SEP) of a cross-validated calibration model is calculated by the following equation (Christy and Kvalheim, 2007):

$$\text{SEP} = \left[\frac{1}{I_p}\sum_{m=1}^{n_v} \quad \sum_{i=1}^{I_{vm}} f_i^{\,2}\right]$$

When I_{vm} is the number of predicted samples in the cross validation of group m. n_v is the number of groups used in the cross validation. I_p is the total number of prediction samples and f_i is the residual variance of the sample i after A factors (Christy and Kvalheim, 2007).

2.5.4 Principal component analysis (PCA) for discrimination analysis

PCA is a data reduction technique that aims to explain most of the variance in the data while reducing the number of variables to a few uncorrelated components. The information carried by the original variables is projected onto a smaller number of underlying ("latent") variables called principal components (PCs). The first principal component (PC_1) covers as much of the variation in the data as possible. The second principal component (PC_2) is orthogonal to the first and covers as much of the remaining variation as possible and so on. By plotting the principal components, one can view inter-relationships between different variables, and detect and interpret sample patterns (CAMO Software AS, 1998; Anderson, 2003).

This method can identify groups of variables or individuals. PCA is used to identify groups of variables based on the loadings, i.e., correlations between the variables and the principal components; and groups of individual based on the principal component scores. The result of PCA is generally called "score" (equivalent to the variables) which is used in estimating the bilinear modeling. Score contains the information of several variables which is concentrated onto a few underlying variables. Each sample has a score along each model component. The scores show the locations of the samples along each model component, and can be used to detect sample patterns, groupings, similarities or differences (Anderson, 2003).

Loading is one result of PCA and is used to estimate the bilinear modeling. The loading is embedded with information of several variables in a new component. Each variable has a loading along each model component. The loading shows how well a variable is taken into account by the model components and can be used to understand how much each variable contributes to the meaningful variation in the data and to interpret variable relationship. The loading is also useful for interpreting the meaning of each model component (Anderson, 2003; Kara, 2009).

In the classification of cereal grains by PCA, Delwiche et al. (1995) applied NIR reflectance spectroscopy and PCA to classify amylose content in rice. Delwiche et al. (1999) later identified wheat varieties using NIR spectra. Kim et al. (2003) determined the authentication of Korean rice also using NIR spectra. In addition, Pitiphonpong and Suwannaporn (2009a) applied PCA to classify the KDML105 variety using pasting and calorimetric properties. It succeeded as an effective tool to classify the KDML105 variety from different cultivated locations using four factors of PCA which accounted for 92.7% of the total variance. However, their works did not take into account the degree of milling that may affect the identification of rice.

2.5.5 Partial least square discriminant analysis (PLS-DA) for classification analysis

This supervised pattern recognition technique is a variation of the previously described PLS regression, with the purpose of making qualitative assignation rather than predicting a qualitative parameter (Kasemsumran et al., 2005; Liu et al., 2008). With this technique, the identified variations in the data set are correlated with class membership; therefore, the PLS is employed to discriminate between different classes. The creation of the PLS-DA model consists of two basic steps: A conventional PLS model is first built on group indicator variables, after which the resultant observations are then classified based on the group indicator variables (Liu et al., 2008).

For class membership identification, a dummy matrix (*Y*) consisting of ones and zeros for classes is paired with *X* spectral data. The developed PLS-DA model can then be employed to classify new samples. This is achieved by predicting the *X* spectral data of each new sample and identifying how good the predicted data belong to each class *Y* (Kasemsumran et al., 2005; Liu et al., 2008; Görlitz et al., 2009). In this case, receiver operating characteristic (ROC) curves can be used to assess and optimize the class specificity and sensitivity with different thresholds (Barker and Rayens, 2003; Ballabio and Todeschini, 2009; Rossini et al., 2011).

2.5.6 Application of NIR spectroscopy for determination of rice quality

Nowadays NIR spectroscopy analysis has replaced wet analysis to a great extent. There exist extensive research studies whose main focus has been on the development of global calibration models that are of commercial and technical values and accurately predict rice quality. Research publications on the application of NIR spectroscopy for the prediction of rice quality are shown in Table 2.16.

Table 2.16 Application of NIR spectroscopy for prediction of rice quality

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Milling quality					
- Degree of milling	Milled rice	surface lipids, total lipids, bran removal	MLR: SEE = 0.112, r^2 = 0.98	NIR: 800 – 1,800	Stermer *et al.* (1977)
- Degree of milling	Brown, milled rice	Bran removal	MLR: SEE = 0.569, r^2 = 0.988 SEP = 0.744, r^2 = 0.985 PLS: SEE = 0.511, r^2 = 0.992 SEP = 1.07, r^2 = 0.965	NIR: 1100 – 2500	Wadsworth *et al.* (1991)
- Degree of milling	Short, medium, long milled rice (n=196)	Milling meter	PLS: SEP = 2.7, r^2 = 0.969	NIR: 450 – 1,048	Delwiche *et al.* (1996)
- Whiteness	Short, medium, long milled rice (n=196)	Milling meter	PLS: SEP = 0.60, r^2 = 0.966	NIR: 450 – 1,048	Delwiche *et al.* (1996)
- Transparency	Short, medium, long milled rice (n=196)	Milling meter	PLS: SEP = 0.15, r^2 = 0.927	NIR: 450 – 1,048	Delwiche *et al.* (1996)
- Degree of milling	Milled rice and rice Flour (n=120)	Milling meter	PLS: Milled rice: SECV = 4.2-6.3 Rice flour : SECV = 8.2 Milled rice : SECV = 4.29-9.90	NIR: 750 – 1,050 NIR: 750 – 1,050 NIT: 750 – 1,050	Barton *et al.* (1998)
- Whiteness	Milled rice and rice Flour (n=120)	Milling meter	PLS: Milled rice: SECV = 0.98-1.28 Rice flour : SECV = 1.90 Milled rice: SECV = 1.01-4.43	NIR: 750 – 1,050 NIR: 750 – 1,050 NIT: 750 – 1,050	Barton *et al.* (1998)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Milling quality					
- Transparency	Milled rice and rice flour (*n*=120)	Milling meter	PLS: Milled rice: SECV = 0.14-0.19 Rice flour : SECV = 0.2 Milled rice: SECV = 0.19-0.21	NIR: 750 – 1,050 NIR: 750 – 1,050 NIT: 750 – 1,050	Barton *et al*. (1998)
- Degree of milling	Milled rice and rice flour (*n*=96)	Milling meter	PLS: Milled rice: SECV = 3.13 Rice flour : SECV = 7.69 Milled rice: SECV = 6.01	NIR: 400 – 2,498 NIR: 400 – 2,498 NIT: 850 – 1,050	Barton *et al*. (2000)
- Whiteness	Milled rice and rice flour (*n*=96)	Milling meter	PLS: Milled rice: SECV = 0.71 Rice flour : SECV = 1.76 Milled rice: SECV = 1.54	NIR: 400 – 2,498 NIR: 400 – 2,498 NIT: 850 – 1,050	Barton *et al*. (2000)
- Transparency	Milled rice and rice flour (*n*=96)	Milling meter	PLS: Milled rice: SECV = 0.20 Rice flour : SECV = 0.22 Milled rice: SECV = 0.24	NIR: 400 – 2,498 NIR: 400 – 2,498 NIT: 850 – 1,050	Barton *et al*. (2000)
- Whiteness	Short grain brown rice, milled rice (*n*=61)	Milling meter	PLS: Brown rice: SECV = 0.52,r = 0.78 Brown rice: SECV = 0.62, r = 0.66 Milled rice: SECV = 0.71, r = 0.87 Milled rice : SECV = 0.88, r = 0.79	NIR: 800 – 1,098 NIR: 1,100 – 2,498 NIR: 800 – 1,098 NIR: 1,100 – 2,498	Natsuga and Kawamura (2006)
- Transparency	Short grain brown rice, milled rice (*n*=61)	Milling meter	PLS: Brown rice: SECV = 6.02,r = 0.82 Brown rice: SECV = 6.63, r = 0.78 Milled rice: SECV = 4.10, r = 0.89 Milled rice : SECV = 6.08, r = 0.75	NIR: 800 – 1,098 NIR: 1,100 – 2,498 NIR: 800 – 1,098 NIR: 1,100 – 2,498	Natsuga and Kawamura (2006)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Moisture content (%)	Brown rice, milled rice (*n*=125)	Hot air oven at 135°C for 3 hrs	PLS: Brown rice: SEP = 0.12, r = 0.990 Milled rice: SEP = 0.17, r = 0.978	NIT: 825 – 1,075 NIT: 825 – 1,075	Shimizu *et al.* (1998)
	Whole grain rough rice (*n*=150)	AOAC (hot air oven)	PLS: Rough rice: SEP = 0.70, r^2 = 0.96	NIT: 400 – 2,498	Kawamura *et al.* (1997)
	Rough rice, brown rice	AOAC (hot air oven)	PLS: Rough rice: SEP = 0.70, r^2 = 0.96 Brown rice: SEP = 0.50, r^2 = 0.97	NIR: 400 – 2,498	Kawamura *et al.* (2003)
	Single grain brown rice (*n*=100)	Hot air oven at 135°C for 15 hrs	PLS: SEP = 0.29, r = 0.99 SEP = 0.24, r = 0.99	NIT: 800 – 1,000 NIT: 1,300 – 1,500	Rittiron *et al.* (2004)
	Short grain brown rice, milled rice (*n*=61)	Hot air oven at 135°C for 24 hrs	PLS: Brown rice: SECV = 0.15, r = 0.98 Brown rice: SECV = 0.19, r = 0.97 Milled rice: SECV = 0.16, r = 0.96 Milled rice: SECV = 0.19, r = 0.99	NIR: 800 – 1,098 NIR: 1,100 – 2,498 NIR: 800 – 1,098 NIR: 1,100 – 2,498	Natsuga and Kawamura (2006)
	Milled rice (*n*=130)	Hot air oven at 105°C for 72 hrs	MLR: SEC = 0.329, r^2 = 0.975, RPD=5.5 PLS: SEP = 0.245, ^{r2} = 0.987, RPD = 8.2	NIR: 960, 930, 980 NIR: 930 – 1,014	Lin *et al.* (2006)
Protein content (%)	Rice flour, long, medium, short grain (*n*=97)	Combustion method (*N* x 5.95)	PLS: SEP = 0.107, r^2 = 0.989	NIR: 1,100 – 2,498	Delwiche *et al.* (1995)
	Milled rice, long, medium, short grin (*n*=95)	Combustion method (*N* x 5.95)	PLS: SEP = 0.13, r^2 = 0.966	NIR: 1,180 – 1,800	Delwiche *et al.* (1996)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Protein content (%)	Milled rice, rice flour (*n*=120)	Kjeldahl method (N x 5.95)	PLS: Milled rice: SECV = 0.22-1.12 Rice flour: SECV = 0.15 Milled rice: SECV = 0.18-0.21	NIR: 1,100 – 2,500 NIR: 1,100 – 2,500 NIT: 1,100 – 2,500	Barton *et al.* (1998)
	Brown rice, milled rice (*n*=125)	Kjeldahl method (N x 5.95)	PLS: Brown rice: SEP = 0.19, r = 0.943 Milled rice: SEP = 0.16, r = 0.961	NIT: 825 – 1,075 NIT: 825 – 1,075	Shimizu *et al.* (1998)
	Whole grain rough rice (*n*=150)	Kjeldahl method (N x 5.95)	PLS: Brown rice: SEP = 0.24, r^2 = 0.70 Milled rice: SEP = 0.22, r^2 = 0.76	NIT: 400 – 2,498 NIT: 400 – 2,498	Kawamura *et al.* (1997)
	Milled rice and rice flour (*n*=96)	Combustion method (N x 5.95)	PLS: Milled rice: SECV = 0.22 Rice flour : SECV = 0.14 Milled rice: SECV = 0.20	NIR: 400 – 2,498 NIR: 400 – 2,498 NIT: 850 – 1,050	Barton *et al.* (2000)
	Long, medium, short milled rice grain (*n*=90)	Combustion method (N x 5.95)	PLS: SEP = 0.138, r^2 = 0.992	NIR: 200-1795, 2,050 – 3,570^{cm-1}	Himmelsbach *et al.* (2001)
	Long, medium, short milled rice grain (*n*=76)	Combustion method (N x 5.95)	PLS: RMSEP = 0.38, r^2 = 0.85	NIR: 400 – 2,500	Champagne *et al.* (2001)
	Rough rice, brown rice	Combustion method (N x 5.95)	PLS: Rough rice: SEP = 0.24, r^2 = 0.70 Brown rice: SEP = 0.23, r^2 = 0.68	NIR: 400 – 2,498	Kawamura *et al.* (2003)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Protein content (%)	Rice flour, long, medium, short grain (*n*=128)	Combustion method (*N* x 5.95)	PLS: SECV = 0.23, r^2 = 0.982	NIR: 400 – 2,498	Sohn *et al.* (2004a)
	Rice flour (*n*=214)	Combustion method (*N* x 5.95)	PLS: SECV = 0.22, r^2 = 0.983	NIR: 1,100 – 2,498	Sohn *et al.* (2004b)
	Single grain brown Rice (*n*=100)	Combustion method (*N* x 5.95)	PLS: SEP = 0.38, r = 0.96 SEP = 0.31, r = 0.97	NIT: 800 – 1,000 NIT: 1,300 – 1,500	Rittiron *et al.* (2004)
	Short grain brown rice, milled rice (*n*=61)	Kjeldahl method (*N* x 5.95)	PLS: Brown rice: SECV = 0.16, r = 0.96 Brown rice: SECV = 0.24, r = 0.92 Milled rice: SECV = 0.18, r = 0.95 Milled rice: SECV = 0.19, r = 0.94	NIR: 800 – 1,098 NIR: 1,100 – 2,498 NIR: 800 – 1,098 NIR: 1,100 – 2,498	Natsuga and Kawamura (2006)
Apparent amylose content (%)	Brown rice (*n*=153), Milled rice (*n*=123)	Iodine colorimetry using a potato (superlose)-waxy (IR29)	PLS: Brown rice: SEP = 2.27, r^2 = 0.757 Milled rice: SEP = 0.79, r^2 = 0.960	NIT: 800 – 1,050	Villareal *et al.* (1994)
	Rice flour, long, medium, short grain (*n*=247)	Colorimetric assay for milled rice, and was performed on autoanaly-zer (Juliano, 1971)	PLS: SEP = 1.04, r^2 = 0.956	NIR: 1,100 – 2,498	Delwiche *et al.* (1995)
	Milled rice, long, medium, short grain (*n*=196)	Colorimetric assay for milled rice, and was performed on autoanaly-zer (Juliano, 1971)	PLS: SEP = 1.33, r^2 = 0.887	NIR: 400 – 2,498	Delwiche *et al.* (1996)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Apparent amylose content (%)	Milled rice, rice flour (*n*=120)	Iodine-blue colorimetric method	PLS: Milled rice: SECV = 0.37-0.43 Rice flour: SECV = 0.53 Milled rice: SECV = 0.53-0.55	NIR: 1,100 – 2,500 NIR: 1,100 – 2,500 NIT: 1,100 – 2,500	Barton *et al.* (1998)
	Brown rice, milled rice (*n*=125)	Iodine-blue colorimetric method (Juliano, 1971)	PLS: Brown rice: SEP = 0.17, r = 0.818 Milled rice: SEP = 0.78, r = 0.921	NIT: 825 – 1,075 NIT: 825 – 1,075	Shimizu *et al.* (1998)
	Whole grain rough rice (*n*=150)	Iodine-blue colorimetric method (Juliano, 1971)	PLS: Milled rice: SEP = 0.27, r^2 = 0.00	NIT: 400 – 2,498	Kawamura *et al.* (1997)
	Milled rice and rice flour (*n*=96)	Iodine-blue colorimetric method (Juliano, 1971)	PLS: Milled rice: SECV = 1.17 Rice flour : SECV = 0.53 Milled rice: SECV = 1.83	NIR: 400 – 2,498 NIR: 400 – 2,498 NIT: 850 – 1,050	Barton *et al.* (2000)
	Long, medium, short milled rice grain (*n*=90)	Colorimetric assays Using an autoanalyzer (Webb, 1972)	PLS: SEP = 1.05, r^2 = 0.985	NIR: 200-1795, 2,050 – 3,570^{cm-1}	Himmelsbach *et al.* (2001)
	Long, medium, short milled rice grain (*n*=76)	Iodine-blue colorimetric method (Juliano, 1971)	PLS: RMSEP = 1.91, r^2 = 0.81	NIR: 400 – 2,500	Champagne *et al.* (2001)
	Rice flour (*n*=162)	Colorimetric assay for milled rice, and was performed on autoanalyzer (Juliano, 1971)	PLS: SEC = 0.89, r^2 = 0.96 SECV = 1.43, r^2 = 0.89 SEP = 1.39, r^2 = 0.91	NIR: 400 – 2,500	Bao *et al.* (2001)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Apparent amylose content (%)	Short grain japonica non-glutinous rice (*n*=125)	Iodine-blue colorimetric method (Juliano, 1971)	PLS: SECV = 0.96, r^2 = 0.63 SECV = 0.56, r^2 = 0.85	NIR: 850 – 1,050 NIR: 850 – 1,050	Shimizu *et al.* (2003)
	Rice flour, long, medium, short grain (*n*=128)	Iodine-blue colorimetric method (AACC, 2000d)	PLS: SECV = 1.0, r^2 = 0.979	NIR: 400 – 2,498	Sohn *et al.* (2004a)
	Rice flour (*n*=214)	Iodine-blue colorimetric method (AACC, 2000d)	PLS: SECV = 0.57, r^2 = 0.994	NIR: 1,100 – 2,498	Sohn *et al.* (2004b)
	Single grain brown rice (*n*=474)	Iodine-blue colorimetric method and expressed as brown rice weight (%)	PLS: SEP = 2.82, r^2 = 0.85	NIR: 1,100- 2,500	Wu and Shi (2004)
	Short grain brown rice, milled rice (*n*=61)	Iodine-blue colorimetric method (Juliano, 1971)	PLS: Milled rice: SECV = 1.42, r = 0.52 Milled rice : SECV = 1.13, r = 0.75	NIR: 800 – 1,098 NIR: 1,100 – 2,498	Natsuga and Kawamura (2006)
	Paddy rice, brown rice, milled rice, rice flour (n=586)	Colorimetric assay for milled rice, and was performed on autoanaly-zer (Juliano, 1971)	MPLS: Milled rice: SECV = 2.13, r^2 = 0.92	NIR: 1,100 – 2,498	Wu and Shi (2007)
	Milled rice (*n*=230)	Iodine-blue colorimetric method (Juliano, 1971)	PLS: Milled rice: SEC = 1.723, r^2 = 0.902 Milled rice: SEP = 2.158, r^2 = 0.843 Rice flour: SEC = 0.969, r^2 = 0.934 Rice flour: SEP = 1.224, r^2 = 0.945	NIR: 1,160 – 1,950 NIR: 1,160 – 1,950 NIR: 1,400 – 2,492 NIR: 1,400 – 2,492	Srisawas (2009)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Alkali spreading value	Milled rice, long, medium, short grain (*n*=196)	Six grains were immersed in 1.7% KOH (Little *et al*., 1958)	PLS: SEP = 0.43, r^2 = 0.966	NIR: 400 – 2,498	Delwiche *et al*. (1996)
	Milled rice and rice flour (*n*=96)	Six grains were immersed in 1.7% KOH (Little *et al*., 1958)	PLS: SECV = 0.64	NIR: 400 – 2,498	Barton *et al*. (2000)
	Rice flour (*n*=162)	Six grains were immersed in 1.7% KOH (Little *et al*., 1958)	PLS: SEP = 0.88, r^2 = 0.70	NIR: 400 – 2,500	Bao *et al*. (2001)
	Paddy rice, brown rice, milled rice, rice flour (n=586)	Six grains were immersed in 1.7% KOH (Little *et al*., 1958)	MPLS: Milled rice: SECV = 0.33, r^2 = 0.84	NIR: 1,100 – 2,498	Wu and Shi (2007)
	Milled rice (*n*=230)	Six grains were immersed in 1.7% KOH (Little *et al*., 1958)	PLS: Milled rice: SEC = 0.524, r^2 = 0.831 Milled rice: SEP = 0.545, r^2 = 0.806 Rice flour: SEC = 0.568, r^2 = 0.809 Rice flour: SEP = 1.224, r^2 = 0.945	NIR: 1,116 - 1,936 NIR: 1,116 - 1,936 NIR: 1,116 – 2,484 NIR: 1,116 – 2,484	Srisawas (2009)
Gel consistency (mm)	Rice flour (*n*=162)	Gel length of rice paste (Cagampang *et al*., 1973)	PLS: SEP = 7.12, r^2 = 0.81	NIR: 400 – 2,500	Bao *et al*. (2001)
	Paddy rice, brown rice, milled rice, rice flour (n=586)	Gel length of rice paste (Cagampang *et al*., 1973)	MPLS: Milled rice: SECV = 11.73, r^2 = 0.76	NIR: 1,100 – 2,498	Wu and Shi (2007)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Gel consistency (mm)	Milled rice (*n*=230)	Gel length of rice paste (Cagampang *et al.*, 1973)	PLS: Milled rice: SEC = 15.06, r^2 = 0.611 Milled rice: SEP = 16.44, r^2 = 0.533 Rice flour: SEC = 14.31, r^2 = 0.670 Rice flour: SEP = 14.52, r^2 = 0.654	NIR: 1,108 – 1,940 NIR: 1,108 – 1,940 NIR: 1,116 – 1,776 NIR: 1,116 – 1,776	Srisawas (2009)
Lipid content (%)	Long grain rice	Soxtec system	PLS: SEC = 0.04, r^2 = 0.97 SEC = 0.03, r^2 = 0.99 SEC = 0.024, r^2 = 0.99 SEC = 0.03, r^2 = 0.99	NIR: 400 - 700 NIR: 1,500 – 2,500 NIR: 400 – 700, 1,500 – 2,500 NIR: 400 – 2,500	Chen *et al.* (1997)
	Long, medium, short milled rice grain (*n*=76)	Soxtec system	PLS: RMSEP = 0.04, r^2 = 0.90	NIR: 400 – 2,500	Champagne *et al.* (2001)
	Japonica, indica, glutinous rice (*n*=248)	Soxtec system	PLS: Brown rice grain: RMSECV = 0.17, r^2 = 0.73 Brown rice flour: RMSECV = 0.15, r^2 = 0.81 Milled rice grain: RMSEC = 0.12, r^2 = 0.81 Milled rice flour: RMSECV = 0.09, r^2 = 0.89	NIR: 1,100 – 2,498	Wang *et al.* (2006)
	Milled rice, rice flour (n=140)	Fat acidity (mg of KOH/100 g dm)	PLS: Milled rice: SEP = 0.83, r^2 = 0.87 Rice flour: SEP = 0.73, r^2 = 0.94	NIR: 1,100 – 2,498	Li and Shaw (1997)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Lipid content (%)	Short grain brown rice, milled rice (*n*=61)	Free fatty acid (mg)	<u>PLS:</u> Milled rice: SECV = 3.39, r = 0.42	NIR: 800 – 1,098	Natsuga and Kawamura (2006)
			Milled rice : SECV = 3.07, r = 0.56	NIR: 1,100 – 2,498	
			Brown rice : SECV = 11.56, r = 0.30	NIR: 800 – 1,098	
			Brown rice : SECV = 9.02, r = 0.67	NIR: 1,100 – 2,498	
Pasting properties (RVU)	Milled rice, long, medium, short grain (*n*=196)	RVA analyzer	<u>PLS:</u> Peak viscosity SEP = 23.7, r^2 = 0.639	NIR: 1,120 – 1,800	Delwiche *et al.* (1996)
			Final viscosity SEP = 20.6, r^2 = 0.424	NIR: 1,120 – 1,800	
			Breakdown viscosity SEP = 14.3, r^2 = 0.719	NIR: 1,140 – 1,800	
			Consistency SEP = 10.6, r^2 = 0.735	NIR: 1,120 – 1,800	
			Setback viscosity SEP = 20.2, r^2 = 0.737	NIR: 1,110 – 1,800	
	Rice flour (*n*=162)	RVA analyzer	<u>PLS:</u> Peak viscosity SEP = 17.15, r^2 = 0.32	NIR: 400 – 2,500	Bao *et al.* (2001)
			Hot paste viscosity SEP = 16.7, r^2 = 0.55		
			Cold paste viscosity SEP = 20.8, r^2 = 0.76		
			Consistency SEP = 12.4, r^2 = 0.78		
			Setback viscosity SEP = 13.6, r^2 = 0.792		

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Pasting properties (RVU)			Breakdown viscosity SEP = 10.2, r^2 = 0.88		
	Short grain japonica non-glutinous rice (n=341)	RVA analyzer	PLS: Maximum viscosity SEP = 17.7, r^2 = 0.75, RPD = 1.9	NIT: 850 – 1,048	Shimizu *et al.* (2001)
	Rice flour (*n*=86)	RVA analyzer	PLS: viscosity at 212 second (r^2 = 0.961) and 228 second (r^2 = 0.903) were correlated with NIR spectroscopy	NIR: 1,100 – 2,500	Meadows and Barton 11 (2002)
	Milled rice (*n*=230)	RVA analyzer	PLS: Peak viscosity SEP = 26.83, r^2 = 0.678	NIR: 1,130 – 2,470	Srisawas (2009)
			Breakdown viscosity SEP = 14.89, r^2 = 0.735	NIR: 1,120 – 2,480	
			Setback viscosity SEP = 33.50, r^2 = 0.602	NIR: 1,108 – 2,492	
			Consistency SEP = 27.83, r^2 = 0.522	NIR: 1,148 – 2,452	
Degree of retrogradation (%)	Cooked rice (*n*=43)	Enzymatic digestibility	MLR: Eq.1: SEP = 3.22, r^2 = 0.968 Eq.2: SEP = 4.66, r^2 = 0.979 Eq.3: SEP = 3.91, r^2 = 0.975	NIR: 400 – 2,498	Cho *et al.* (1998)
Sensory attributes (0-15 scale)	Milled rice (*n*=60)	Sensory evaluation	PLSR: Manual adhesiveness, visual Adhesiveness, stickiness to lip, RAP = 0.54-0.56	NIR	Windham *et al.* (1997)

Table 2.16 (continued)

Parameters	Samples	Reference methods	Results	Mode: Wavelength (nm)	Author (Year)
Sensory attributes (0-15 scale)	Long, medium, short milled rice grain (*n*=76)	Sensory texture attribute (0-15 scale)	PLS: RMSEP = 1.91, r^2 = 0.81 PLS: Initial starchy coating RMSEP = 0.20, r^2 = 0.76 Stickiness RMSEP = 0.38, r^2 = 0.53 Hardness RMSEP = 0.32, r^2 = 0.67 Cohesiveness of mass RMSEP = 0.22, r^2 = 0.83	NIR: 400 – 2,500	Champagne *et al.* (2001)
Texture of rice gel (g)	Rice flour (*n*=162)	Texture analyzer	PLS: Hardness: SEP = 2.4, r^2 = 0.86 Adhesiveness: SEP=3.6, r^2 = 0.67 Springiness: SEP = 0.06, r^2 = 0.01 Cohesiveness: SEP=0.03, r^2 = 0.58 Gumminess: SEP = 1.24, r^2 = 0.77 Chewiness: SEP = 1.00, r^2 = 0.86	NIR: 400 – 2,500	Bao *et al.* (2001)
Thermal properties	Rice flour (*n*=162)	DSC.(°C)	PLS: To: SEP = 1.79, r^2 = 0.86 Tp: SEP = 1.33, r^2 = 0.89 Tc: SEP = 2.23, r^2 = 0.64 ΔHg (J/g): SEP=0.03, r^2 = 0.58	NIR: 400 – 2,500	Bao *et al.* (2001)

2.5.6.1 Milling quality

Numerous researchers investigated the milling quality and degree of milling using NIR spectroscopy. Stermer et al. (1977) used MLR methods to compare the reflectance data (800—1,800 nm) with surface lipids, total lipids and bran removal. The results showed that the reflectance at three principle oil absorption bands (0.928, 1.215, 1.725) was found to be highly correlated with surface and total lipid contents and to a lesser degree with weight loss due to milling.

Wadsworth et al. (1991) and Delwiche et al. (1996) found that PLSR calibration equation models strongly correlated with the degree of milling expressed as percentage of bran removal and the optical degree of milling measured by Satake MM-1B milling meter. The calibration model was able to evaluate milling quality using NIR spectroscopy with whiteness (SEP = 0.60% reflectance, r^2 = 0.97), transparency (SEP = 0.15% transmittance, r^2 = 0.93) and milling degree (SEP = 2.7 dimensionless units on a 0-199 scale, r^2 = 0.97). In addition, Barton et al. (1998) evaluated whiteness, transparency, and milling degree. The NIR models showed that the physical properties of whiteness, transparency, and milling degree were best modeled in the 750-1,050 nm range.

2.5.6.2 Moisture content

Most researchers achieved both high coefficient of determination (r^2) and high correlation coefficient (r) in determining the moisture content in rice grains of brown rice, milled rice, rough rice (Shimizu et al., 1998; Kawamura et al., 1997; Kawamura et al., 2003; Natsuga and Kawamura, 2006; Lin et al., 2006) and single grain brown rice (Rittiron et al., 2004).

2.5.6.3 Protein and apparent amylose content

The protein and apparent amylose contents of rice are important factors in the estimation of rice quality. The Kjeldahl method has been traditionally used for the determination of protein content. This method is however unfriendly to environment and time-consuming. The determination of apparent amylose content using the iodine-blue colorimetric method, amperometric, or potentiometric titration against a standard curve has disadvantages because the long linear chains of α-(1,4) glucans, occurring in the α-(1,6) branched amylopectin, could form amylose-iodine complex which causes the standard curve error (Himmelsbach et al., 2001). NIR spectroscopy has been used to overcome these problems. Villareal et al. (1994) successfully applied the near infrared transmittance (NIT) spectroscopy to predict the apparent amylose content in rice with more accuracy.

Delwiche et al. (1995) developed NIR calibration models for amylose and protein analysis of ground milled rice. Good results were obtained but a large number of factors were required, including 18 factors for amylose and 16 factors for protein content. Delwiche et al. (1996) one year later extended the application of NIR spectroscopy to whole grain milled rice samples. The results obtained were acceptable for both constituents even though the standard error of the model was slightly higher compared with the ground samples. The results of PLSR modeling indicated SEP = 1.3% and r^2 = 0.89 for apparent amylose content and SEP = 0.13% and r^2 = 0.97 for protein content.

Barton et al. (2000) examined three types of spectroscopic techniques for rice quality and reported the optimal geometry for development of an NIR model. In their studies, the protein and amylose models had acceptable error levels but were developed using a sample set with a narrow range of protein and an uneven distribution of apparent amylose content. Samples with a greater range and distribution for protein and better distribution of apparent amylose content (particularly 0-10%) were required to adequately predict a more diverse population.

Himmelsnach et al. (2001) determined the protein and apparent amylose contents of milled rice using NIR-FT/Raman spectroscopy. The best model for protein was obtained using 6 factors, giving r^2 = 0.992, SEP = 0.138%, and bias = -0.009%. The best model for apparent amylose content was obtained using 8 factors, yielding r^2 = 0.985, SEP = 1.05%, and bias = -0.006%. In the same year, Bao et al. (2001) developed NIR technique to measure rice starch quality parameters. PLSR modeling indicated that NIR spectroscopy was reasonably accurate in predicting apparent amylose content (SEP = 1.39%, r^2 = 0.91).

Sohn et al. (2004a) used the derivative method for NIR calibration to determine the protein and apparent amylose contents in rice flour. The calibration models developed using the data for two years resulted in good precision with a standard error of cross validation (SECV) of 0.23% for protein using 4 factors and an SECV of 1.0% for amylose using

10 factors. Additionally, Sohn et al. (2004b) used NIR spectroscopy together with PLSR to determine the protein and apparent amylose contents. The best NIR models were obtained with second derivative of orthogonal signal correction (OSC) spectra for protein (SECV = 0.22%, 4 factors) and with OSC spectra for apparent amylose content (SECV 0.57%, 11 factors).

2.5.6.4 Alkali spreading value and gel consistency

Alkali spreading value and gel consistency of rice grain are major factors to evaluate gelatinization temperature and texture of cooked rice. The test of alkali spreading value relies on visual observation of the degree of dispersion of milled rice after immersing into alkali solution. In addition, the complex procedure for gel consistency gives poor repeatability of gel length (Bao et al., 2001). Calibrations of NIR spectroscopy for evaluating both constituents have been developed. Delwiche et al. (1996) developed NIR models for evaluating alkali spreading value but the models were ineffective (SEP = 0.43 units on a 2-7 scales, r^2 = 0.82). However, this accuracy is probably sufficient for initial screening in breeding programs.

Bao et al. (2001) developed NIR spectroscopy to determine the gel consistency of rice starch. They demonstrated that PLSR modeling was reasonably accurate in predicting gel consistency. On the other hand, NIR models obtained from milled rice and rice flour showed the coefficient of determination (r^2) of 0.82 (Srisawas, 2009).

2.5.6.5 Lipid content and fat acidity

The complexity of determination of lipid content and fat acidity could produce incorrect results. Li and Shaw (1997) applied the MLR and PLSR calibration models to evaluate the fat acidity of rough rice. The PLSR provided the optimal calibration model for fat acidity with the coefficient of 0.92 at sample moisture contents of 12.7-16.7%. In the year, Chen et al. (1997) used visible/near infrared calibration to determine surface lipid content of milled long grain rice. The reflectance calibration equation from the set with three variables was more accurate in predicting surface lipid content than the calibration from the two-variable set. The best calibration yielded a coefficient of determination (r^2) of 0.99 and a SEP of 0.04% of surface lipid content.

2.5.6.6 Pasting properties of rice

However, NIR spectroscopy could not accurately assess RVA parameters. Delwiche et al. (1996) were unsuccessful in developing the effective NIR models for predicting RVA values. On the other hand, Bao et al. (2001) showed that PLSR modeling was reasonably accurate in predicting pasting parameters of setback viscosity (SEP = 13.6 RVU, r^2 = 0.92), breakdown (SEP = 10.2 RVU, r^2 = 0.88) and gelatinization peak temperature (T_p) (SEP = 1.33°C, r^2 = 0.89).

Shimizu et al. (2001) developed a PLSR calibration method of maximum viscosity determination of Japanese milled rice flours using NIT spectroscopy. The variations of spectral and maximum viscosity were found to influence PLS loading weights. C-H and O-H in ROH and H_2O absorbance presented by the loading weights were significant in the 8th loading of the PLS model for Japonica type rice. The performance of PLS calibration model (11 components) for maximum viscosity of a RVA was SEP of 17.7, r^2 of 0.75, and RPD of 1.9. The results indicated that NIT spectroscopy can be applied to the determination of maximum viscosity of Japonica type rice. Meadows and Barton-II (2002) later predicted RVA parameters in rice, including short-, medium- and long grain rice cultivars by NIR spectroscopy. PLSR models generated for the entire NIR spectra against the RVA curve showed the feasibility to determine RVA parameters by NIR spectroscopy. Recently, Srisawas (2009) reported that the modeling of NIR spectroscopy was reasonably accurate for evaluating the pasting properties of milled rice.

2.5.6.7 Sensory evaluation and cooking quality

Few studies on the potential of NIR spectroscopy to determine sensory attributes and cooking quality including texture of cooked rice have been published. Windham et al. (1997) examined NIR spectroscopy in cooked rice texture of three cultivars grown in four locations, dried by five processes to 12 and 15% moisture contents, and milled at 4 and 8% degree of milling. NIR spectroscopy showed potential for predicting descriptive texture attributes perceived in the initial oral phases of sensory evaluation. Champagne et al. (2001) later applied NIR spectroscopy to predict descriptive texture attributes of 88 samples including short-, medium-, and long grain cultivars by PLSR.

Cho et al. (1998) determined the degree of retrogradation of cooked rice samples using NIR spectroscopy. Spectral differences, due to retrogradation of cooked rice, were observed at 1,434, 1,700, 1,928, 2,100, 2,284, and 2,320 nm. The results suggested that NIR spectroscopy might be used as a potential method for determining the degrees of retreogradation and gelatinization of cooked rice.

2.6 Discrimination of rice

There are many types of rice varieties in Thailand with the variation in the apparent amylose content. Rice can be classified into various categories based on growth cultivations; cultivating durations and seasons; physical characteristics such as kernel length, shape, and degree of milling; and physicochemical properties such as apparent amylose content, alkali spreading value, gel consistency, texture properties, and their aroma (Bett-Garber et al., 2001; Aphithanaphong, 2004). Based on the growth cultivations and cultivating durations, rice can be classified as upland rice, lowland rice, floating rice, sensitive and non-sensitive photoperiod rice. Additionally, there are two groups of rice depending on cultivating seasons: in-season rice and off-season rice. In-season rice refers to rice that produces one crop per year (e.g., KDML105, RD15, and LPT123) while off-season rice is rice varieties that can produce two crops per year (e.g., PTT1, PSL1, CNT1, and SPR2) (Kongseree, 2002b; Rice Department, 2009).

By physical characteristics, rice can be grouped as extra long, long, medium, and short grain rice, depending on kernel size (Naivikul, 2004). Archer and Siebenmorgen (1995) reported that the Federal Grain Inspection (FGIS) standards identified rice grain by degree of milling into four groups: well-milled, reasonably well-milled, lightly milled, and under-milled.

Based on the physicochemical properties, Juliano (1985) classified rice into four groups according to the apparent amylose contents: waxy, low, intermediate, and high amylose content. In addition, rice is classified as waxy or glutinous rice (mainly amylopectin or less than 2% apparent amylose content) and non-waxy or non-glutinous rice (containing more than 5% apparent amylose content) on the basis of starch content in rice grain. Furthermore, rice is categorized into three groups according to gel consistency value: soft (61-100 mm), medium (41-60 mm), and hard (26-40) gel consistency (Cagampang et al., 1973).

There are three groups of rice on the basis of their gelatinization temperature: low (55-70°C), intermediate (70-74°C), and high (75-79°C) gelatinization temperature (Kongseree, 2002a). Rice is divided into four types depending on the texture of cooked rice: very soft texture, soft texture, fluffy and medium, and fluffy and hard (Champagne et al., 2001). As reviewed by the Department of Foreign Trade (1997), rice can be classified into two groups according to their aroma: aromatic and non-aromatic rice. Among aromatic rice varieties, KDML105 and RD15 are of most economic value to Thailand because of their higher prices which are two or three times higher than those of non-aromatic rice varieties.

Nowadays, the classification of rice varieties and the detection of adulteration are major issues of the rice industry and are attracting an increasing amount of attention from rice producers, researchers, and consumers. There are several methods for classifying rice varieties, such as visual observation, physical, chemical and DNA analysis. The visual observation is limited in its ability to provide information on the quality of the grain and unable to use for classifying rice varieties (Bhattacharya et al., 1982).

In addition, the chemical analysis conventionally used for the classification of rice is perceived as environmentally unfriendly, time-consuming, and fraught with errors (Himmelsbach et al., 2001). The DNA analysis is suitable for authentication because DNA information is identical for cultivars or species. However, this method is rather expensive (Kim et al., 2003). Thus, there is significant interest in an accurate and practical method for classification of rice to prevent blending or adulteration. NIR spectroscopy coupled with multivariate analysis, such as PCA, DA and PLS-DA, has been successfully applied to interpret the properties of samples and allows a classification without the use of chemical information. Research studies on application of NIR spectroscopy for classification rice varieties are presented in Table 2.17.

Table 2.17 Application of NIR spectroscopy for discrimination of rice varieties

Methods	Samples	Multivariate methods	Results	Mode: Wavelength (nm)	Author (Year)
Multivariate analysis	Milled rice (*n*=91)	Ward's cluster analysis	Categorizing rice cultivars into seven groups based on grain dimension, apparent amylose content, and alkali spreading value	-	Bett-Garber *et al.* (2001)
	Red rice grain (*n*=16)	Hierarchical cluster analysis	Classifying red rice samples into two groups based on kernel properties	-	Patindol *et al.* (2006)
	Milled rice (*n*=9)	Discriminant analysis	Classifying rice amylose content varieties using only pasting properties	-	Suwannaporn *et al.* (2007)
	Long grain rice starch (*n*=20)	Ward's cluster analysis	Classifying long grain rice according to their swelling, pasting, and gelatinization properties	-	Patindol *et al.* (2009)
	KDML105 milled rice	PCA	Classifying KDML105 based on its Cultivated location into five regions	-	Pitiphunpong and Suwannaporn (2009)
NIR spectroscopy	Basmatic rice (n=16) and other rice (n=100)	Fisher linear discriminant	Classifying Basmatic rice from other rice varieties	NIT: 850 – 1,050	Osborne *et al.* (1993b)
	Milled rice (*n*=19)	Soft Independent Modelling of Class Analogy (SIMCA)	FT-NIR DRIFT reasonably classified glutinous rice from non-glutinous rice	FT-NIR DRIFT: 400 – 11,000^{cm-1}	Ootake and Kokot (1998a)

Table 2.17 (continued)

Methods	Samples	Multivariate methods	Results	Mode: Wavelength (nm)	Author (Year)
NIR spectroscopy	Milled rice (*n*=19)	Soft Independent Modelling of Class Analogy (SIMCA)	Second derivative: Glutinous classify correctly 63.9 Non-glutinous classify correctly 66.7 MSC: Glutinous classify correctly 58.3 Non-glutinous classify correctly 50.0	FT-NIR DRIFT: 400 – 11,000^{cm-1}	Ootake and Kokot (1998b)
	Rice variety		Rice highly identified up to 90% based on their shape	NIR spectroscopy With CCD camara	Kwon and Cho (1998)
	Short, medium, long Grain (*n*=280)	Modified PLS (MPLS)	1st calibration: SECV = 0.165, r2 = 0.91 2nd calibration: SECV = 0.165, r= 0.93 Korean domestic rice correctly identified of 80% samples	NIR: 400 – 2,500	Kim *et al.* (2003)
	Whole grain Thai aromatic rice	PCA	PCA was not sufficient to classify Thai rice variety by NIR spectroscopy without chemical properties	NIR: 1,100 – 2,500	Theanjumpool *et al.* (2005)
	Milled Japanese rice	PLS	Detection blended the Koshihiakari with >5% of Akitakomachi varieties by single kernel NIT spectroscopy	NIT: 1,100 – 2,500	Rittiron *et al.* (2005)
	Paddy rice from four crop year (n=1,408)	Discriminant analysis (DA)	Eight models were used to classify paddy rice	NIR: 1,100 – 2,500	Liu *et al.* (2006)

2.6.1 Discrimination of rice by multivariate analysis

Several reports have found the benefits of multivariate analysis and NIR spectroscopy in discriminating rice according to rice properties. Bett-Garber et al. (2001) categorized ninety-one rice samples into seven groups based on amylose, protein, flavor and texture properties by Ward's cluster analysis. Patindol et al. (2006) classified red rice samples into two major clusters (Wells and Bengal) according to their kernel properties by hierarchical cluster analysis. Suwannaporn et al. (2007) suggested that the discriminant analysis using pasting attributes could classify rice varieties of different amylose contents.

Patindol et al. (2009) classified long grain rice starch using chemometric analysis based on swelling, pasting, and gelatinization properties. Pitiphunpong and Suwannaporn (2009) applied PCA to classify different cultivated locations of KDML 105 into five groups: the upper central region, the upper northeast region, the lower central region, the lower northeast region, and the lower northern and upper northeast region using pasting and calorimetric properties.

2.6.2 Discrimination of rice by NIR spectroscopy

NIR spectroscopy is a tool with many advantages in discrimination and it has been used in conjunction with chemometric techniques (Kim et al., 2003). Osborne et al. (1993b) investigated the feasibility of NIT spectroscopy to discriminate between individual grains of Basmati and other long grain rice using 16 Basmati and 100 other rice samples. The results showed that 8% of the Basmati and 14% of the others were misclassified on the basis of a rule based on spectra of 930 individual grains.

Ootake and Kokot (1998a) applied diffuse reflectance infrared Fourier transform spectroscopy (FT-NIR DRIFT), photo-acoustic spectroscopy (PAS) and FT-Raman spectroscopy for discrimination of glutinous and non-glutinous rice varieties. The soft independent modeling of class analogy (SIMCA) was used to classify raw spectral data. The best discrimination model was achieved with the FT-Raman results, followed by those from the PAS measurements. In the same year, they studied the effects of spectral pre-treatments, such as MSC and second derivative, for discrimination of glutinous and non-glutinous rice by vibrational spectroscopy. The results showed that the best classification of FT-NIR DRIFT was obtained with the second derivative pre-treatment. With the PAS spectral sampling method, the best classification model was the NIR spectra transformed with MSC. For FT-Raman, the best result was obtained with the MSC pre-treatment (Ootake and Kokot, 1998b).

In Korea, Kwon and Cho (1998) developed NIR spectroscopy with a CCD camera to identify rice varieties. An image processing technique using a CCD camera could identify rice varieties of different shapes, and the predictive accuracy reached 90% for similarly shaped rice varieties. In addition, the authentication of Korean domestic rice from foreign rice using NIR spectroscopy was studied by Kim et al. (2003). Two sample sets were used to develop calibration equation and the spectral regions used for this experiment were 500-600 nm, 700-900 nm, and 980-2,498 nm. Modified partial least square (MPLS) regression was used to develop the prediction model. The SECV and the r^2 were 0.165 and 0.91 respectively for 1st calibration set and 0.165 and 0.93 for 2nd calibration set, respectively. In addition, the Korean domestic rice was correctly identified from the other foreign rice samples.

For Thai rice, Theanjumpol et al. (2005) applied PCA to identify PTT1 and KDML105 from other rice varieties. Principal component-1 (PC_1) and PC_3 showed better results in separating rice varieties than PC_2. The PCA score plots clearly identified differences in the quality of RD15, PTT1 and KDML105. However, they concluded that the PCA technique alone could not be used to identify aromatic Thai rice varieties from non-aromatic rice varieties.

Rittiron et al. (2005) identified milled Japanese rice using kernel NIT spectroscopy. The results showed that a blend rice sample could be separated from a pure rice sample. Kim et al. (2006) later reported that NIR spectroscopy could classify paddy rice which was harvested in the summer of 2000 using the discriminant analysis and back propagation neural network.

CHAPTER 3

METHODOLOGY

3.1 Materials

Two varieties (KDML105 and RD15) of Hom Mali rough rice from 50 different planting locations and 10 varieties of rough rice of low (HKLG, PTT1, and PSL1), intermediate (SPR2 and SPR60) and high amylose (CNT1, CNT2, LPT123, PSL2, and PTT60) were obtained from the rice research centers, the rice seed centers, and the agriculture co-operatives in Thailand. The rice samples were divided into four groups; Hom Mali rice, low, intermediate and high amylose rice groups (Table 3.1). The 60 samples were harvested during November 2007 and April 2008. Each sample was cleaned to remove the impurities and then sun-dried to obtain the final moisture content of 12-13%. The sample was then individually vacuum-packed and stored at 10±1°C before milling process (Figure 3.1).

Table 3.1 Rough rice samples in the experiment

Groups	Variety	Nomenclature	Geological cultivation	No. of sample
Thai Hom Mali	1. Kao Dawk Mali 105 2. Rice Department15	1. KDML105 2. RD15	1. Lower northen region (Chainat, Lopburi, Nakornsawan and Pitsanulok province)	11
			2, Central region (Suphanburi and Pathumthani province)	9
			3. Upper northeast region (Mahasarakham, Roiet, Nakhon-phanom, Sakonnakorn and Udonthani province)	14
			4. Lower northeast region (Yasothon, Amnartcharoen, Sisaket, Ubonratchathani, Buriram, Surin and Nakornratchasima province)	16
Low amylose	1. Hom Klong Luang	1. HKLG	1. Pitsanulok rice research center	1
	2. Pathum Thani-1	2. PTN1	2. Pathum Thani rice research center	1
	3. Pitsanulok-1	3. PL1	3. Pitsanulok rice research center	1
Intermediate amylose	1. Suphan Buri-2	1. SPR2	1. Suphan Buri rice research center	1
	2. Suphan Buri-60	2. SPR60	2. Suphan Buri rice research center	1
High amylose	1. Chainat-1	1. CNT1	1. Chai Nat rice research center	1
	2. Chainat-2	2. CNT2	2. Chai Nat rice research center	1
	3. Luang Pra Tew-123	3. LPT123	3. Pitsanulok rice research center	1
	4. Pitsanulok-2	4. PL2	4. Pitsanulok rice research center	1
	5. Pathum Thani-60	5. PTN60	5. Nakhon Sawan rice seed center	1
			Total rice samples	60

Figure 3.1 Rough rice samples in vacuum packaging

3.2 Reagents

Ethanol (95%)	Merck	Germany
Glacial acetic acid (1.0 N)	Merck	Germany
Hydrochloric acid	Merck	Germany
Iodine solution (0.2% I_2 and 2.0% KI in distilled water)	Ajax	Australia
Potassium hydroxide	Ajax	Australia
Sodium hydroxide (2.0 N)	Merck	Germany
Standard potato amylose (about 16% iodine affinity, dry basis)	Fluka	Switzerland
Standard amylopectin	Fluka	Switzerland
Ethylene diamine tetraacetic acid (EDTA)	Merck	Germany

3.3 Equipment

Dehusker	Satake, Model SB	Japan
Satake miller	Satake, Model SKB	Japan
Screening machine	Satake, Model SB	Japan
UV-Visible Spectrophotometer	Shimadzu, UV-1601	Japan

FT-NIR Spectrophotometer	Buchi NIRLab N-200	Switzerland
Nitrogen combustion analyzer	Leco model FP-2000	USA
Rapid Visco Analyzer (RVA)	Model 3-D	Australia
Milling meter	Satake, MM-1B	Japan
Cyclone sample mill	Udy Crop	USA
Soxhlet extractor	Foss, Model 1043	Sweden
Digital balance	Mettler, AE50	Japan
Hot air oven	Memmert	Germany
Rice grader equipment	Thaisang netting	Thailand
Rice pre-cleaner equipment	Thaisang netting	Thailand
Air-tight desiccators	Scott-Duran	Germany
Unscrambler software version 9.7, 10.1	CAMO software	Norway

3.4 Research stations

Faculty of Agro-Industry, King Mongkut's Institute of Technology Ladkrabang, Bangkok, Thailand.

Department of Horticulture, Faculty of Agriculture, Kasetsart University, Kamphaeng Saen Campus, Nakhonpathom, Thailand.

Suan Dusit Rice Mill Company Limited, Suan Dusit Rajabhat University, Prachinburi, Thailand

3.5 Methodology

3.5.1 Degree of milling compensation

To achieve the equilibrium moisture content, the rough rice samples were kept at room temperature for 2 days (Delwiche et al., 1995). The 300 g rough rice samples were dehusked using a Satake dehusker. Each brown rice sample was subsequently milled using four different degrees of milling: 0, 5, 10, and 15% using a Satake miller. For instance, 5% degree of milling indicated that 5% of bran was removed from brown rice (w/w). Each degree of milling was obtained from the calibration curve between the degree of milling (Y, %) and the milling time (x, second) of each rice group. The calibration curve of four rice groups was expressed in Table 3.2. The equations of Hom Mali rice, low, intermediate and high amylose rice groups were used to calculate the duration time of rice milling at 5, 10 and 15% degrees of milling.

Table 3.2 Regression equations of four rice groups for rice preparation at different degrees of milling

Rice groups	Regression equation (Y = ax + b)	R^2
Hom Mali rice	$Y = 0.219x + 1.359$	0.988
Low amylose group	$Y = 0.181x + 1.306$	0.988
Intermediate amylose group	$Y = 0.176x + 1.367$	0.992
High amylose group	$Y = 0.183x + 1.586$	0.991

Note: Y = degree of milling (%) and x = milling time (second)

The samples were next graded by the rice grader equipment to remove broken rice. The whole grain differed in shape, degree of chalkiness, and degree of milling. The samples with different degrees of milling were then ground using a Cyclone Sample Mill.

The rice flour was separated with a 1.0 mm screen to measure the apparent amylose content, gel consistency, moisture content, and pasting properties with an RVA, while a 0.5 mm screen was applied for evaluation of the rice protein. Each rice flour sample was packed in an aluminum foil bag and stored at room temperature.

3.5.2 Measurement of NIR spectra of milled rice samples

Before collecting the NIR spectra of the milled rice samples, the room temperature was strictly controlled at 25°C. Spectral data were collected over the range of 1,100 to 2,500 nm (10,000-4,000 cm^{-1}) in reflectance mode using a fourier transform near infrared reflectance (FT-NIR) spectroscopy equipped with an integrating sphere. Each sample was weighed approximately 80 g and filled into standard glass petri dishes. The spectra were collected continuously over the NIR wavelength region. Each spectrum was recorded as log (*1/R*) at 2 nm increments. Duplicates of each sample were scanned to minimize the effects of particle size and sample temperature. These original spectra of each sample were collected by the NIRCal 5.21 software program.

3.5.3 Analysis of physicochemical properties

Following the measurement of NIR spectra, the rice samples were evaluated for the physicochemical properties as follows:

3.5.3.1 Moisture content

The moisture contents of brown and milled rice were determined according to AACC 45-15A (2000a). Each sample was weighed 5 g and dried in the hot air oven at 130°C for 16 hours. The samples were then cooled in desiccators for 1 hour and weighed. The moisture content was finally calculated based on weight loss using the following formula:

$$\text{Moisture content (\% } d.b\text{)} = \frac{\text{(initial weight – final weight) x 100}}{\text{final weight}}$$

3.5.3.2 Apparent amylose content

The apparent amylose content was determined by AACC 61-03 (1999) using the starch-iodine blue method. Each rice flour sample was weighed 150 mg and defatted by refluxing with 95% ethanol for 16 hours in a Soxhlet extractor at the rate of 6 drops/second. The defatted sample was kept at room temperature for 2 days. Afterward, each sample was weighed 100 mg and added in a 100 ml volumetric flask. Then, 1 ml of 95% ethanol was added and followed by 9 ml of 2 N NaOH for washing down all the flour clinging to the sides of the flask and kept at room temperature for 10 minutes. The filtrate was heated in a waterbath at 90°C for 10 minutes in order to gelatinize the flours. The sample was then cooled and adjusted to 100 ml with distilled water. The samples were swirled to mix the solution and kept at room temperature (25°C) for 23 hours.

After storing for 23 hours, 5 ml of each sample was transferred into another 100 ml volumetric flask. Then, about 70 ml of distilled water, 1 ml of 1N acetic acid, and 2 ml of iodine solution were added. The volume of the solution in each flask was adjusted to 100 ml by distilled water and thoroughly mixed. The samples were allowed to develop dark purple color under room temperature for 20 minutes. The above procedure was also repeated to prepare a blank.

An intensity of the developed color was measured in terms of an absorbance using a spectrophotometer at 620 nm when the blank treatment was set as zero. The values of the absorbance were transformed into the percentage of apparent amylose content using pure potato amylose and amylopectin as a standard curve shown in Table 3.3.

Table 3.3 Concentration ratios of pure potato amylose and amylopectin

Amylose in sample (% dry basis)	Volume ratio of stock solutions		
	Amylose (1 mg/ml)	Amylopectin (1 mg/ml)	0.09 N NaOH
0	0.0	7.0	3
10	1.0	6.0	3
20	2.0	5.0	3
25	2.5	4.5	3
30	3.0	4.0	3

Source: AACC 61-03 (1999)

Furthermore, the moisture content affected apparent amylose content due to 3-4% loss of the former during grinding whole milled rice grain into rice flour (Phil Williams, Personal contract). Thus, the calculation of apparent amylose content took into consideration the moisture content of rice grain. The apparent amylose content of whole brown and milled rice samples at different moisture contents (% *d.b*) were reported using the following formula according to Phil Williams.

$$AAC_{WMR}(\%) = \frac{AAC_{FL} \times (100 - MC_{WMR})}{100 - MC_{FL}}$$

where AAC_{WMR} = apparent amylose content of whole milled rice (%)

AAC_{FL} = apparent amylose content of flour milled rice (%)

MC_{WMR} = moisture content of whole milled rice (%)

MC_{FL} = moisture content of flour milled rice (%)

3.5.3.3 Protein content

The total nitrogen content was assessed by nitrogen combustion analyzer (Leco model FP-2000) according to the nitrogen combustion method (AACC, 2000b). The total nitrogen content was expressed as "protein content" by multiplying as a conversion factor of 5.95. The instrument was calibrated against 150 mg of EDTA, which was dried overnight at 100°C and cooled in desiccators before use. The instrument was calibrated by blank 8 times and performed EDTA test before running actual tests. The tin foil was weighed and tared before rice flour of about 250 mg was put onto the tin foil. The flour was then tightly compressed into a pellet by hand and the pellet was transferred to the instrument and tested for protein content. For every 20 samples analysis, the instrument would be checked for accuracy using EDTA sample.

3.5.3.4 Gel consistency

Gel consistency was determined according to Cagampang et al. (1973). Each sample was weighed 100 ± 1 mg and placed in 13 mm x 100 mm test tubes. Then, 0.2 ml of 95% ethanol containing 0.025% thymol blue was added and followed by 2 ml of 0.2N KOH. The samples were dispersed thoroughly with Vortex mixer (setting No.6) for 10 seconds. The tubes were then covered with glass marbles and boiled in vigorously boiling water bath for 8 minutes. Afterward, the tubes were removed from the bath and shaken well using the test tube mixer again for 15 seconds. The samples were cooled in ice waterbath for 20 minutes. Then, the tubes were laid horizontally on the table for 30 minutes. Total moving length of the blue color gel was measured as gel consistency value as shown in Figure 3.2. Hard, medium, and soft gel consistencies referred to as the range of moving range gel were less than 40, 41-60, and 61-100 mm, respectively.

(a) (b) (c)

Figure 3.2 Gel consistency (a) hard gel, (b) medium gel, (c) soft gel

3.5.3.5 Alkali spreading value

Alkali spreading value was determined using a modification of Little et al. (1958). The standard of disintegrated rice grain was detected by 25 grains of each rice group in 1.7% KOH solution for 23 hours. The degree of disintegration was evaluated by comparing to

KDML105, SPR2 and LPT123, which referred to as a low, intermediate, and high value of disintegration in rice grain, respectively. For analysis of alkali spreading value of rice grain, 100 grains of each sample were placed in a 140 mm-diameter petri dish containing 50 ml of 1.7% KOH solution. The petri dish was placed on a black or blue paper for clear assessment. The grains were clearly separated from one another. The petri dish was covered and kept for 23 hours at room temperature. The individual grains were evaluated according to their degrees of alkali spreading values as shown in Table 2.10

3.5.3.6 Pasting properties of rice

Pasting properties were determined using an RVA analyzer (Model 3-D) according to AACC 61-02 (2000c). Each of rice flour was weighed about 3.0 ± 1 g, then added 25 ml of distilled water into a metal RVA. The temperature was raised from 50 to 95°C ± 1°C in 0 to 5 minutes. The temperature of 95°C ± 1°C was maintained for 2 minutes and then cooled to 50°C over 7 to 12.5 minutes. Each experiment was started with 960 rpm paddle speed for 10 seconds and followed by a 160 rpm paddle speed throughout the experiment. The result was obtained by RVA amylograph and values for viscosity were reported in units termed "rapid visco units" (RVU) (Figure 3.3).

As seen in Figure 3.3, the definitions of the abbreviations are as follows (Delwiche et al., 1996):

-*"Peak viscosity (PV)"* or maximum viscosity (*Max*) represents the maximum viscosity which is recorded during the heating and holding cycles and occurs soon after the temperature reaches 95°C.

- *Trough viscosity (TV)"* (no analogous amylograph term) is the maximum viscosity after peak and occurs during the cooling.

- *"Final viscosity (FV)"* is the viscosity at the finish test.

- *'Breakdown viscosity (BD)"* is the viscosity of the paste during the 95°C holding period.

-*"Setback viscosity (SB)"* is an indicator of the retrogradation of the paste and is calculated from the differences of final viscosity and peak viscosity.

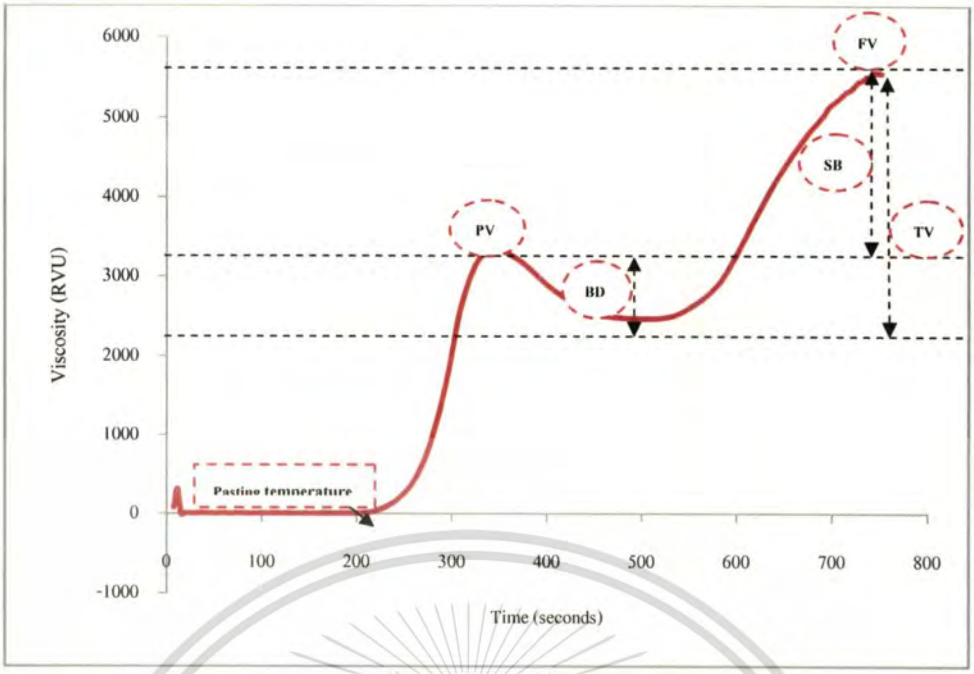


Figure 3.3 Typical RVA curve of CNT1 variety

3.5.4 Statistical and chemometric analysis

3.5.4.1 Evaluation of the effect of degree of milling on rice quality

Each physicochemical parameter was calculated as a mean ± standard deviation by SPSS software and determined the differences between means by the two-way analysis of variance (ANOVA) using Duncan's multiple range test at 5% probability level.

3.5.4.2 Calibration model to predict the physicochemical properties of rice

A) Detection of outlier of reference data

Prior to calculation, the physicochemical data were considered as outlier according to Sirisomboon et al. (2007) and Rittiron (2009) using the following formula:

$$t_i = \frac{x_i - \bar{x}}{SD} \geq 3$$

where; x_i = the chemical data

$\bar{x}$ = the average value

SD = the standard deviation

If t_i was more than or equal to 3, the sample was outlier.

B) Pre-processing of NIR spectral data

Spectra were exported from the NIRCal software in JCAMP-DX format into the Unscrambler version X 10.1 (CAMO software, ASA, Norway) for chemometric analysis. The three reference spectra for each sample were averaged into one spectrum. The models were developed after averaging both original and pre-processed data. The spectra were pre-processed using the MSC, SNV, and second derivative. The MSC and SNV were applied to remove the multiplicative interferences of scatter, particle size, and the change of light distance.

The second derivative was performed using Savitzky-Golay algorithm with a second-order polynomial equation. The data points on the left and right sides in the mathematical treatment were 10 nm gap size of the second derivative (Rittiron et al., 2005). Besides, the average spectra were pre-processed using MSC and then transformed into second derivative (MSC + Savitzky-Golay second derivative; 10 nm averaging for left and right sides) and SNV and then pre-processed into second derivative (SNV + Savitzky-Golay second derivative; 10 nm averaging for left and right sides).

C) Partial least square regression (PLSR) analysis

For the calibration equation, the physicochemical data were dependent variables (*Y*-variables) and original spectra were independent variables (*X*-variables). The data were divided into two sets: calibration and validation sets with the ratio of 2:1. The calibration set was mainly required to develop a model while the validation set was applied to evaluate the calibration equation. PCA was used to detect the outlier of NIR spectra. After removing the outlier from reference analysis and NIR spectra, PLSR was applied to calculate the regression equations between physicochemical data (*Y*-variables) and the absorption of sample at each wavelength (*X*-variables) from 1,100 to 2,500 nm. In the development of the PLSR model, full cross-validation was used to validate the quality and to prevent over-fitting of the calibration model.

The performance of the PLS calibration model was evaluated by standard error of calibration (SEC), standard error of prediction (SEP), and the coefficient of determination (r^2). The best model should have not only low SEC and SEP with a high coefficient of determination but also a small difference between SEC and SEP. For the evaluation of the regression model, the relative performance determinant (RPD), the ratio of SEP to the standard deviation (SD) of the reference data, was performed. For specific applications, RPD was defined using the following 6 ranges: 0.0 to 2.3 as not recommended, 2.4 to 3.0 as very rough screening quality, 3.1 to 4.9 as screening quality, 5.0 to 6.4 as quality control, 6.5 to 8.0 as process control, and >8.1 suitable for any application (William and Norris, 2001).

After the calibration equations were established, the rice samples at different degrees of milling in the validation set were used to assess the prediction accuracy of the calibration equation by SEP, coefficient of determination, and bias.

3.5.4.3 Discrimination of Hom Mali rice from the other rice varieties at various degrees of milling

Data obtained from physicochemical properties of rice and NIR spectra were used to discriminate Hom Mali rice from other rice varieties at different degrees of milling. The principal component analysis (PCA) and partial least square-discriminant analysis (PLS-DA), members of the multivariate analysis, were used to classify Hom Mali rice.

A) Discrimination of Hom Mali rice from the aromatic and non-aromatic rice varieties based on physicochemical measurements by PCA

The physicochemical data of samples with different degrees of milling were analyzed by PCA using the Unscrambler software package version 9.7 (CAMO software ASA, Norway). The data were presented in terms of the loadings of the physicochemical properties and the scores of each model principal component (Li et al., 2007).

B) Discrimination of Hom Mali rice from other rice varieties based on the spectral of NIR by PCA

PCA was performed using original and pre-processing spectra. PCA was applied to discriminate the grouping of samples, based on loadings and the principal component (PC) scores. The loadings show not merely how well a variable is taken into account by the model components but also how close the variable relationships are. The PC scores indicate the locations of the samples along each model component and can be used to detect sample patterns, grouping, similarities or differences (Anderson, 2003).

C) Discrimination of Hom Mali rice from other rice varieties using PLS-DA

PLS-DA was used in this study to establish calibration models for discrimination of Hom Mali rice and the other rice varieties on the basis of the spectral profile differences. It is partial least square application for the optimum separation of classes. Each sample was assigned a dummy variable of 1 or 0 as a reference value. It is an arbitrary number that indicate whether the sample is belonged to a particular group or not. In this case, the spectral data from Hom Mali rice samples were assigned a numeric value of 1, and those of the aromatic and non-aromatic rice samples were assigned as 0 (Table 3.4).

Table 3.4 Assigned values of dummy variables of Hom Mali rice and the aromatic and non-aromatic rice varieties

	Hom Mali rice	Low AMM*	Intermediate AMM*	High AMM*
Hom Mali rice	1	0	0	0
Low AMM	0	1	0	0
Intermediate AMM	0	0	1	0
High AMM	0	0	0	1

* Low AMM, Intermediate AMM and High AMM means low, intermediate and high apparent amylose rice group

The PLS-DA model was then developed by assigning the reference value for each sample. Hom Mali rice samples would be discriminated correctly only if the values were in the range of 0.5 and 1.5 and the samples would be discriminated as aromatic or non-aromatic if the values were between -0.5 and 0.5.

The coefficient of determination (r^2) in calibration and the root mean square of the standard error of calibration (RMSEC) were used to evaluate the accuracy of the PLS-DA calibration models for the prediction of unknown samples. Rice samples were split randomly into calibration (n = 64) and validation sets (n = 62). The validation set was used to evaluate the accuracy of the models to discriminate samples according to their physicochemical properties. The PLS-DA calibration models were validated using full cross validation. The best performance of models was selected as the values giving the minimum RMSEC, and the maximum of the coefficient of determination and the discrimination rate.

CHAPTER 4

RESULTS AND DISCUSSION

To evaluate the discrimination methods of Hom Mali rice from the other aromatic and non-aromatic rice varieties, this chapter is thus concerned with: 1) physicochemical properties of Hom Mali rice and the aromatic and non-aromatic rice varieties, 2) the effect of degree of milling on physicochemical properties of rice varieties, 3) establishment of the calibration model to predict the physicochemical properties of rice, and 4) discrimination of Hom Mali rice from the other aromatic and non-aromatic rice varieties by FT-NIR spectroscopy according to their physicochemical properties and NIR spectra at different degrees of milling.

4.1 Physicochemical properties of Hom Mali rice and the aromatic and non-aromatic rice varieties

4.1.1 Moisture content

Moisture content is one of the key parameters determining grain quality. At present, the price of rice relies on its moisture content in that the price of rice with low moisture content is higher than that with high moisture content (Kongseree, 1979). Moisture contents of all rice samples kept in a refrigerator for 4 months are shown in Table 4.1., which varied between 11.10 and 12.13% and were not statistically different ($p \geq 0.05$). This result attributed to the strict control of final moisture content of all rice samples at 12-13% by sun-drying since the moisture content significantly affected NIR spectra. The changing moisture content dramatically influenced the peak of spectrum in that the latter could shift upward or downward depending on the moisture content (Kasemsumran, 2009). Thus, moisture content should be regarded as an important variable that needed to remain constant in determining the physicochemical properties of rice by NIR spectroscopy.

Table 4.1 Moisture and protein contents of rice samples

Groups / Varieties	Moisture content (%)^{ns}	Protein content (%)
Hom Mali group (*n*=50)		
1. KDML105 (*n*=31)	11.99 ± 0.44	7.01 ± 0.70^{bc}
2. RD15 (*n*=19)	12.13 ± 0.82	6.97 ± 0.83^{bc}
Low amylose group (*n*=3)		
1. HKLG (*n*=1)	11.35 ± 0.07	6.49 ± 0.01^{c}
2. PTT1 (*n*=1)	11.45 ± 0.09	8.13 ± 0.02^{ab}
3. PSL1 (*n*=1)	11.10 ± 0.13	6.91 ± 0.00^{bc}
Intermediate amylose group (*n*=2)		
1. SPR2 (*n*=1)	11.35 ± 0.05	7.56 ± 0.02^{bc}
2. SPR60 (*n*=1)	11.15 ± 0.08	9.05 ± 0.07^{a}
High amylose group (*n*=5)		
1. CNT1 (*n*=1)	11.55 ± 0.23	7.51 ± 0.15^{bc}
2. CNT2 (*n*=1)	11.55 ± 0.07	5.26 ± 0.02^{d}
3. LPT123 (*n*=1)	11.70 ± 0.11	6.85 ± 0.04^{bc}
4. PSL2 (*n*=1)	11.60 ± 0.11	7.01 ± 0.12^{bc}
5. PTT60 (*n*=1)	11.45 ± 0.06	6.93 ± 0.00^{bc}

^{ns} denotes that the mean values are insignificantly different ($p \geq 0.05$). Meanwhile, any other superscript (e.g., ab, bc, c) indicates that the mean values are significantly different ($p \leq 0.05$).

4.1.2 Protein content

Protein content of the rice samples varied between 5.26 and 9.05% (Table 4.1). Additionally, SPR60 showed the highest protein content and was statistically higher than those of both Hom Mali rice samples ($p \leq 0.05$). Between the samples of Hom Mali rice, the protein contents of KDML 105 and RD15 were not statistically different ($p \geq 0.05$) (Table 4.1). The results hence showed that different growing regions had no influence the protein content of Hom Mali rice, which was in contrast to the work of Somrith (1996). The result indicated that differences in the growing regions led to different physicochemical properties of rice grain, particularly in protein content.

Furthermore, the results showed insignificant differences in protein contents of Hom Mali rice, low amylose group, and SPR2 which was identified as intermediate amylose group ($p \geq 0.05$). The protein content of Hom Mali rice was not different from that of the high amylose group except CNT2 ($p \geq 0.05$). The results contradicted the work of Juliano (1993) who discovered that protein contents of rice differed among rice varieties. In addition, Yadav and Jindal (2008) demonstrated that the protein contents of the aromatic rice were less than those of the non-aromatic rice varieties except HKLG, which was attributable to nitrogen fertilizer application. However, the different protein contents of HKLG, SPR60, CNT2 and other rice samples may attribute to rice variety, geological cultivation, environment, and nitrogen fertilizer application. These factors influenced the variations in the level of protein content (Somrith, 1996; Singh et al., 2005, Bahmaniar and Ranjbar, 2007; Cameron et al., 2007).

As previously mentioned, these results indicated that the protein content could not be used to discriminate Hom Mali rice from low, intermediate, and high amylose groups except for SPR2 of the intermediate group and CNT2 of the high group.

4.1.3 Apparent amylose content

Apparent amylose content is the major constituent of rice grain. Rice is usually classified according to the apparent amylose content into five groups: waxy (0.0-5.0%), very low (5.1-12.0%), low (12.1-20.0%), intermediate (20.1-25.0%), and high amylose content (>25.0%) (Juliano,1993). Hom Mali rice is normally identified with the low amylose group due to their resemblance (Kongseree, 2002a). The apparent amylose contents of rice samples are presented in Table 4.2. The apparent amylose contents of the Hom Mali rice varied between 16.02 and 16.09%, which were similar to the low amylose rice group ($p \geq 0.05$) except HKLG in which this experiment indicated that it belonged more to the intermediate amylose group. In the low amylose group, the apparent amylose content of HKLG (18.25%) was the highest (Table 4.2). However, the apparent amylose content of HKLG in this study was lower than that in the works of Kongseree (2002a) and Srisawas (2009), who both reported that HKLG was classified as a rice variety with intermediate apparent amylose content.

However, the apparent amylose contents of Hom Mali rice group were lower than those of both intermediate and high amylose groups ($p \leq 0.05$). The results have showed the apparent amylose contents of SPR2 (19.65%) and SPR60 (22.45%) were grouped as intermediate amylose group, while those of CNT1, CNT2, LPT123, PSL2 and PTT60 were classified as high amylose group, ranging from 26.60 to 28.65% (Table 4.2). These results corresponded with the report of Williams et al. (1958) who found that long grain rice varieties have the higher apparent amylose content than medium and short grain rice varieties. In addition, they reported that the differentiation of apparent amylose content among these rice varieties was attributed to the structural differences of rice grain, genetic factors, and composition.

Table 4.2 Apparent amylose contents, gel consistency and alkali spreading values of rice samples

Groups / Varieties	Apparent amylose content (%)	Gel consistency (mm)	Alkali spreading value (units on a 1—7 visual scale)
Hom Mali group (n = 50)			
1. KDML105 (n=31)	16.09 ± 1.12^{ef}	79.06 ± 4.15^{a}	7.00 ± 0.00^{a}
2. RD15 (n=19)	16.02 ± 1.46^{ef}	73.63 ± 5.76^{bc}	6.00 ± 0.00^{b}
Low amylose group (n = 3)			
1. HKLG (n=1)	18.25 ± 0.20^{cd}	71.50 ± 0.64^{bc}	7.00 ± 0.00^{a}
2. PTT1 (n=1)	16.60 ± 0.13^{de}	77.50 ± 0.70^{b}	6.00 ± 0.00^{b}
3. PSL1 (n=1)	14.35 ± 0.05^{f}	71.00 ± 1.50^{bc}	6.00 ± 0.00^{b}
Intermediate amylose group (n = 2)			
1. SPR2 (n=1)	19.65 ± 0.45^{c}	59.50 ± 0.65^{de}	5.00 ± 0.00^{c}
2. SPR60 (n=1)	22.45 ± 0.35^{b}	55.00 ± 1.45^{e}	4.00 ± 0.00^{c}
High amylose group (n = 5)			
1. CNT1 (n=1)	26.60 ± 0.29^{a}	65.50 ± 0.57^{cd}	1.00 ± 0.00^{d}
2. CNT2 (n=1)	28.65 ± 0.21^{a}	39.00 ± 1.39^{f}	1.00 ± 0.00^{d}
3. LPT123 (n=1)	27.25 ± 0.19^{a}	41.00 ± 1.43^{f}	1.00 ± 0.00^{d}
4. PSL2 (n=1)	26.65 ± 0.26^{a}	41.25 ± 0.95^{f}	1.00 ± 0.00^{d}
5. PTT60 (n=1)	28.55 ± 0.18^{a}	42.00 ± 0.18^{f}	1.00 ± 0.00^{d}

$^{ab, bc, c}$ indicates that the mean values are significantly different ($p \leq 0.05$).

Furthermore, these results also corresponded with the report of Navasearttavisoort (2004). Results showed that the starch content of aromatic rice was slightly lower than that of non-aromatic rice, resulting in lower apparent amylose content in Hom Mali rice and in the low amylose group compared with the intermediate and high amylose groups.

On apparent amylose content basis, Hom Mali rice, PTT1, HKLG and PSL1 were classified as low amylose. SPR60 was grouped as intermediate amylose and the rest of the samples were identified as high amylose. This fact substantiated the findings of Juliano (1993) except SPR2 (19.65 ± 0.45%), which was classified to the intermediate group according to the work by Kongseree (2002a). The differences in the apparent amylose content among rice samples were attributable to variety, temperature during grain ripening, and nitrogen fertilization (Juliano, 1985).

Therefore, it could be inferred that the apparent amylose content could be used to discriminate Hom Mali rices from the intermediate and high amylose groups but was unable to do so from the low amylose group.

4.1.4 Gel consistency

Gel consistency was originally developed to differentiate high-amylose rice with contrasting amylograph pasting viscosities. Rice is normally categorized into three groups according to gel consistency: soft (61-100 mm), medium (41-60 mm), and hard (26-40 mm) gel consistency (Cagampang et al., 1973). The gel consistency of the rice samples are shown in Table 4.2. Gel consistency of Hom Mali rice ranged between 73.63 and 79.06 mm, which it was in the soft gel consistency group, and so was the low amylose group with gel consistency between 71.00 and 77.50 mm. However, the gel length of KDML105 was significantly higher than those of RD15 and low amylose rice group ($p \leq 0.05$). On the other hand, gel consistency of the intermediate and high amylose groups varied between 55.00 to 59.50 and 39.00 to 65.50 mm, respectively. Both groups can be classified as medium and hard gel consistency. This classification agreed with the classification reported by Cagampang et al. (1973).

In addition, the results showed that the gel consistencies of Hom Mali rice and low amylose groups were significantly higher than those of intermediate (55.00 to 59.50 mm) and high amylose groups (39.00 to 65.50 mm) (Appendix C: Table 1C). The results were also consistent with those found by Kongseree (2000a). The negative correlation between gel consistency and apparent amylose content in rice samples was probably due to the fact that the high amylose rice group tended to retrograde more than the low amylose rice group. Consequently, rice gel paste of the high amylose rice group was lower than that of the low amylose rice group. Therefore, the gel consistency values increased with the decrease of apparent amylose content of rice grain. Juliano and Pascual (1981) explained that the gel length of low amylose group was higher than intermediate and high amylose groups because the rice paste could flow rapidly during cooling. Furthermore, Cagampang et al. (1973) reported that this phenomenon resulted from the retrogradation of amylose molecules after gelatinization in alkali dilution and then cooling to room temperature.

Moreover, it should be noted that CNT1 was high amylose rice like CNT2, LPT123, PSL2 and PTT60 but its gel length was significantly higher than the others ($p \leq 0.05$). This result corresponded to the works of Kongseree (2000a) and Cheaupun et al. (2005) who implied that the longer gel length of CNT1 (60.5 ± 0.8 mm) was due to its unique characteristics, thereby identified as soft-medium gel consistency.

The results revealed that Hom Mali rice could be discriminated from the intermediate and high amylose groups according to the gel consistency. However, the gel consistency parameter was incapable of classifying Hom Mali rice from the low amylose group and CNT1.

4.1.5 Alkali spreading value

Alkali spreading value, which is related to the gelatinization temperature of starch granules, involves incubating six grains of milled rice in weak base for 23 hours. The alkali spreading value measures the degree of spreading using a seven-point scale (1 = grain not affected, 7 = grain completely dispersed) and corresponds to gelatinization temperature as follows: 1-2 as high (74.5-80°C); 3 as high-intermediate; 4-5 as intermediate (70-74°c); and 6-7 as low (<70°C) gelatinization temperature (Little et al., 1958; Juliano, 1985). Alkali spreading values of rice samples are shown in Table 4.2.

Alkali spreading values of Hom Mali rice and low amylose rice group varied from 6.0 to 7.0 and 6.0 to 7.0, respectively, which were insignificant different ($p \geq 0.05$). Both types of rice grains fell under low gelatinization temperature. However, the scores of alkali spreading values of both groups were significantly higher than those of intermediate and high amylose groups ($p \leq 0.05$). In the intermediate amylose rice group, the alkali spreading values of SPR2 and SPR60 were respectively 5.0 and 4.0, while the alkali spreading values of all rice varieties in the high amylose rice group were 1.0. Thus, intermediate and high amylose rice groups were classified as high and high-intermediate gelatinization temperatures, respectively. These findings agreed with the works of Little et al. (1958) and Juliano (1985) for rice classification on gelatinization temperature basis.

Different alkali spreading values among rice groups might be attributable to the apparent amylose content. The work of Nayak et al. (2002) in which alkali spreading value showed a significant negative correlation with apparent amylose content suggested that gelatinization temperature decreased when apparent amylose content of rice increased. This fact indicated that the high amylose rice group would absorb more water at high gelatinization temperature and produce a greater volume of cooked rice. Thus, the alkali spreading values of Hom Mali rice and the low amylose rice group were higher than the intermediate and high amylose rice groups.

Furthermore, amylopectin chain-length in rice grain affected the alkali spreading value. Starch granules of low amylose rice varieties which were mostly composed of short chains of amylopectin showed high levels of disintegration in alkali solution, while those of high amylose rice varieties were significantly more resistant to alkali digestibility (Prathepha et al., 2005; Umemoto et al., 2002). In this study, Hom Mali rice could be discriminated from intermediate and high amylose rice groups according to their alkali spreading values. However, the alkali spreading values were unable to discriminate Hom Mali rice from the low amylose group since they were all identified as belonging to the same low amylose rice group.

4.1.6 Pasting properties of rice

Pasting properties of four rice groups are shown in Figure 4.1. Peak viscosity and breakdown viscosity of Hom Mali rice and those of low amylose rice group were higher than those of intermediate and high amylose rice groups. The decrease in peak viscosity of intermediate and high amylose rice groups suggested that the starch granules of both rice groups were more resistant to swelling than those of Hom Mali rice and low amylose rice group. Furthermore, the reduction of breakdown viscosity indicated that the capacity of the starch granules of intermediate and high amylose rice groups to rupture after cooking decreased significantly.

Final viscosity is the viscosity at the finish test while setback viscosity is an indicator of the retrogradation of the paste (Delwiche et al., 1996). However, the final viscosity and setback viscosity increased with the increasing apparent amylose content of rice grain. These results were due to the starch granules of intermediate and high amylose rice groups retrograding rapidly after cooling period (Figure 4.1).

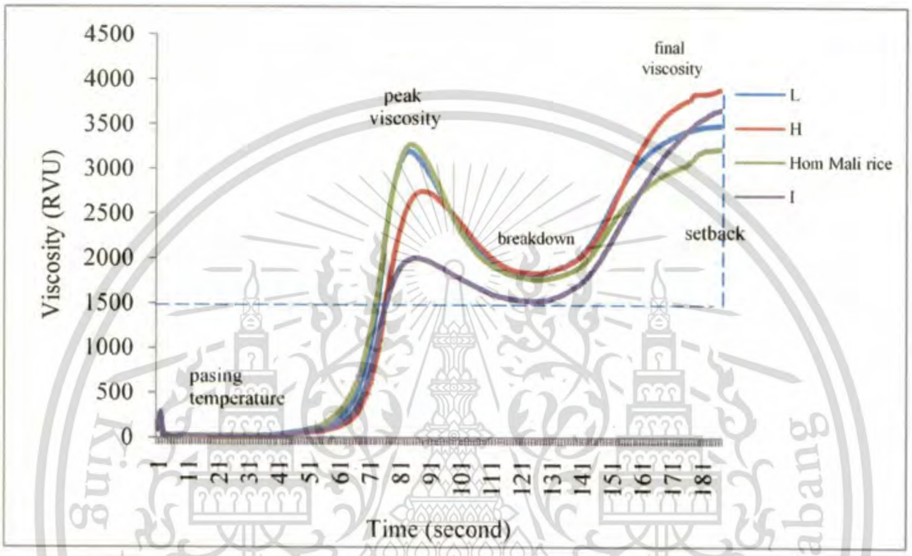


Figure 4.1 The RVA curves of four rice groups: L = low, I = intermediate, and H = high amylose rice groups

4.1.6.1 Peak viscosity

Peak viscosity, the maximum viscosity during heating cycle, is influenced by apparent amylose content and protein content. Apparent amylose content is inversely proportional to the degree of granule swelling during pasting (Perdon et al., 2001). Noda et al. (2003) reported that apparent amylose content of rice starch was negatively correlated with peak viscosity. The amylose molecules inhibited the swelling properties of amylopectin in rice grain granules (Meadows and Barton-II, 2002). Martin and Fitzgerald (2002) reported that proteins in rice grain influenced RVA viscosity curves through binding water, which increased the concentration of the dispersed and viscous phases of gelatinized starch. Peak viscosity values of rice samples are shown in Table 4.3. The values of the low amylose group ranged from 2,036 to

2,180 RVU, which were significantly higher than those of Hom Mali rice (1,753 and 1,841 RVU) ($p \leq 0.05$). However, those of KDML105 and RD15 were not statistically different ($p \geq 0.05$).

Furthermore, these results indicated that peak viscosity of low amylose group was significantly higher than those of intermediate and high amylose groups which ranged from 1,247 to 1,544 RVU and 957 to 1,061 RVU, respectively (Table 4.3). The obtained results were correlated with the apparent amylose content in rice grain which could inhibit the swelling properties of rice grain. Thus, peak viscosity of high amylose rice group was lower than those of intermediate and low amylose rice groups.

In this study, the peak viscosity values of HKLG, PTT1, and PSL1, all of which belong to the low amylose rice group, were higher than that of Hom Mali rice. This result could be attributed to the unique characteristics of these varieties of low amylose group and the cultivation conditions (Kongseree, Personal contact). However, peak viscosity could be the major parameter which could clearly discriminate Hom Mali rice from other rice groups, especially from the low amylose rice group.

4.1.6.2 Breakdown viscosity

Breakdown viscosity is caused by breakdown of gelatinized starch granules, of which the degree of breakdown is dependent on rigidity of the swollen granules (Perdon et al., 2001). Like peak viscosity, breakdown viscosity was also negatively correlated with apparent amylose content (Noda et al., 2003). The results of breakdown viscosity of all rice samples are shown in Table 4.3. Breakdown viscosity values of Hom Mali rice (1,061 to 1,103 RVU) and low amylose group (1,024 to 1,082 RVU) were not significantly different ($p \geq 0.05$). Furthermore, RD15 (1,061 RVU) of Hom Mali rice variety was not statistically different from low amylose group ($p \geq 0.05$). However, the breakdown viscosity of Hom Mali rice was higher than those of intermediate and high amylose rice groups which varied between 967 to 976 RVU and 333 to 512 RVU, respectively ($p \leq 0.05$). This result was in accordance with the report of Kongseree (2002a) that the breakdown viscosity of non-aromatic rice was lower than that of Hom Mali rice.

Table 4.3 Pasting properties of rice samples

Groups / Variety	Peak viscosity (RVU)	Breakdown viscosity (RVU)	Setback viscosity (RVU)	Final viscosity (RVU)	Pasting temperature (°C)	Trough viscosity (RVU)
Hom Mali rice (n=50)						
1. KDML105 (n=31)	$1,841 \pm 11^{b}$	$1,103 \pm 8^{a}$	-763 ± 16^{e}	$3,045 \pm 13^{e}$	81 ± 1^{d}	$1,660 \pm 5^{e}$
2. RD15 (n=19)	$1,753 \pm 11^{b}$	$1,061 \pm 5^{b}$	-595 ± 11^{e}	$3,010 \pm 28^{e}$	80 ± 1^{d}	$1,612 \pm 7^{e}$
Low amylose group (n=3)						
1. HKLG (n=1)	$2,180 \pm 2^{a}$	$1,059 \pm 1^{b}$	127 ± 3^{d}	$3,164 \pm 3^{de}$	85 ± 1^{cd}	$1,949 \pm 2^{d}$
2. PTT1 (n=1)	$2,072 \pm 2^{a}$	$1,024 \pm 2^{b}$	220 ± 1^{d}	$3,436 \pm 2^{bcd}$	85 ± 2^{cd}	$1,953 \pm 2^{d}$
3. PSL1 (n=1)	$2,036 \pm 3^{a}$	$1,082 \pm 4^{b}$	161 ± 2^{d}	$3,236 \pm 2^{cde}$	88 ± 0^{ab}	$1,868 \pm 2^{d}$
Intermediate amylose group (n=2)						
1. SPR2 (n=1)	$1,247 \pm 1^{d}$	976 ± 4^{c}	931 ± 2^{c}	$3,561 \pm 2^{abc}$	86 ± 0^{c}	$2,145 \pm 2^{c}$
2. SPR60 (n=1)	$1,544 \pm 3^{c}$	967 ± 2^{c}	997 ± 2^{c}	$3,546 \pm 4^{abc}$	88 ± 0^{ab}	$2,146 \pm 5^{c}$
High amylose group (n=5)						
1. CNT1 (n=1)	$1,038 \pm 7^{e}$	484 ± 3^{d}	$1,305 \pm 4^{b}$	$3,679 \pm 4^{ab}$	89 ± 1^{a}	$2,465 \pm 7^{a}$
3. CNT2 (n=1)	934 ± 3^{e}	463 ± 5^{d}	$1,464 \pm 2^{b}$	$3,742 \pm 1^{ab}$	89 ± 1^{a}	$2,313 \pm 2^{b}$
4. LPT123 (n=1)	957 ± 2^{e}	512 ± 2^{d}	$1,887 \pm 2^{a}$	$3,755 \pm 2^{ab}$	89 ± 1^{a}	$2,443 \pm 5^{a}$
5. PSL2 (n=1)	982 ± 4^{e}	417 ± 4^{d}	$1,400 \pm 4^{b}$	$3,629 \pm 17^{ab}$	87 ± 2^{b}	$2,311 \pm 6^{b}$
6. PTT60 (n=1)	$1,061 \pm 2^{e}$	333 ± 5^{d}	$1,558 \pm 2^{b}$	$3,856 \pm 6^{a}$	86 ± 0^{c}	$2,442 \pm 2^{a}$

[ab, bc, c] indicates that the mean values are significantly different ($p \leq 0.05$).

Differences among rice groups were attributable to amylopectin chain length and apparent amylose content (Meadows and Barton-II, 2002; Patindol et al., 2009). Breakdown viscosity positively correlated with the proportion of short amylopectin chains and negatively correlated with apparent amylose content. Thus, the breakdown viscosity of low amylose rice group was higher than those of intermediate and high amylose rice groups. According to the results, the Hom Mali rice group, especially KDML 105, could be identified with low, intermediate and high amylose rice groups according to its breakdown viscosity, while RD15 could classify only from the intermediate and high amylose rice groups.

4.1.6.3 Setback viscosity

Setback viscosity refers to starch retrogradation which positively correlates with apparent amylose content (Perdon et al., 2001). The setback viscosity of Hom Mali rice (-765 to -595 RVU) was significantly lower than those of low (161 to 220 RVU), intermediate (931 to 997 RVU) and high amylose groups (1,305 to 1,558 RVU), respectively ($p \leq 0.05$) (Table 4.3). The results also showed that the setback viscosity tended to increase with an increase in the apparent amylose content. Consequently, the setback viscosity of high amylose rice varieties was highest. In comparison with high amylose rice varieties, LPT123 exhibited the highest setback viscosity (1,887 RVU), which could be attributed to the retrogradation of amylose molecules during cooling period of RVA measurement.

Therefore, Hom Mali rice could clearly be discriminated from the other rice groups, depending on its setback viscosity. These results also indicated that setback viscosity should be used as a parameter for discriminating Hom Mali rice from the low amylose group. Furthermore, this result was in agreement with that found in Pitiphonpong and Suwannaporn (2009a) who suggested that the setback viscosity could be used as a variable to classify KDML105 from the other rice varieties by the PCA technique.

4.1.6.4 Final viscosity

Final viscosity positively correlates with apparent amylose content. The higher the apparent amylose content, the greater the final viscosity (Perdon et al., 2001). The result exhibited significant differences in final viscosity among rice groups (Table 4.3). Final viscosity of Hom Mali rice ranged from 3,010 to 3,045 RVU, which were not significantly different from the low amylose group ($p \geq 0.05$) except PTT1. In addition, the final viscosity of PTT1 showed no significant difference from that of intermediate amylose rice group, namely SPR2 and SPR60. Moreover, the data exhibited that the final viscosity of intermediate amylose group was also not significantly different from that of high amylose rice group ($p \geq 0.05$) except PTT60. Among rice varieties in the high amylose group, PTT60 showed the highest final viscosity.

The results of this study revealed that Hom Mali rice could not be discriminated from HKLG and PSL1 according to its final viscosity. However, it was important to note that the final viscosity could be used for discriminating Hom Mali rice from PTT1 which was typically mixed with Hom Mali rice. The mixing causes the customers to complain about the impurity of Hom Mali rice. Furthermore, Hom Mali rice could be discriminated from the intermediate and high amylose groups on the basis of the final viscosity.

4.1.6.5 Pasting temperature

According to the RVA measurement of rice samples, the pasting temperature ranged from 80 to 89°C. The pasting temperature was lowest in RD15 and highest in CNT1, CNT2, and LPT123 (Table 4.3). The pasting temperature tended to increase with an increase in apparent amylose content. Thus, all high amylose rice varieties were significantly different from Hom Mali rice and low amylose rice group ($p \leq 0.05$) except PSL1. The results agreed with the report of Yoon et al. (2009) who found that the pasting temperature of intermediate amylose rice (Llpumbyeo variety) was lower than high amylose rice (Dobongbyeo variety). Ghiashi et al. (1982) explained that since the internal starch granule of high amylose starch was tightly packed, the swelling slowed during heating, which subsequently increased the pasting properties. However, there was no difference between the pasting temperature of low and intermediate amylose rice groups ($p \geq 0.05$).

Thus, this parameter could identify Hom Mali rice from the intermediate and high amylose rice groups but was unable to discriminate Hom Mali rice from the low amylose rice group.

4.1.6.6 Trough viscosity

Similar to the results on setback viscosity, trough viscosity of Hom Mali rice was lower than those of low, intermediate and high amylose rice ($p \leq 0.05$) (Table 4.3). The results could be attributed to the retrogradation of apparent amylose content in rice grain, which affected the trough viscosity (Perdon et al., 2001). Consequently, the trough viscosity of high amylose group was higher than those of the other rice groups. Therefore, the trough viscosity can discriminate Hom Mali rice from the other rice groups in the same manner as setback viscosity.

In this study, the results indicated that Hom Mali rice could be discriminated from low, intermediate and high amylose rice groups according to the physicochemical properties except protein content. The apparent amylose content, gel consistency, and alkali spreading value could be used for discriminating Hom Mali rice from intermediate and high amylose groups. However, Hom Mali rice was unable to be discriminated from low amylose group by these properties due to the fact both groups were identified as belonging to the same group of low amylose. Furthermore, the pasting properties of rice could discriminate Hom Mali rice from low amylose group, especially peak viscosity, setback viscosity, and trough viscosity. Moreover, the results indicated that Hom Mali rice could be classified from PTT1 using the final viscosity parameter.

4.2 Effect of degree of milling on physicochemical properties of rice

Generally rice grain consume as a whole grain of milled rice or white rice obtained by milling (dehulling and polishing) rough rice. The degree of milling depends on the purposes of milling. Therefore, degree of milling is one of the key factors affecting several aspects of rice quality, such as nutritional and physicochemical properties, and cooking and eating quality (Sadeghi et al., 2012). Wadsworth (1994) reported that the degree of milling did not affect milling quality, but the composition of rice resulted in the change of physicochemical properties. To investigate the effect of degree of milling on these properties, the degrees of milling of rice samples were varied from 0 (brown rice), 5, 10, and 15% degree of milling.

4.2.1 Protein content

The degree of milling significantly affected the protein content (Table 4.4). The results showed that increasing degree of milling resulted in the reduction of protein content of all rice varieties (Figure 4.2). The highest values of protein contents were observed in the degree of milling of 0%, whereas the lowest values were obtained in the degree of milling of 15%. These results are confirmed by the earlier studies reported by Sadeghi et al. (2012). The process of polishing further decrease the nutrient contents after bran removal since rice bran layer contains several important nutrients such as protein and lipid contents (Lamberts et al., 2007; Sadeghi et al., 2012). A similar effect of degree of milling on protein contents had been reported by Lamberts et al. (2007), who found that protein content decreased from outer to inner layers of rice grain. Additionally, Lyon et al. (1999) found that deep-milled samples had generally lower protein content than regular-milled samples. However, at the same degrees of milling (0, 5, 10, and 15% degree of milling), the protein contents of KDML105 were not statistically different from those of the other rice varieties ($p \geq 0.05$).

Moreover, the degree of milling changed both the protein content of Hom Mali rice and those of rice varieties of low, intermediate or high amylose groups. For example, the protein content of KDML105 at 5% degree of milling was similar to the protein contents of low, intermediate and high amylose groups at 0 and 5% degrees of milling except CNT2 variety (Table 4.4). The results indicated that the changes in the degree of milling among various rice varieties could lead to the changes in their protein content. Previous results found that protein content could not be used for discriminating Hom Mali rice from the other rice varieties, but these results exhibited that degree of milling affected the protein content of rice grain. Thus, in the discrimination of Hom Mali rice from low, intermediate and high amylose rice, the effect of the degree of milling on the protein content should be taken into consideration.

4.2.2 Apparent amylose content

The effects of degree of milling on the apparent amylose content of all rice varieties are presented in Table 4.4. Each variety of rice sample showed significant differences in apparent amylose contents for different degrees of milling ($p \leq 0.05$). The results also illustrated that the apparent amylose contents of all rice varieties tended to increase with the increasing degree of milling up to 15%. However, the protein content decreased with the increasing degree of milling. The increase in apparent amylose content was attributable to the disproportional losses of protein and lipid of rice grain with milling (Normand et al., 1996). This result corresponded with the work of Perdon et al. (2001) who reported that apparent amylose content positively correlated with degree of milling. Zhang et al. (2003) also reported the corresponding correlation between degree of milling and apparent amylose content. The apparent amylose contents of japonica and indica rice varieties respectively increased 1.36 and 1.95% when the degree of milling increased by 10%. The results indicated that apparent amylose content was affected by degree of milling. Milling to a greater degree produced significantly ($p \leq 0.05$) higher apparent amylose content.

Furthermore, the changing degree of milling during rice milling brought the apparent amylose content of Hom Mali rice closer to those of the other rice varieties (Table 4.4). At 10% degree of milling, the apparent amylose content of Hom Mali rice (KDML105, 18.70 ± 1.26%; and RD15, 18.47 ± 1.05%) was not significantly different from PTT1 at 10% degree of milling (18.65 ± 0.18%) and PSL1 at 15% degree of milling (18.60 ± 0.11%) ($p \geq 0.05$). Moreover, the results showed that the apparent amylose content of Hom Mali rice with 15% degree of milling (KDML105, 20.25 ± 1.39% and RD15, 20.04 ± 0.85%) was similar to HKLG at 0, 5, and 10% degrees of milling (18.25 ± 0.20%, 20.35 ± 0.07%, 21.50 ± 0.57%), PTT1 (20.40 ± 0.06%) and PSL1 (18.60 ± 0.11%) at 15% degree of milling ($p \geq 0.05$). The results indicated that the degree of milling greatly affected the apparent amylose content of rice grain. Consequently, Hom Mali rice was unable to be discriminated from the low amylose rice group with different degrees of milling.

The comparison among Hom Mali rice, low, intermediate and high amylose rice varieties exhibited that Hom Mali rice was not significantly different from low amylose rice and SPR2 ($p \geq 0.05$). Additionally, Hom Mali rice differed from SPR60 and high amylose rice varieties ($p \leq 0.05$). The results were correlated to rice variety and degree of milling. As previously mentioned, degree of milling is an important factor to be fixed for discriminating Hom Mali rice from low amylose rice group. However, the results indicated that Hom Mali rice could not be discriminated from low amylose rice group and SPR2 with different degrees of milling using merely the apparent amylose content measurement.

Table 4.4 Effect of degrees of milling on physicochemical properties of rice varieties

Rice variety	Degree of milling (%)	Protein content (%)	Apparent amylose content (%)	Gel consistency (mm)	Alkali spreading value (units on a 1-7 visual scale)
KDML105	0	$7.01 \pm 0.70^{c-g}$	$16.09 \pm 1.12^{r-t}$	79.06 ± 4.15^{a}	7.00 ± 0.00^{a}
	5	$6.68 \pm 0.73^{d-j}$	$16.88 \pm 1.10^{q-s}$	$71.93 \pm 3.64^{a-d}$	7.00 ± 0.00^{a}
	10	$6.19 \pm 0.63^{e-n}$	$18.70 \pm 1.26^{o-q}$	$64.62 \pm 5.14^{d-j}$	7.00 ± 0.00^{a}
	15	$5.53 \pm 0.55^{i-o}$	$20.25 \pm 1.39^{m-o}$	$61.48 \pm 4.40^{f-k}$	7.00 ± 0.00^{a}
RD15	0	$6.97 \pm 0.83^{c-h}$	$16.02 \pm 1.46^{r-t}$	$73.63 \pm 5.76^{a-c}$	6.00 ± 0.00^{b}
	5	$6.71 \pm 0.81^{d-j}$	$17.18 \pm 1.16^{q-s}$	$68.42 \pm 3.27^{c-f}$	7.00 ± 0.00^{a}
	10	$6.17 \pm 0.58^{e-n}$	$18.47 \pm 1.05^{o-q}$	$63.39 \pm 3.15^{e-k}$	7.00 ± 0.00^{a}
	15	$5.57 \pm 0.77^{h-o}$	$20.04 \pm 0.85^{n-o}$	55.57 ± 4.36^{k}	7.00 ± 0.00^{a}
HKLG	0	$6.49 \pm 0.01^{d-l}$	$18.25 \pm 0.20^{o-r}$	$71.50 \pm 0.64^{a-d}$	7.00 ± 0.00^{a}
	5	$6.19 \pm 0.01^{e-n}$	$20.35 \pm 0.07^{m-o}$	$68.50 \pm 0.70^{c-f}$	7.00 ± 0.00^{a}
	10	$5.25 \pm 0.02^{k-o}$	$21.50 \pm 0.57^{l-n}$	$61.50 \pm 0.71^{f-k}$	7.00 ± 0.00^{a}
	15	$5.05 \pm 0.08^{m-o}$	$22.25 \pm 0.07^{k-m}$	$56.50 \pm 2.12^{j-k}$	6.00 ± 0.00^{b}
PTT1	0	$8.13 \pm 0.02^{a-c}$	$16.60 \pm 0.13^{q-s}$	$77.50 \pm 0.70^{a-b}$	6.00 ± 0.00^{b}
	5	$7.83 \pm 0.03^{b-d}$	$17.45 \pm 0.04^{p-s}$	$67.50 \pm 0.71^{c-g}$	6.00 ± 0.00^{b}
	10	$5.34 \pm 0.01^{j-o}$	$18.65 \pm 0.18^{o-q}$	$61.00 \pm 1.31^{f-k}$	7.00 ± 0.00^{a}
	15	$5.25 \pm 0.01^{k-o}$	$20.40 \pm 0.16^{m-o}$	$58.50 \pm 0.81^{h-k}$	7.00 ± 0.00^{a}
PSL1	0	$6.91 \pm 0.00^{c-i}$	14.35 ± 0.05^{t}	$71.00 \pm 1.50^{b-c}$	6.00 ± 0.00^{b}
	5	$6.61 \pm 0.01^{d-k}$	$15.55 \pm 0.46^{s-t}$	$65.00 \pm 1.38^{d-i}$	5.00 ± 0.00^{c}
	10	$5.86 \pm 0.02^{f-o}$	$16.75 \pm 0.11^{q-s}$	$60.50 \pm 0.74^{f-k}$	6.00 ± 0.00^{b}
	15	$5.64 \pm 0.09^{g-o}$	$18.60 \pm 0.11^{o-q}$	$57.00 \pm 1.35^{i-k}$	6.00 ± 0.00^{b}
SPR2	0	$7.56 \pm 0.02^{c-e}$	$19.65 \pm 0.45^{n-p}$	$59.50 \pm 0.65^{g-k}$	5.00 ± 0.00^{c}
	5	$7.26 \pm 0.02^{c-f}$	$21.25 \pm 0.35^{l-n}$	$57.50 \pm 0.65^{h-k}$	5.00 ± 0.00^{c}
	10	$6.94 \pm 0.05^{c-i}$	$22.80 \pm 0.17^{k-l}$	56.00 ± 0.92^{k}	5.00 ± 0.00^{c}
	15	$5.20 \pm 0.02^{k-o}$	$23.35 \pm 0.35^{k-l}$	$46.41 \pm 1.53^{l-m}$	5.00 ± 0.00^{c}
SPR60	0	9.05 ± 0.07^{a}	$22.45 \pm 0.35^{k-m}$	55.00 ± 1.45^{k}	4.00 ± 0.00^{d}
	5	$8.97 \pm 0.01^{a-b}$	$24.35 \pm 0.13^{i-k}$	45.00 ± 0.01^{-n}	4.00 ± 0.00^{d}
	10	$6.24 \pm 0.24^{e-n}$	$25.20 \pm 0.28^{h-j}$	$42.00 \pm 0.87^{l-o}$	4.00 ± 0.00^{d}
	15	$5.82 \pm 0.03^{g-o}$	$26.30 \pm 0.28^{g-i}$	$37.00 \pm 1.21^{n-p}$	4.00 ± 0.00^{d}
CNT1	0	$7.51 \pm 0.15^{c-e}$	$26.60 \pm 0.29^{f-h}$	$65.50 \pm 0.57^{c-h}$	1.00 ± 0.00^{f}
	5	$6.39 \pm 0.10^{e-m}$	$27.73 \pm 0.17^{d-g}$	$60.75 \pm 0.50^{f-k}$	2.00 ± 0.50^{e}
	10	$5.99 \pm 0.13^{f-n}$	$28.67 \pm 0.15^{c-f}$	47.00 ± 4.96^{l}	1.00 ± 0.00^{f}
	15	$5.11 \pm 0.08^{l-o}$	$29.57 \pm 0.22^{b-d}$	$45.25 \pm 2.87^{l-n}$	1.00 ± 0.00^{f}
CNT2	0	$5.26 \pm 0.02^{k-o}$	$28.65 \pm 0.21^{c-f}$	$39.00 \pm 1.39^{l-p}$	1.00 ± 0.00^{f}
	5	$5.11 \pm 0.05^{l-o}$	$29.45 \pm 0.21^{b-e}$	$36.00 \pm 1.28^{o-q}$	1.00 ± 0.00^{f}
	10	$4.86 \pm 0.02^{n-o}$	$30.70 \pm 0.28^{a-c}$	$32.50 \pm 2.12^{p-s}$	1.00 ± 0.00^{f}
	15	4.49 ± 0.01^{o}	32.65 ± 0.18^{a}	$27.50 \pm 0.81^{r-s}$	1.00 ± 0.00^{f}
LPT123	0	$6.85 \pm 0.04^{c-i}$	$27.25 \pm 0.19^{e-h}$	$41.00 \pm 1.43^{l-o}$	1.00 ± 0.00^{f}
	5	$6.55 \pm 0.04^{d-k}$	$28.45 \pm 0.11^{c-g}$	$35.50 \pm 0.84^{o-r}$	1.00 ± 0.00^{f}
	10	$5.93 \pm 0.03^{f-n}$	$29.40 \pm 0.44^{b-e}$	$32.00 \pm 1.51^{p-s}$	1.00 ± 0.00^{f}
	15	$5.22 \pm 0.08^{k-o}$	$31.50 \pm 0.31^{a-b}$	27.00 ± 2.43^{s}	1.00 ± 0.00^{f}
PSL2	0	$7.01 \pm 0.12^{c-g}$	$26.65 \pm 0.26^{f-h}$	$41.25 \pm 0.95^{l-o}$	1.00 ± 0.00^{f}
	5	$6.68 \pm 0.16^{d-j}$	$27.25 \pm 0.23^{e-h}$	$37.75 \pm 1.25^{m-p}$	1.00 ± 0.00^{f}
	10	$6.25 \pm 0.05^{e-n}$	$28.55 \pm 0.36^{c-g}$	$32.25 \pm 1.89^{p-s}$	1.00 ± 0.00^{f}
	15	$5.69 \pm 0.19^{g-o}$	$30.62 \pm 0.30^{a-c}$	27.25 ± 1.50^{s}	1.00 ± 0.00^{f}
PTT60	0	$6.93 \pm 0.00^{c-i}$	$28.55 \pm 0.18^{c-g}$	$42.00 \pm 0.18^{l-o}$	1.00 ± 0.00^{f}
	5	$6.83 \pm 0.00^{c-i}$	$29.95 \pm 0.26^{b-d}$	$37.50 \pm 2.12^{m-p}$	1.00 ± 0.00^{f}
	10	$6.00 \pm 0.01^{f-n}$	$31.60 \pm 0.15^{a-b}$	$32.00 \pm 1.53^{p-s}$	2.00 ± 0.00^{e}
	15	$5.92 \pm 0.18^{f-n}$	32.30 ± 0.31^{a}	$28.50 \pm 0.94^{q-s}$	2.00 ± 0.00^{e}

$^{a, b, c}$ indicates that the mean values are significantly different ($p \leq 0.05$).

al. (2005) and Umemoto et al. (2002) found that the increasing apparent amylose following an increase in the degree of milling resulted in the decrease in scoring of alkali spreading value of rice grain.

Although Hom Mali rice and low amylose rice groups had different levels of apparent amylose contents at different degrees of milling, no significant differences were found, except in RD15 (0% degree of milling), HKLG (15% degree of milling), and PTT1 (0 and 5% degree of milling). Hom Mali rice and low amylose rice group showed the highest score of alkali spreading value among the four rice groups, followed by intermediate and high amylose rice groups (Table 4.4). Thus, the increase in degree of milling up to 15% had no influence on the alkali spreading value of all rice groups. However, Hom Mali rice could not be discriminated from the low amylose rice group according to the alkali spreading value, but Hom Mali rice could be identified from the intermediate and high amylose rice groups.

4.2.5 Pasting properties of rice

The effect of degree of milling on the pasting properties of brown rice and milled rice is shown in Table 4.5 and appendix (Figures 1F-4F). The increases of the RVA curves with increasing degree of milling of four rice groups are shown in Figures 1F-4F. The curves of four rice groups, i.e., Hom Mali rice, low, intermediate and high amylose groups treated with various degrees of milling, were very similar to one another. Figures 1F-4F show that RVA peak viscosity values of four rice groups at 15% degree of milling were higher than those at 10, 5, and 0% degrees of milling. The differences was attributed to the reduction of amylase activity, protein and lipid contents in rice grain at 15% degree of milling, causing higher peak viscosity (Lim et al., 1999; Perdon et al., 2001; Fitzgerald et al., 2003; Mariotti et al., 2005, Mariotti et al., 2009).

4.2.5.1 Peak viscosity

Degree of milling significantly ($p \leq 0.05$) impacts peak viscosity (Table 4.5). Peak viscosities of all rice varieties increased with the degree of milling. Milled rice with 15% degree of milling showed the highest peak viscosity, followed by milled rice with 10, 5, and 0% degree of milling. The increase in peak viscosity with milling was attributed to the removal of a greater amount of bran as well as to the increased apparent amylose content and decreased proteins and lipids with the longer milling duration (Wadsworth, 1994). This is confirmed by

Mariotti et al. (2005) who found that low amylose rice flour showed the higher water binding capacity, swelling power, solubility and peak viscosity than high amylose rice flour. Lim et al. (1999) noted that protein removal caused peak viscosity to increase and starch to decrease. Fitzgerald et al. (2003) also reported that amylase is located mainly in the bran layer which is removed during milling. Rice with a higher degree of milling will have less amylase and thus higher peak viscosity.

Of the same degree of milling, peak viscosity was the highest for PTT1 and the lowest for CTN2 (Table 4.5). These observations were in agreement with the results of Perdon et al. (2001). Additionally, the peak viscosity values of KDML105 (2,740 ± 13 RVU) and RD15 (2,631 ± 15 RVU) at 5% degree of milling were not significantly indifferent from the HKLG variety at 5% degree of milling (2,945 ± 3RVU), SPR2 variety at 10 (2,514 ± 2 RVU) and 15% (2,778 ± 2 RVU) degree of milling, and SPR60 at 15% degree of milling (2,631 ± 2 RVU). Therefore, these results showed that degree of milling affected peak viscosity which was closely related to Hom Mali rice and made its discrimination from low amylose group and SPR2 impossible according to their peak viscosity.

4.2.5.2 Breakdown viscosity

The changes in breakdown viscosity of all rice varieties with different degrees of milling are presented in Table 4.5, which were similar to the results of the peak viscosity of all rice varieties. The breakdown viscosity values of all rice varieties were found to increase with the increasing degree of milling. The highest values of breakdown viscosity of all rice varieties were observed at the 15% degree of milling while the lowest values were found at the 0% degree of milling. The removal of bran layers that are rich in proteins and lipids and the increase of apparent amylose content, compared to the degree of milling at 0%, probably inhibited the rupture of starch granules of rice grain during gelatinization. These results were similar to those reported by Lim et al., 1999; Perdon et al., 2001; Noosuk et al., 2003. The breakdown viscosities were positively correlated with the degree of milling. Furthermore, Juliano (1993) found that low amylose rice varieties had lower capacity of breaking down the starch granules during gelatinization than high amylose rice samples.

Moreover, the results showed that the degree of milling influenced the discrimination of Hom Mali rice. The breakdown viscosity of Hom Mali rice, especially RD15 at 5% degree of milling (1,351 ± 10 RVU), was not significantly different from HKLG at 5% (1,185 ± 5 RVU), 10% degree of milling (1,320 ± 2 RVU), PSL1 at 5% (1,286 ± 2 RVU), 10% (1,337 ± 3 RVU), 15% degree of milling (1,435 ± 4 RVU), SPR2 at 10% (1,183 ± 3 RVU), 15% degree of milling (1,247 ± 1 RVU), SPR 60 at 10% (1,250 ± 2 RVU) and 15% degree of milling (1,341 ± 2 RVU) ($p \geq 0.05$). This indicated that the changes in rice composition were a result of the milling degree, thereby causing the breakdown viscosity of Hom Mali rice to be similar to those low amylose rice varieties. Therefore, Hom Mali rice could not be discriminated from low and intermediate rice varieties.

4.2.5.3 Setback viscosity

Setback viscosity showed significant differences among the rice varieties with different degrees of milling ($p \leq 0.05$) (Table 4.5). Milled rice at 0% degree of milling exhibited the lowest setback viscosity, whereas it was found to be highest for milled rice at 15% degree of milling of all rice varieties. These results indicated that setback viscosities were positively correlated with the degree of milling. These results corresponded with the work by Park et al. (2001) who found that the higher the degree of milling, the higher the setback viscosity. A similar finding was also reported of Perdon et al. (2001). They proposed that high amylose rice varieties had higher capacity of retrogradation during cooling period in RVA measurement than low amylose rice varieties, resulting in the highest setback viscosity obtained in milled rice at 15% degree of milling which showed the highest apparent amylose content.

However, results obtained in this study did not show significant differences ($p \geq 0.05$) in setback viscosity of Hom Mali rice and low amylose rice varieties. On the other hand, Hom Mali rice was significantly different from intermediate and high amylose rice varieties. Therefore, the results indicated the possibility of discriminating Hom Mali rice from intermediate and high amylose rice groups, except from low amylose rice, with different degrees of milling on the basis of their setback viscosity.

Table 4.5 Effect of degrees of milling on pasting properties of rice varieties

Rice variety	Degree of milling (%)	Peak viscosity (RVU)	Breakdown viscosity (RVU)	Setback viscosity (RVU)	Final viscosity (RVU)	Trough viscosity (RVU)
KDML105	0	$1,841 \pm 11^{k-o}$	$1,103 \pm 7^{g-j}$	-763 ± 16^{s}	$3,045 \pm 13^{u-v}$	$1,660 \pm 5^{u-v}$
	5	$2,740 \pm 13^{e-f}$	$1,463 \pm 10^{c-d}$	-668 ± 16^{s}	$3,172 \pm 11^{t-v}$	$1,791 \pm 7s^{-u}$
	10	$3,205 \pm 16^{b-c}$	$1,684 \pm 11^{a-b}$	$-376 \pm 12^{q-r}$	$3,232 \pm 10^{t-v}$	$1,882 \pm 8^{r-t}$
	15	$3,523 \pm 18^{a}$	$1,838 \pm 11^{a}$	60 ± 9^{p}	$3,326 \pm 10^{r-u}$	$1,949 \pm 9^{r-s}$
RD15	0	$1,753 \pm 11^{l-p}$	$1,061 \pm 5^{h-k}$	$-595 \pm 11^{r-s}$	$3,010 \pm 28^{v}$	$1,612 \pm 7^{v}$
	5	$2,631 \pm 15^{f-g}$	$1,351 \pm 10^{d-f}$	$-515 \pm 12^{r-s}$	$3,263 \pm 18^{s-v}$	$1,774 \pm 13^{t-u}$
	10	$3,123 \pm 21^{c}$	$1,597 \pm 10^{b-c}$	-218 ± 9^{q}	$3,335 \pm 18^{q-u}$	$1,884 \pm 11^{r-t}$
	15	$3,446 \pm 19^{a-b}$	$1,750 \pm 12^{a-b}$	$239 \pm 18^{o-p}$	$3,439 \pm 19^{p-t}$	$1,955 \pm 11^{r-s}$
HKLG	0	$2,180 \pm 2^{i-j}$	$1,059 \pm 1^{h-k}$	$127 \pm 3^{o-p}$	$3,164 \pm 3^{t-v}$	$1,949 \pm 2^{r-s}$
	5	$2,945 \pm 3^{c-e}$	$1,185 \pm 5^{f-i}$	$387 \pm 2^{n-o}$	$3,442 \pm 3^{o-t}$	$2,174 \pm 5^{n-q}$
	10	$3,174 \pm 5^{b-c}$	$1,320 \pm 2^{d-f}$	531 ± 2^{n}	$3,577 \pm 7^{n-r}$	$2,237 \pm 4^{m-p}$
	15	$3,592 \pm 2^{a}$	$1,574 \pm 5^{b-c}$	$980 \pm 3^{k-m}$	$3,668 \pm 4^{k-p}$	$2,385 \pm 2^{i-m}$
PTT1	0	$2,072 \pm 2^{i-k}$	$1,024 \pm 2^{i-l}$	$220 \pm 1^{o-p}$	$3,436 \pm 2^{p-t}$	$1,953 \pm 2^{r-s}$
	5	$3,063 \pm 4^{c}$	$1,117 \pm 2^{g-j}$	$359 \pm 1^{n-o}$	$3,747 \pm 3^{i-p}$	$2,050 \pm 2^{q-r}$
	10	$3,189 \pm 3^{b-c}$	$1,380 \pm 2^{d-e}$	544 ± 6^{n}	$3,833 \pm 4^{h-n}$	$2,128 \pm 3^{p-q}$
	15	$3,550 \pm 2^{a}$	$1,475 \pm 3^{c-d}$	$869 \pm 1^{l-m}$	$3,989 \pm 2^{d-j}$	$2,259 \pm 2^{l-p}$
PSL1	0	$2,036 \pm 3^{i-l}$	$1,082 \pm 4^{h-k}$	$161 \pm 2^{o-p}$	$3,236 \pm 2^{t-v}$	$1,868 \pm 2^{s-t}$
	5	$3,044 \pm 3^{c-d}$	$1,286 \pm 2^{d-g}$	$373 \pm 3^{n-o}$	$3,542 \pm 2^{n-s}$	$2,153 \pm 1^{o-q}$
	10	$3,237 \pm 3^{d-e}$	$1,337 \pm 3^{d-f}$	543 ± 4^{n}	$3,642 \pm 3^{l-q}$	$2,256 \pm 2^{l-p}$
	15	$3,541 \pm 1^{a}$	$1,435 \pm 4^{c-e}$	836 ± 6^{m}	$3,763 \pm 2^{h-n}$	$2,319 \pm 3^{j-o}$
SPR2	0	$1,247 \pm 1^{r-t}$	$976 \pm 4^{j-m}$	$931 \pm 2^{k-m}$	$3,561 \pm 2^{n-s}$	$2,145 \pm 2^{o-q}$
	5	$1,937 \pm 7^{j-n}$	$1,024 \pm 5^{i-l}$	$1,140 \pm 1^{j-l}$	$3,632 \pm 3^{l-r}$	$2,272 \pm 3^{k-p}$
	10	$2,514 \pm 2^{f-h}$	$1,183 \pm 3^{f-i}$	$1,416 \pm 4^{g-i}$	$3,725 \pm 5^{j-p}$	$2,373 \pm 4^{i-m}$
	15	$2,778 \pm 3^{d-f}$	$1,247 \pm 1^{e-h}$	$1,633 \pm 5^{e-g}$	$3,959 \pm 1^{d-k}$	$2,477 \pm 4^{g-j}$
SPR60	0	$1,544 \pm 3^{o-q}$	$967 \pm 2^{j-m}$	$997 \pm 2^{k-m}$	$3,546 \pm 4^{n-s}$	$2,146 \pm 5^{o-q}$
	5	$2,164 \pm 4^{i-j}$	$1,034 \pm 3^{i-k}$	$1,177 \pm 2^{i-k}$	$3,635 \pm 1^{l-q}$	$2,346 \pm 2^{j-n}$
	10	$2,452 \pm 3^{g-h}$	$1,250 \pm 2^{e-h}$	$1,416 \pm 4^{e-h}$	$4,059 \pm 2^{d-h}$	$2,448 \pm 9^{h-k}$
	15	$2,631 \pm 2^{f-g}$	$1,341 \pm 2^{d-f}$	$1,474 \pm 6^{e-g}$	$4,174 \pm 5^{c-f}$	$2,638 \pm 4^{e-g}$

^{ns} denotes that the mean values are insignificantly different ($p \geq 0.05$). Meanwhile, any other superscript (e.g., ab, bc, c) indicates that the mean values are significantly different ($p \leq 0.05$).

Table 4.5 (continued)

Rice variety	Degree of milling (%)	Peak viscosity (RVU)	Breakdown viscosity (RVU)	Setback viscosity (RVU)	Final viscosity (RVU)	Trough viscosity (RVU)
CNT1	0	$1,038 \pm 7^{s-u}$	$484 \pm 3^{u-w}$	$1,305 \pm 4^{h-j}$	$3,679 \pm 4^{k-p}$	$2,465 \pm 7^{h-j}$
	5	$1,470 \pm 9^{p-r}$	$757 \pm 4^{n-r}$	$1,629 \pm 5^{e-g}$	$4,255 \pm 8^{c-d}$	$2,525 \pm 3^{f-i}$
	10	$1,730 \pm 2^{m-p}$	$824 \pm 3^{m-q}$	$1,941 \pm 4^{c-d}$	$4,733 \pm 5^{b}$	$2,893 \pm 3^{c-d}$
	15	$2,116 \pm 9^{i-k}$	$931 \pm 4^{j-n}$	$2,216 \pm 5^{b-c}$	$5,055 \pm 4^{a}$	$3,023 \pm 4^{c}$
CNT2	0	934 ± 3^{u}	$463 \pm 5^{u-w}$	$1,464 \pm 2^{g-h}$	$3,742 \pm 1^{i-p}$	$2,313 \pm 2^{j-o}$
	5	$1,293 \pm 5^{q-s}$	$565 \pm 4^{s-v}$	$1,974 \pm 1^{c-d}$	$3,931 \pm 2^{e-l}$	$2,432 \pm 4^{h-l}$
	10	$1,645 \pm 4^{n-p}$	$698 \pm 1^{q-t}$	$2,106 \pm 7^{b-d}$	$4,255 \pm 4^{c-e}$	$2,550 \pm 3^{f-i}$
	15	$2,071 \pm 2^{i-k}$	$717 \pm 7^{p-t}$	$2,692 \pm 3^{a}$	$4,742 \pm 3^{b}$	$2,774 \pm 7^{d-e}$
LPT123	0	$957 \pm 2^{t-u}$	$512 \pm 2^{u-w}$	$1,887 \pm 2^{d-e}$	$3,755 \pm 2^{i-o}$	$2,443 \pm 5^{h-k}$
	5	$1,297 \pm 2^{q-s}$	$837 \pm 3^{l-q}$	$2,317 \pm 24^{b}$	$4,038 \pm 3^{d-i}$	$2,768 \pm 4^{d-e}$
	10	$1,743 \pm 3^{l-p}$	$920 \pm 6^{j-o}$	$2,695 \pm 6^{a}$	$4,417 \pm 4^{c}$	$2,985 \pm 4^{c}$
	15	$2,164 \pm 3^{i-j}$	$1,037 \pm 2^{i-k}$	$2,833 \pm 4^{a}$	$4,928 \pm 5^{a-b}$	$3,233 \pm 1^{a}$
PSL2	0	$982 \pm 4^{t-u}$	$417 \pm 4^{v-w}$	$1,400 \pm 4^{g-j}$	$3,629 \pm 17^{l-r}$	$2,311 \pm 6^{j-o}$
	5	$1,069 \pm 7^{s-u}$	$539 \pm 4^{t-v}$	$1,830 \pm 5^{d-f}$	$3,884 \pm 9^{f-m}$	$3,583 \pm 4^{f-h}$
	10	$1,635 \pm 7^{o-p}$	$738 \pm 3^{o-s}$	$2,651 \pm 10^{a}$	$4,144 \pm 10^{c-g}$	$2,879 \pm 3^{c-d}$
	15	$2,022 \pm 3^{i-m}$	$894 \pm 6^{k-p}$	$2,723 \pm 10^{a}$	$4,757 \pm 3^{b}$	$3,044 \pm 7^{b-c}$
PTT60	0	$1,061 \pm 2^{s-u}$	333 ± 5^{w}	$1,558 \pm 2^{f-h}$	$3,856 \pm 6^{g-n}$	$2,442 \pm 2^{h-k}$
	5	$1,475 \pm 4^{p-r}$	$487 \pm 1^{u-w}$	$1,953 \pm 5^{c-d}$	$4,238 \pm 3^{c-d}$	$2,665 \pm 5^{e-f}$
	10	$1,830 \pm 1^{k-o}$	$630 \pm 1^{r-u}$	$2,259 \pm 1^{b}$	$4,714 \pm 4^{b}$	$2,968 \pm 2^{c}$
	15	$2,259 \pm 2^{h-i}$	$754 \pm 2^{n-r}$	$2,748 \pm 4^{a}$	$4,870 \pm 1^{a-b}$	$3,191 \pm 3^{a-b}$

[ns] denotes that the mean values are insignificantly different ($p \geq 0.05$). Meanwhile, any other superscript (e.g., ab, bc, c) indicates that the mean values are significantly different ($p \leq 0.05$).

4.2.5.4 Final viscosity

The degree of milling also impacted the final viscosity. The results showed an increase of final viscosity of all rice varieties with an increase in degree of milling. Milled rice at 15% degree of milling showed the highest final viscosity, whereas the lowest final viscosity was found in milled rice at 0% degree of milling. The differences in final viscosity of all rice varieties were attributed to the increasing apparent amylose content and decreasing protein content during rice milling (Lim et al., 1999; Mariotti et al., 2005). Furthermore, Miles et al. (1985) reported that increase in final viscosity might be due to the aggregation of the amylose molecules.

Additionally, the result depicted that the final viscosity values obtained from KDML105 and RD15 were not significantly different from those of low amylose group ($p \geq 0.05$) but differed from intermediate and high amylose rice groups ($p \leq 0.05$).Although the degree of milling affected the final viscosity of rice samples, it could be used to discriminate Hom Mali rice from intermediate and high amylose rice varieties. However, the final viscosity could not be used for discriminating Hom Mali rice from low amylose rice varieties.

4.2.5.5 Trough viscosity

Various results reported on the effect of degree of milling on pasting properties, such as peak, breakdown, setback and final viscosity. This study showed that degree of milling also affected trough viscosity in a similar fashion that it did the setback and final viscosity (Table 4.5). The highest trough viscosity was of milled rice at 15% degree of milling, followed by milled rice at 10, 5, and 0% degree of milling. The increase in trough viscosity with increased degree of milling might be explained by the higher apparent amylose content in milled rice at 15% degree of milling. The effect of apparent amylose content on the trough viscosity was due to the retrogradation of amylose molecules during cooling period of RVA measurement, resulting in the increased trough viscosity.

However, the result revealed that trough viscosity of Hom Mali rice was not significantly different from that of low amylose group ($p \geq 0.05$). On the other hand, this property significantly differed from intermediate and high amylose groups ($p \geq 0.05$). Therefore, Hom Mali rice could be discriminated from intermediate and high amylose groups according to trough viscosity, whereas trough viscosity could not be used for discriminating Hom Mali rice from low amylose varieties.

Thus, it could be inferred that not all pasting properties of rice could be used for discriminating Hom Mali rice from the low amylose group with different degrees of milling. However, the setback, final and trough viscosity could be used to discriminate Hom Mali rice from intermediate and high amylose groups, whereas the peak and breakdown viscosity could differentiate Hom Mali rice from high amylose group. These results were related to the effect of degree of milling on the apparent amylose content and protein content in that the degree of milling changed the rheology of starch during RVA measurement.

It could be concluded from these results that the degree of milling changed the composition of rice grain and greatly affected the physicochemical properties of rice. With increasing degree of milling, protein content and gel consistency decreased whereas apparent amylose content and pasting properties, i.e., peak, breakdown, setback, final and trough viscosity, increased. Furthermore, the degree of milling affects not only the physicochemical properties but also the discrimination of rice. For instance, Hom Mali rice is generally classified as having low apparent amylose content and soft gel consistency (Kongseree, 2002b). By increasing the degree of milling, the apparent amylose content increases whereas the gel consistency decreases. These changes make its physicochemical properties similar to those of rice varieties with intermediate or high amylose contents. It is possible that the changes in the degree of milling among various rice varieties could lead to the changes in their physicochemical properties. As such, the pre-determined degree of milling during rice milling was preferred for the discrimination of Hom Mali rice from the other aromatic and non-aromatic rice varieties.

As previously stated, the removal of bran during milling increases the starch level and pasting properties but lowers the protein content of the remaining grain. Therefore, the changes in rice composition affected the discrimination of Hom Mali rice from low, intermediate, and high amylose rice varieties.

4.3 Prediction of physicochemical properties of rice with different degrees of milling by FT-NIR spectroscopy

4.3.1 An overview of the distribution in physicochemical properties of rice with different degrees of milling

The range (minimum to maximum), mean and standard deviation values of the physicochemical properties of brown rice (0% degree of milling) and milled rice samples with different degrees of milling are shown in Table 4.6. The moisture and protein contents ranged between 11.10 to 14.00% and 4.07 to 9.10%, respectively. The apparent amylose content widely varied from 13.40 to 36.20% with the standard deviation of 4.29. In addition, alkali spreading value and gel consistency ranged from 1.00 to 7.00 units of 1-7 visual scale and 39.00 to 87.00, respectively.

For pasting properties, the peak, breakdown, setback, final viscosity, pasting temperature, and trough viscosity were between 934 to 4,156 RVU, -140 to 2,044 RVU, -1,130 to 1,887 RVU, 2,126 to 4,603 RVU, 5.30 to 6.60°C, and 1,888 to 2,472 RVU, respectively. The mean ± standard deviation of these properties were 2,905 ± 838 RVU, 1,356 ± 412 RVU, -315 ± 620 RVU, 3,306 ± 1,229 RVU, 4.46 ± 1.86°C, and 1,834 ± 207 RVU, respectively. These standard deviations were wide ranging and higher than those reported in Delwiche et al.'s (1996). Bao et al. (2001) described that the high standard deviation caused the calibration equations not to be an accurate prediction of the constituents since the standard deviation was often referred to as the standard error of calibration (SEC) set. The higher the SEC, the unsuitable it is to predict the constituents.

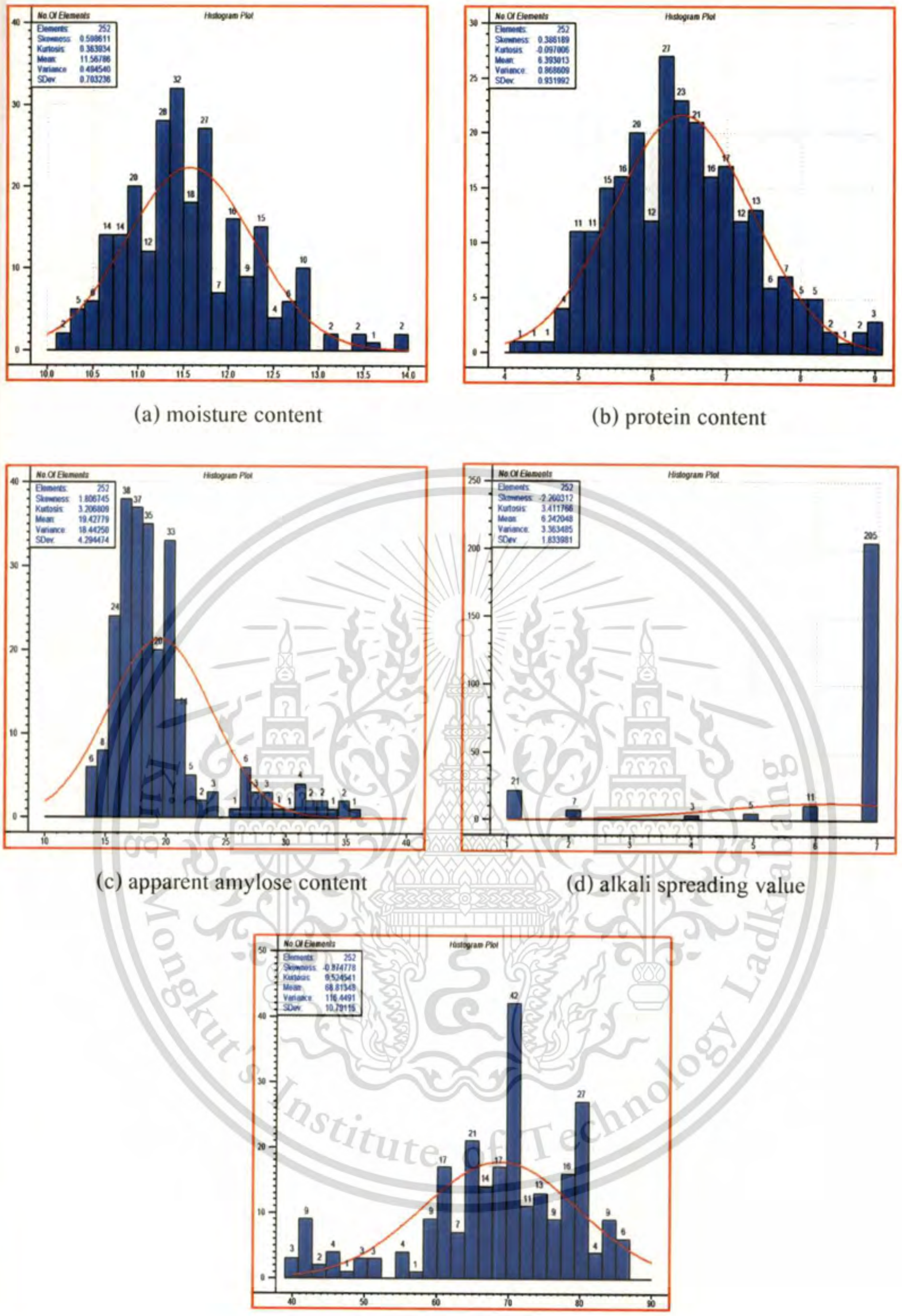
The distribution of moisture and protein contents of rice samples with four different degrees of milling is given in Figures 4.2a and 4.2b. The phenotypic distributions of the two traits showed continuous and approximately normal variations with wider ranges frequency; both figures represented all moisture and protein contents with different degrees of milling. On the other hand, the frequency of apparent amylose content, alkali spreading value and gel consistency did not present the normal distribution curve. The apparent amylose content of 15-20% in the rice samples was approximately 14 times higher than the apparent amylose content of 1-2% (Figure 4.2c). Simultaneously, the alkali spreading value and gel consistency of rice samples in different degrees of milling of 7.00 (Figure 4.2d) and 70 mm (Figure 4.2e), respectively, showed a higher frequency mean than the other values.

Table 4.6 Statistical parameters of chemical analysis for rice varieties with different degrees of milling

Rice properties	Unit	*n*	Range	Mean ± Standard of deviation
Moisture content	%wb	252	11.10 - 14.00	11.56 ± 0.70
Protein content	%db	252	4.07 - 9.10	6.39 ± 0.93
Apparent amylose content	%db	252	13.40 - 36.20	19.42 ± 4.29
Alkali spreading value	units of 1-7 visual scale	252	1.00 - 7.00	6.24 ± 1.83
Gel consistency	mm	252	39.00 - 87.00	68.81 ± 10.79
Pasting properties				
Peak viscosity	RVU	252	934 - 4,156	2,905 ± 838
Breakdown viscosity	RVU	252	-140 - 2,044	1,356 ± 412
Setback viscosity	RVU	252	-1,130 - 1,887	-135 ± 620
Final viscosity	RVU	252	2,126 - 4,603	3,306 ± 1,229
Pasting temperature	°C	252	5.30 - 6.60	4.46 ± 1.86
Trough viscosity	RVU	252	1,888 - 2,472	1,834 ± 207

The rice samples in this study were comprised mostly of fifty Hom Mali rice grown in the lower north, central, lower northeast, and upper northeast of Thailand (Table 3.1). Thus, the diversity of spectra and reference values of rice samples at various degrees of milling were found in Hom Mali rice more than those of low, intermediate, and high amylose rice groups. This indicated that the two samples of Hom Mali rice (KDML105 and RD15) influenced the calibration models of rice physicochemical properties.

Similarly, the distribution of pasting properties, i.e., peak, breakdown, setback, final viscosity, pasting temperature and trough viscosity, exhibited the non-distribution variations (Figures 4.3a and 4.3f). These frequencies of the pasting properties of rice samples fell in the category of Hom Mali rice. Tsuchikawa (2007) suggested that the distribution of the constituents being calibrated for over the calibration samples is also important. The range of the variability should be as large as that expected in any future sample. This has the advantage of providing more precise estimating of the calibration equations. Furthermore, the histogram of differences between NIR and chemical results, where the smooth curve is a fitted normal distribution generally shows the accuracy of calibration model (Osborne et al., 1993a).



(a) moisture content

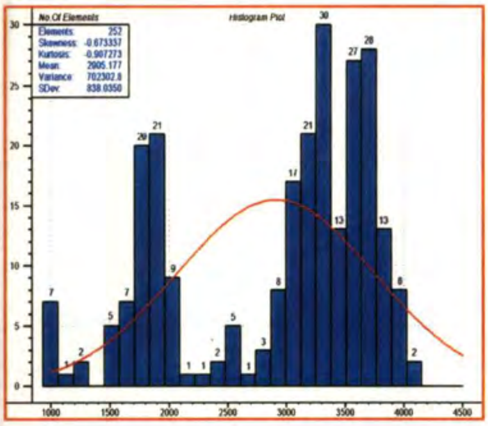
(b) protein content

(c) apparent amylose content

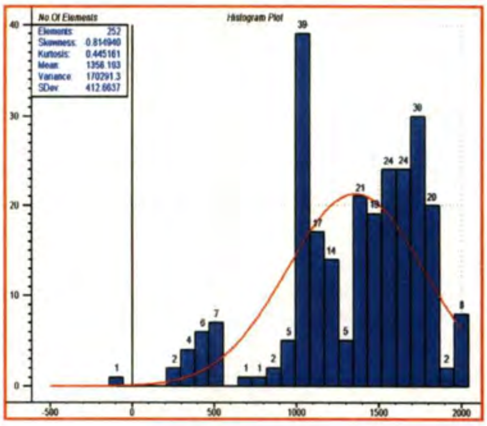
(d) alkali spreading value

(e) gel consistency

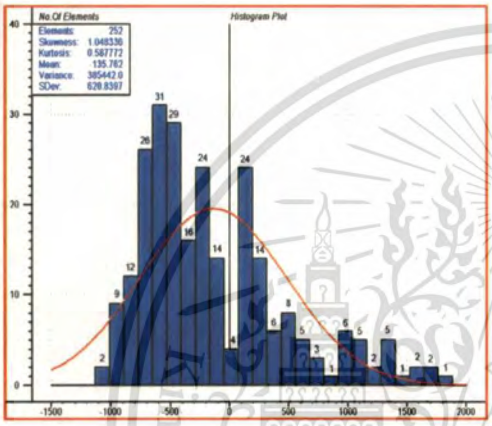
Figure 4.2 Histogram of 252 rice samples with four degrees of milling; moisture content (a), protein content (b), apparent amylose content (c), alkali spereading value, and gel consistency (e)



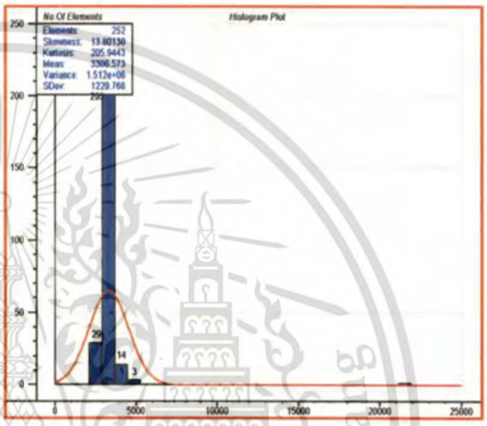
(a) peak viscosity



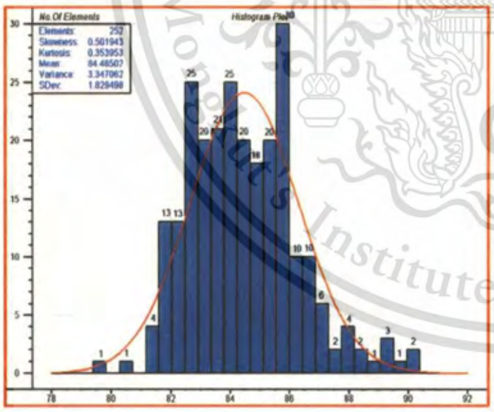
(b) breakdown viscosity



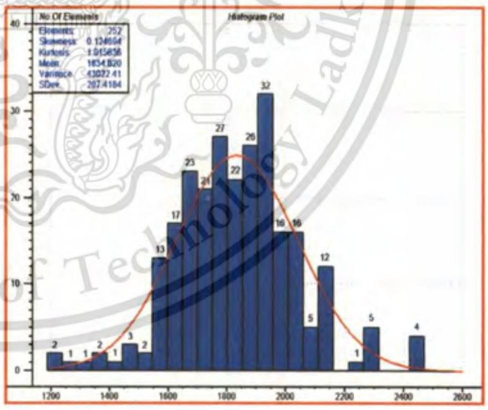
(c) setback viscosity



(d) final viscosity



(e) pasting temperature



(f) trough viscosity

Figure 4.3 Histogram of 252 samples with four degrees of milling; peak viscosity (a), breakdown viscosity (b), setback viscosity (c), final viscosity (d), pasting temperature (e), and trough viscosity (f)

4.3.2 Original and pre-processing of NIR spectra

Spectral data of rice samples with four different degrees of milling were collected over the range of 1,100-2,500 nm (10,000-4,000 cm^{-1}) using 2 nm intervals. In this study, rice samples varied widely in color of rice grain and physicochemical properties due to the effect of degree of milling on the samples (Tables 4.4 and 4.5). Color of rice grain varied from brown (0% degree of milling) to white milled rice grain (15% degree of milling). Figure 4.4 illustrates differences in the mean spectra of rice samples with four different degrees of milling.

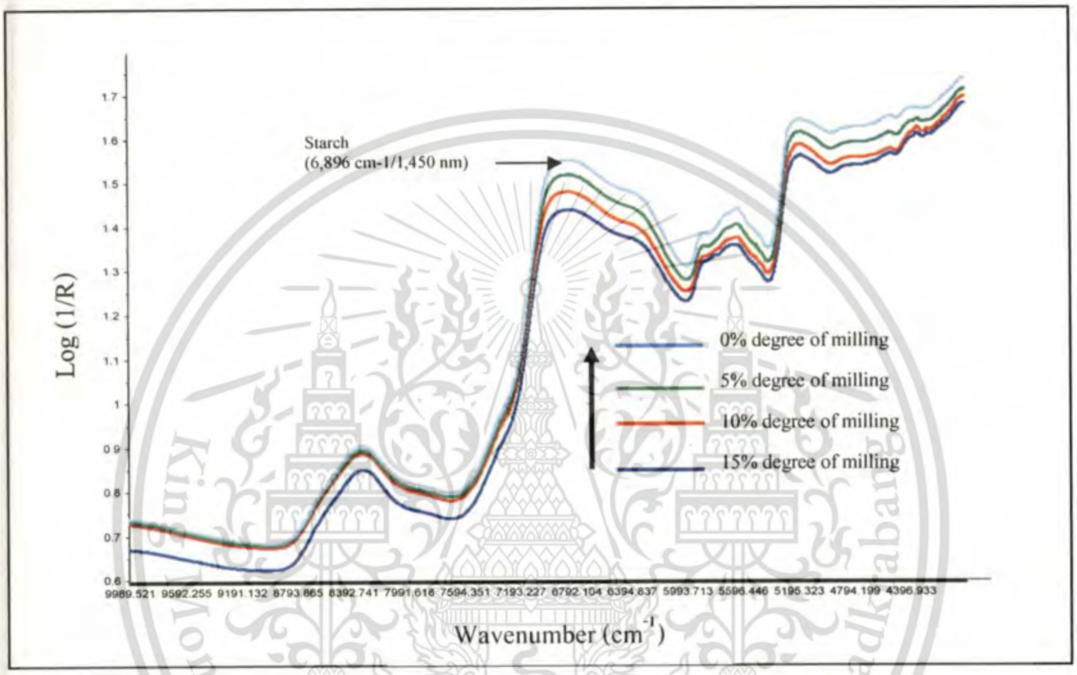


Figure 4.4 Original spectra of rice samples with four different degrees of milling

The upper spectrum was of milled rice with 15% degree of milling and the lowest was of brown rice (0% degree of milling). The spectra were shifted upward when the degree of milling increased up to 15%. Since the degree of milling increased with diminishing mean particle size and increasing whiteness, the scattering increased and the radiation penetrated shorter and therefore log 1/R decreased. Furthermore, all spectra were similar in their moisture content, so the changes in spectral form could not be attributed to differences in moisture content in rice grains (Rittiron, 2009). In this study, the spectra of four rice samples changed about 6,896 cm^{-1} (1,450 nm) due to the increasing starch, especially apparent amylose content (Figure 4.4).

Various pre-processing methods were employed in this study, including MSC, SNV, Savizky-Golay second derivative, MSC + Savizky-Golay second derivative, and SNV + Savizky-Golay second derivative. The pre-processing of NIR spectra is showed in Figure 4.5.

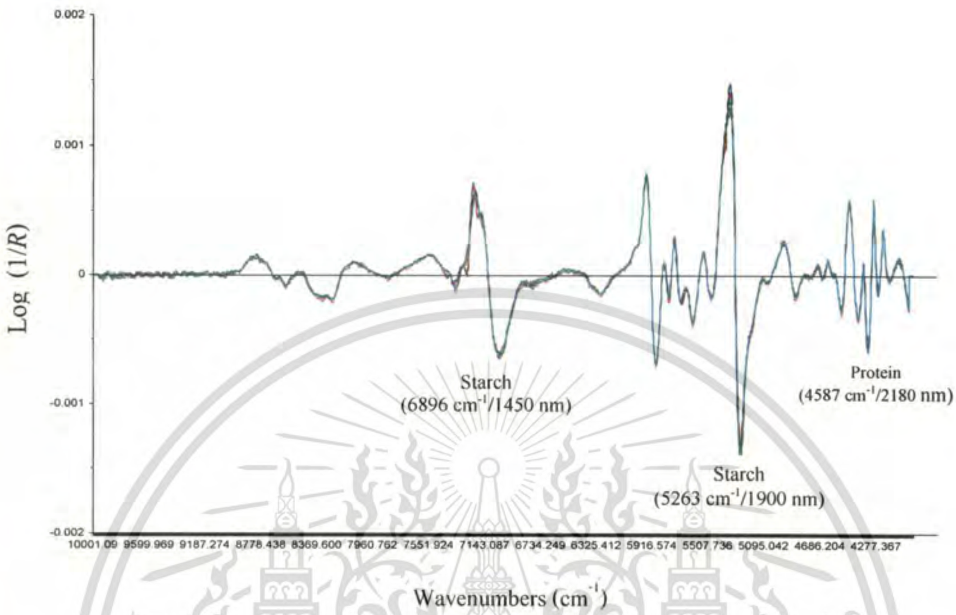


Figure 4.5 NIR spectra of rice samples after SNV + second derivative pre-processing

It appeared that the informative regions of NIR spectra of rice samples after SNV + second derivative pre-processing in 6,896 cm^{-1} (1,450 nm) (the stretch of O-H molecular bonds, first overtone) and 5,263 cm^{-1} (1,900 nm) (the stretch of O-H bonds and O-H deformations) were starch (Figure 4.5). Furthermore, the NIR spectrum of rice shows the enlargement of starch bands of O-H group stretching vibrations, intense peaks centered around 5,102 cm^{-1} (1,960 nm) and 4,761 cm^{-1} (2,100 nm) corresponding to O-H stretching, O-H bending and C-O stretching combination and several sharp peaks in the 4,386-4,000 cm^{-1} (2,280-2,500 nm) characteristics of several chemical groups. (Workmand and Weyer, 2008). Additionally, the spectra of apparent amylose content revealed a CH_2 stretching band at 5,128 cm^{-1} (1,950 nm), 4,063 cm^{-1} (2,461 nm) and 4,019 cm^{-1} (2,488 nm) (Parker, 1983).

Figure 4.5 also shows that the presence of protein in rice was detected by amides and various C-H functional groups. The major band locations associated with protein were found at 6,667-6,536 cm^{-1} (1,500-1,530 nm) as N-H stretching first overtone and 4,878-4,854 cm^{-1}

(2,050-2,060 nm) showed N-H stretching combinations. The 4,613-4,857cm^{-1} (2,168-2,180 nm) region is associated with the N-H bend second overtone and C=O stretch/N-H in-plane bending/C-H stretch combination bands (Osborn et al., 1993a; Workmand and Weyer, 2008).

This indicated that these regions were feasible to use for the determination of starch content, especially the apparent amylose content which could affect gel consistency, alkali spreading value, and pasting properties of rice with different degrees of milling.

4.3.3 PLSR models of physicochemical of rice with different degrees of milling

4.3.3.1 Moisture content

The PLSR model was used to evaluate the prediction capability of the different wavelength ranges. The results of PLSR models developed from brown and milled rice spectra are shown in Table 4.7. Performance was evaluated using the determination of correlation coefficient of validation set (r^2_{val}), standard error of prediction (SEP), and bias. Good calibration results in a larger r^2 value and smaller bias. The spectra indicating by "original" implied no chemometric pre-processing of data. These models were selected from the best model of each degree of milling (Appendix H; Table 1H). Among these PLSR models, the best model was obtained from original spectra of milled rice at 10% degree of milling in 10,000-4,000 cm^{-1} wavenumbers range with SEP, r^2_{val}, and bias of 0.11%, 0.94, and -0.00%, respectively.

The larger wavenumbers range of 10,000-4,000 cm^{-1} could offer more information, resulting in the best model. However, the wavenumbers of 8,333-6,896 cm^{-1} also gave the best models for all degrees of milling (0, 5, 10, and 15% degree of milling), for milled rice at 5%, and for milled rice at 15% degree of milling. Additionally, Workmand and Weyer (2008) reported that a wider wavenumbers range did not necessarily result in better prediction results. They indicated that these ranges are combination bands involving the first and second symmetric and the first and second asymmetric overtones of the OH stretching modes of the water molecule. However, the weak band of 8,333 cm^{-1} (1,200 nm) could shift toward high wavenumbers (lower wavelength) with increasing temperature.

Furthermore, a fairly small range of moisture content (10.10-14.00%) caused low RPD (Williams, 2007). The comparison between actual and predicted moisture contents from the calibration and validation data sets based on the best model is presented in Figure 4.6. The scatter plot of the model demonstrated that NIR values were highly correlated with the reference values.

Table 4.7 Summary of PLSR models for prediction of moisture, protein, and apparent amylose content using different pre-processing and wavenumbers regions selected from NIR spectra of rice samples with different degrees of milling

Rice sample	Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
				SEC	r^2_{cal}	SEP	r^2_{val}		
Moisture content									
All degrees of milling*	Original	8,333–6,896	6	0.24	0.87	0.24	0.86	0.00	2.71
Brown rice	Original	10,000–4,000	7	0.29	0.67	0.34	0.52	-0.03	1.46
Milled rice at 5% degree of milling	MSC + Sav.Gol_2nd derv**	8,333–6,896	5	0.08	0.97	0.14	0.92	-0.01	3.28
Milled rice at 10% degree of milling	**Original**	**10,000–4,000**	**7**	**0.09**	**0.96**	**0.11**	**0.94**	**-0.00**	**4.16**
Milled rice at 15% degree of milling	original	8,333–6,896	7	0.13	0.94	0.16	0.92	0.00	3.11
Protein content									
All degrees of milling*	**Original**	**10,000–4,000**	**6**	**0.24**	**0.87**	**0.23**	**0.88**	**-0.02**	**2.90**
Brown rice	MSC	10,000–4,000	13	0.95	0.98	1.51	0.89	-0.07	2.84
Milled rice at 5% degree of milling	SNV	10,000–4,000	11	1.18	0.93	1.51	0.89	-0.08	2.83
Milled rice at 10% degree of milling	MSC	10,000–4,000	13	1.01	0.95	1.64	0.87	0.10	2.58
Apparent amylose content									
All degrees of milling*	MSC	10,000–4,000	7	2.01	0.75	2.14	0.72	-0.05	1.88
Brown rice	**SNV**	**7,142–4,012**	**5**	**1.27**	**0.90**	**1.47**	**0.87**	**0.23**	**2.64**
Milled rice at 5% degree of milling	MSC + Sav.Gol_2nd derv	10,000–4,000	7	0.40	0.98	2.04	0.66	0.18	1.55
Milled rice at 10% degree of milling	Original	8,620–5,128	3	1.02	0.89	1.14	0.88	-0.15	2.26
Milled rice at 15% degree of milling	Original	7,142–4,012	7	1.18	0.87	1.49	0.81	0.22	1.95

* All degrees of milling means rice samples with 0, 5, 10 and 15% degrees of milling

**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

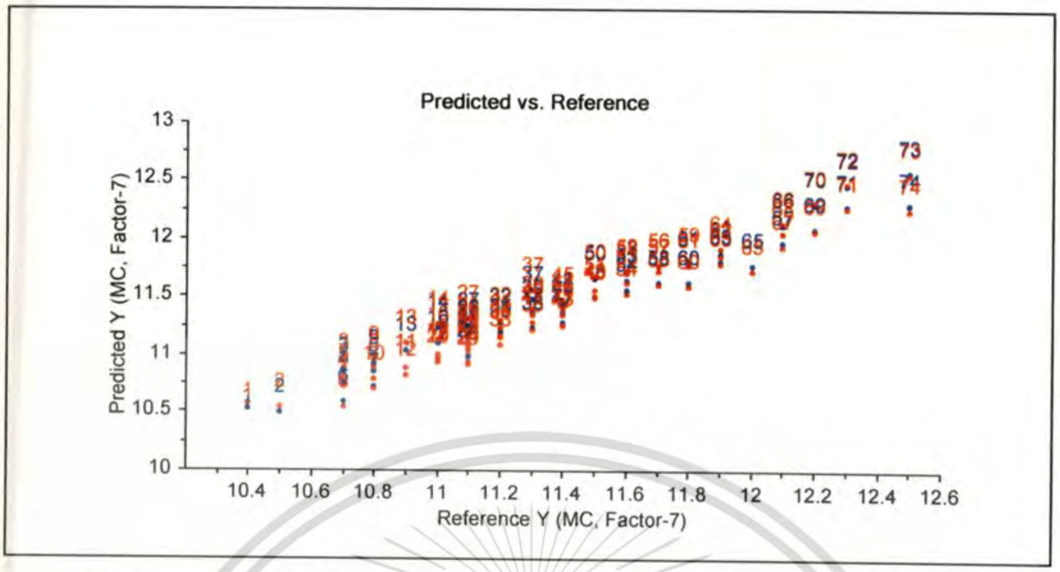


Figure 4.6 Comparison of reference and predicted values of moisture content by PLSR model for calibration (blue) and validation (red) data sets of milled rice samples at 10% degree of milling

4.3.3.2 Protein content

Table 4.7 shows the results obtained by applying the multivariate method of PLSR models to various calibration setups for protein content. These calibrations included those best models of each rice sample at different degrees of milling. The tabulated data in Table 4.7 revealed that the best calibration obtained for protein content was produced using the original spectra of all degrees of milling samples. This resulted in using six principal components (PC) or factors giving SEP, r^2_{val} and bias of 0.23%, 0.88 and -0.02%, respectively. An SEP of 0.23% protein was marginally greater than that reported for ground rice samples (SEP = 0.11% protein, Delwiche et al., 1995). Additionally, as seen in Figure 4.7, the scatter plot of model and reference protein values showed that the NIR predictions were of a relatively clustered line.

In all respects, this was better than the model of 0, 5, 10 and 15% degree of milling of rice samples. The use of pre-processing NIR spectra, including MSC, SNV, second derivative, MSC + second derivative and SNV + second derivative, generally reduced the number of factors but they did not increase r^2_{val} appreciably reduced the SEP compared with that of the original spectra (Appendix H; Table 2H). The reduced number of factors slightly decreased the

r^2_{val} but increased the SEP. Parker (1983) suggested that the presence of protein in rice was easily detected by the amide I band at 1,660 cm^{-1} with a shoulder at 1,613 cm^{-1}, indicative of aromatic amino acids. This agreed with the results of Himmelsbach et al. (2001) who found that the best model of protein content was predicted at the 200-1,795 cm^{-1} and 2,050-3,570 cm^{-1} wavenumbers range by NIR-FT/Raman spectroscopy.

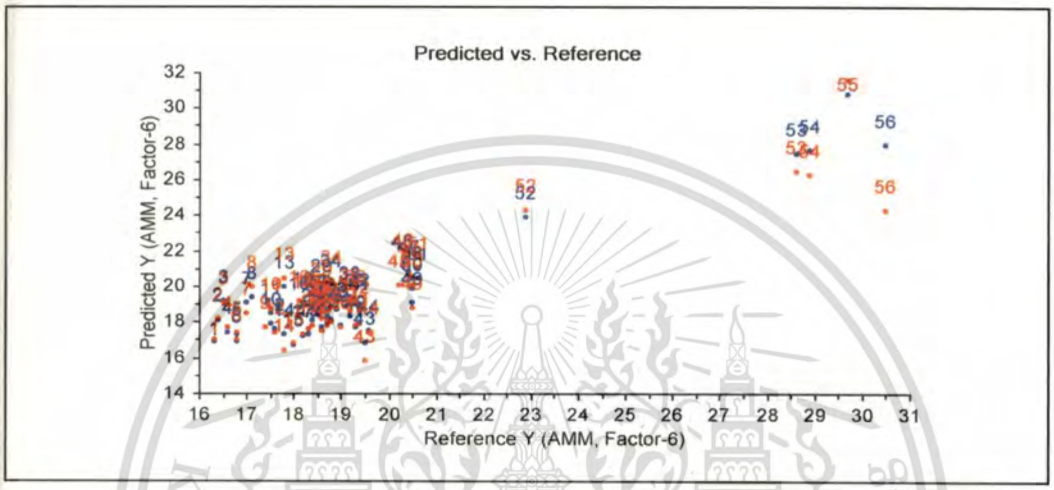


Figure 4.7 Comparison of reference and predicted values of protein content by PLSR model for calibration (blue) and validation (red) data sets of milled rice samples at all degrees of milling

4.3.3.3 Apparent amylose content

The presence of apparent amylose content in rice revealed a CH_2 stretching band at 2,905 cm^{-1} with a shoulder at 2,940 cm^{-1} (Himmelsbach et al., 2001). Additionally, the spectra of apparent amylose content revealed a CH_2 stretching band at 5,128 cm^{-1} (1,950 nm), 4,063 cm^{-1} (2,461 nm) and 4,019 cm^{-1} (2,488 nm) (Parker, 1983). In this study, the results were generally improved by eliminating spectral regions where no bands were presented. Therefore, the regions of the NIR spectra from 10,000-8,624 cm^{-1} were typically excluded from the spectral data set. However, both wavenumbers ranges, i.e., 8,620-5,128 cm^{-1} and 7,142-4,012 cm^{-1}, were selected and compared to the PLSR model with full wavenumbers range.

The comparison of the PLSR models for 8,620-5,128 cm^{-1} and 7,142-4,012 cm^{-1} wavenumbers range versus full region wavenumbers (10,000-4,000 cm^{-1}) of NIR spectra with the different pre-processing is shown in Appendix H (Table 3H). By evaluating the most effective

PLSR model for rice samples at each degree of milling, it was concluded that the use of pre-processing methods did not improve the SEP and RPD, even though the number of factors required was reduced. However, the MSC and SNV applied to the milled rice samples at 5% degree of milling at 7,142-4,012 cm^{-1} tended to increase the SEP and RPD.

Table 4.7 presents the PLSR models for predicting apparent amylose content using different pre-processing and wavenumbers regions selected from the NIR spectra of rice samples with different degrees of milling. The best models of all degrees of milling, brown rice, and 5% degree of milling were performed with MSC, SNV, MSC + second derivative (MSC + Sav.Gol_2nd derv) in 10,000-4,000, 7,142-4,102 and 10,000-4,000 cm^{-1} wavenumbers range, respectively. On the other hand, the best models of milled rice at 10 and 15% degrees of milling were the original spectra in 8,620-5,128 and 7,142-4,012 cm^{-1} wavenumbers range, respectively. The results illustrated that these PLSR models were reasonably accurate in predicting apparent amylose content compared with the previous apparent amylose content models using paddy rice, brown rice, milled rice and rice flour by Wu and Shi (2007) and Srisawas (2009), which resulted in an SECV of 2.13% and SEP of 2.158%, respectively.

Among these models, brown rice after pre-processing by the SNV method in 7,142-4,012 cm^{-1} wavenumbers range demonstrated the best model to predict the apparent amylose content using five factors and gave SEP, r^2_{val} and bias of 1.47%, 0.87 and 0.23%, respectively (Table 4.7). This model was slightly better than the apparent amylose content model of single grain brown rice (Wu and Shi, 2004 with r^2 of 0.85 and SEP of 2.82). A scatter plot of the model and reference apparent amylose content values are illustrated in Figure 4.8. The model presented the slightly poorer performance of the rice samples since most of the samples were of Hom Mali rice with different degrees of milling.

However, the apparent amylose contents estimated by PLSR models in the wavenumbers of 10,000-4,000 cm^{-1} were similar to those reported by Natsuga et al. (1992) and Kawamura et al. (1997). Villareal et al. (1994) and Delwiche et al. (1995, 1996) previously reported similar SEP values but higher r values. However, their set sample included a wider range of rice samples such as medium, long-grain rice, and waxy-type rice. A wider range constituent range usually yields a higher r value with similar SEP (Williams, 2007). Thus, in this study it could be concluded that the results were in good agreement with those studies.

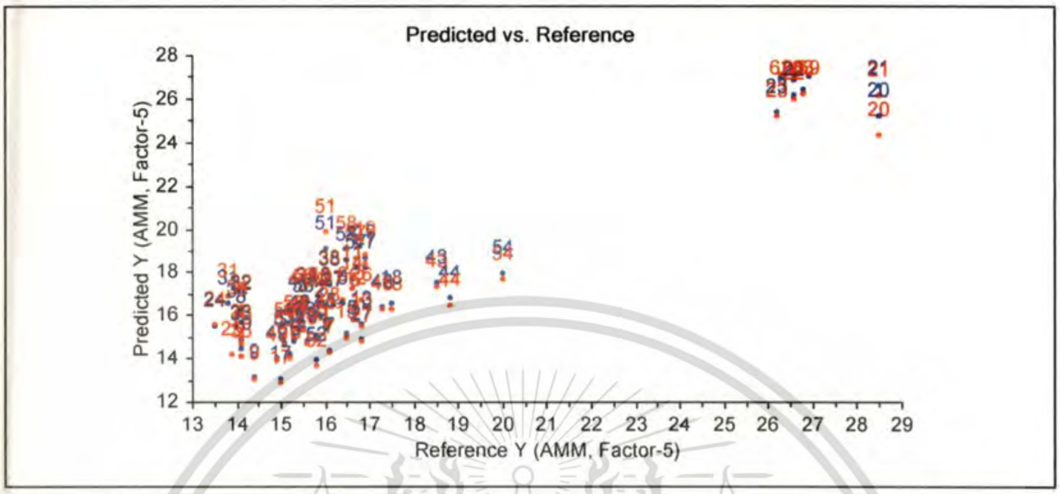


Figure 4.8 Comparison of reference and predicted values of apparent amylose content by PLSR model for calibration (blue) and validation (red) data sets of rice sample in brown rice form

4.3.3.4 Alkali spreading value

Good calibration models of all degrees of milling, brown rice, 5, 10 and 15% degree of milling were obtained from the NIR spectra after SNV + second derivative (SNV + Sav.Gol_2nd derv), SNV, original NIR spectra, MSC and MSC, respectively. However, the RPD values from all degrees of milling, 5, 10 and 15% degree of milling were not recommended for the prediction of the alkali spreading value due to the very low RPD values. By comparison, brown rice appeared among all the best model for predicting the alkali spreading value that took place at seven factors with SEP, r^2_{val} and bias of 0.67, 0.86, and -0.03 units on a 1-7 visual scale, respectively. This brown rice model showed a low RPD value, indicating its use as merely a model for very rough quality screening (Table 4.8).

NIR values for alkali spreading value were not highly correlated to reference values as were moisture and apparent amylose content. However, the alkali spreading value of brown rice model demonstrated a reasonable ability to predict the scoring alkali spreading value of Hom Mali rice, intermediate and high amylose rice varieties (Figure 4.9).

Table 4.8 Summary of PLSR models for prediction of alkali spreading value and gel consistency using different pre-processing and wavenumbers regions selection in NIR spectra of rice samples with different degrees of milling

Rice sample	Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
				SEC	r^2_{cal}	SEP	r^2_{val}		
Alkali spreading value									
All degrees of milling*	MSC	10,000–4,000	7	0.10	0.69	1.08	0.65	-0.00	1.63
Brown rice	**SNV**	**10,000–4,000**	**7**	**0.52**	**0.91**	**0.67**	**0.86**	**-0.03**	**2.69**
Milled rice at 5% degree of milling	Original	10,000–4,000	3	0.37	0.92	0.43	0.90	-0.09	1.26
Milled rice at 10% degree of milling	MSC	10,000–4,000	6	0.44	0.91	0.52	0.86	0.14	2.43
Milled rice at 15% degree of milling	MSC	10,000–4,000	6	0.66	0.82	0.83	0.73	0.14	1.96
Gel consistency									
All degrees of milling*	MSC, SNV + Sav.Gol_2nd derv	10,000–4,000	7	5.13	0.81	6.84	0.66	0.22	1.66
Brown rice	SNV	10,000–4,000	4	5.01	0.82	5.63	0.78	0.26	1.87
Milled rice at 5% degree of milling	Original	10,000–4,000	7	3.40	0.88	4.86	0.77	0.73	1.86
Milled rice at 10% degree of milling	**SNV + Sav.Gol_2nd derv**	**10,000–4,000**	**5**	**2.01**	**0.95**	**3.20**	**0.88**	**0.08**	**2.41**
Milled rice at 15% degree of milling	Original	10,000–4,000	7	3.38	0.91	4.35	0.85	-0.48	2.27

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling

**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

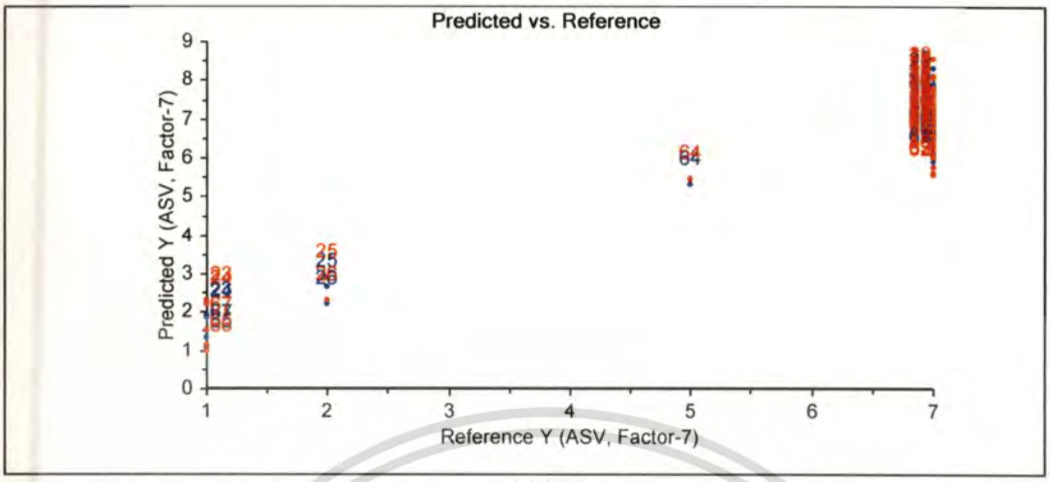


Figure 4.9 Comparison of reference and predicted values of alkali spreading value by PLSR model for calibration (blue) and validation (red) data sets of milled rice sample at all degrees of milling

This experiment found that NIR values for alkali spreading value were not correlated with reference values. Delwiche et al. (1996), however, showed the correlation of NIR spectra to the alkali spreading value based on 1.5% KOH with the calibration equation that required six factors with SEP of 0.43 of visual score (r^2 = 0.822, bias = -0.08, second derivative in 1,140-1,800 nm). Wadsworth et al. (1991) explained that the poor calibration model was the result of the correlation between alkali spreading value and the water bands at 1,930 and 1,450 nm. Recently, Srisawas (2009) found that a good calibration model for the alkali spreading value was obtained from the NIR milled rice spectra after smoothing, but it required as many as nineteen factors to reach the r^2_{val} of 0.806 with SEP of 0.545 visual score. The use of a large number of PCs only indicated that the alkali spreading value could not be modeled with high accuracy.

4.3.3.5 Gel consistency

Gel consistency is a good index of cooked rice texture (Bao et al., 2001). The statistics summary of the models developed for predicting gel consistency is showed in Table 4.8. The best models for all degrees of milling, brown rice, 5, 10 and 15% degree of milling were the rice NIR spectra performed with MSC or SNV + second derivative (MSC, SNV + Sav.Gol_2nd derv), SNV, original spectra, second derivative (Sav.Gol_2nd derv) and original spectra, respectively, in 10,000-4,000 cm^{-1}.

Among these models, the NIR spectra of milled rice at 10% degree of milling after second derivative performed with SNV + Savitzky-Golay algorithm gave the best model for predicting the gel consistency. This model revealed five factors with SEP, r^2_{val} and bias of 3.20 mm, 0.88 and 0.08mm, respectively. Similarly, the scatter plot of reference and predicted values of gel consistency showed that, like alkali spreading values, the NIR values were not highly correlated to reference values due to its distribution data were not of normal variation (Figure 4.10).

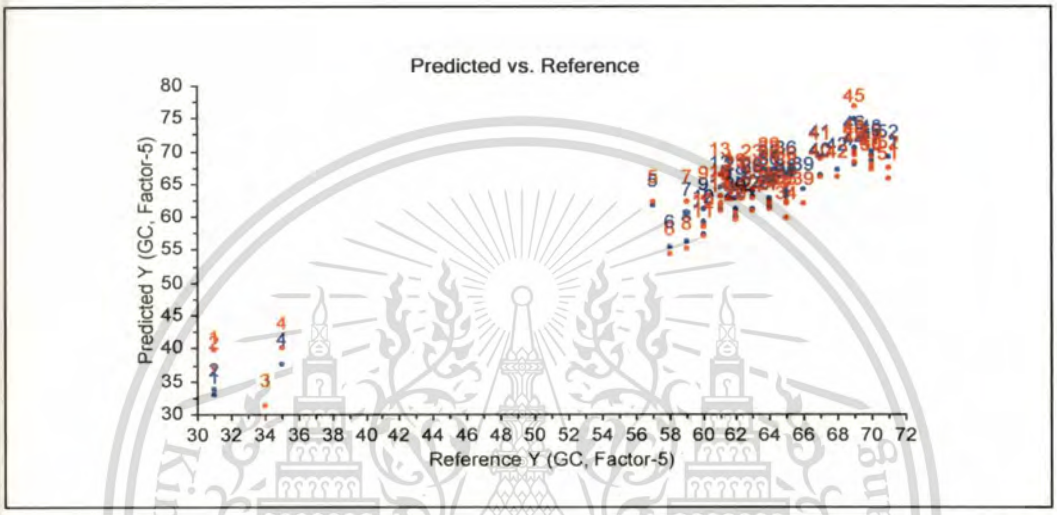


Figure 4.10 Comparison of reference and predicted values of gel consistency by PLSR model for calibration (blue) and validation (red) data sets of milled rice sample at 10% degree of milling

However, Bao et al. (2001) found that the best model of the gel consistency with high r^2_{val} = 0.81 and low SEP (7.12) from the NIR spectra of rice flour samples was applicable to the rice breeding program.

4.3.3.6 Pasting properties of rice

PLSR models of the pasting properties of rice, i.e., peak, breakdown, setback, final, trough viscosity and pasting temperature, are represented as follows:

A) Peak viscosity

The results in Table 4.9 summarized the good calibration of PLSR models for predicting peak viscosity of rice samples. For each degree of milling, the best calibration for all degrees of milling, brown rice, milled rice at 5, 10 and 15% degree of milling, were obtained from the NIR spectra performed with MSC, SNV, original spectra, MSC and original spectra, respectively, in 10,000-4,000 cm^{-1}. It was found that the SEPs of these models were very high, resulting in very low RPD values. However, the PLSR model of milled rice at all degrees of milling showed better performance for predicting peak viscosity with seven factors that gave SEP, r^2_{val} and bias of 267 RVU, 0.90 and 3.34 RVU, respectively (Figure 4.11).

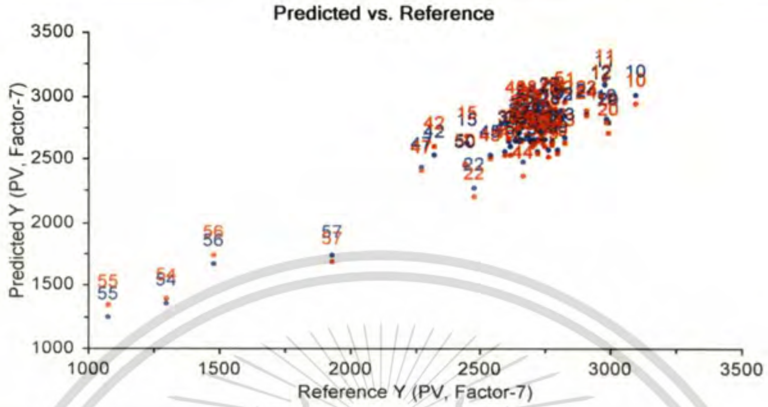


Figure 4.11 Comparison of reference and predicted values of peak viscosity by PLSR model for calibration (blue) and validation (red) data sets of milled rice samples at 5% degree of milling

B) Breakdown viscosity

Breakdown viscosity is inhibited by phospholipids that combine with amylose and with the long branch chains of amylopectin, resulting in limited granular swelling (Lin and Czuchajowska, 2000). Therefore, the breakdown viscosity values of brown rice were lower than the other milled rice samples at the high degree of milling. In this study, brown rice samples showed the best performance for predicting the breakdown viscosity with the NIR spectra transformed with MSC method which gave the same results as SNV method. Both model used five factors with SEP, r^2_{val} and bias of 71 RVU, 0.90 and -7.15 RVU, respectively (Table 4.9 and Figure 4.12).

Table 4.9 Summary of PLSR models for prediction of peak, breakdown, and setback viscosity using different pre-processing and wavenumbers regions selection in NIR spectra of rice samples with different degrees of milling

Rice sample	Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
				SEC	r^2_{cal}	SEP	r^2_{val}		
Peak viscosity									
All degrees of milling*	**SNV + Sav.Gol_2nd derv**	**10,000–4,000**	**7**	**219**	**0.93**	**267**	**0.90**	**-21.5**	**3.34**
Brown rice	SNV	10,000–4,000	5	115	0.78	137	0.71	-11.90	1.89
Milled rice at 5% degree of milling	Original	10,000–4,000	7	118	0.90	153	0.83	15.82	2.27
Milled rice at 10% degree of milling	MSC	10,000–4,000	7	147	0.89	209	0.78	4.22	1.79
Milled rice at 15% degree of milling	Original	10,000–4,000	6	172	0.89	208	0.84	-35.35	2.34
Breakdown viscosity									
All degrees of milling*	MSC	10,000–4,000	11	118	0.92	135	0.90	-19.31	3.00
Brown rice	**MSC, SNV**	**10,000–4,000**	**5**	**60**	**0.92**	**71**	**0.90**	**-7.15**	**2.87**
Milled rice at 5% degree of milling	MSC + SNV Sav.Gol_2nd derv	10,000–4,000	6	33	0.98	99	0.81	-2.65	2.19
Milled rice at 10% degree of milling	Original	10,000–4,000	5	88	0.85	106	0.79	-15.64	1.83
Milled rice at 15% degree of milling	Original	10,000–4,000	7	93.8	0.91	121	0.86	-1.03	2.48
Setback viscosity									
All degrees of milling*	SNV	10,000–4,000	13	175	0.90	233	0.83	26.80	2.60
Brown rice	MSC, SNV	10,000–4,000	4	219	0.91	245	0.88	33.47	2.88
Milled rice at 5% degree of milling	Sav.Gol_2nd derv	10,000–4,000	7	76	0.98	356	0.76	29.50	1.82
Milled rice at 10% degree of milling	**Original**	**10,000–4,000**	**6**	**195**	**0.92**	**237**	**0.89**	**-43.26**	**2.68**
Milled rice at 15% degree of milling	SNV	10,000–4,000	7	242	0.90	361	0.78	10.21	1.91

* All degrees of milling means rice samples with 0, 5, 10 and 15% degrees of milling.

**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

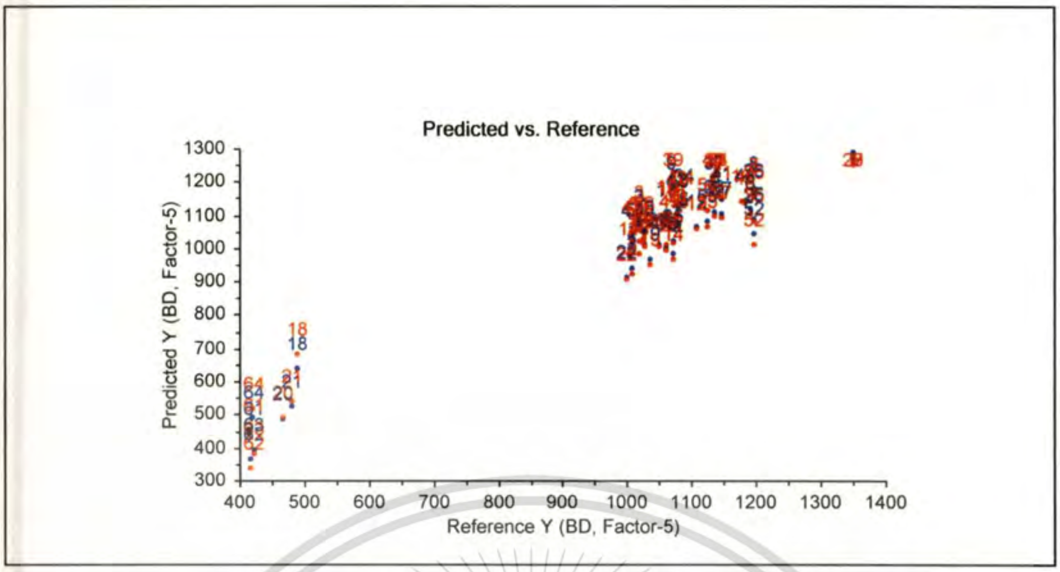


Figure 4.12 Comparison of reference and predicted values of breakdown viscosity by PLSR model for calibration (blue) and validation (red) data sets of rice sample in brown rice form

C) Setback viscosity

Table 4.9 presents the details of PLSR model developed for predicting setback viscosity of different pre-processing methods in the NIR spectra of rice samples with different degrees of milling. Milled rice samples at 10% degree of milling could be successfully modeled by PLSR with reasonable accuracy. The maximum values of r^2_{val} and RPD was 0.89 and 2.68, respectively. The scatter plots of predicted and reference values of setback viscosity are presented in Figure 4.13. Srisawas (2009) reported that the positive significant correlation between apparent amylose content and setback viscosity was likely to cause the moderate performance of the NIR spectroscopy models.

D) Final viscosity

The calibration and validation statistics for the best model of rice samples at different degrees of milling are shown in Table 4.10. The final viscosity equations developed from milled rice at 10% degree of milling was superior to those from rice at other degrees of milling. Good calibration equation of this model showed lower SEP value of 181, high value r^2_{val} of 0.80 and RPD of 2.68. Comparison of reference and predicted values of final viscosity by PLSR model is shown in Figure 4.14.

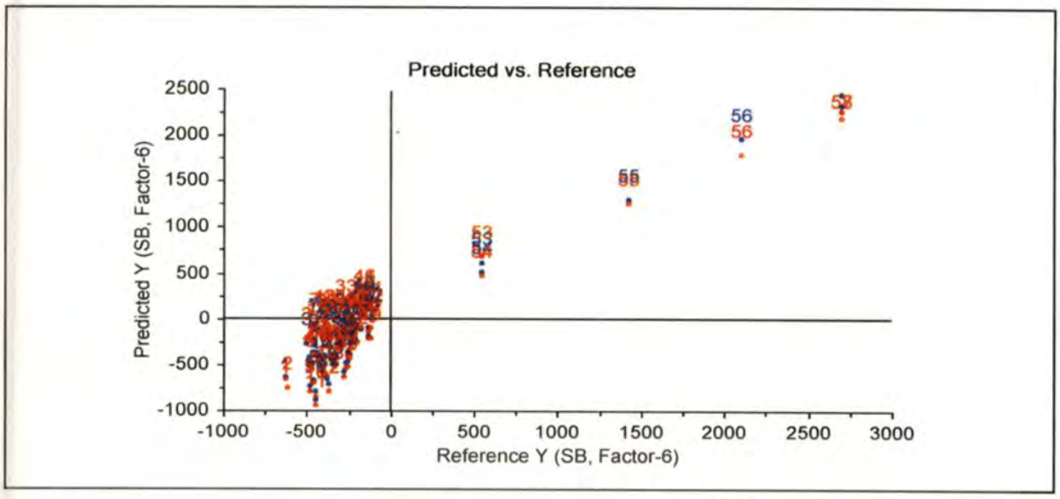


Figure 4.13 Comparison of reference and predicted values of setback viscosity by PLSR model for calibration (blue) and validation (red) data sets of milled rice samples at 10% degree of milling

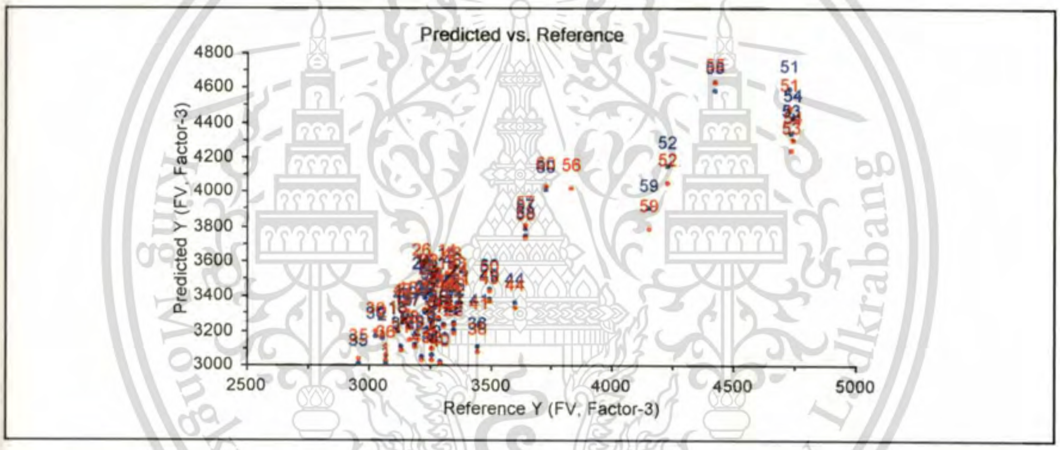


Figure 4.14 Comparison of reference and predicted values of final viscosity by PLSR model for calibration (blue) and validation (red) data sets of milled rice samples at 10% degree of milling

D) Pasting temperature

Table 4.10 shows the statistical values of PLSR models for predicting pasting temperature using different pre-processing methods of rice samples with different degrees of milling. The equation of pasting temperature from the spectra of milled rice at 10% degree of milling was more reliable than those from all degrees of milling, brown rice, and milled rice with 5 and 15% degree of milling according to the lower of SEP and higher of r^2_{val} and RPD. This model performed with MSC or SNV with ten factors gave SEP, r^2_{val} and bias of 0.46°C, 0.82 and

-0.22°C, respectively. Comparison of predicted and reference values for pasting temperature of validation samples is showed as a straight line similar to that of moisture content (Figure 4.15).

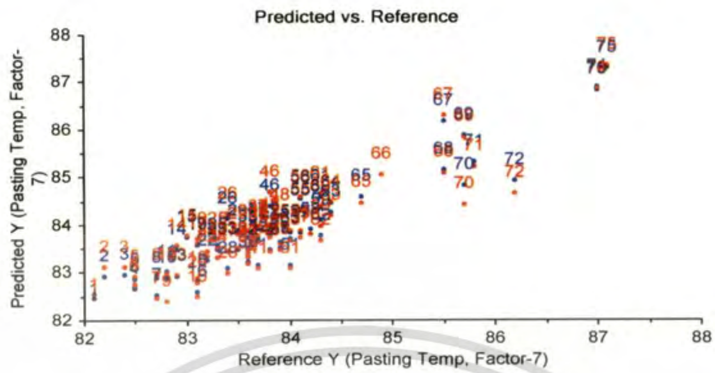


Figure 4.15 Comparison of reference and predicted values of pasting temperature by PLSR model for calibration (blue) and validation (red) data sets of milled rice samples at 10% degree of milling

E) Trough viscosity

The result in Table 4.10 presents the best PLSR models for predicting trough viscosity of rice samples at different degrees of milling. The trough viscosity PLSR model from the rice samples at all degrees of milling transformed with MSC was better than those of rice samples of brown rice and milled rice samples at 5, 10 and 15% degree of milling. This calibration equation was for milled rice at all degree of milling in predicting trough viscosity. The scatter plot of predicted and reference values of trough viscosity of validation samples is presented in Figure 4.16.

Table 4.10 Summary of PLSR models for prediction of final viscosity, pasting temperature, and trough viscosity using different pre-processing and wavenumbers regions selection in NIR spectra of rice samples with different degrees of milling

Rice sample	Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
				SEC	r^2_{cal}	SEP	r^2_{val}		
Final viscosity									
All degrees of milling*		10,000–4,000	7	242	0.68	252	0.64	-5.38	1.69
Brown rice	Sav.Gol_2nd derv	10,000–4,000	5	69	0.93	141	0.71	0.84	1.48
Milled rice at 5% degree of milling	MSC, SNV	10,000–4,000	7	116	0.84	151	0.74	-11.65	1.92
Milled rice at 10% degree of milling	**MSC + Sav.Gol_2nd derv**	**10,000–4,000**	**3**	**151**	**0.86**	**181**	**0.80**	**17.00**	**2.68**
Milled rice at 15% degree of milling	MSC	10,000–4,000	7	162	0.90	222	0.82	3.17	2.25
Pasting temperature									
All degrees of milling*	Sav.Gol_2nd derv	10,000–4,000	6	0.56	0.88	0.66	0.84	0.03	2.69
Brown rice	MSC + Sav.Gol_2nd derv	10,000–4,000	5	0.45	0.93	0.86	0.74	-0.01	1.80
Milled rice at 5% degree of milling	Sav.Gol_2nd derv	10,000–4,000	7	0.07	0.99	0.43	0.73	-0.02	1.59
Milled rice at 10% degree of milling	**MSC, SNV**	**10,000–4,000**	**7**	**0.38**	**0.88**	**0.46**	**0.82**	**-0.02**	**2.06**
Milled rice at 15% degree of milling	Original	10,000–4,000	7	0.38	0.84	0.56	0.68	0.10	1.70
Trough viscosity									
All degrees of milling*	**MSC**	**10,000–4,000**	**4**	**57**	**0.91**	**79**	**0.82**	**22.40**	**2.57**
Brown rice	MSC + Sav.Gol_2nd derv	10,000–4,000	5	0.45	0.93	0.86	0.74	-0.01	1.80
Milled rice at 5% degree of milling	Sav.Gol_2nd derv	10,000–4,000	7	0.07	0.99	0.43	0.73	-0.02	1.59
Milled rice at 10% degree of milling	SNV	10,000–4,000	5	111	0.85	141	0.77	0.32	1.72
Milled rice at 15% degree of milling	MSC, SNV	10,000–4,000	7	99	0.90	127	0.85	-5.65	2.21

* All degrees of milling means rice samples with 0, 5, 10 and 15% degrees of milling. ** Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order.

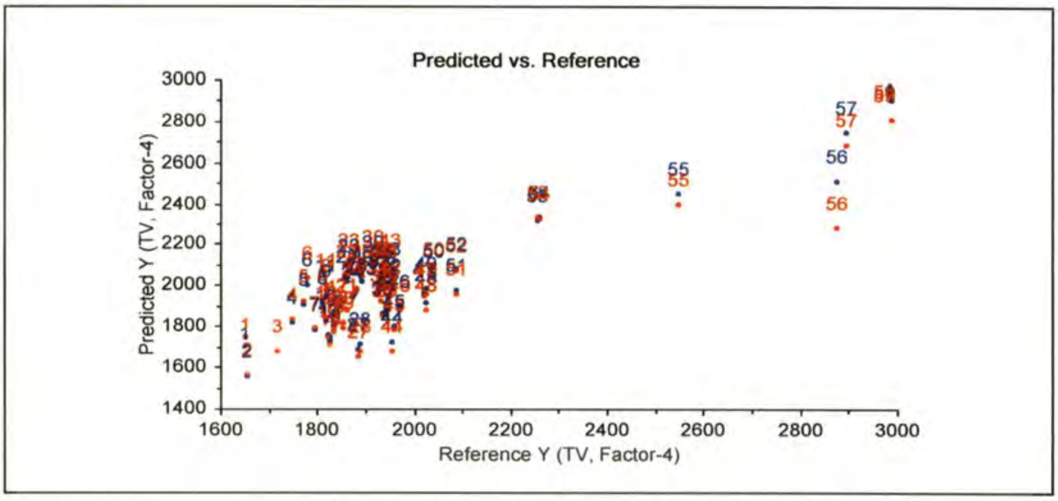


Figure 4.16 Comparison of reference and predicted values of trough viscosity by PLSR model for calibration (blue) and validation (red) data sets of milled rice samples at 15% degree of milling

The PLSR models for predicting the pasting properties of rice indicated that these models were reasonably predictive of the pasting properties of rice. However, the scatter plot of the model demonstrated that NIR values were not related to reference values of peak, breakdown, setback, final and trough viscosity, similar to those of the apparent amylose content, alkali spreading value, and gel consistency. The results by Shimizu *et al.* (2001), Bao et al. (2001) and Meadows and Barton-II (2002) were better than the result in this study. Additionally, Radhika Reddy et al. (1994) demonstrated that the rheological properties of rice viscosity were influenced by the long-B chains of the amylopectin molecules. They also found that variations in the ratio of amylose to amylopectin might be the primary reason why the NIR models for RVA constituents were not highly accurate.

It could be concluded from all the results that the best model of moisture content was the original spectra of milled rice at 10% degree of milling in 10,000-4,000 cm^{-1} wavenumbers ranges with SEP, r^2_{val} and bias of 0.11%, 0.94 and -0.00%, respectively. The best model of protein content was the original spectra of all degree of milling samples in 10,000-4,000 cm^{-1} wavenumbers ranges with SEP, r^2_{val} and bias of 0.23%, 0.88 and -0.02%, respectively. Brown rice after pre-processing by SNV method in 7,142-4,012 cm^{-1} wavenumbers ranges seemed to be the best model to predict the apparent amylose content with SEP, r^2_{val} and bias of 1.47%, 0.87 and -0.23%, respectively.

The RPD from various models were not recommended for predicting the alkali spreading value and gel consistency. However, a comparison of these models showed brown rice to be the best model for predicting the alkali spreading value and milled rice at 10% degree of milling after second derivative performed with SNV + Savitzky-Golay algorithm the best model for gel consistency. This may be attributable to the frequency distributions of alkali spreading value and gel consistency were not of normal distribution because most of the rice samples were Hom Mali rice (Figures 4.2 d and e).

These results showed that the PLSR models could reasonably predict the pasting properties of rice. It was found that the SEPs of these models were very high, resulting in low RPD. In addition, the frequency distribution of the pasting properties, i.e., peak, breakdown, setback, final and trough viscosity, did not exhibit normal distribution (Figures 4.3a-f). Regarding the physicochemical properties of rice, although pasting properties could not be accurately predicted by FT-NIR spectroscopy due to relatively low r^2 values, high SEP and high bias of the pasting parameters, these values were slightly more accurate than those reported by Bao *et al.* (2001). Results showed that PLSR modeling for predicting setback viscosity (SEP = 13.6 RVU, r^2 = 0.92), breakdown viscosity (SEP = 10.2 RVU, r^2 = 0.88), and gelatinization peak temperature (T_p) (SEP = 1.33°C, r2 = 0.89).

4.4 Discrimination of Hom Mali rice with different degrees of milling from the aromatic and non-aromatic rice varieties

The discrimination of Hom Mali rice from other aromatic and non-aromatic rice varieties is important to maintain the quality of Hom Mali rice for consumer. Aromatic rice varieties, especially PTT1 and CNT1, are the major varieties to blend with Hom Mali rice and thereby cause the changes in cooking quality of Hom Mali rice (Cheaupun et al., 2005). As such, the difference between Hom Mali rice and the other aromatic and non-aromatic rice varieties can be based not only on the presence or absence of aroma but also on the differences in the physicochemical properties in the rice grains, which are influenced by the degree of milling (Table 4.4 and 4.5). In this section, the classification of Hom Mali rice from the other aromatic and non-aromatic rice varieties using PCA and PLS-DA technique was presented as follows:

4.4.1 Discrimination of Hom Mali rice from other aromatic and non-aromatic rice varieties based on the physicochemical properties by PCA technique

The physicochemical properties of brown and milled rice at four different degrees of milling are shown in Tables 4.4 and 4.5. According to the physicochemical data, the moisture contents were similar among the rice groups for all degrees of milling (Table 4.1), therefore, the data were discarded for the rice classification process. Thai rice could be discriminated using PCA into four groups with two principal components (PCs). Table 4.11 shows the correlation coefficients and the variance obtained for milled rice with different degrees of milling. The two PCs (PC_1 and PC_2) for the five conditions, i.e., all degrees of milling, 0, 5, 10, and 15% of milling, respectively account for 76.83, 77.29, 80.77, 76.14 and 83.57% of the total variance.

However, the correlation coefficients of certain variables in the physicochemical data were unclear, which affected the variable arrangement in the two PCs. As shown in Table 4.11, the gel consistency at all degrees of milling had the correlation coefficients for PC_1 and PC_2 of -0.77 and -0.67, respectively. These values showed a slight difference between the two PCs, resulting in difficulty in arranging the new variables in the two PCs. Therefore, a varimax rotation was employed to minimize the number of variables that influenced the original PCs. Merely two PCs were considered in the rotation because these PCs had an eigenvalue that was greater than zero. The results are shown in Table 4.12.

The PCA involved all degrees of milling (0, 5, 10 and 15%) and the value of correlation of the rotated PC_1 was related to the apparent amylose content, alkali spreading value, gel consistency, trough and setback viscosity. These parameters explained 43.62% of the variance. The rotated PC_2 was related to the maximum or peak viscosity and breakdown viscosity, which explained 33.21% of the variance. Once combined, the rotated PC_1 and PC_2 could account for 76.83% of the total variance. The rotated first (PC_1) and rotated second (PC_2) components of brown rice, 5, 10 and 15% degree of milling accounted for 77.29, 80.77, 76.14 and 83.57%, respectively (Table 4.12). The correlation values for the rotated PC_1 of brown rice comprised eight variables, i.e., apparent amylose content, alkali spreading value, gel consistency, maximum, breakdown, trough, final and setback viscosity. The rotated PC_2 related to only one variable, i.e., the protein content. Similar results were obtained with the 5, 10, and 15% degrees of milling.

Table 4.11 Correlation coefficients of physicochemical properties of milled rice from all and each level at different degrees of milling

Variables	Principal components (PCs)									
	All degrees of milling[1]		0% degree of milling		5% degree of milling		10% degree of milling		15% degree of milling	
	PC_1	PC_2	PC_1	PC_2	PC_1	PC_2	PC_1	PC_2	PC_1	PC_2
Protein content		0.76		0.96		0.73		0.95		0.86
Apparent amylose content	0.88	-0.37	0.93		0.93		0.93		0.93	
Alkali spreading value	-0.97	-0.31	-0.97		-0.97		-0.96		-0.97	
Gel consistency	-0.77	-0.67	-0.87		-0.90		-0.90		-0.88	
Pasting properties										
Peak viscosity	-0.51	-0.77	-0.86		-0.88		-0.92		-0.92	
Breakdown viscosity	-0.68		-0.93		-0.92		-0.94		-0.95	
Setback viscosity	0.92	-0.36	0.96		0.98		0.98		0.97	
Final viscosity	0.38		0.80		0.88		0.38	0.24	0.94	
Trough viscosity	0.87	0.51	0.94		0.93		0.93		0.95	
Eigenvalue	5.12	3.32	7.42	1.08	7.73	1.15	7.34	1.03	8.06	1.12
Variance (%)	46.62	30.21	67.46	9.83	70.29	10.48	66.72	9.41	73.31	10.23
Cumulative (%)	46.62	76.83	67.46	77.29	70.29	80.77	66.72	76.14	73.31	83.57

[1] Physicochemical data were analyzed using PCA including 0, 5, 10, and 15% degree of milling.

Table 4.12 Correlation coefficients of physicochemical properties from all and each level at different degrees of milling rotated by varimax method

Variables	Principal components (PCs)									
	All degrees of milling[1]		0% degree of milling		5% degree of milling		10% degree of milling		15% degree of milling	
	PC_1	PC_2	PC_1	PC_2	PC_1	PC_2	PC_1	PC_2	PC_1	PC_2
Protein content	0.38	0.65		0.96		0.72		0.96		0.83
Apparent amylose content	0.95		0.94		0.94		0.93		0.93	
Alkali spreading value	-0.87	-0.42	-0.98		-0.97		-0.96		-0.97	
Gel consistency	-0.91		-0.88		-0.89		-0.89		-0.89	
Pasting properties										
Peak viscosity		-0.92	-0.86		-0.89		-0.93		-0.91	
Breakdown viscosity	-0.33	-0.90	-0.93		-0.90	-0.23	-0.94		-0.94	
Setback viscosity	0.96		0.96		0.96		0.98		0.98	
Final viscosity	0.40		0.80		0.90		0.39	0.22	0.95	
Trough viscosity	0.95		0.93		0.93		0.93		0.95	
Eigenvalue	4.79	3.65	7.40	1.09	7.55	1.33	7.32	1.05	8.01	1.19
Variance (%)	43.62	33.21	67.32	9.97	68.64	12.13	66.56	9.58	72.83	10.73
Cumulative (%)	43.62	76.83	67.32	77.29	68.64	80.77	66.56	76.14	72.83	83.57

[1] Physicochemical data were analyzed using PCA including 0, 5, 10, and 15% degree of milling.

The factor scores of rotated PC_1 and PC_2 for all degrees of milling are presented in Figure 4.17. It was feasible to discriminate Thai milled rice into four groups according to the physicochemical properties; Hom Mali rice, low, intermediate, and high amylose rice groups (Figure 4.17). Hom Mali rice and the low amylose rice group could be separated from the intermediate and high amylose rice groups but Hom Mali rice could not be differentiated from the low amylose rice group due to their similar physicochemical properties (Table 4.18). Moreover, Hom Mali rice with different degrees of milling had different positions at PC_2, resulting from the maximum and breakdown viscosity (Table 4.11 and Figure 4.17).

However, the PCA could not explicitly discriminate the Thai rice varieties at all degrees of milling (0, 5, 10, and 15% degree of milling). Therefore, the feasibility of discriminating Thai milled rice was studied at different degrees of milling using PCA. Since each degree of milling affected the discrimination performance in a similar manner, the factor scores of the rotated PC_1 and PC_2 of the 0% degree of milling are thus presented in Figure 4.18.

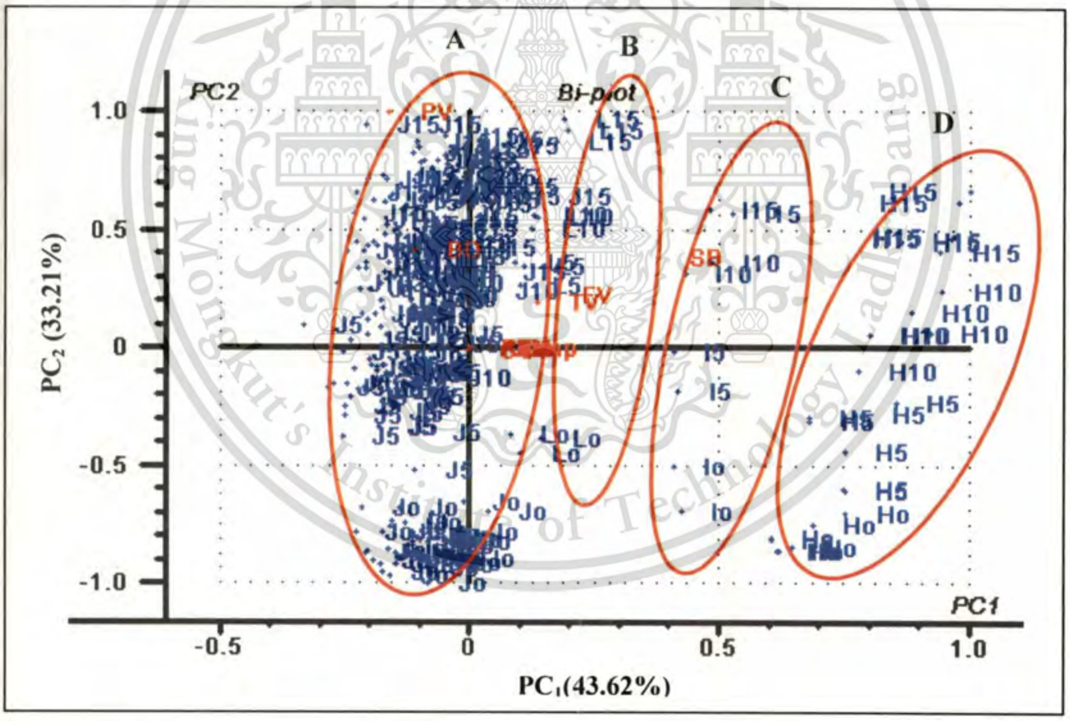


Figure 4.17 Score plot of the rotated PC_1 and rotated PC_2 from physicochemical data of all degrees of milling

where A = J0, J5, J10, J15 = Hom Mali rice at 0, 5, 10, 15% degree of milling; B = L0, L5, L10, L15 = Low amylose rice at 0, 5, 10, 15% degree of milling; C = I0, I5, I10, I15 = Intermediate amylose rice at 0, 5, 10, 15% degree of milling; and D = H0, H5, H10, H15 = high amylose rice at 0, 5, 10, 15% degree of milling

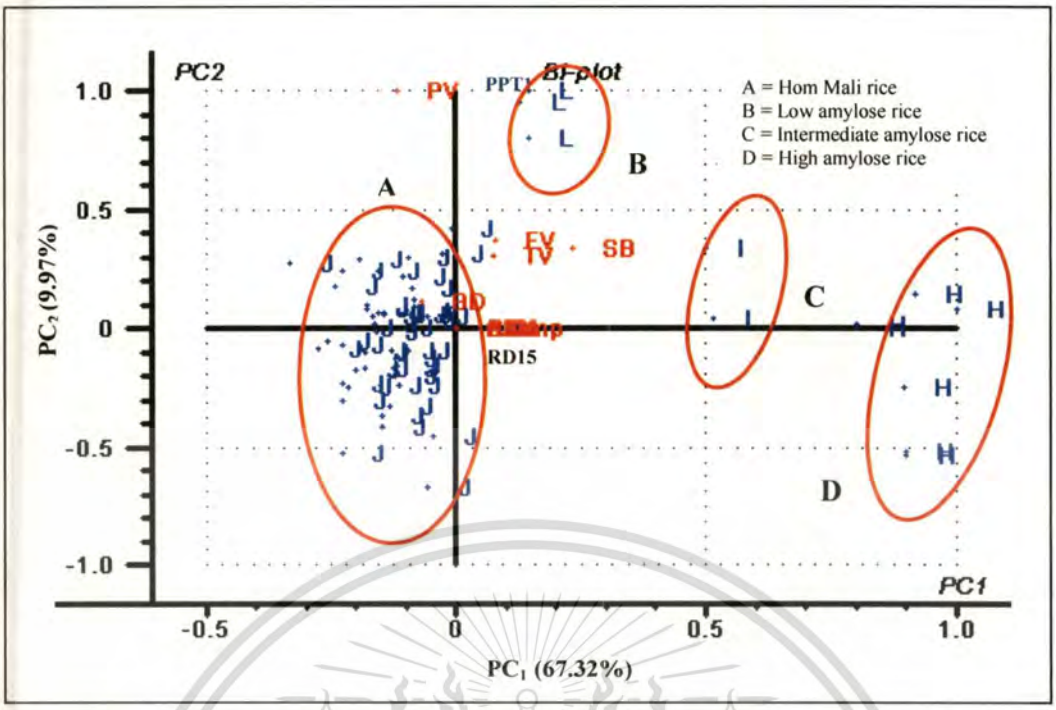


Figure 4.18 Score plot of the rotated PC_1 and PC_2 of the physicochemical properties at 0% degree of milling

From the PCA score plot of Figure 4.18, at the same degree of milling the score on the PC_1 axis could discriminate Thai milled rice into four groups: Hom Mali rice, low, intermediate and high amylose rice groups. On the other hand, the score on the PC_2 axis could not discriminate Thai milled rice into four groups because the protein content among the four groups was not sufficiently different (Table 4.12). However, it was possible to discriminate the RD15 variety (Hom Mali rice group) from PTT1 (low amylose rice group) at the same degree of milling by PCA due to their different pasting properties, especially peak or maximum viscosity (Table 4.9). The results of the discrimination of rice samples in Figure 4.18 were similar to those obtained from 5, 10 and 15% degree of milling (Appendix I; Figures I1-3I).

These results confirmed that the degree of milling greatly affected the physicochemical properties of rice and discrimination of Hom Mali rice from the other rice varieties. Therefore, it was important to note that the discrimination of Hom Mali rice with different degrees of milling from the other aromatic and non-aromatic rice varieties, especially the low amylose rice group based on their physicochemical properties, should be performed at the same degree of milling.

4.4.2 Discrimination of Hom Mali rice from the other aromatic and non-aromatic rice varieties based on NIR spectra characteristics by the PCA and PLS-DA techniques

4.4.2.1 Discrimination of Hom Mali rice from the other aromatic and non-aromatic rice varieties by the PCA technique

The original spectra of four rice groups are shown in Figure 4.19. The mean spectra of the four rice groups represented Hom Mali rice (labeled as J), low (as L), intermediate (as I) and high (as H) amylose rice groups. The spectrum of high amylose rice group was the uppermost while Hom Mali rice and low amylose group were the lowest. As a general rule, spectra of rice with high amylose content are of higher density of crystalline starch region than those of intermediate and low amylose rice groups. This can be complicated by factors such as size, shape, and seed density (Williams, 2007). However, the spectrum of Hom Mali rice was closely similar to that of low amylose rice due to both groups being identified as belonging to the low amylose rice group (Figure 4.19).

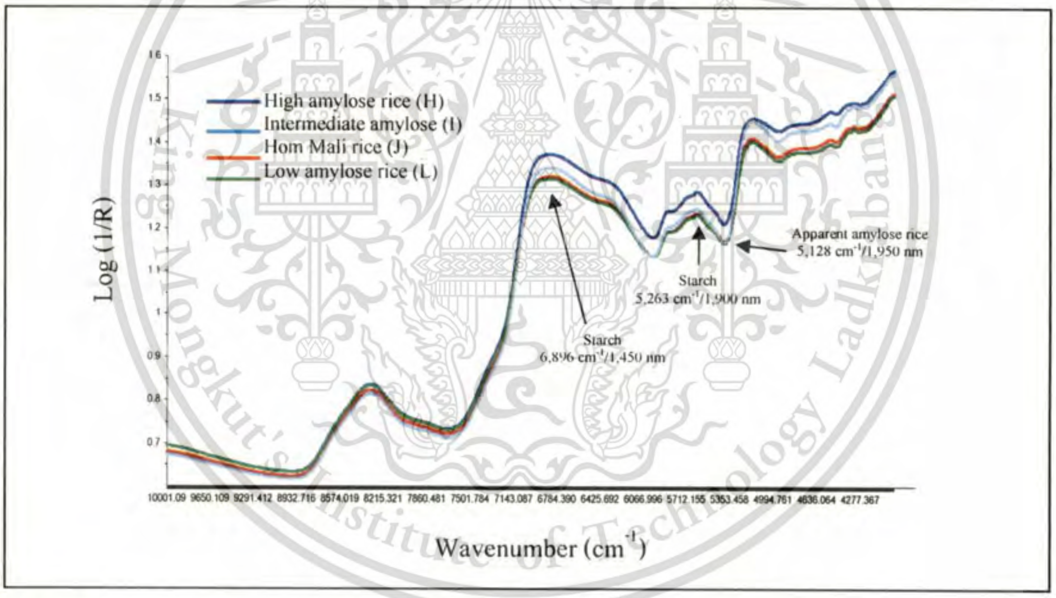


Figure 4.19 Original spectra of four rice groups

The most noticeable differences between these curves were attributed to apparent amylose content in rice grain: Hom Mali rice (16.02-16.09%), low (14.34-18.25%), intermediate (19.65-22.45%) and high (26.65-28.65%) amylose rice groups (Table 4.2) as spectra differences between the curves were found in many regions: 6,896 cm^{-1} (1,450 nm), 5,263 cm^{-1} (1,900 nm), 5,102 cm^{-1} (1,960 nm) and 5,126 cm^{-1} (1,950 nm) (Parker, 1983; Workmand and Weyer, 2008). Thus, the differences in NIR spectra of four rice groups were possible to use to classify Hom Mali rice from the other groups. In this study, PCA was performed on the spectral region of 10,000-4,000 cm^{-1}. Table 4.13 summarizes the PCA classification resulted on the basis of original and pre-processing NIR spectra of rice samples at various degrees of milling using PCA. The table showed the number of false negative, number of false positive, number of correct classify, false negative (%), false positive (%) and correctly classify (%). False positive is a measure of the ability to reject the true object. On the other hand, false negative is the proportion of samples not belonging to a certain class classified as foreign, i.e., it is a measure of the ability to discriminate against "false positive" (Esteban-Díez et al., 2007).

In spite of the good results obtained in false negative, false positive and correct discrimination, the model developed from original NIR spectra of milled rice at 10% degree of milling, presented the best performance for classifying Hom Mali rice from the other aromatic and non-aromatic rice varieties. The false negative, false positive and correct discrimination of this model were 4.76, 1.98 and 87.30%, respectively (Table 4.13), indicating that many Hom Mali rice varieties could be discriminated as "true" Hom Mali rice, leading to a high correct discrimination.

The results could be also confirmed graphically. Figure 4.20 shows the score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 10% degree of milling. By the category discrimination, the upper and lower quadrants would correspond to the sample of Hom Mali rice (labeled as J), whereas the other two quadrants would correspond to the low (labeled as L), intermediate (labeled as I) and high (labeled as H) amylose rice varieties. In this study, the samples expected to be located in the upper and lower right quadrants would be Hom Mali rice samples (labeled as J). Rice samples contained in the upper and lower left quadrants were plotted as low (labeled as L), intermediate (labeled as I) and high (labeled as H) amylose rice varieties. However, this model found the indiscrimination of some Hom Mali rice samples due to their presence in the upper and lower left quadrants, causing a decrease in the correct discrimination.

Table 4.13 PCA discrimination results using the NIR spectral data

Samples	Number of false negative (n)	Number of false positive (n)	Number of correct classify (n)	False negative (%)	False positive (%)	Correct discrimination (%)
All degrees of milling						
No pre–processing	35	68	149	13.89	26.98	59.13
MSC	41	36	175	16.27	14.29	69.44
SNV	27	52	173	10.71	20.63	68.65
Sav.Gol_2nd derv*	45	59	148	17.86	23.41	58.73
MSC + Sav.Gol_2nd derv	64	77	111	25.40	30.56	44.05
SNV + Sav.Gol_2nd derv	75	81	96	29.76	32.14	38.10
0% degree of milling						
No pre–processing	9	6	48	14.29	2.38	76.19
MSC	8	16	39	12.70	6.35	61.90
SNV	8	16	39	12.70	6.35	61.90
Sav.Gol_2nd derv*	3	15	45	4.76	5.95	41.43
MSC + Sav.Gol_2nd derv	4	20	39	6.35	7.94	61.90
SNV + Sav.Gol_2nd derv	4	21	38	6.35	8.33	60.32
5% degree of milling						
No pre–processing	4	5	54	6.32	1.98	85.71
MSC	15	6	42	23.81	2.38	66.67
SNV	13	7	43	20.63	2.78	68.25
Sav.Gol_2nd derv*	18	13	32	28.57	5.16	50.79
MSC + Sav.Gol_2nd derv	15	17	31	23.81	6.75	49.21
SNV + Sav.Gol_2nd derv	15	19	29	23.81	7.54	46.03

* Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 4.13 (continued)

Samples	Number of false negative (n)	Number of false positive (n)	Number of correct classify (n)	False negative (%)	False positive (%)	Correct discrimination (%)
10% degree of milling						
No pre–processing	**3**	**5**	**55**	**4.76**	**1.98**	**87.30**
MSC	13	8	42	20.63	3.17	66.67
SNV	14	8	41	22.22	3.17	65.08
Sav.Gol_2nd derv*	14	16	33	22.22	6.35	52.38
MSC + Sav.Gol_2nd derv	15	16	32	23.81	6.35	50.79
SNV + Sav.Gol_2nd derv	15	20	28	23.81	7.94	44.44
15% degree of milling						
No pre–processing	9	9	45	14.29	3.57	71.43
MSC	21	13	29	33.33	5.16	46.03
SNV	20	13	30	31.75	5.16	47.62
Sav.Gol_2nd derv*	24	16	23	38.10	6.35	36.51
MSC + Sav.Gol_2nd derv	18	12	33	28.57	4.76	52.38
SNV + Sav.Gol_2nd derv	19	9	35	30.16	3.57	55.56

* Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

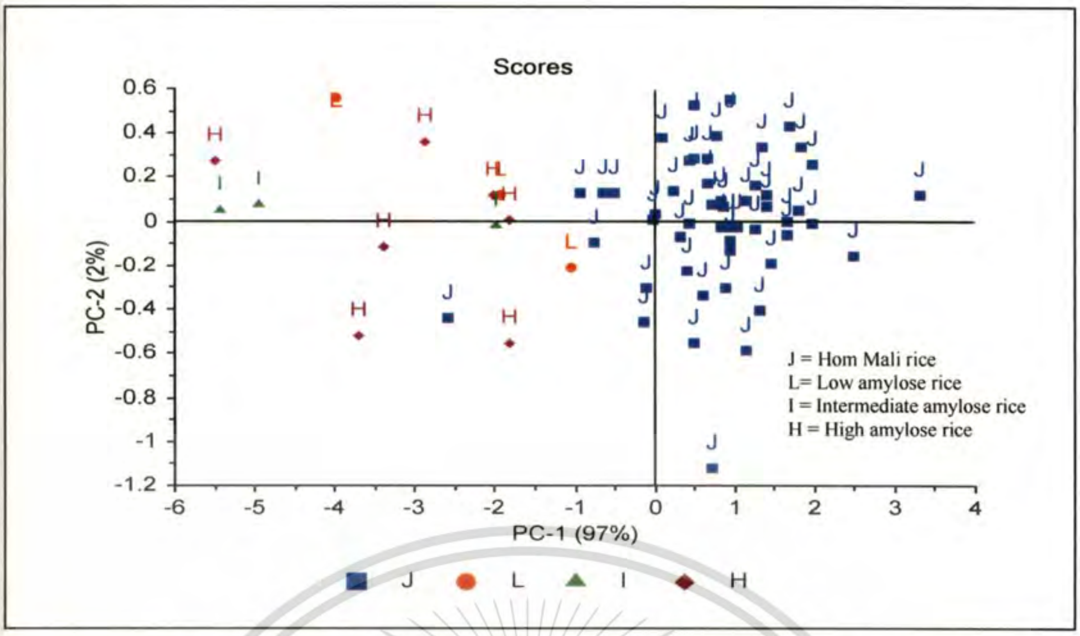


Figure 4.20 Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice groups of milled rice at 10% degree of milling

Furthermore, this result showed the original NIR spectra of milled rice at 5% degree of milling to be a good model for discriminating Hom Mali rice from the other rice varieties. This model gave the false negative, false positive and correct discrimination of 6.32, 1.98 and 85.71%, respectively (Table 4.13). The score plot of PC_1 and PC_2 of milled rice at 5% degree of milling was very similar to the score plot of milled rice at 10% degree of milling (Figure 4.21). This score plot depicted that Hom Mali rice samples (labeled as J) were placed in the upper and lower right quadrants, whereas low (labeled as L), intermediate (labeled as I) and high (labeled as H) were located in the upper and lower left quadrants. Additionally, some Hom Mali rice samples (labeled as J) were found in the upper and lower left quadrants, causing the misclassification from the aromatic and non-aromatic rice varieties.

Of the Hom Mali rice samples plotted in the two score plots of PC_1 and PC_2 models, 5 and 10% degrees of milling represented Hom Mali rice that could be discriminated from the other rice varieties based on original spectra by PCA. Both models exhibited the large correct classify of 85.71 and 87.30%, respectively. Esteban-Díez et al. (2007) suggested that the correct classify value more than 80% indicated the suitability for applying the NIR spectra to develop classification models for coffee variety identification. Therefore, these results indicated that the discrimiantion models of 5 and 10% degrees of milling were good models for discriminating Hom Mali rice from the other aromatic and non-aromatic rice varieties.

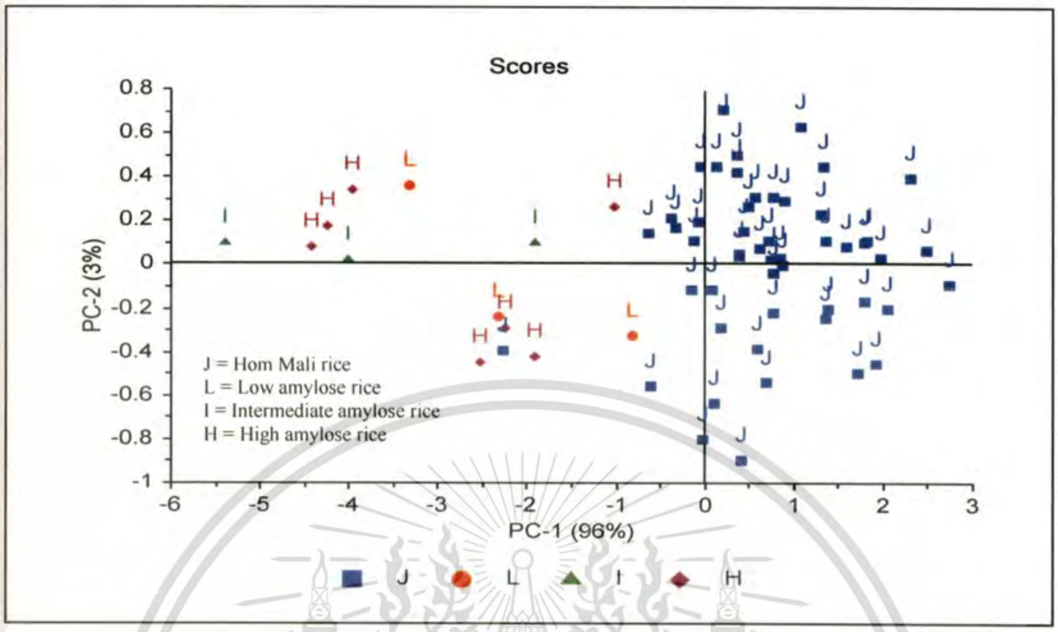


Figure 4.21 Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice groups of milled rice at 5% degree of milling

However, the results showed that all degrees of milling, including 0, 5, 10 and 15% degree of milling, could reasonably discriminate Hom Mali rice from the other rice varieties, especially the NIR spectra transformed with MSC and SNV which gave correct discrimination of 69.44 and 68.65%, respectively (Table 4.13). On the other hand, the results for those NIR spectra with other pre-processing were much worse, presumably due to the effect of degree of milling on the physicochemical properties. The score plots of PC_1 and PC_2 of four rice groups at all degrees of milling are presented in Figure 4.22. The results exhibited that Hom Mali rice samples (labeled as J) were located in all four quadrants and thereby could not be discriminated from low (labeled as L), intermediate (labeled as I) and high amylose rice samples (labeled as H) by PCA. These results were attributed to the effect of degree of milling on physicochemical properties of rice, giving rise to the similarity in the properties of the four rice groups (Tables 4.4 and 4.5).

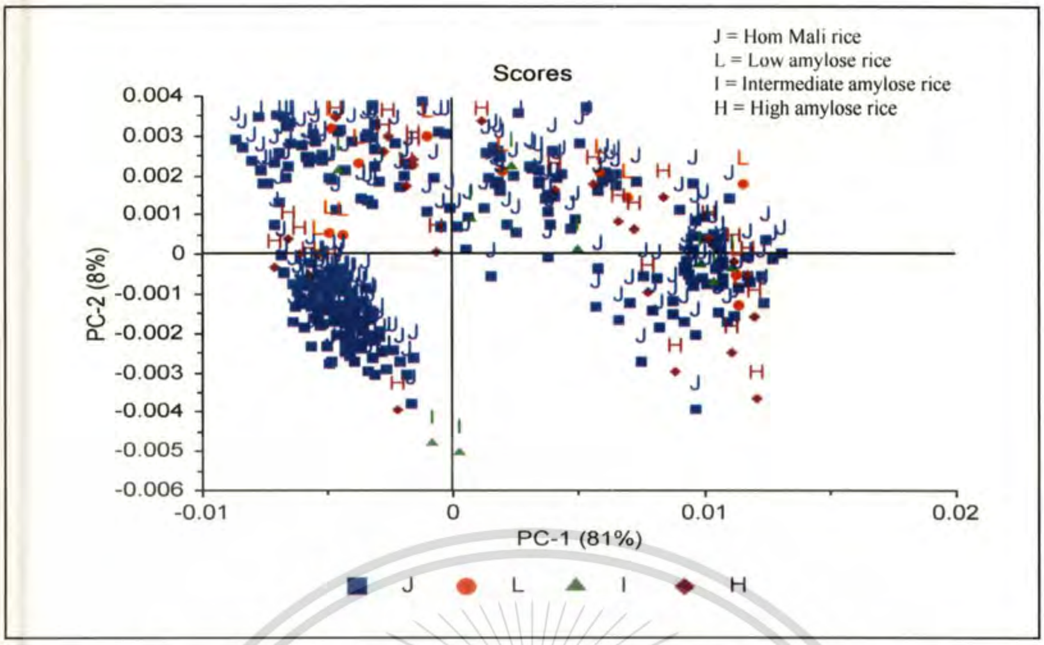


Figure 4.22 Score plots of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice groups at all degrees of milling

Additionally, the NIR spectra of brown rice samples (0% degree of milling) could reasonably discriminate Hom Mali rice from the aromatic and non-aromatic rice varieties. Discrimination accuracies of 0% degree of milling obtained from the original spectra, MSC, SNV, MSC + second derivative and SNV + second derivative were respectively 76.19, 61.90, 61.90, 61.90 and 60.32% except the NIR spectra transformed with second derivative (Table 4.13). The comparison of the pre-processing methods indicated that the original spectra method of 5 and 10% degree of milling was the best models for discriminating Hom Mali rice. At 15% degree of milling, the original NIR spectra were merely a reasonable model for discrimination of Hom Mali rice from the other rice varieties, while the other NIR spectra pre-processed with MSC, SNV, second derivative, MSC + second derivative and SNV + second derivative were unsuitable for discriminating Hom Mali rice (Table 4.13).

By comparison of the pre-processing methods, the original NIR spectra appeared to be the best model for classifying Hom Mali rice for 0, 5, 10 and 15% degree of milling except the NIR spectra of all degrees of milling. Moreover, the PCA discrimination model of the original spectra of milled rice at 10% degree of milling was better than those of milled rice at 5, 0, 15% degree of milling and all degrees of milling (Table 4.13).

In spite of the PCA discrimination results and score plots of PC_1 and PC_2 derived from the original NIR spectra, the application of PCA enabled to the discrimination of Hom Mali rice from the aromatic and non-aromatic rice varieties, consistent with the work of Wang et al. (1999) who applied PCA to reduce the number of neural network inputs and achieved 98% classification accuracy for six classes of wheat. In this study, the findings revealed that the original NIR spectra with the degree of milling of 10% was considered the best model for classifying Hom Mali rice from the other rice varieties.

4.4.2.2 Discrimination of Hom Mali rice from the other aromatic and non-aromatic rice varieties by the PLS-DA technique

In this section, the discrimination of Hom Mali rice from the other aromatic and non-aromatic rice varieties based on the NIR spectra by PLS-DA was investigated. Hom Mali rice samples would be correctly discriminated only if the values were in the range of 0.5 and 1.5. On the other hand, the rice samples were of the aromatic and non-aromatic varieties if the values were between -0.5 and 0.5. PLS-DA regression statistics obtained from the original and pre-processed NIR spectra of rice samples are shown in Table 4.14. The results exhibited that the best performance PLS-DA discrimination model of all degrees of milling was the original NIR spectra which gave number of factors, r^2_{cal} and SEC of 8, 0.71 and 0.19, respectively. For brown rice samples (0% degree of milling), the NIR spectra transformed with SNV appeared the best discrimination model for discriminating Hom Mali rice (number of factors = 5, r^2_{cal} = 0.78 and SEC = 0.17).

Additionally, the best PLS-DA discrimination model of 5% degree of milling was NIR transformed with SNV + second derivative presenting the number of factors, r^2_{cal} and SEC of 3, 0.75 and 0.19, respectively. The NIR spectra pre-processed by MSC of milled rice at 10% degree of milling gave the number of factors, r^2_{val} and SEP of 6, 0.81 and 0.17, respectively, which exhibited the best performance for discriminating Hom Mali rice. Furthermore, the results presented that the best discrimination model of milled rice at 15% degree of milling was NIR spectra transformed with MSC (number of factors = 8, r^2_{val} = 0.53, SEP = 0.28).

In this study, the rice samples with all degrees of milling (0, 5, 10, and 15% degree of milling), 0, 5, 10 and 15% degree of milling could reasonably discriminate Hom Mali rice from the other rice varieties.

Table 4.14 PLS-DA regression statistics obtained from original and pre-processed NIR spectra of rice samples

Rice samples	Pre-processing	Number of samples (*n*)	Number of factors	r^2_{cal}	r^2_{val}	SEC	SEP
All degrees of milling	No-Pre-processing	504	8	0.71	0.68	0.19	0.20
	MSC	504	7	0.66	0.59	0.20	0.22
	SNV	504	7	0.67	0.61	0.20	0.22
	Sav.Gol_2nd derv	504	3	0.59	0.55	0.22	0.23
	MSC + Sav.Gol_2nd derv	504	4	0.62	0.58	0.22	0.23
	SNV + Sav.Gol_2nd derv	504	4	0.62	0.58	0.21	0.23
Brown rice (0% degree of milling)	No-Pre-processing	126	3	0.70	0.64	0.20	0.22
	MSC	126	5	0.78	0.66	0.17	0.22
	SNV	126	5	0.79	0.69	0.17	0.21
	Sav.Gol_2nd derv	126	3	0.67	0.56	0.21	0.25
	MSC + Sav.Gol_2nd derv	126	3	0.68	0.59	0.21	0.24
	SNV + Sav.Gol_2nd derv	126	3	0.69	0.60	0.20	0.24
Milled rice (5% degree of milling)	No-Pre-processing	126	1	0.68	0.67	0.22	0.23
	MSC	126	2	0.55	0.50	0.26	0.28
	SNV	126	2	0.55	0.50	0.26	0.28
	Sav.Gol_2nd derv	126	2	0.70	0.59	0.21	0.25
	MSC + Sav.Gol_2nd derv	126	3	0.75	0.64	0.19	0.24
	SNV + Sav.Gol_2nd derv	126	3	0.75	0.64	0.19	0.24

*Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 4.14 (continued)

Rice samples	Pre-processing	Number of samples (n)	Number of factors	r^2_{cal}	r^2_{val}	SEC	SEP
Milled rice (10% degree of milling)	No-Pre-processing	126	1	0.66	0.65	0.23	0.24
	MSC	126	6	0.81	0.64	0.17	0.24
	SNV	126	6	0.81	0.64	0.17	0.24
	Sav.Gol_2nd derv*	126	2	0.73	0.68	0.20	0.24
	MSC + Sav.Gol_2nd derv	126	3	0.74	0.65	0.20	0.23
	SNV + Sav.Gol_2nd derv	126	3	0.74	0.65	0.20	0.23
Milled rice (15% degree of milling)	No-Pre-processing	126	1	0.57	0.56	0.26	0.27
	MSC	126	8	0.87	0.53	0.14	0.28
	SNV	126	8	0.87	0.53	0.14	0.27
	Sav.Gol_2nd derv	126	2	0.68	0.53	0.22	0.27
	MSC + Sav.Gol_2nd derv	126	1	0.62	0.55	0.24	0.27
	SNV + Sav.Gol_2nd derv	126	1	0.62	0.55	0.24	0.27

*Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

The above results corresponded to those in Table 4.15. This table presented number of false negative, number of false positive, number of correct discrimination, false negative, false positive and correct discrimination. In this part, false negative sample was the other rice groups: low, intermediate and high amylose rice groups that were considered as Hom Mali rice group. On the contrary, false positive sample was Hom Mali rice sample that was considered as the other rice groups.

It could be observed that the optimal discrimination model corresponded to the result of Table 4.14. The results exhibited that the best discrimination results for all degrees of milling (0, 5, 10 and 15% degree of milling) were obtained from the original NIR spectra with number of false negative samples being 29 samples (11.51%). The NIR spectra of brown rice pre-processed by SNV appeared the best model for discriminating Hom Mali rice with false negative, false positive and correct discrimination of 6.35, 2.78 and 82.54%, respectively (Table 4.15). The best performance for discriminating Hom Mali rice of milled rice at 5% degree of milling was the NIR spectra transformed with SNV + second derivative. This model presented number of false negative of 6 samples, which gave false negative and correct discrimination of 4.36 and 85.71%, respectively.

Additionally, the NIR spectra after MSC pre-processing of milled rice at 10% degree of milling appeared the best discrimination model which gave false negative, false positive and correct discrimination of 6.35, 1.59 and 87.30%, respectively. Furthermore, the NIR spectra of milled rice at 15% degree of milling transformed with MSC seemed to be the best discrimination model, which was similar to the case of milled rice at 10% degree of milling. However, this model showed lower false negative (3.17%) than the model of milled rice at 10% degree of milling, but false positive (1.98%) and correct discrimination (88.89%) were higher than those of the 10% degree of milling model (Table 4.15).

Considering all the models based on NIR spectra, it was observed that Hom Mali rice could be discriminated from low, intermediate and high amylose rice groups at all degrees of milling, 0, 5, 10 and 15% degree of milling. These were attributed to the differences in the physicochemical properties of rice grains, especially the pasting properties of rice grains (peak, setback and trough viscosity). In this study, results found that the pasting properties caused Hom Mali rice to differ from the other rice groups, leading to different NIR spectra of the four rice groups and thereby allowing the discrimination of Hom Mali rice from the other rice groups.

Table 4.15 PLS-DA discrimination results using the NIR spectral data

Samples	Number of false negative (n)	Number of false positive (n)	Number of correct classify (n)	False negative[1] (%)	False positive[2] (%)	Correct discrimination (%)
All degrees of milling						
No pre–processing	**29**	**65**	**158**	**11.51**	**25.79**	**62.70**
MSC	49	54	149	19.44	21.43	59.13
SNV	34	64	154	13.49	25.40	61.11
Sav.Gol_2nd derv[3]	55	59	138	21.83	23.41	54.76
MSC + Sav.Gol_2nd derv	32	67	153	12.70	26.59	60.71
SNV + Sav.Gol_2nd derv	28	71	153	11.11	28.17	60.71
0% degree of milling						
No pre–processing	4	13	46	6.35	5.16	73.02
MSC	3	11	49	4.76	4.37	77.78
SNV	**4**	**7**	**52**	**6.35**	**2.78**	**82.54**
Sav.Gol_2nd derv[3]	2	14	47	3.17	5.56	74.60
MSC + Sav.Gol_2nd derv	3	9	51	4.76	3.57	80.95
SNV + Sav.Gol_2nd derv	3	10	50	4.76	3.97	79.37
5% degree of milling						
No pre–processing	5	9	49	7.94	3.57	77.78
MSC	7	5	51	11.11	1.98	80.95
SNV	8	7	48	12.70	2.78	76.19
Sav.Gol_2nd derv*	6	8	49	9.52	3.17	77.78
MSC + Sav.Gol_2nd derv*	6	7	50	9.52	2.78	79.37
SNV + Sav.Gol_2nd derv*	**3**	**6**	**54**	**4.36**	**3.57**	**85.71**

[1] False negative was the other rice groups that were considered as Hom Mali rice group,
[2] False positive was Hom Mali rice sample that was considered as the other rice groups and
[3] Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 4.15 (continued)

Samples	Number of false negative (n)	Number of false positive (n)	Number of correct classify (n)	False negative[1] (%)	False positive[2] (%)	Correct discrimination (%)
10% degree of milling						
No pre–processing	5	8	50	7.94	3.17	79.37
MSC	**4**	**4**	**55**	**6.35**	**1.59**	**87.30**
SNV	7	8	48	11.11	3.17	76.19
Sav.Gol_2nd derv[3]	6	9	48	9.52	3.57	76.19
MSC + Sav.Gol_2nd derv	8	10	45	12.70	3.97	71.43
SNV + Sav.Gol_2nd derv	6	11	46	9.52	4.37	73.02
15% degree of milling						
No pre–processing	11	3	41	7.46	1.19	77.78
MSC	**2**	**5**	**56**	**3.17**	**1.98**	**88.89**
SNV	5	11	47	7.94	4.37	74.60
Sav.Gol_2nd derv[3]	6	12	45	9.52	4.76	71.43
MSC + Sav.Gol_2nd derv	4	10	49	6.35	3.97	77.78
SNV + Sav.Gol_2nd derv	6	11	46	9.52	4.37	73.02

[1] False negative was the other rice groups that were considered as Hom Mali rice group,
[2] False positive was Hom Mali rice sample that was considered as the other rice groups and
[3] Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

However, wavenumbers range of starch regions, such as 6,896 cm^{-1} (1,450 nm), 5,263 cm^{-1} (1,900 nm), 5,102 cm^{-1} (1,960 nm) and 5,126 cm^{-1} (1,950 nm), were important for discriminating Hom Mali rice from the other rice groups (Parker, 1983). The reason was that these regions presented the peak of starch and apparent amylose content, both of which influenced the pasting properties of rice grain which were a major parameter for discriminating Hom Mali rice. Of all the discrimination models discussed, the results showed that the degree of milling at 15% would be recommended for discriminating Hom Mali rice by PLS-DA. Therefore, NIR spectroscopy was found to be the most efficient in discrimination of Hom Mali rice from the other rice varieties by PLS-DA. Osborne et al. (1993b) applied the NIT spectroscopy for discriminating Basmati rice from the other long grain rices by PLS-DA. The results showed that 8% of the Basmati and 14% of the other were misclassified on the basis of NIR spectra of 930 individual grains, which is in agreement with this study.

The predicted and reference values of milled rice at 15% degree of milling pr-processed with MSC plot displayed in Figure 4.23 also confirmed the high quality of the discrimination model developed from NIR spectra for discrimination between Hom Mali rice (labeled as J), and low (labeled as L), intermediate (labeled as I) and high (labeled as H) amylose rice varieties. Figure 4.23 shows that 56 samples (88.89%) of Hom Mali rice samples were classified correctly which lied between 0.5 to 1.5 while the aromatic and non-aromatic rice samples were placed in the range of -0.5 to 0.5. There were 5 samples (1.98%) of Hom Mali rice which were placed above 1.5. Therefore, they were discriminated as "false negative", leading to a low correct discrimination. Meanwhile, some samples of other rice varieties were placed between 0.5 to 1.5, causing them to be discriminated as "false negative", which decreased the percentage of correct discrimination.

Figure 4.23 illustrates a high correct discrimination and clear discrimination between Hom Mali and the other rice varieties. In this study, the results showed that PLS-DA had potential for classifying rice varieties. Moreover, it was found that the fixed degree of milling at 15% would be recommended in the discrimination of Hom Mali rice.

These results indicated that PLS-DA models successfully discriminated Hom Mali rice samples from the aromatic and non-aromatic rice samples because of their differences in peak of NIR spectra, especially apparent amylose content. Moreover, this study found that the PLS-DA models better classified Hom Mali rice from the other rice samples than PCA. The PLS-DA discrimination model at 10% degree of milling performed with MSC and SNV achieved the correct discrimination rate up to 70.42%. These results verified that the differences existed between the rice samples in terms of different physicochemical properties; and confirmed that NIR spectra contained information applicable to the discrimination of rice samples by PLS-DA.

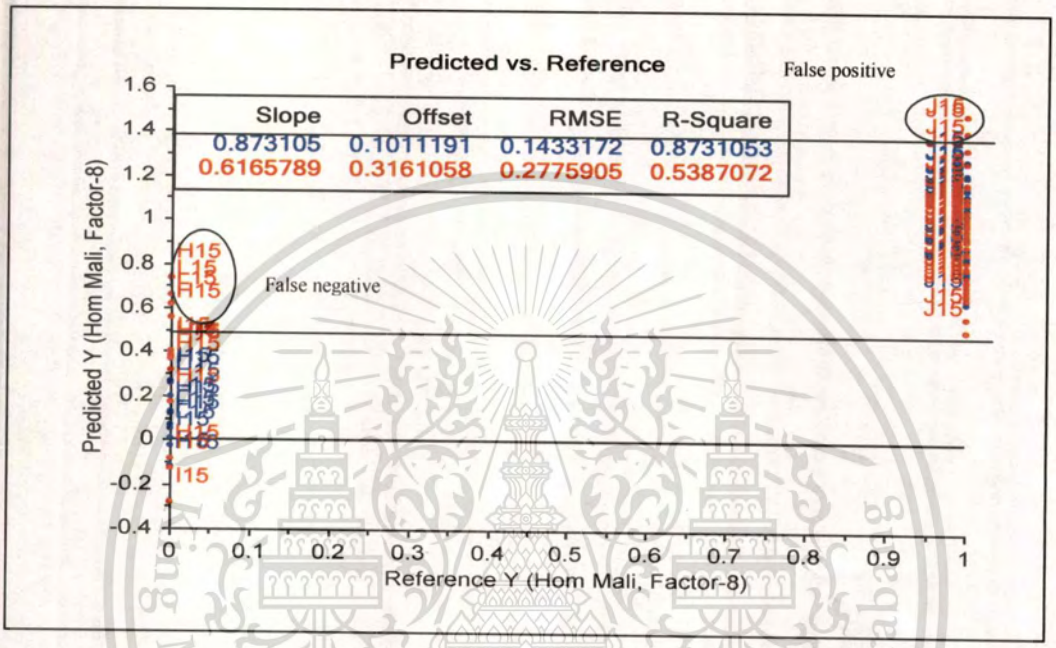


Figure 4.23 Predicted vs. reference of milled rice at 15% degree of milling pre-processing with MSC of PLS-DA model

CHAPTER 5

CONCLUSION

5.1 Conclusion

The physicochemical properties of Hom Mali rice were very similar to the low amylose rice group but differed from the intermediate and high amylose rice groups. Hom Mali rice could be discriminated from low, intermediate, and high amylose rice groups according to their physicochemical properties except protein content. The apparent amylose content, gel consistency, and alkali spreading value could be used for discriminating Hom Mali rice from the intermediate and high amylose groups, but not from low amylose group due to the fact that they were belonging to the low amylose group. The pasting properties of rice were the major parameters for classifying Hom Mali rice from the low amylose group, especially peak viscosity, setback viscosity, and trough viscosity. In this study, it be noted that Hom Mali rice could be discriminated from PTT1 using the final viscosity parameter.

The degree of milling affected the physicochemical properties of brown and milled rice. The apparent amylose content, alkali spreading value, maximum (peak), trough, breakdown, final and setback viscosity increased with an increase in the degree of milling up to 15% degree of milling for all rice groups, while the protein content and gel consistency decreased. This indicated that changes in the degree of milling among rice varieties could be related to the changes in their physicochemical properties. Thus, the classification of Hom Mali rice from the other rice varieties should take into consideration the effect of degree of milling on their properties.

FT-NIR spectroscopy with PLSR technique had potential for predicting physicochemical properties of rice samples with different degrees of milling. PLSR models for moisture, protein, apparent amylose contents, alkali spreading value, gel consistency and pasting properties of rice were demonstrated a reasonable evaluated these properties. The results concluded that the fixed degree of milling of rice samples showed the better model than all degrees of milling (0, 5, 10, and 15% degree of milling).

PCA could be used for discriminating Thai milled rice into four groups: Hom Mali rice, low, intermediate and high amylose rice groups using two principal components. Rotated PC_1 and

PC_2 using the varimax method provided a better arrangement with new variables than the un-rotated principal components. Hom Mali rice was clearly differentiated from the low, intermediate and high amylose rice groups. At the same degree of milling, the RD15 variety could be differentiated from PTT1 variety due to their different pasting properties. Thus, rice samples with the fixed degree of milling were shown the greater models than rice samples various degrees of milling.

FT-NIR spectroscopy with PCA and PLS-DA had potential for discrimination between the NIR spectra of Hom Mali rice and the low, intermediate and high amylose rice varieties. It should be noted that 10% degree of milling was considered as the best discrimination model for discriminating Hom Mali rice from the other rice varieties by PCA. Likewise, the NIR spectra of milled rice at 15% degree of milling transformed with MSC exhibiting the best model for discriminating Hom Mali rice by PLS-DA. These results showed that the fixed degree of milling was more suitable for discriminating Hom Mali rice than all degree of milling (0, 5, 10 and 15% degree of milling).

This study has clearly demonstrated that FT-NIR spectroscopy had a potential method for determination of physicochemical properties of rice and discrimination of Hom Mali rice from the other aromatic and non-aromatic rice varieties.

5.2 Recommendations

To further explore the possibility of near infrared spectroscopy in evaluation of rice quality and classification of Hom Mali rice, future research should focus on:

5.2.1 The quantity of rice samples with low, intermediate and high amylose rice varieties should be nearly as much as Hom Mali rice samples to improve the accuracy of the calibration equation.

5.2.2 The investigation of changes in physicochemical properties of rice in relation with NIR spectra during storage due to the storage of rice is important factor affecting the physicochemical properties and classifing Hom Mali rice.

5.2.3 More variations in samples with respect to varieties, geological cultivation and handling conditions should be included in the calibration model.

5.2.4 The discrimination of Hom Mali rice from PTT1 and CNT1 varieties in different ratios should be investigated because both varieties are very popular to blend with Hom Mali rice.

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APPENDIX

Appendix A

Chemical preparations

The following is a list of the solutions and chemicals required throughout this research.

1. Glacial acetic acid (1.0 N)

Glacial acetic acid is 99.6% (w/v) acetic acid and is 17.4 M. Add 57.5 ml of glacial acetic acid to 800 ml of distilled water and then make to 1,000 ml with distilled water.

2. Iodine solution

Pour 10 g of potassium iodine into a 500 ml beaker. Add 100 ml of distilled water and mix the solution with a metal stirring rod until the potassium iodine dissolves in the water. Pour 1 g of iodine into another 500 beaker. Add 100 ml of distilled water and mix the solution until the iodine dissolves in the water. After that, mix the potassium iodine solution and iodine solution in 1,000 ml beaker and then make to 500 ml with distilled water. This solution should keep in brown bottle at room temperature.

3. Sodium hydroxide (2.0 N)

Add 80 g of sodium hydroxide to 900 ml of distilled water and then make to 1,000 ml with distilled water.

Appendix B

Standard curve of apparent amylose content

(AACC, 1999)

Table 1B Concentration of amylose to amylopectin ratio

Amylose content in milled rice (% dry basis)[1]	Composition of mixture (ml)		
	Amylose (1 mg/ml)	Amylopectin (1 mg/ml)	0.09 N NaOH
0	0.0	7.0	3
10	1.0	6.0	3
20	2.0	5.0	3
25	2.5	4.5	3
30	3.0	4.0	3

1) These values have been calculated on the basis of an average starch content of 90% (m/m) in milled rice

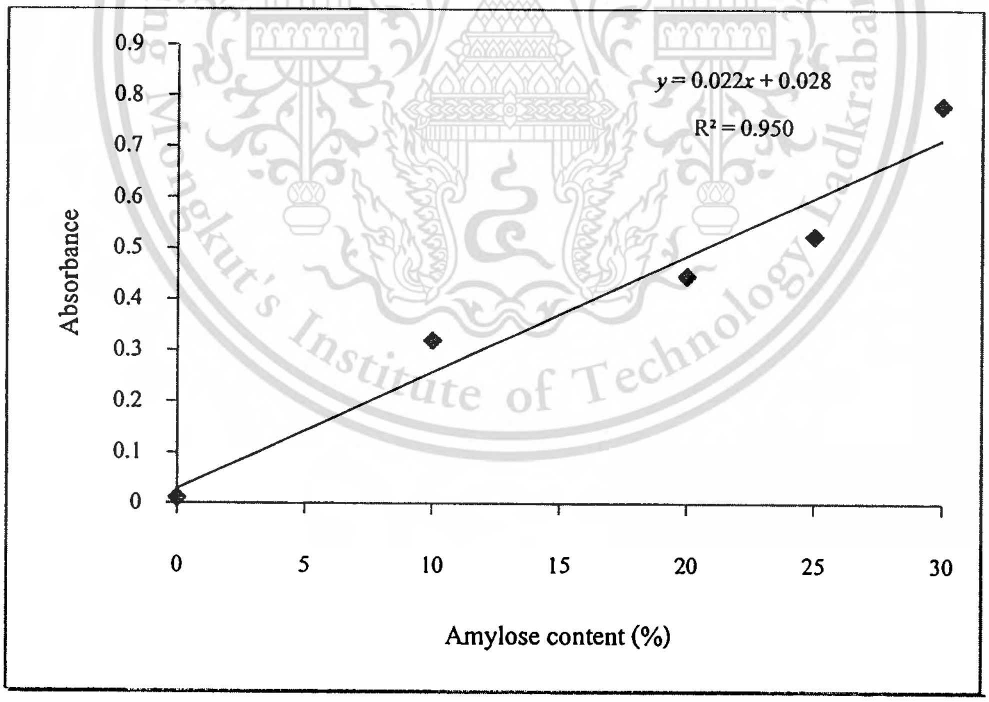
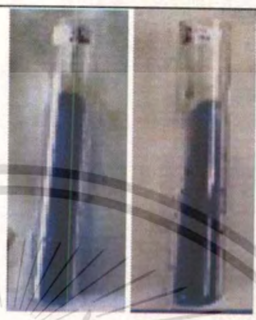
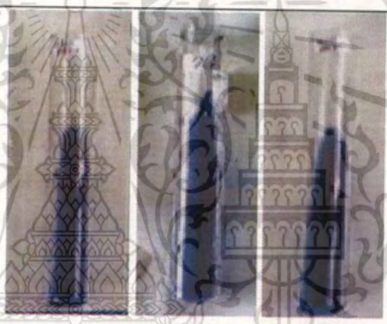
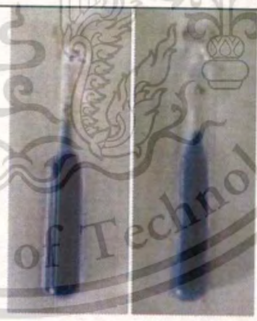
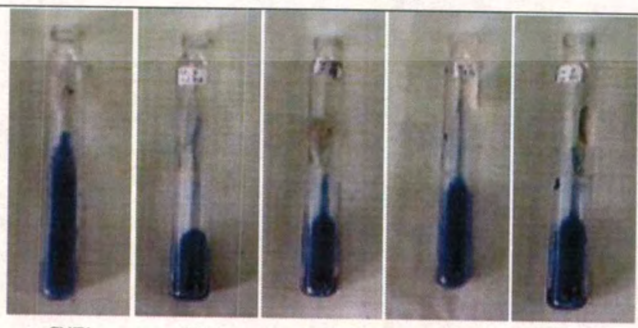


Figure 1B Standard curve of amylose content

Appendix C

Gel consistency of four rice groups

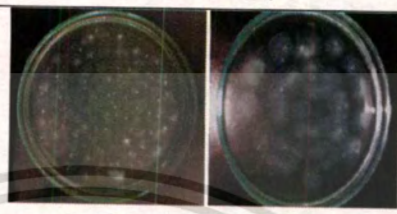
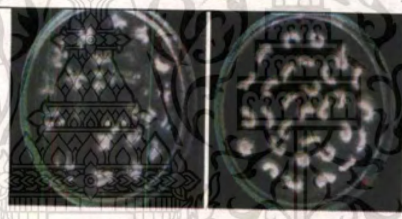
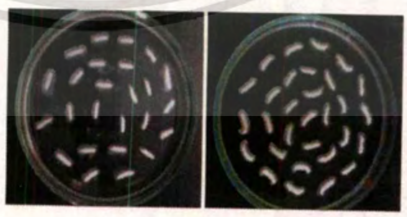
Table 1C Gel consistency of four rice group; Hom Mali rice, low, intermediate, and high amylose rice group

Rice groups	Gel consistency
Hom Mali rice	 KDML105 RD15
Low amylose rice	 HKLG PTT1 PSL1
Intermediate amylose rice	 SPR SPR60
High amylose rice	 CNT1 CNT2 LPT123 PSL2 PTT60

Appendix D

Alkali spreading value of four rice groups

Table 1D Alkali spreading value of four rice group; Hom Mali rice, low, intermediate, and high amylose rice group

Rice groups	Gel consistency
Hom Mali rice	 KDML105 RD15
Low amylose rice	 HKLG PTT1 PSL1
Intermediate amylose rice	 SPR SPR60
High amylose rice	 CNT1 CNT2 LPT123  PSL2 PTT60

Appendix E

Effect of degree of milling on gel consistency and alkali spreading value

Table 1E Effect of degree of milling on gel consistency of rice groups

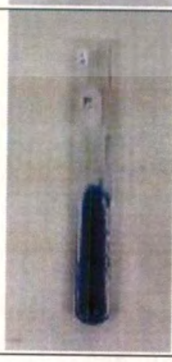
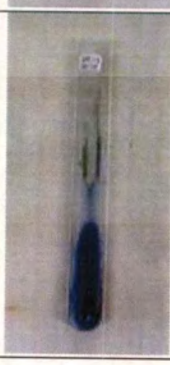
Rice group	Degree of milling (%)			
	0	5	10	15
Hom Mali rice				
Low amylose rice				
Intermediate amylose rice				
High amylose rice				

Table 2E Effect of degree of milling on alkali spreading value of rice groups

Rice group	Degree of milling (%)			
	0	5	10	15
Hom Mali rice				
Low amylose group				
Intermediate amylose group				
High amylose group				

Appendix F

RVA curve of four rice groups

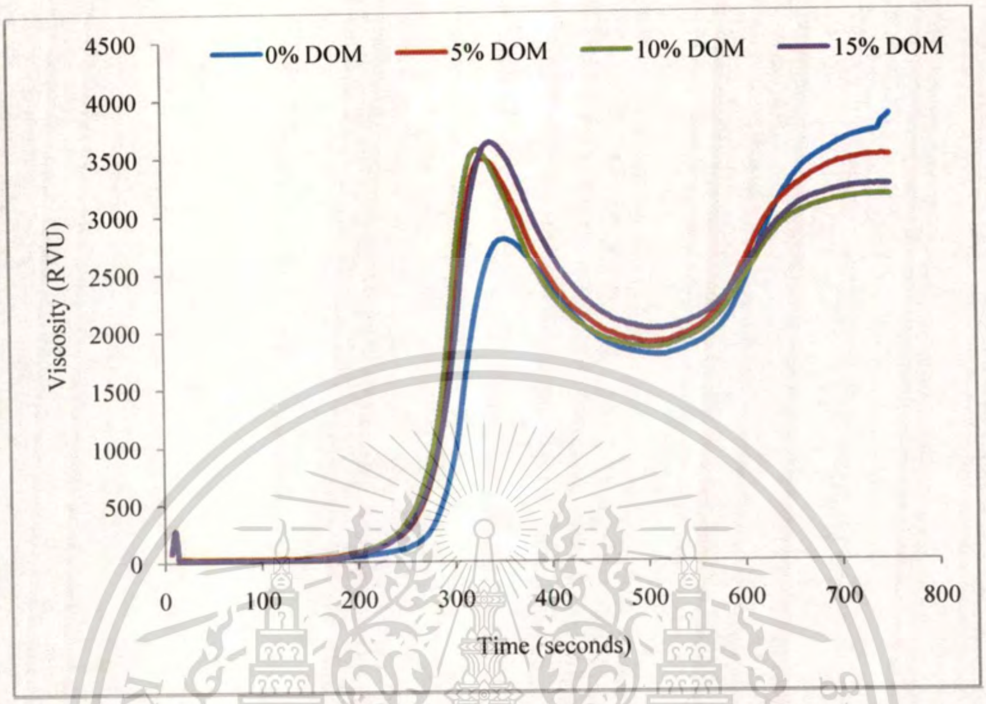


Figure 1F The RVA curves of Hom Mali rice with different degrees of milling

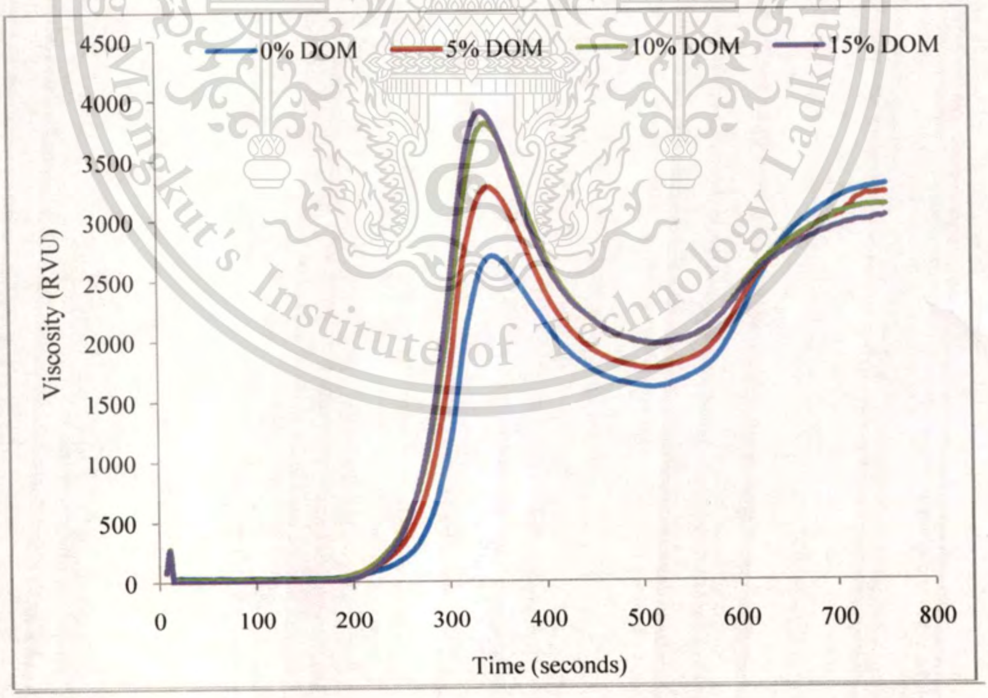


Figure 2F The RVA curves of low amylose rice group with different degrees of milling

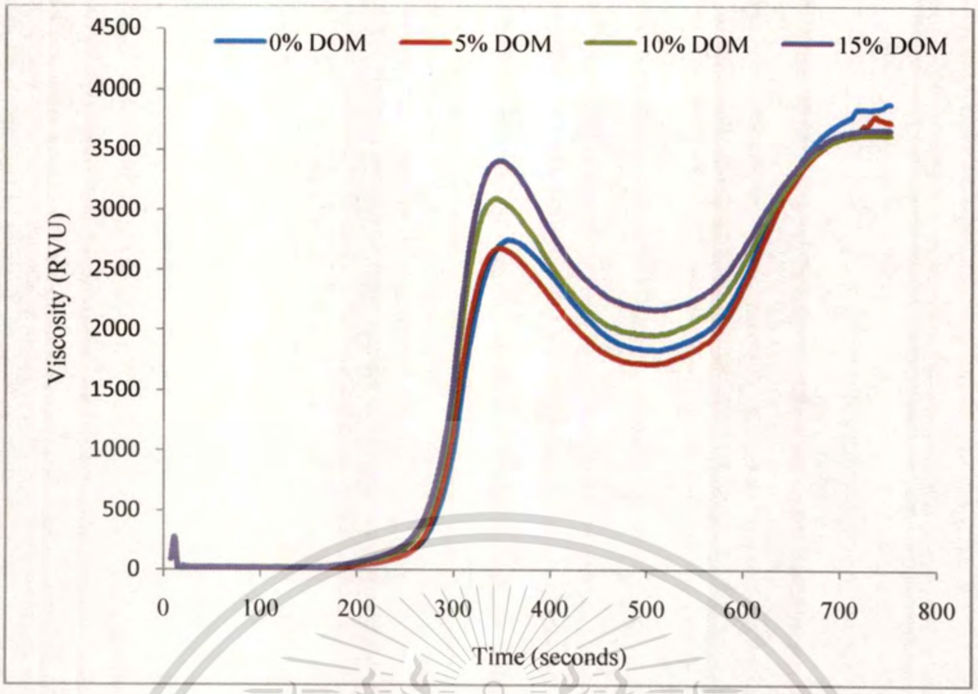


Figure 3F The RVA curves of intermediate amylose rice group with different degrees of milling

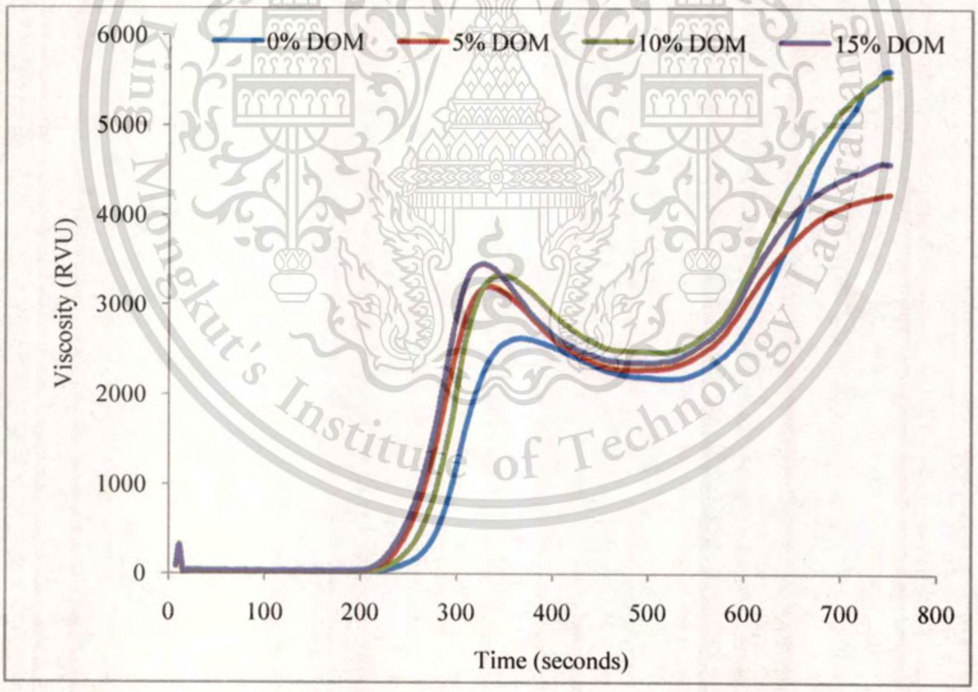
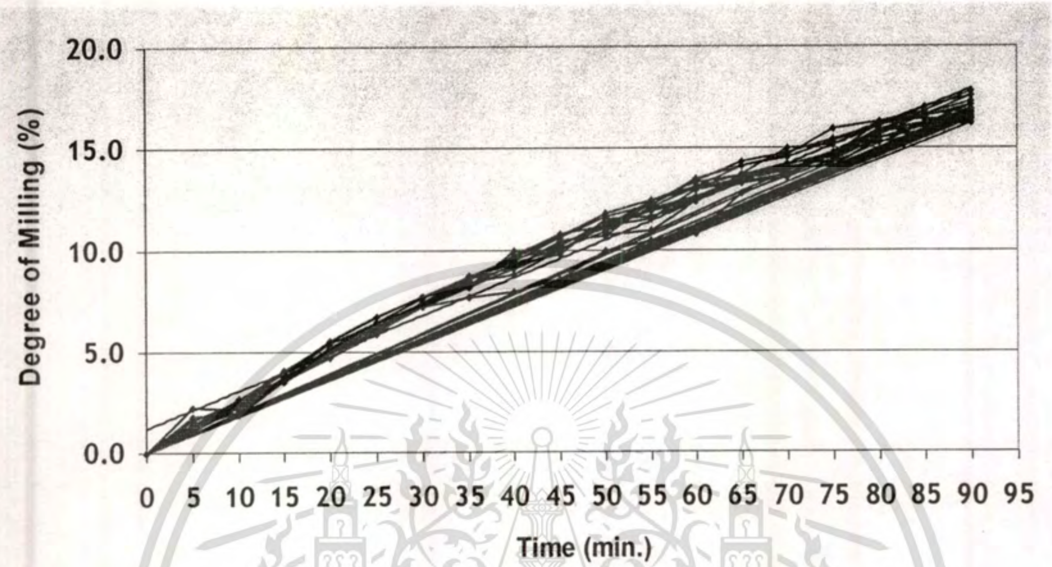


Figure 4F The RVA curves of high amylose rice group with different degrees of milling

Appendix G

Correlation between degree of milling and milling time of rice samples



Appendix H

The statistics of PLSR models for physicochemical properties prediciton using differences pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Table 1H The calibration and validation statistics of PLSR models for moisture content prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	10,000–4,000	7	0.25	0.85	0.26	0.84	-0.00	2.51
MSC		6	0.26	0.85	0.27	0.84	-0.01	2.42
SNV		6	0.26	0.85	0.27	0.84	-0.01	2.42
Sav.Gol_2nd derv**		6	0.24	0.87	0.26	0.85	0.01	2.51
MSC + Sav.Gol_2nd derv		6	0.24	0.87	0.26	0.85	0.01	2.51
SNV + Sav.Gol_2nd derv		6	0.24	0.88	0.25	0.86	0.00	2.61
Original	5,620–5,102	7	0.27	0.84	0.28	0.82	0.00	2.33
MSC		7	0.27	0.84	0.28	0.82	0.00	2.33
SNV		7	0.27	0.84	0.29	0.82	0.00	2.25
Sav.Gol_2nd derv		6	0.28	0.83	0.29	0.81	0.00	2.29
MSC + Sav.Gol_2nd derv		7	0.27	0.83	0.29	0.81	0.00	2.29
SNV + Sav.Gol_2nd derv		7	0.27	0.83	0.29	0.80	0.00	2.25
Original	**8,333–6,896**	6	**0.24**	**0.87**	**0.24**	**0.86**	**0.00**	**2.71**
MSC		5	0.25	0.86	0.26	0.85	0.00	2.51
SNV		5	0.25	0.86	0.26	0.84	0.00	2.51
Sav.Gol_2nd derv		6	0.24	0.87	0.26	0.84	0.01	2.51
MSC + Sav.Gol_2nd derv		5	0.26	0.85	0.28	0.82	0.00	2.33
SNV + Sav.Gol_2nd derv		5	0.26	0.85	0.28	0.82	0.00	2.33
Brown rice (0% degree of milling)								
Original	10,000–4,000	7	**0.29**	**0.67**	**0.34**	**0.52**	**-0.03**	**0.46**
MSC		6	0.29	0.64	0.35	0.51	-0.04	1.31
SNV		6	0.29	0.64	0.35	0.51	-0.04	1.31
Sav.Gol_2nd derv		4	0.34	0.53	0.40	0.36	-0.00	1.15
MSC + Sav.Gol_2nd derv		3	0.33	0.54	0.38	0.41	-0.01	1.21
SNV + Sav.Gol_2nd derv		3	0.33	0.54	0.38	0.41	-0.01	1.21
Original	5,620–5,102	7	0.32	0.57	0.40	0.36	-0.02	1.15
MSC		6	0.33	0.54	0.40	0.36	-0.02	1.15
SNV		6	0.33	0.54	0.39	0.37	-0.02	1.18
Sav.Gol_2nd derv		4	0.38	0.39	0.41	0.32	-0.00	1.12
MSC + Sav.Gol_2nd derv		3	0.41	0.30	0.43	0.24	-0.00	1.07
SNV + Sav.Gol_2nd derv		3	0.41	0.30	0.42	0.24	-0.00	1.07
Original	8,333–6,896	4	0.35	0.48	0.37	0.43	-0.04	1.24
MSC		3	0.38	0.41	0.40	0.36	-0.02	1.15
SNV		3	0.38	0.41	0.40	0.36	-0.02	1.15
Sav.Gol_2nd derv		3	0.39	0.37	0.41	0.30	-0.00	1.12
MSC + Sav.Gol_2nd derv		2	0.38	0.40	0.41	0.32	-0.00	1.13
SNV + Sav.Gol_2nd derv		4	0.35	0.48	0.37	0.43	-0.00	1.16

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling

**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 1H (continued)

Spectra pre-processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
Milled rice (5% degree of milling)								
Original	10,000–4,000	7	0.12	0.94	0.15	0.91	-0.00	3.06
MSC		6	0.12	0.94	0.14	0.91	-0.00	3.06
SNV		7	0.11	0.95	0.14	0.92	-0.00	3.28
Sav.Gol_2nd derv**		5	0.12	0.94	0.17	0.89	-0.02	2.70
MSC + Sav.Gol_2nd derv		6	0.08	0/97	0.16	0.91	-0.01	2.87
SNV + Sav.Gol_2nd derv		6	0.08	0.97	0.15	0.91	-0.01	2.87
Original	5,620–5,102	5	0.14	0.92	0.15	0.91	-0.01	3.06
MSC		5	0.14	0.92	0.17	0.90	-0.01	2.70
SNV		5	0.14	0.92	0.16	0.90	-0.01	2.70
Sav.Gol_2nd derv		5	0.14	0.91	0.17	0.88	-0.01	2.70
MSC + Sav.Gol_2nd derv		5	0.15	0.91	0.19	0.86	-0.00	2.42
SNV + Sav.Gol_2nd derv		6	0.13	0.93	0.18	0.87	-0.00	2.55
Original	8,333–6,896	6	0.14	0.93	0.16	0.91	-0.01	2.87
MSC		5	0.13	0.93	0.15	0.91	-0.01	2.87
SNV		5	0.13	0.93	0.15	0.91	-0.01	2.87
Sav.Gol_2nd derv		6	0.07	0.98	0.15	0.92	-0.01	3.06
MSC + Sav.Gol_2nd derv		**5**	**0.08**	**0.97**	**0.14**	**0.92**	**-0.01**	**3.28**
SNV + Sav.Gol_2nd derv		5	0.08	0.97	0.15	0.92	-0.01	3.28
Milled rice (10% degree of milling)								
Original	**10,000–4,000**	**7**	**0.09**	**0.96**	**0.11**	**0.94**	**-0.00**	**4.16**
MSC		7	0.10	0.95	0.12	0.93	-0.01	3.81
SNV		7	0.10	0.95	0.13	0.93	-0.01	3.81
Sav.Gol_2nd derv		6	0.06	0.98	0.15	0.90	0.00	3.05
MSC + Sav.Gol_2nd derv		6	0.08	0.97	0.15	0.90	0.00	3.05
SNV + Sav.Gol_2nd derv		6	0.08	0.97	0.15	0.91	0.00	3.05
Original	5,620–5,102	7	0.13	0.93	0.16	0.89	-0.00	2.86
MSC		6	0.15	0.90	0.20	0.84	-0.02	2.29
SNV		6	0.15	0.90	0.19	0.85	-0.00	2.41
Sav.Gol_2nd derv		5	0.16	0.88	0.21	0.83	0.00	0.18
MSC + Sav.Gol_2nd derv		5	0.17	0.88	0.20	0.82	0.00	0.18
SNV + Sav.Gol_2nd derv								
Original	8,333–6,896	7	0.11	0.95	0.14	0.92	0.01	3.27
MSC		6	0.10	0.95	0.13	0.93	-0.00	3.52
SNV		6	0.10	0.95	0.13	0.93	-0.00	3.52
Sav.Gol_2nd derv		6	0.09	0.96	0.17	0.88	0.01	2.69
MSC + Sav.Gol_2nd derv		4	0.12	0.94	0.16	0.89	0.00	2.86
SNV + Sav.Gol_2nd derv		4	0.12	0.94	0.16	0.89	0.00	2.86

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling

**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 1H (continued)

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
Milled rice								
(15% degree of milling)								
Original	10,000–4,000	5	0.17	0.90	0.19	0.86	0.00	2.62
MSC		7	0.15	0.92	0.19	0.88	0.00	2.62
SNV		5	0.18	0.86	0.21	0.85	-0.00	2.37
Sav.Gol_2nd derv**		4	0.17	0.90	0.21	0.85	0.23	2.37
MSC + Sav.Gol_2nd derv		6	0.10	0.96	0.19	0.87	0.01	2.62
SNV + Sav.Gol_2nd derv		6	0.10	0.96	0.19	0.87	0.01	2.62
Original	5,620–5,102	6	0.17	0.90	0.20	0.87	0.00	2.49
MSC		3	0.20	0.86	0.21	0.85	-0.03	2.36
SNV		3	0.20	0.86	0.21	0.85	-0.03	2.36
Sav.Gol_2nd derv		6	0.16	0.91	0.20	0.87	-0.00	2.49
MSC + Sav.Gol_2nd derv		5	0.17	0.90	0.21	0.86	-0.01	2.37
SNV + Sav.Gol_2nd derv		5	0.17	0.90	0.21	0.85	-0.0	2.37
Original	**8,333–6,896**	**7**	**0.13**	**0.94**	**0.16**	**0.92**	**0.00**	**3.11**
MSC		5	0.16	0.92	0.19	0.89	-0.00	2.62
SNV		5	0.16	0.92	0.18	0.89	-0.00	2.62
Sav.Gol_2nd derv		5	0.14	0.94	0.21	0.86	-0.00	2.37
MSC + Sav.Gol_2nd derv		4	0.14	0.93	0.19	0.87	-0.00	2.67
SNV + Sav.Gol_2nd derv		4	0.14	0.93	0.20	0.86	-0.00	2.67

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling
**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 2H The calibration and validation statistics of PLSR models for protein content prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	**10,000–4,000**	**6**	**0.24**	**0.87**	**0.23**	**0.88**	**-0.02**	**2.90**
MSC		4	0.29	0.84	0.29	0.83	-0.01	2.31
SNV		4	0.30	0.83	0.29	0.83	-0.01	2.31
Sav.Gol_2nd derv**		5	0.27	0.85	0.28	0.82	-0.02	2.38
MSC + Sav.Gol_2nd derv		5	0.27	0.86	0.26	0.83	-0.03	2.35
SNV + Sav.Gol_2nd derv		5	0.27	0.86	0.26	0.83	-0.03	2.35
Brown rice (0% degree of milling)								
Original	10,000–4,000	15	0.97	0.95	1.73	0.89	-0.07	2.49
MSC		**13**	**0.95**	**0.98**	**1.51**	**0.89**	**-0.07**	**2.84**
SNV		12	1.14	0.94	1.79	0.88	-0.02	2.41
Sav.Gol_2nd derv		8	1.27	0.92	2.35	0.74	0.10	1.83
MSC + Sav.Gol_2nd derv		8	1.23	0.93	2.28	0.75	0.08	1.83
SNV + Sav.Gol_2nd derv		8	1.26	0.92	2.37	0.74	0.08	1.82
Milled rice (5% degree of milling)								
Original	10,000–4,000	13	1.14	0.94	1.46	0.88	-0.11	2.75
MSC		11	1.19	0.93	1.52	0.89	-0.08	2.81
SNV		**11**	**1.18**	**0.93**	**1.51**	**0.89**	**-0.08**	**2.83**
Sav.Gol_2nd derv		6	1.89	0.83	2.47	0.71	-0.16	1.74
MSC + Sav.Gol_2nd derv		8	1.24	0.93	2.24	0.75	-0.24	1.92
SNV + Sav.Gol_2nd derv		8	1.23	0.93	2.29	0.75	-0.24	1.88
Milled rice (10% degree of milling)								
Original	10,000–4,000	14	1.06	0.94	1.60	0.87	0.02	2.56
MSC		**13**	**1.01**	**0.95**	**1.64**	**0.87**	**0.10**	**2.58**
SNV		11	1.36	0.91	1.78	0.85	0.52	2.38
Sav.Gol_2nd derv		8	1.47	0.89	2.36	0.74	0.17	1.79
MSC + Sav.Gol_2nd derv		8	1.31	0.91	2.10	0.79	0.12	1.75
SNV + Sav.Gol_2nd derv		8	1.29	0.92	2.07	0.80	0.12	1.73
Milled rice (15% degree of milling)								
Original	10,000–4,000	12	0.30	0.94	0.92	0.60	-0.12	2.00
MSC		**10**	**0.53**	**0.91**	**0.89**	**0.76**	**-0.50**	**2.09**
SNV		10	0.79	0.82	0.95	0.74	-0.07	1.96
Sav.Gol_2nd derv		4	1.17	0.61	1.24	0.57	0.04	1.50
MSC + Sav.Gol_2nd derv		4	1.14	0.64	1.20	0.59	-0.06	2.01
SNV + Sav.Gol_2nd derv		4	1.11	0.64	1.20	0.59	-0.05	2.00

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling
**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 3H The calibration and validation statistics of PLSR models for apparent amylose content prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre-processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	10,000–4,000	7	2.26	0.69	2.37	0.66	-0.01	1.64
MSC		**7**	**2.01**	**0.75**	**2.14**	**0.72**	**-0.05**	**1.88**
SNV		7	2.00	0.75	2.13	0.72	-0.05	1.87
Sav.Gol_2nd derv**		7	1.91	0.78	2.48	0.62	0.04	1.60
MSC + Sav.Gol_2nd derv		7	1.84	0.79	2.42	0.64	-0.05	1.64
SNV + Sav.Gol_2nd derv		6	2.14	0.72	2.45	0.63	0.08	1.62
Original	8,620–5,128	7	2.21	0.70	2.34	0.67	-0.02	1.70
MSC		7	2.03	0.75	2.13	0.72	-0.22	1.87
SNV		7	2.03	0.75	2.13	0.73	-0.22	1.87
Sav.Gol_2nd derv		7	2.06	0.74	2.50	0.62	-0.12	1.59
MSC + Sav.Gol_2nd derv		7	2.01	0.75	2.44	0.64	-0.12	1.63
SNV + Sav.Gol_2nd derv		7	2.01	0.75	2.44	0.64	-0.12	1.63
Original	7,142–4,012	7	2.18	0.71	2.29	0.68	0.06	1.74
MSC		7	2.06	0.74	2.17	0.71	0.06	1.83
SNV		7	2.04	0.75	2.15	0.72	0.07	1.85
Sav.Gol_2nd derv		7	2.05	0.74	2.46	0.63	0.09	1.62
MSC + Sav.Gol_2nd derv		7	1.90	0.78	2.36	0.65	0.05	1.68
SNV + Sav.Gol_2nd derv		7	1.90	0.78	2.35	0.66	0.05	1.69
Brown rice (0% degree of milling)								
Original	10,000–4,000	1	1.77	0.81	1.83	0.81	0.21	3.88
MSC		4	1.28	0.90	1.48	0.87	0.30	2.62
SNV		4	1.28	0.90	1.47	0.87	0.30	2.64
Sav.Gol_2nd derv		5	1.10	0.93	1.69	0.83	0.26	2.30
MSC + Sav.Gol_2nd derv		5	1.20	0.91	1.81	0.81	0.25	2.14
SNV + Sav.Gol_2nd derv		5	1.20	0.91	1.81	0.81	0.25	2.14
Original	8,620–5,128	2	1.68	0.83	1.77	0.82	0.28	2.19
MSC		7	1.16	0.92	1.51	0.88	0.22	2.57
SNV		7	1.16	0.92	1.51	0.87	0.21	2.57
Sav.Gol_2nd derv		5	1.18	0.92	1.71	0.83	0.34	2.27
MSC + Sav.Gol_2nd derv		5	1.31	0.90	1.86	0.80	0.26	2.09
SNV + Sav.Gol_2nd derv		5	1.31	0.90	1.86	0.80	0.26	2.09
Original	7,142–4,012	4	1.42	0.88	1.60	0.85	0.29	2.43
MSC		4	1.42	0.88	1.60	0.85	0.29	2.43
SNV		**5**	**1.27**	**0.90**	**1.47**	**0.87**	**0.23**	**2.64**
Sav.Gol_2nd derv		3	1.62	0.84	1.82	0.81	0.38	2.13
MSC + Sav.Gol_2nd derv		3	1.67	0.83	1.93	0.79	0.25	2.01
SNV + Sav.Gol_2nd derv		3	1.65	0.84	1.91	0.79	0.25	2.03
Milled rice (5% degree of milling)								
Original	10,000–4,000	3	1.94	0.68	2.21	0.60	-0.04	1.43
MSC		3	1.78	0.73	2.15	0.64	0.11	1.47
SNV		3	1.78	0.73	2.13	0.63	0.11	1.47
Sav.Gol_2nd derv		3	1.94	0.68	2.22	0.56	0.09	1.42
MSC + Sav.Gol_2nd derv		**7**	**0.40**	**0.98**	**2.04**	**0.66**	**0.18**	**1.55**
SNV + Sav.Gol_2nd derv		7	0.40	0.98	2.02	0.65	0.18	1.55
Original	8,620–5,128	4	1.83	0.71	2.10	0.64	-0.05	1.50
MSC		3	1.85	0.71	2.10	0.64	-0.04	1.50
SNV		3	1.85	0.71	2.09	0.65	0.03	1.51
Sav.Gol_2nd derv**		3	1.94	0.68	2.27	0.55	0.08	1.39

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling

**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 3H (continued)

Spectra pre-processing	Wavenumbers (cm^{-1})	PC	Calibration SEC	Calibration r^2cal	Validation SEP	Validation r^2val	Bias	RPD
Milled rice (5% degree of milling)								
MSC + Sav.Gol_2nd derv	8,620–5,128	4	1.35	0.85	2.22	0.58	0.07	1.42
SNV + Sav.Gol_2nd derv		4	1.35	0.85	2.18	0.61	0.07	1.42
Original	7,142–4,012	3	1.91	0.69	2.18	0.61	-0.07	1.45
MSC		**3**	**1.73**	**0.75**	**1.97**	**0.68**	**0.08**	**1.60**
SNV		3	1.73	0.75	1.99	0.68	0.08	1.60
Sav.Gol_2nd derv		2	2.01	0.66	2.21	0.59	0.01	1.43
MSC + Sav.Gol_2nd derv		3	1.81	0.72	2.11	0.63	0.30	1.48
SNV + Sav.Gol_2nd derv		3	1.81	0.71	2.11	0.63	0.30	1.48
Milled rice (10% degree of milling)								
Original	10,000–4,000	4	1.01	0.89	1.17	0.86	-0.16	2.20
MSC		5	1.17	0.85	1.58	0.74	0.00	1.63
SNV		5	1.17	0.85	1.63	0.71	0.00	1.58
Sav.Gol_2nd derv		5	0.81	0.93	1.68	0.70	-0.18	1.53
MSC + Sav.Gol_2nd derv		5	0.96	0.90	1.67	0.73	-0.11	1.54
SNV + Sav.Gol_2nd derv		5	0.96	0.90	1.70	0.70	-0.11	1.51
Original	**8,620–5,128**	**3**	**1.02**	**0.89**	**1.14**	**0.88**	**-0.15**	**2.26**
MSC		3	1.31	0.82	1.59	0.73	-0.00	1.62
SNV		6	1.12	0.87	1.52	0.76	-0.09	1.69
Sav.Gol_2nd derv		5	0.96	0.90	1.74	0.70	-0.19	1.45
MSC + Sav.Gol_2nd derv		5	0.88	0.92	1.64	0.73	-0.22	1.57
SNV + Sav.Gol_2nd derv		5	0.85	0.92	1.70	0.70	-0.22	1.57
Original	7,142–4,012	3	1.03	0.86	1.15	0.85	-0.15	2.24
MSC		5	1.24	0.83	1.65	0.71	-0.04	1.56
SNV		4	1.28	0.82	1.62	0.74	-0.05	0.06
Sav.Gol_2nd derv		5	1.10	0.87	1.83	0.61	-0.12	1.41
MSC + Sav.Gol_2nd derv		3	1.45	0.77	1.81	0.65	-0.16	1.42
SNV + Sav.Gol_2nd derv		3	1.45	0.77	1.77	0.67	-0.16	1.42
Milled rice (15% degree of milling)								
Original	10,000–4,000	1	1.67	0.75	1.76	0.73	0.07	1.65
MSC		7	1.15	0.88	1.80	0.72	0.29	1.61
SNV		7	1.15	0.88	1.54	0.79	0.29	1.88
Sav.Gol_2nd derv**		3	1.88	0.68	2.17	0.58	0.11	1.34
MSC + Sav.Gol_2nd derv		5	1.07	0.90	2.26	0.56	0.20	1.28
SNV + Sav.Gol_2nd derv		5	1.07	0.90	2.16	0.59	0.20	1.34
Original	8,620–5,128	7	1.16	0.88	1.50	0.80	0.23	1.93
MSC		6	1.30	0.85	1.67	0.75	0.18	1.74
SNV		6	1.30	0.85	1.77	0.72	0.18	1.64
Sav.Gol_2nd derv		4	1.38	0.83	2.07	0.62	0.42	1.40
MSC + Sav.Gol_2nd derv		5	1.09	0.89	2.02	0.58	0.21	1.44
SNV + Sav.Gol_2nd derv		5	1.09	0.89	2.12	0.60	0.21	1.37
Original	**7,142–4,012**	**7**	**1.18**	**0.87**	**1.49**	**0.81**	**0.22**	**1.95**
MSC		6	1.37	0.83	1.74	0.73	0.17	1.67
SNV		6	1.37	0.83	1.69	0.75	0.17	1.72
Sav.Gol_2nd derv		2	1.92	0.67	2.19	0.58	0.12	1.32
MSC + Sav.Gol_2nd derv		5	1.22	0.87	2.15	0.59	0.31	1.35
SNV + Sav.Gol_2nd derv		5	1.22	0.87	2.10	0.61	0.31	1.35

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling

**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 4H The calibration and validation statistics of PLSR models for alkali spreading value prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	10,000–4,000	6	1.09	0.64	1.13	0.62	0.01	1.60
MSC		**7**	**1.01**	**0.69**	**1.08**	**0.65**	**-0.00**	**1.63**
SNV		7	1.01	0.69	1.10	0.65	-0.00	1.64
Sav.Gol_2nd derv**		6	1.06	0.66	1.17	0.58	-0.00	1.64
MSC + Sav.Gol_2nd derv		6	0.97	0.72	1.14	0.61	0.00	1.58
SNV + Sav.Gol_2nd derv		6	0.90	0.76	1.15	0.60	-0.01	1.57
Brown rice (0% degree of milling)								
Original	10,000–4,000	1	0.85	0.76	0.89	0.75	-0.05	2.00
MSC		6	0.59	0.89	0.71	0.84	-0.04	2.52
SNV		**7**	**0.52**	**0.91**	**0.67**	**0.86**	**-0.03**	**2.69**
Sav.Gol_2nd derv		5	0.48	0.93	0.87	0.76	0.05	2.05
MSC + Sav.Gol_2nd derv		6	0.35	0.96	0.90	0.75	0.05	1.99
SNV + Sav.Gol_2nd derv		6	0.35	0.96	0.90	0.75	0.05	1.99
Milled rice (5% degree of milling)								
Original	10,000–4,000	**3**	**0.37**	**0.92**	**0.43**	**0.90**	**-0.09**	**1.26**
MSC		7	0.35	0.92	0.52	0.88	-0.06	1.05
SNV		7	0.36	0.92	0.52	0.83	-0.06	1.05
Sav.Gol_2nd derv		5	0.24	0.97	0.55	0.83	-0.03	0.99
MSC + Sav.Gol_2nd derv		4	0.31	0.94	0.56	0.83	-0.02	0.97
SNV + Sav.Gol_2nd derv		4	0.31	0.94	0.56	0.83	-0.02	0.97
Milled rice (10% degree of milling)								
Original	10,000–4,000	3	0.56	0.86	0.63	0.82	0.06	2.01
MSC		**6**	**0.44**	**0.91**	**0.52**	**0.86**	**0.14**	**2.43**
SNV		5	0.46	0.90	0.53	0.88	0.11	2.39
Sav.Gol_2nd derv		5	0.43	0.92	0.68	0.81	0.14	1.86
MSC + Sav.Gol_2nd derv		5	0.39	0.93	0.55	0.87	0.14	2.30
SNV + Sav.Gol_2nd derv		5	0.39	0.93	0.56	0.86	0.14	2.26
Milled rice (15% degree of milling)								
Original	10,000–4,000	3	0.77	0.76	0.85	0.72	0.20	1.91
MSC		**6**	**0.66**	**0.82**	**0.83**	**0.73**	**0.14**	**1.96**
SNV		5	0.69	0.81	0.86	0.70	0.14	1.96
Sav.Gol_2nd derv		5	0.45	0.92	0.84	0.70	0.14	1.94
MSC + Sav.Gol_2nd derv		4	0.60	0.85	0.86	0.71	0.08	1.89
SNV + Sav.Gol_2nd derv		5	0.50	0.90	0.84	0.72	0.10	1.94

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling
**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 5H The calibration and validation statistics of PLSR models for gel consistency prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	10,000–4,000	6	6.59	0.68	6.89	0.66	0.06	1.65
MSC		7	6.21	0.72	6.61	0.68	0.03	1.72
SNV		7	6.21	0.72	6.62	0.68	0.03	1.72
Sav.Gol_2nd derv**		7	5.22	0.80	6.84	0.66	0.32	1.67
MSC + Sav.Gol_2nd derv		**7**	**5.13**	**0.81**	**6.84**	**0.66**	**0.22**	**1.66**
SNV + Sav.Gol_2nd derv		**7**	**5.13**	**0.81**	**6.84**	**0.66**	**0.22**	**1.66**
Brown rice (0% degree of milling)								
Original	10,000–4,000	1	5.65	0.77	5.86	0.76	0.20	1.79
MSC		4	5.03	0.82	5.67	0.78	0.26	1.85
SNV		**4**	**5.01**	**0.82**	**5.63**	**0.78**	**0.26**	**1.87**
Sav.Gol_2nd derv		3	5.66	0.77	6.64	0.69	0.21	1.58
MSC + Sav.Gol_2nd derv		3	5.84	0.76	6.70	0.66	0.37	1.57
SNV + Sav.Gol_2nd derv		3	5.84	0.76	6.71	0.66	0.37	1.67
Milled rice (5% degree of milling)								
Original	10,000–4,000	**7**	**3.40**	**0.88**	**4.86**	**0.77**	**0.73**	**1.86**
MSC		7	3.70	0.86	5.03	0.75	0.44	1.80
SNV		7	3.69	0.86	5.03	0.75	0.44	1.80
Sav.Gol_2nd derv		3	5.17	0.73	5.90	0.66	0.99	1.53
MSC + Sav.Gol_2nd derv		4	3.81	0.85	5.52	0.70	0.36	1.64
SNV + Sav.Gol_2nd derv		4	3.81	0.85	5.52	0.70	0.36	1.64
Milled rice (10% degree of milling)								
Original	10,000–4,000	6	2.79	0.91	3.60	0.84	-0.18	2.14
MSC		6	2.98	0.89	3.83	0.82	-0.30	2.02
SNV		6	2.98	0.89	3.70	0.82	-0.31	2.09
Sav.Gol_2nd derv		5	2.03	0.95	3.29	0.88	0.11	2.35
MSC + Sav.Gol_2nd derv		5	2.00	0.95	3.30	0.88	0.09	2.34
SNV + Sav.Gol_2nd derv		**5**	**2.01**	**0.95**	**3.20**	**0.88**	**0.08**	**2.41**
Milled rice (15% degree of milling)								
Original	10,000–4,000	**7**	**3.38**	**0.91**	**4.35**	**0.85**	**-0.48**	**2.27**
MSC		7	3.56	0.90	4.42	0.84	1.88	2.23
SNV		7	3.55	3.90	4.56	0.83	0.19	2.16
Sav.Gol_2nd derv		5	3.11	0.92	5.39	0.78	0.28	1.83
MSC + Sav.Gol_2nd derv		5	2.95	0.93	5.24	0.78	0.47	1.88
SNV + Sav.Gol_2nd derv		5	2.95	0.93	5.27	0.79	0.46	1.87

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling
**Savitzky Golay 2^{nd} derivative, 10 points averaging, 2^{nd} polynomial order

Table 6H The calibration and validation statistics of PLSR models for peak viscosity prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	10,000–4,000	5	266	0.87	278	0.86	6.07	2.63
MSC		5	266	0.87	276	0.86	6.07	2.64
SNV		7	228	0.91	275	0.86	6.07	2.65
Sav.Gol_2nd derv**		7	233	0.92	279	0.89	-40.33	2.99
MSC + Sav.Gol_2nd derv		5	266	0.87	278	0.87	6.07	2.63
SNV + Sav.Gol_2nd derv		**7**	**219**	**0.93**	**267**	**0.90**	**-21.5**	**3.34**
Brown rice (0% degree of milling)								
Original	10,000–4,000	3	135	0.70	154	0.62	-12.4	1.68
MSC		4	117	0.77	137	0.73	-13.8	1.89
SNV		**5**	**115**	**0.78**	**137**	**0.71**	**-11.9**	**1.89**
Sav.Gol_2nd derv		7	25	0.98	142	0.70	-1.52	1.83
MSC + Sav.Gol_2nd derv		5	68	0.92	145	0.72	-4.41	1.79
SNV + Sav.Gol_2nd derv		4	106	0.81	147	0.68	-5.78	1.76
Milled rice (5% degree of milling)								
Original	10,000–4,000	**7**	**118**	**0.90**	**153**	**0.83**	**15.82**	**2.27**
MSC		6	130	0.87	159	0.82	15.06	2.19
SNV		6	131	0.87	159	0.82	15.06	2.19
Sav.Gol_2nd derv		3	182	0.75	208	0.69	16.29	1.67
MSC + Sav.Gol_2nd derv		4	157	0.82	201	0.71	5.23	1.73
SNV + Sav.Gol_2nd derv		4	157	0.82	201	0.71	5.23	1.73
Milled rice (10% degree of milling)								
Original	10,000–4,000	1	190	0.81	201	0.81	6.48	1.86
MSC		**7**	**147**	**0.89**	**209**	**0.78**	**4.22**	**1.79**
SNV		7	147	0.89	220	0.79	4.04	1.70
Sav.Gol_2nd derv		6	61	0.98	218	0.76	10.61	1.72
MSC + Sav.Gol_2nd derv		6	59	0.98	220	0.75	8.90	1.70
SNV + Sav.Gol_2nd derv		6	59	0.98	217	0.76	8.91	1.72
Milled rice (15% degree of milling)								
Original	10,000–4,000	6	**172**	0.89	208	**0.84**	-35.35	**2.34**
MSC		6	178	0.88	223	0.82	-37.93	2.18
SNV		5	187	0.87	235	0.80	-47.80	2.07
Sav.Gol_2nd derv		5	137	0.93	262	0.75	-61.88	1.86
MSC + Sav.Gol_2nd derv		5	136	0.93	262	0.75	-61.88	1.86
SNV + Sav.Gol_2nd derv		5	136	0.93	259	0.75	-62.11	1.88

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling

**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 7H The calibration and validation statistics of PLSR models for breakdown viscosity prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	**10,000–4,000**	**11**	**118**	**0.92**	**135**	**0.90**	**-19.31**	**3.00**
MSC		7	131	0.90	145	0.88	-22.71	2.80
SNV		7	132	0.90	145	0.88	-25.39	2.79
Sav.Gol_2nd derv**		8	95	0.95	148	0.88	5.72	2.75
MSC + Sav.Gol_2nd derv		5	266	0.87	276	0.86	6.07	2.64
SNV + Sav.Gol_2nd derv		8	91	0.95	139	0.89	0.58	2.90
Brown rice (0% degree of milling)								
Original	10,000–4,000	7	61	0.92	75	0.89	-9.51	2.71
MSC		**5**	**60**	**0.92**	**71**	**0.90**	**-7.15**	**2.87**
SNV		**5**	**60**	**0.92**	**71**	**0.90**	**-7.15**	**2.87**
Sav.Gol_2nd derv		6	26	0.98	81	0.88	-9.31	2.51
MSC + Sav.Gol_2nd derv		5	51	0.95	86	0.86	-7.79	2.37
SNV + Sav.Gol_2nd derv		5	51	0.95	90	0.84	-7.83	2.26
Milled rice (5% degree of milling)								
Original	10,000–4,000	1	105	0.78	114	0.77	23.18	1.90
MSC		7	72	0.90	102	0.81	-3.16	2.12
SNV		7	72	0.90	102	0.81	-3.16	2.12
Sav.Gol_2nd derv		6	33	0.98	99	0.81	-2.65	2.19
MSC + Sav.Gol_2nd derv		**6**	**36**	**0.97**	**98**	**0.82**	**-3.29**	**2.21**
SNV + Sav.Gol_2nd derv		**6**	**36**	**0.97**	**98**	**0.82**	**-3.29**	**2.21**
Milled rice (10% degree of milling)								
Original	10,000–4,000	**5**	**88**	**0.85**	**106**	**0.79**	**-15.64**	**1.83**
MSC		5	97	0.82	118	0.74	-8.48	1.64
SNV		5	97	0.82	119	0.76	-8.50	1.63
Sav.Gol_2nd derv		5	73	0.90	116	0.74	-10.8	1.67
MSC + Sav.Gol_2nd derv		5	62	0.92	112	0.76	-15.5	1.73
SNV + Sav.Gol_2nd derv		5	62	0.93	113	0.77	-15.5	1.74
Milled rice (15% degree of milling)								
Original	10,000–4,000	7	**93.8**	**0.91**	**121**	**0.86**	**-1.03**	**2.48**
MSC		7	94.6	0.91	127	0.85	-19.90	2.37
SNV		7	94.5	0.91	130	0.84	-19.94	2.31
Sav.Gol_2nd derv		5	94.4	0.91	179	0.70	7.47	1.68
MSC + Sav.Gol_2nd derv		5	92	0.92	173	0.72	-1.66	1.74
SNV + Sav.Gol_2nd derv		5	92	0.92	169	0.73	-1.65	1.78

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling
**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 8H The calibration and validation statistics of PLSR models for setback viscosity prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre-processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	10,000–4,000	10	265	0.83	306	0.77	-55.00	1.98
MSC		10	211	0.86	248	0.81	43.70	2.45
SNV		**13**	**175**	**0.90**	**233**	**0.83**	**26.80**	**2.60**
Sav.Gol_2nd derv**		6	241	0.81	278	0.75	42.50	2.18
MSC + Sav.Gol_2nd derv		6	265	0.83	322	0.75	44.60	2.24
SNV + Sav.Gol_2nd derv		6	265	0.828	322	0.75	40.10	2.20
Brown rice (0% degree of milling)								
Original	10,000–4,000	7	212	0.91	267	0.86	35.55	2.64
MSC		**4**	**219**	**0.91**	**245**	**0.88**	**33.47**	**2.88**
SNV		**4**	**219**	**0.91**	**244**	**0.88**	**33.47**	**2.88**
Sav.Gol_2nd derv		3	279	0.85	325	0.80	52.80	2.18
MSC + Sav.Gol_2nd derv		3	256	0.87	303	0.82	30.7	2.34
SNV + Sav.Gol_2nd derv		5	180	0.94	292	0.84	37.1	2.42
Milled rice (5% degree of milling)								
Original	10,000–4,000	1	338	0.77	356	0.77	-41.3	1.82
MSC		6	288	0.84	372	0.73	-8.89	1.74
SNV		6	288	0.84	372	0.74	-8.89	1.74
Sav.Gol_2nd derv		7	73	0.92	368	0.74	33.40	1.76
MSC + Sav.Gol_2nd derv		7	73	0.92	368	0.74	33.40	1.76
SNV + Sav.Gol_2nd derv		**7**	**76**	**0.98**	**356**	**0.76**	**29.5**	**1.82**
Milled rice (10% degree of milling)								
Original	10,000–4,000	**6**	**195**	**0.92**	**237**	**0.89**	**-43.26**	**2.68**
MSC		7	189	0.92	255	0.87	-24.22	2.57
SNV		5	225	0.89	272	0.85	-21.40	2.41
Sav.Gol_2nd derv		5	210	0.91	342	0.76	-18.44	1.92
MSC + Sav.Gol_2nd derv		4	241	0.88	388	0.69	-3.92	1.69
SNV + Sav.Gol_2nd derv		5	184	0.93	309	0.80	-11.30	2.12
Milled rice (15% degree of milling)								
Original	10,000–4,000	1	410	0.70	433	0.68	-11.35	1.60
MSC		7	243	0.90	394	0.74	9.99	1.75
SNV		**7**	**242**	**0.90**	**361**	**0.78**	**10.21**	**1.91**
Sav.Gol_2nd derv		5	188	0.94	420	0.70	-17.17	1.65
MSC + Sav.Gol_2nd derv		5	197	0.93	410	0.71	-12.76	1.69
SNV + Sav.Gol_2nd derv		3	362	0.77	425	0.69	12.55	1.63

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling

**Savitzky Golay 2^{nd} derivative, 10 points averaging, 2^{nd} polynomial order

Table 9H The calibration and validation statistics of PLSR models for final viscosity prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	10,000–4,000	7	247	0.67	260	0.64	-9.41	1.63
MSC		**7**	**242**	**0.68**	**252**	**0.64**	**-5.38**	**1.69**
SNV		7	242	0.68	254	0.65	-5.36	1.68
Sav.Gol_2nd derv**		6	241	0.68	265	0.62	-9.92	1.61
MSC + Sav.Gol_2nd derv		3	260	0.63	267	0.61	-10.67	1.60
SNV + Sav.Gol_2nd derv		3	260	0.63	268	0.61	-10.68	1.59
Brown rice (0% degree of milling)								
Original	10,000–4,000	3	131	0.73	140	0.68	-5.88	1.49
MSC		6	115	0.79	149	0.67	-5.00	1.40
SNV		7	109	0.81	146	0.67	2.26	1.43
Sav.Gol_2nd derv		**5**	**69**	**0.93**	**141**	**0.71**	**0.84**	**1.48**
MSC + Sav.Gol_2nd derv		7	19	0.97	143	0.68	0.18	1.46
SNV + Sav.Gol_2nd derv		5	61	0.94	146	0.68	1.74	1.43
Milled rice (5% degree of milling)								
Original	10,000–4,000	1	121	0.83	126	0.82	-1.11	2.31
MSC		**7**	**116**	**0.84**	**151**	**0.74**	**-11.65**	**1.92**
SNV		**7**	**116**	**0.84**	**151**	**0.74**	**-11.65**	**1.92**
Sav.Gol_2nd derv		3	139	0.77	155	0.72	-7.50	1.87
MSC + Sav.Gol_2nd derv		3	132	0.79	152	0.73	-11.42	1.91
SNV + Sav.Gol_2nd derv		3	132	0.79	152	0.73	-11.42	1.91
Milled rice (10% degree of milling)								
Original	10,000–4,000	1	146	0.87	153	0.86	19.00	2.68
MSC		4	157	0.85	183	0.80	10.11	2.24
SNV		5	149	0.86	179	0.81	9.57	2.29
Sav.Gol_2nd derv		5	104	0.93	167	0.83	2.85	2.46
MSC + Sav.Gol_2nd derv		**3**	**151**	**0.86**	**181**	**0.80**	**17.00**	**2.68**
SNV + Sav.Gol_2nd derv		5	108	0.93	179	0.81	2.69	2.29
Milled rice (15% degree of milling)								
Original	10,000–4,000	1	242	0.78	249	0.77	34.82	2.00
MSC		**7**	**162**	**0.90**	**222**	**0.82**	**3.17**	**2.25**
SNV		7	162	0.90	224	0.81	3.05	2.23
Sav.Gol_2nd derv		3	244	0.77	277	0.71	58.23	1.80
MSC + Sav.Gol_2nd derv		3	216	0.82	253	0.77	39.58	1.97
SNV + Sav.Gol_2nd derv		3	216	0.82	271	0.73	39.42	1.84

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling
**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Table 10H The calibration and validation statistics of PLSR models for pasting temperature prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	10,000–4,000	12	0.89	0.78	1.05	0.70	0.14	1.69
MSC		11	0.74	0.83	0.86	0.77	0.17	2.06
SNV		11	0.48	0.82	0.55	0.76	0.11	2.11
Sav.Gol_2nd derv**		**6**	**0.56**	**0.88**	**0.66**	**0.84**	**0.03**	**2.69**
MSC + Sav.Gol_2nd derv		6	0.60	0.88	0.70	0.71	0.03	2.01
SNV + Sav.Gol_2nd derv		6	0.60	0.88	0.70	0.84	0.03	2.12
Brown rice (0% degree of milling)								
Original	10,000–4,000	1	0.89	0.71	0.92	0.70	-0.01	1.68
MSC		3	0.83	0.75	0.93	0.71	0.03	1.66
SNV		2	0.90	0.70	0.96	0.69	0.09	1.61
Sav.Gol_2nd derv		2	0.84	0.74	0.91	0.71	0.07	1.70
MSC + Sav.Gol_2nd derv		**5**	**0.45**	**0.93**	**0.86**	**0.74**	**-0.01**	**1.80**
SNV + Sav.Gol_2nd derv		3	0.73	0.80	0.88	0.72	0.01	1.76
Milled rice (5% degree of milling)								
Original	10,000–4,000	1	0.44	0.68	0.46	0.67	-0.07	1.48
MSC		4	0.44	0.69	0.51	0.58	-0.08	1.34
SNV		4	0.44	0.69	0.51	0.58	-0.08	1.34
Sav.Gol_2nd derv		**7**	**0.07**	**0.99**	**0.43**	**0.73**	**-0.02**	**1.59**
MSC + Sav.Gol_2nd derv		7	0.08	0.97	0.46	0.67	-0.02	1.48
SNV + Sav.Gol_2nd derv		7	0.08	0.97	0.46	0.67	-0.02	1.48
Milled rice (10% degre of milling)								
Original	10,000–4,000	7	0.38	0.87	0.49	0.79	-0.01	1.94
MSC		**7**	**0.38**	**0.88**	**0.46**	**0.82**	**-0.02**	**2.06**
SNV		**7**	**0.37**	**0.88**	**0.46**	**0.80**	**-0.02**	**2.06**
Sav.Gol_2nd derv		7	0.16	0.98	0.59	0.70	-0.05	1.61
MSC + Sav.Gol_2nd derv		7	0.16	0.98	0.55	0.74	-0.04	1.73
SNV + Sav.Gol_2nd derv		6	0.28	0.93	0.57	0.72	-0.03	1.66
Milled rice (15% degree of milling)								
Original	10,000–4,000	**7**	**0.38**	**0.84**	**0.56**	**0.68**	**0.10**	**1.70**
MSC		5	0.44	0.79	0.59	0.64	0.09	1.61
SNV		6	0.42	0.81	0.56	0.69	0.12	1.70
Sav.Gol_2nd derv		6	0.20	0.96	0.62	0.60	0.11	1.53
MSC + Sav.Gol_2nd derv		7	0.11	0.97	0.66	0.55	0.11	1.44
SNV + Sav.Gol_2nd derv		6	0.10	0.96	0.64	0.58	0.12	1.49

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling
**Savitzky Golay 2^{nd} derivative, 10 points averaging, 2^{nd} polynomial order

Table 11H The calibration and validation statistics of PLSR models for trough viscosity prediction using difference pre-processings by NIR spectra of brown and milled rice at different degrees of milling

Spectra pre–processing	Wavenumbers (cm^{-1})	PC	Calibration		Validation		Bias	RPD
			SEC	r^2cal	SEP	r^2val		
All degrees of milling*								
Original	10,000–4,000	15	71	0.87	95	0.77	12.40	2.13
MSC		**14**	**57**	**0.91**	**79**	**0.82**	**22.40**	**2.57**
SNV		10	116	0.71	136	0.61	-14.00	1.50
Sav.Gol_2nd derv**		8	95	0.80	141	0.58	-21.70	1.44
MSC + Sav.Gol_2nd derv		7	98	0.80	135	0.61	12.80	1.50
SNV + Sav.Gol_2nd derv		7	98	0.80	135	0.61	15.40	1.50
Brown rice (0% degree of milling)								
Original	10,000–4,000	1	0.89	0.71	0.92	0.70	-0.01	1.68
MSC		3	0.83	0.75	0.93	0.71	0.03	1.66
SNV		2	0.90	0.70	0.96	0.69	0.09	1.61
Sav.Gol_2nd derv		2	0.84	0.74	0.91	0.71	0.07	1.70
MSC + Sav.Gol_2nd derv		**5**	**0.45**	**0.93**	**0.86**	**0.74**	**-0.01**	**1.80**
SNV + Sav.Gol_2nd derv		3	0.73	0.80	0.88	0.72	0.01	1.76
Milled rice (5% degree of milling)								
Original	10,000–4,000	1	0.44	0.68	0.46	0.67	-0.07	1.48
MSC		4	0.44	0.69	0.51	0.58	-0.08	1.34
SNV		4	0.44	0.69	0.51	0.58	-0.08	1.34
Sav.Gol_2nd derv		**7**	**0.07**	**0.99**	**0.43**	**0.73**	**-0.02**	**1.59**
MSC + Sav.Gol_2nd derv		7	0.08	0.97	0.46	0.67	-0.02	1.48
SNV + Sav.Gol_2nd derv		7	0.08	0.97	0.46	0.67	-0.02	1.48
Milled rice (10% degree of milling)								
Original	10,000–4,000	1	130	0.80	139	0.78	5.24	1.74
MSC		5	112	0.85	143	0.77	0.28	1.69
SNV		**5**	**111**	**0.85**	**141**	**0.77**	**0.32**	**1.72**
Sav.Gol_2nd derv		2	135	0.79	154	0.73	-16.9	1.57
MSC + Sav.Gol_2nd derv		4	111	0.85	144	0.77	-8.67	1.68
SNV + Sav.Gol_2nd derv		4	111	0.85	144	0.76	-8.67	1.68
Milled rice (15% degree of milling)								
Original	10,000–4,000	6	117	0.86	148	0.79	11.71	1.90
MSC		**7**	**99**	**0.90**	**127**	**0.85**	**-5.65**	**2.21**
SNV		**7**	**99**	**0.90**	**127**	**0.85**	**-5.65**	**2.21**
Sav.Gol_2nd derv		4	111	0.88	161	0.74	10.75	1.74
MSC + Sav.Gol_2nd derv		4	107	0.89	148	0.79	7.07	1.90
SNV + Sav.Gol_2nd derv		4	107	0.89	146	0.79	7.08	1.92

* All degrees of milling means rice samples with 0, 5, 10 and 15% degree of milling
**Savitzky Golay 2nd derivative, 10 points averaging, 2nd polynomial order

Appendix I

Score plot of the rotated PC_1 and PC_2 of the physicochemical properties of rice samples with different degrees of milling

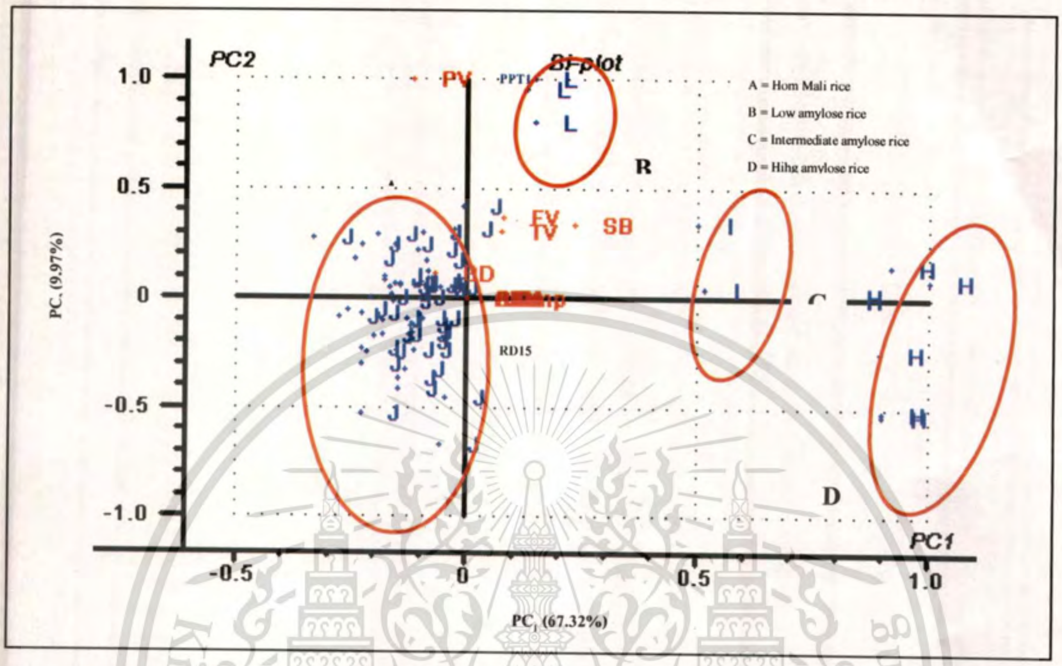


Figure 1I Score plot of the rotated PC_1 and PC_2 of the physicochemical properties at 0% degree of milling

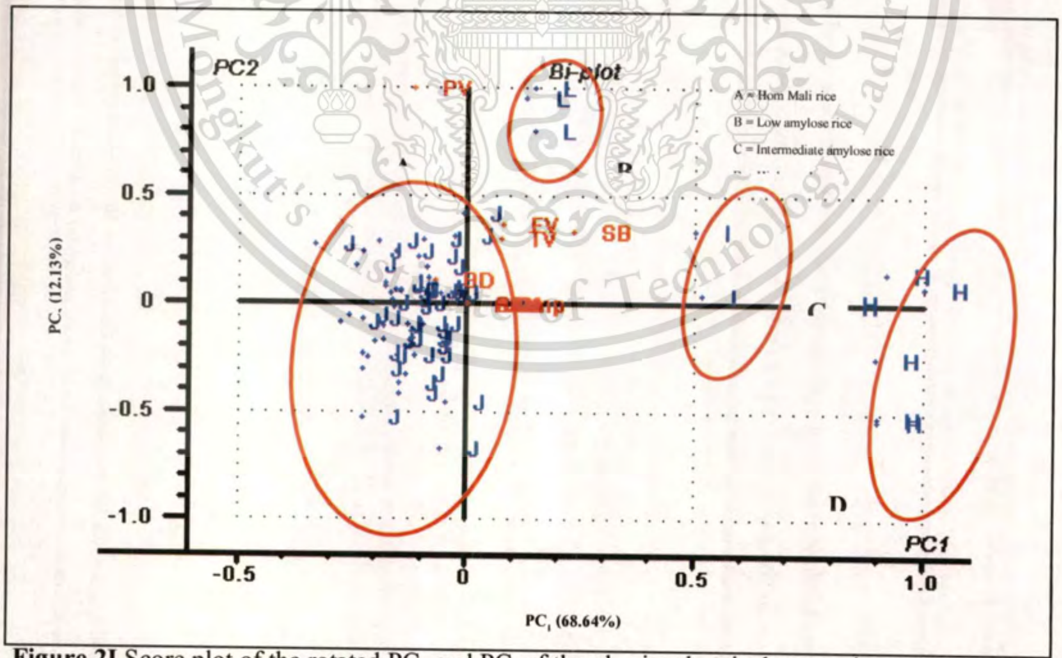


Figure 2I Score plot of the rotated PC_1 and PC_2 of the physicochemical properties at 5% degree at 5% degree of milling

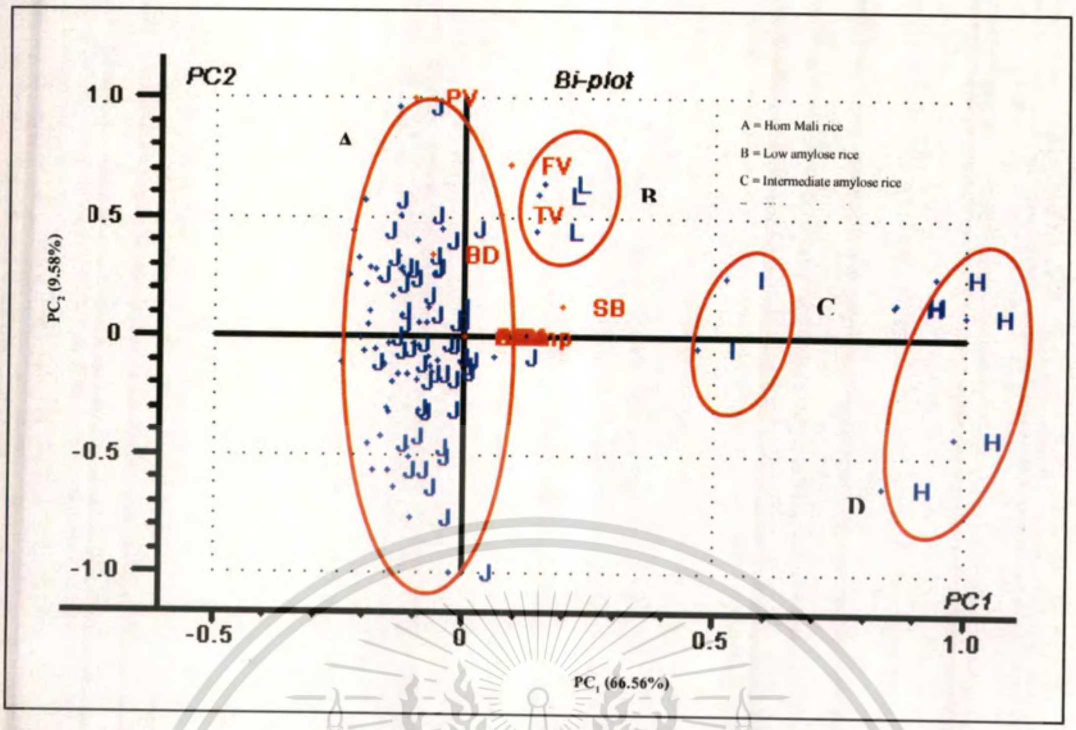


Figure 3I Score plot of the rotated PC$_1$ and PC$_2$ of the physicochemical properties at 10% degree of milling

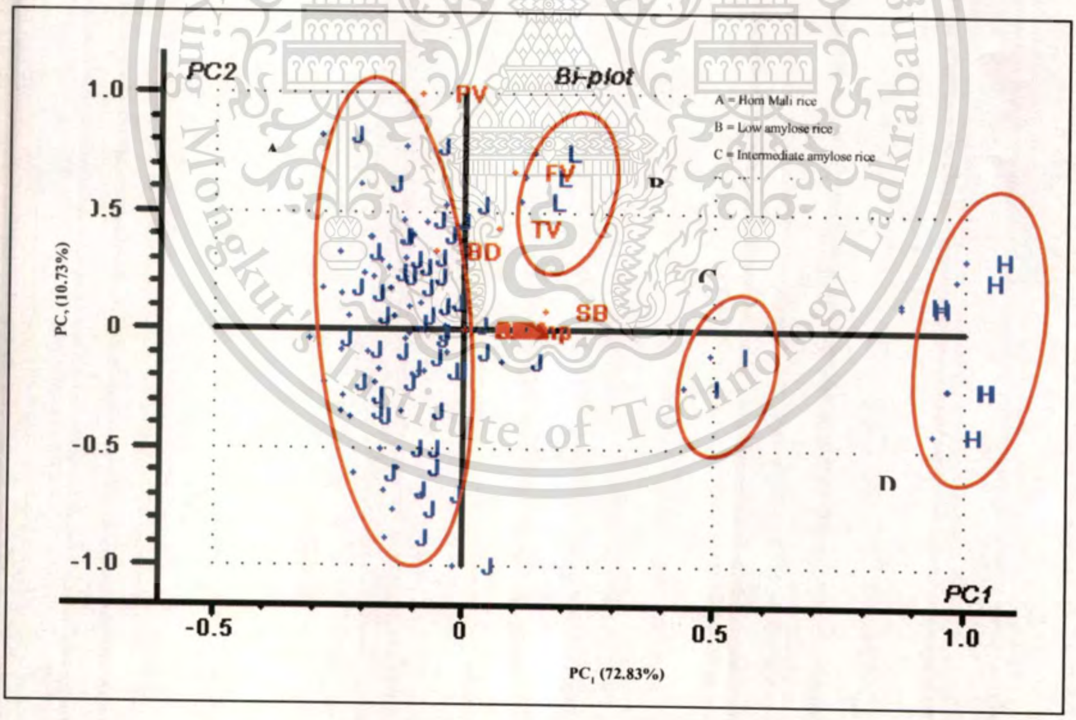
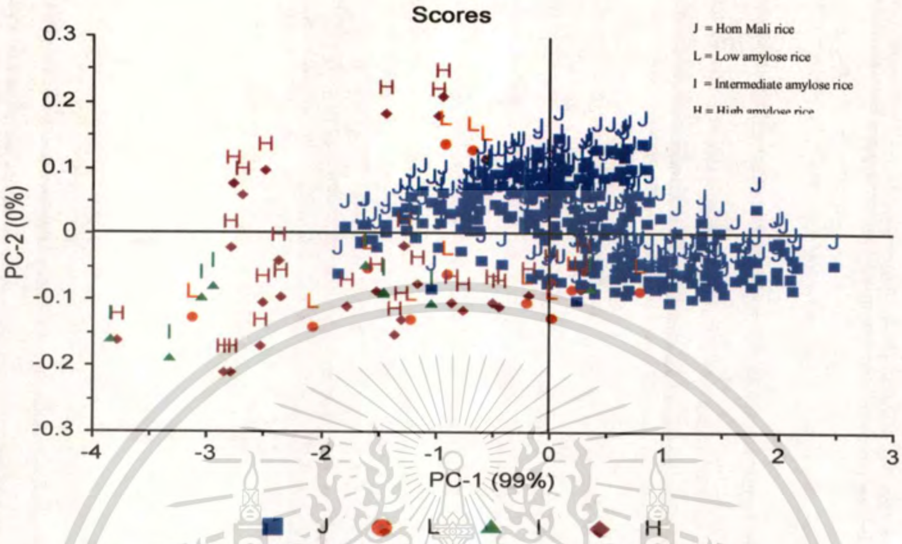


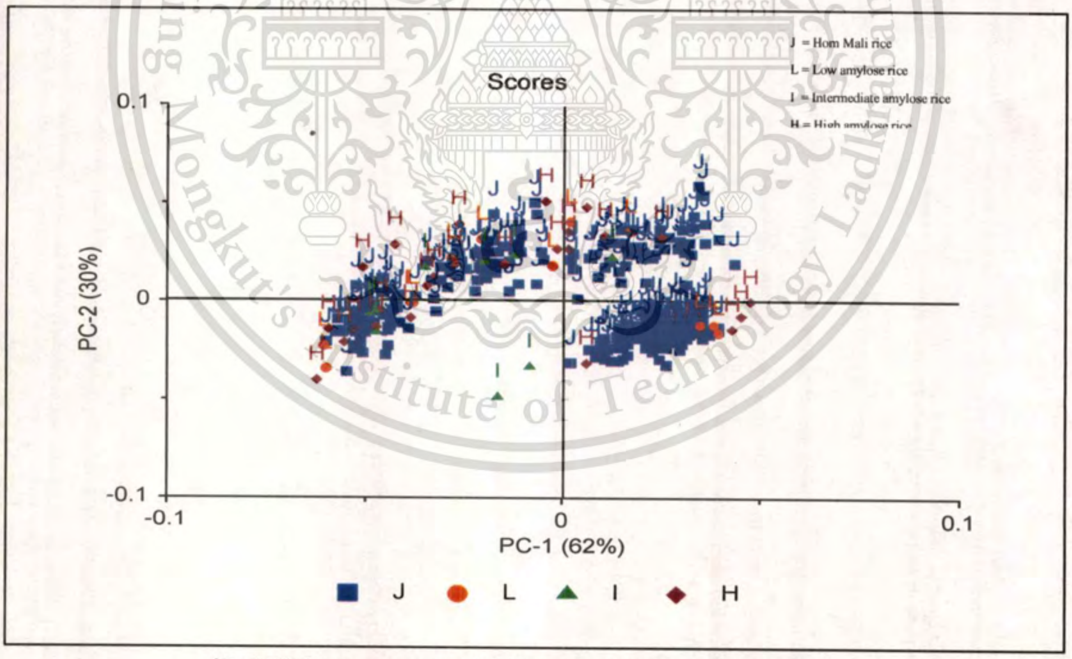
Figure 4I Score plot of the rotated PC$_1$ and PC$_2$ of the physicochemical properties at 15% degree of milling

Appendix J

Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups by PCA

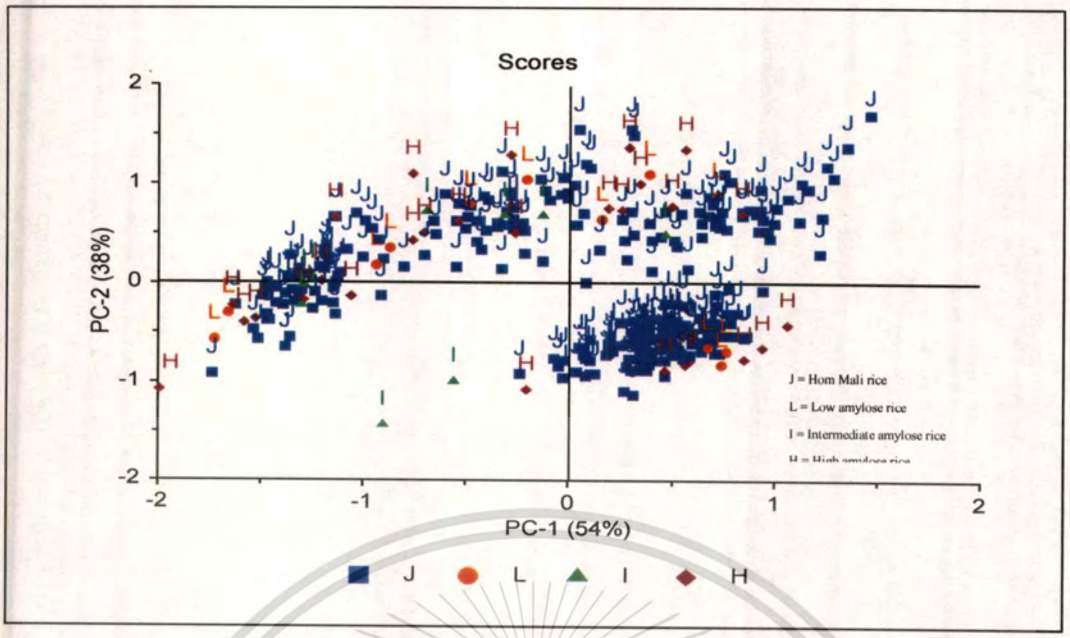


(A: Original spectra of four rice groups)

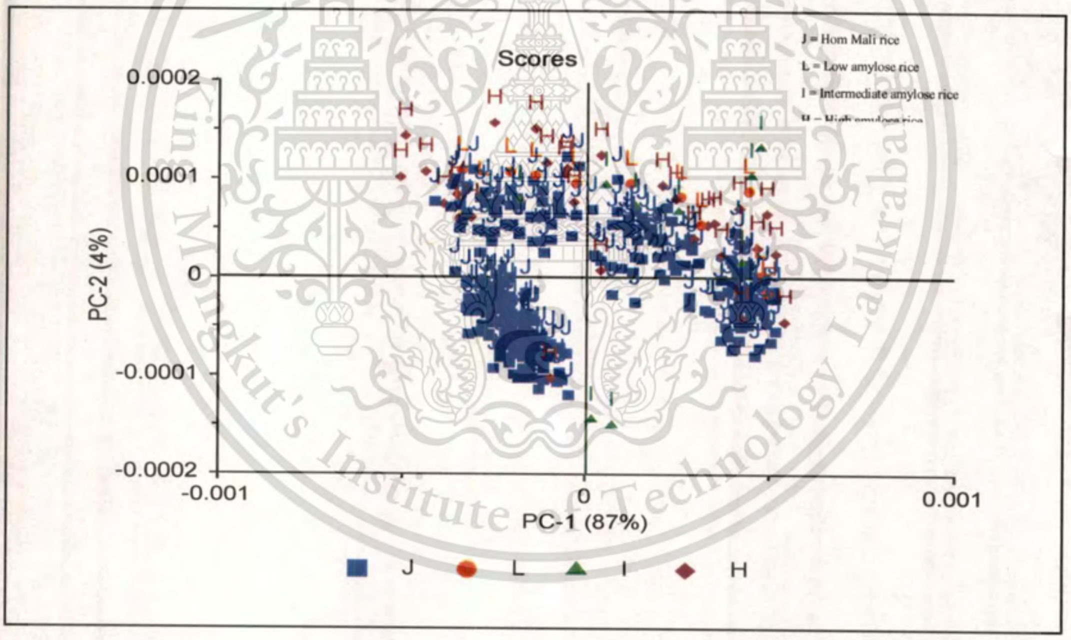


(B: MSC preprocessed NIR spectra of four rice groups)

Figure 1J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose group at all degree of milling

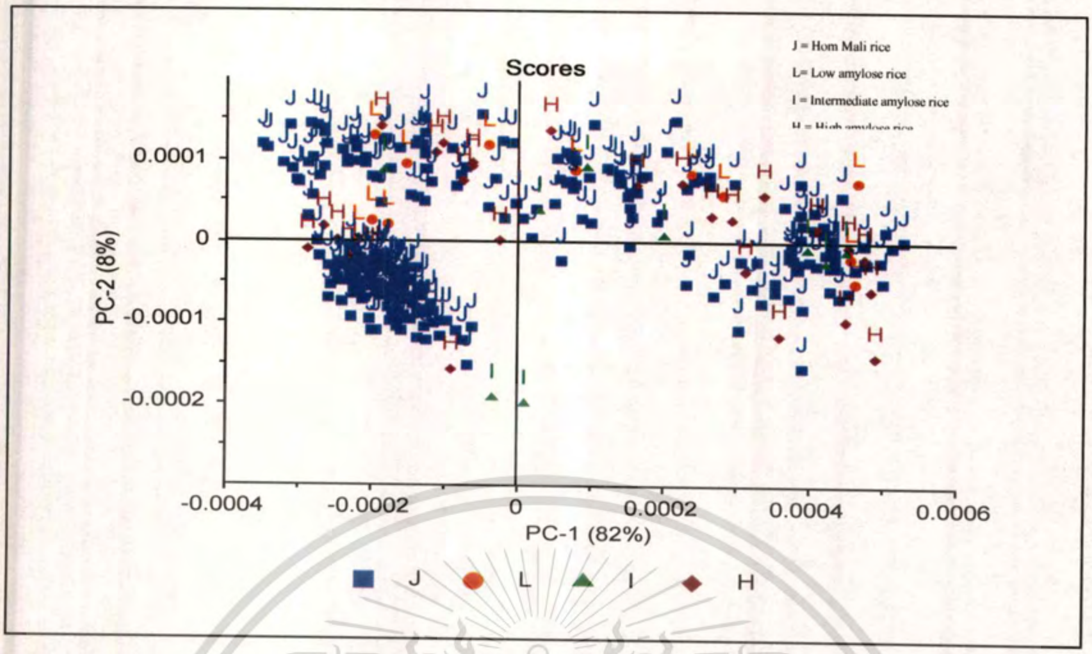


(C: SNV pre-processed NIR spectra of four rice groups)



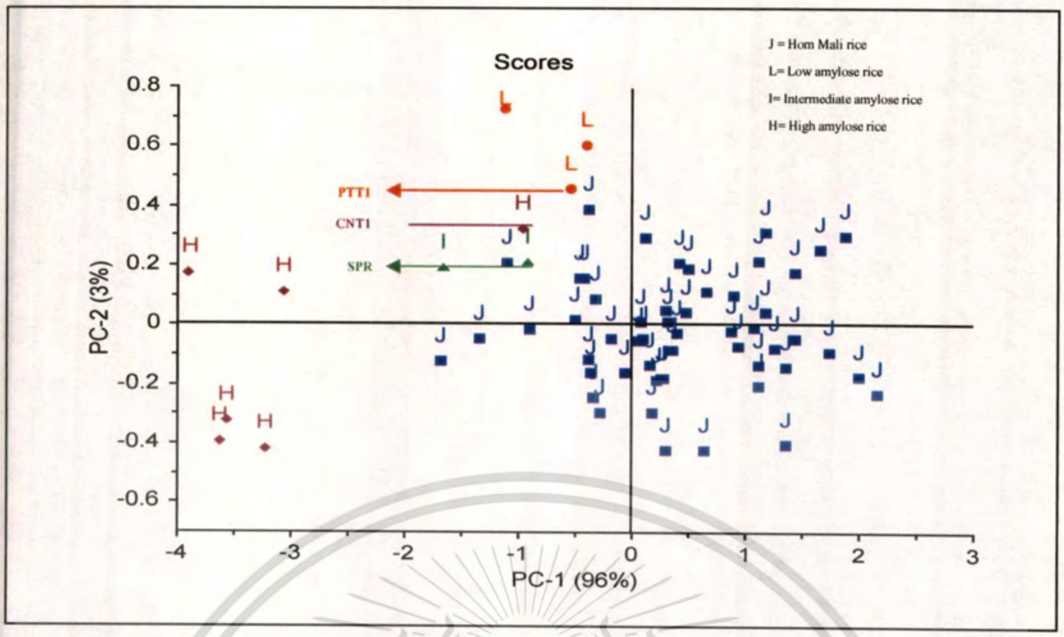
(D: Second derivative pre-processed NIR spectra of four rice groups)

Figure 2J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group at all degrees of milling (continued)

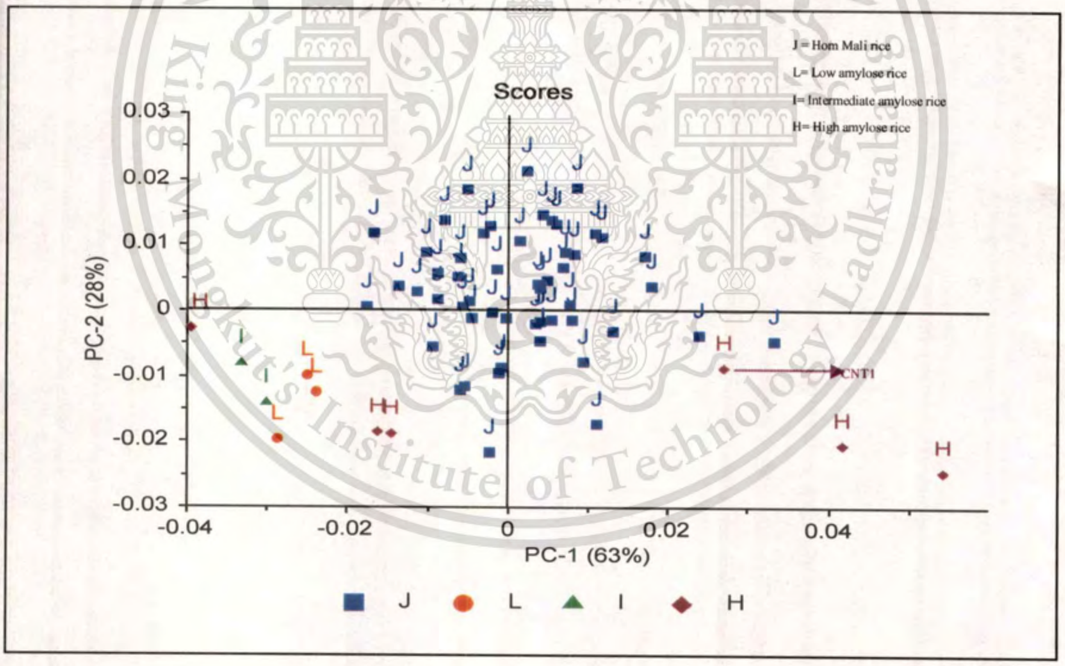


(E: MSC + Second derivative pre-processed NIR spectra of four rice groups)

Figure 2J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group at all degrees of milling (continued)

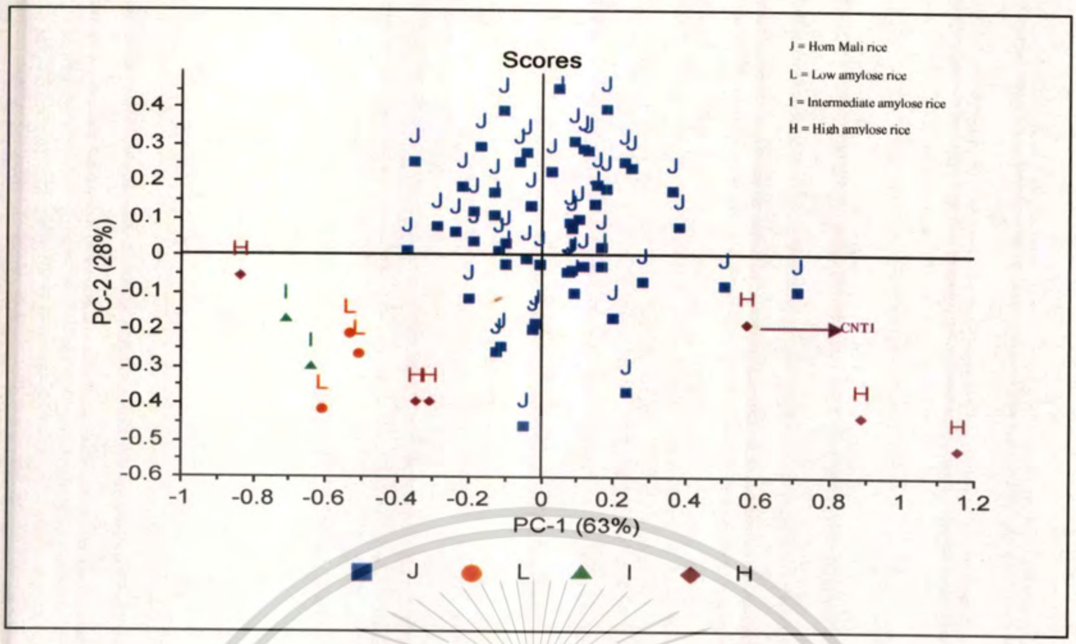


(A: Original spectra of four rice groups)

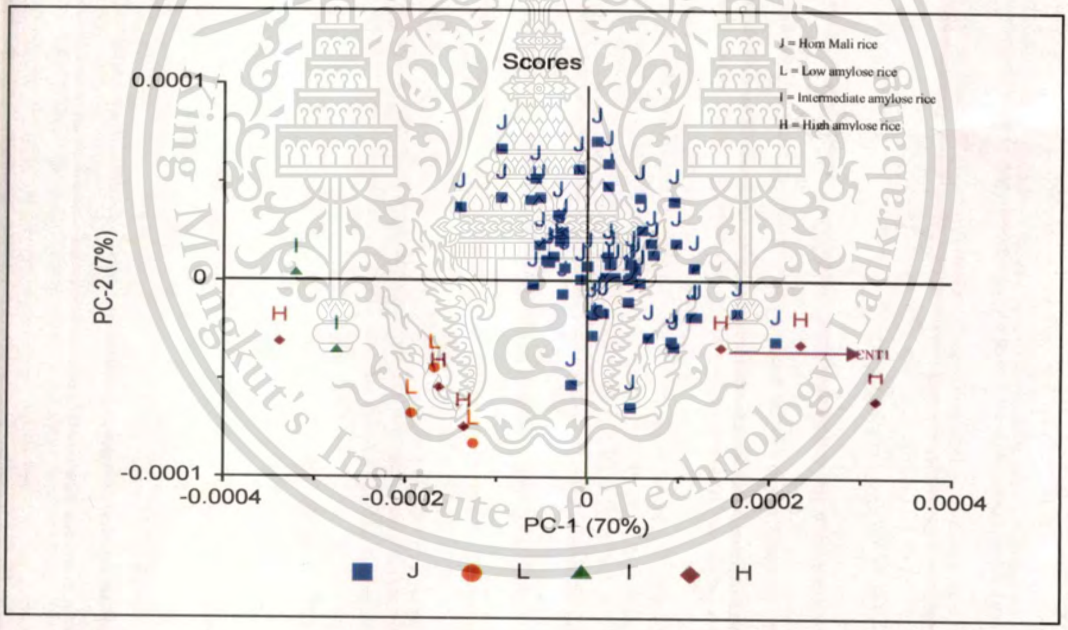


(B: MSC pre-processed NIR spectra of four rice groups)

Figure 3J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group in brown rice form

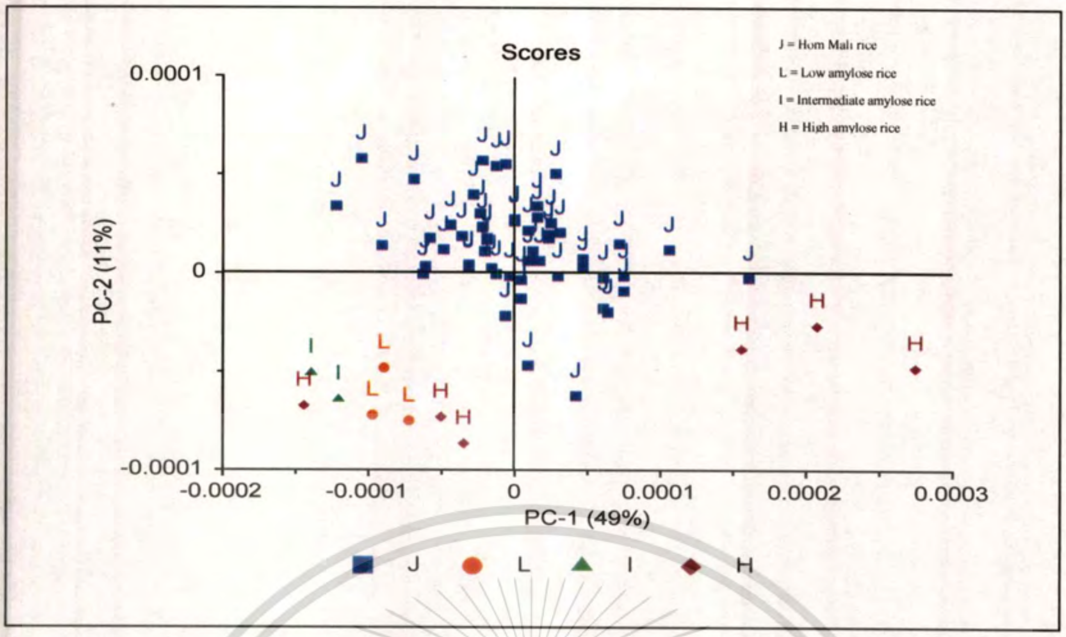


(C: SNV pre-processed NIR spectra of four rice groups)

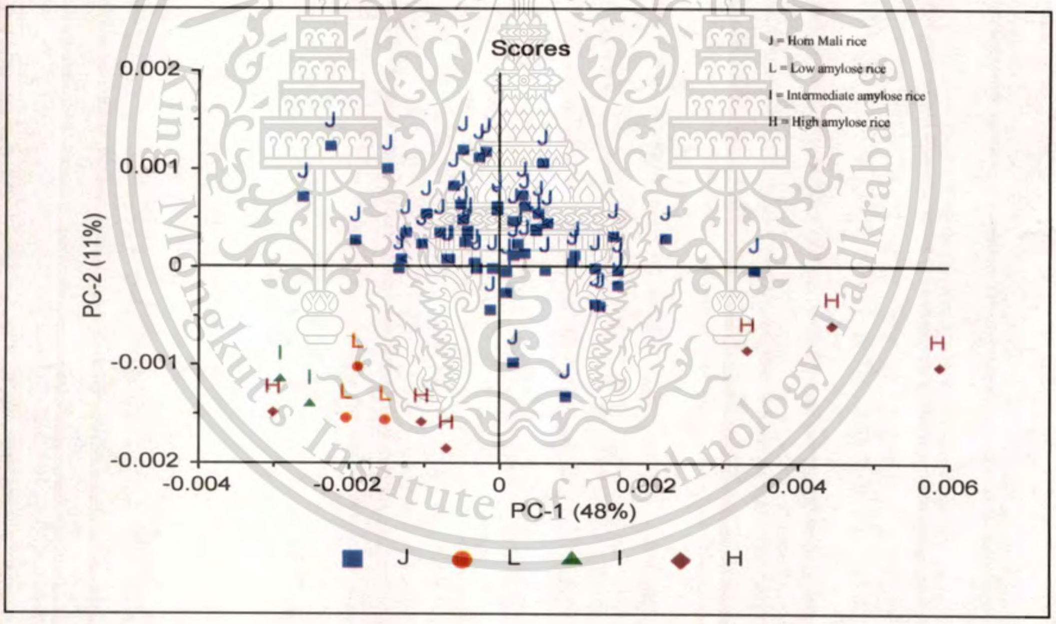


(D: Second derivative pre-processed NIR spectra of four rice groups)

Figure 3J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group in brown rice form (continued)

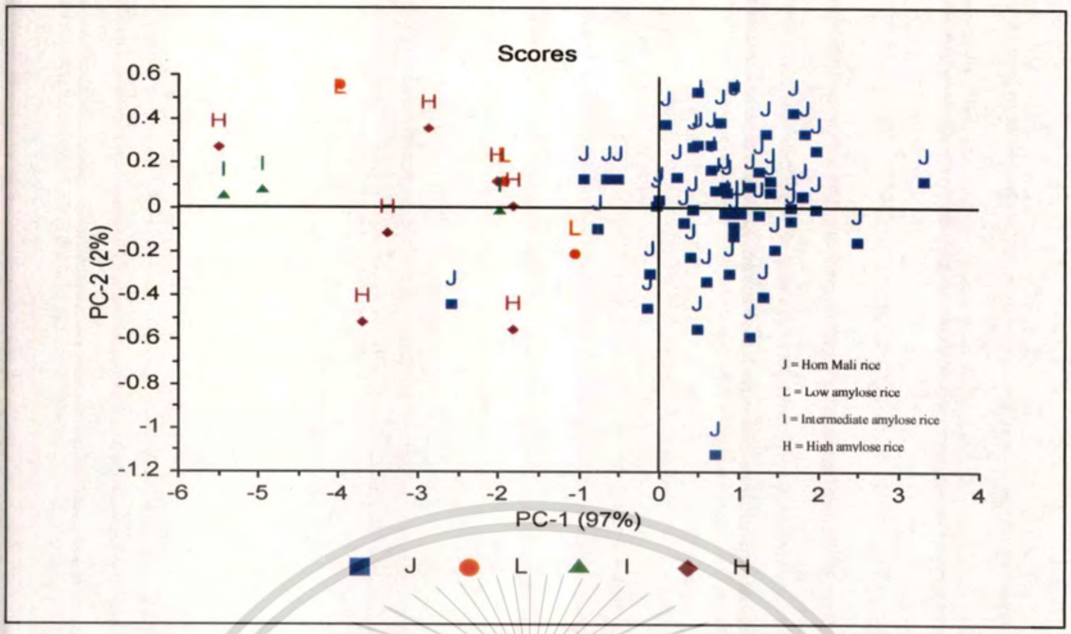


(E: MSC + Second derivative pre-processed NIR spectra of four rice groups)

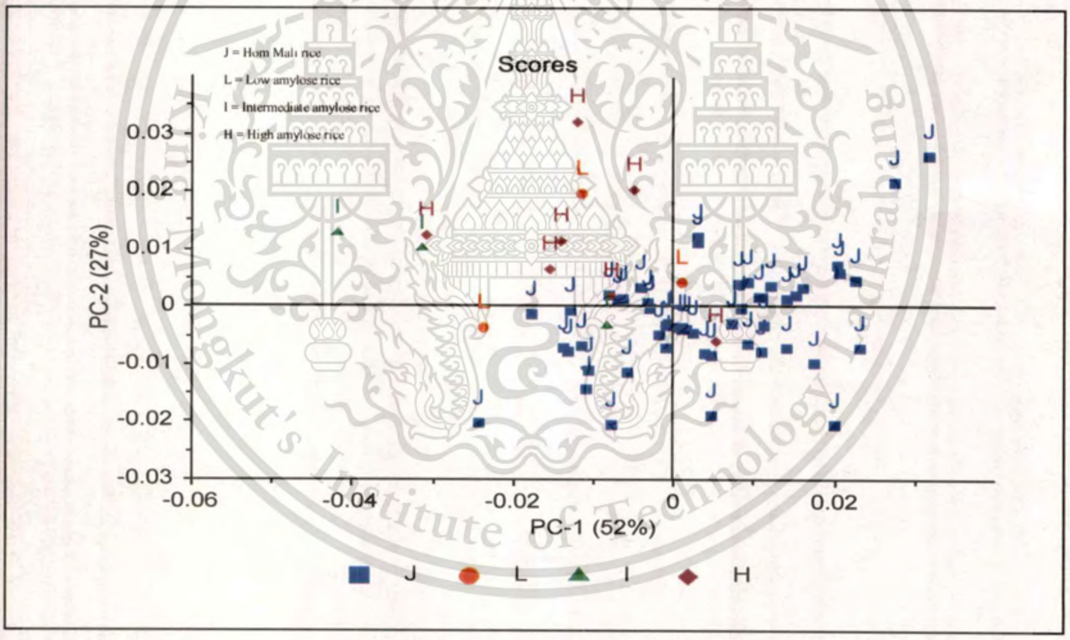


(F: SNV + Second derivative pre-processed NIR spectra of four rice groups)

Figure 3J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group in brown rice form (continued)

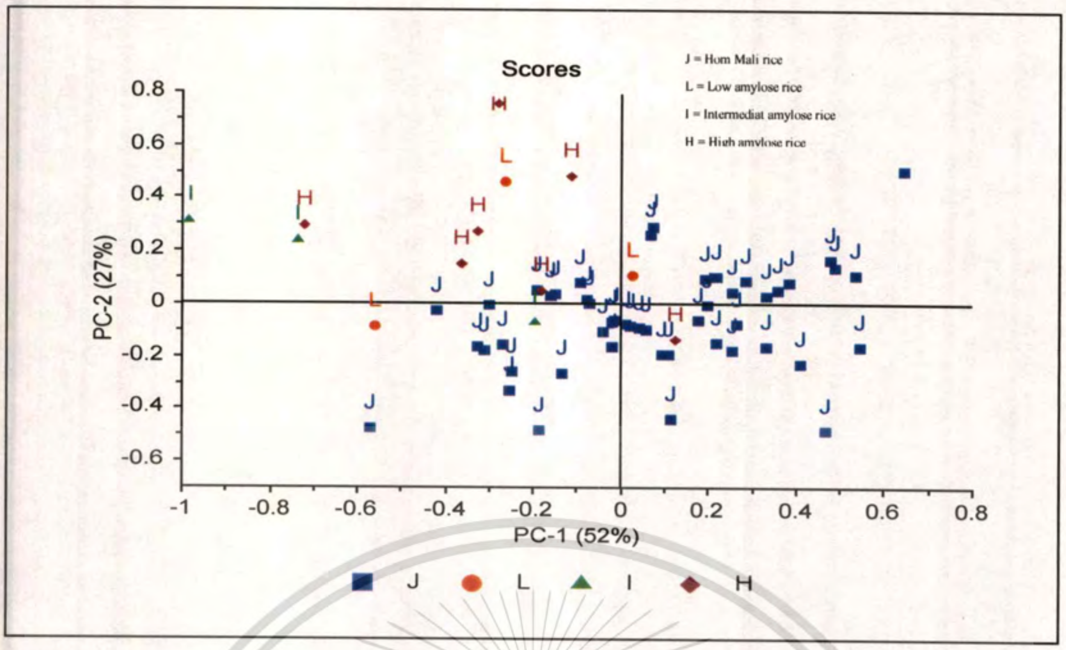


(A: Original spectra of four rice groups)

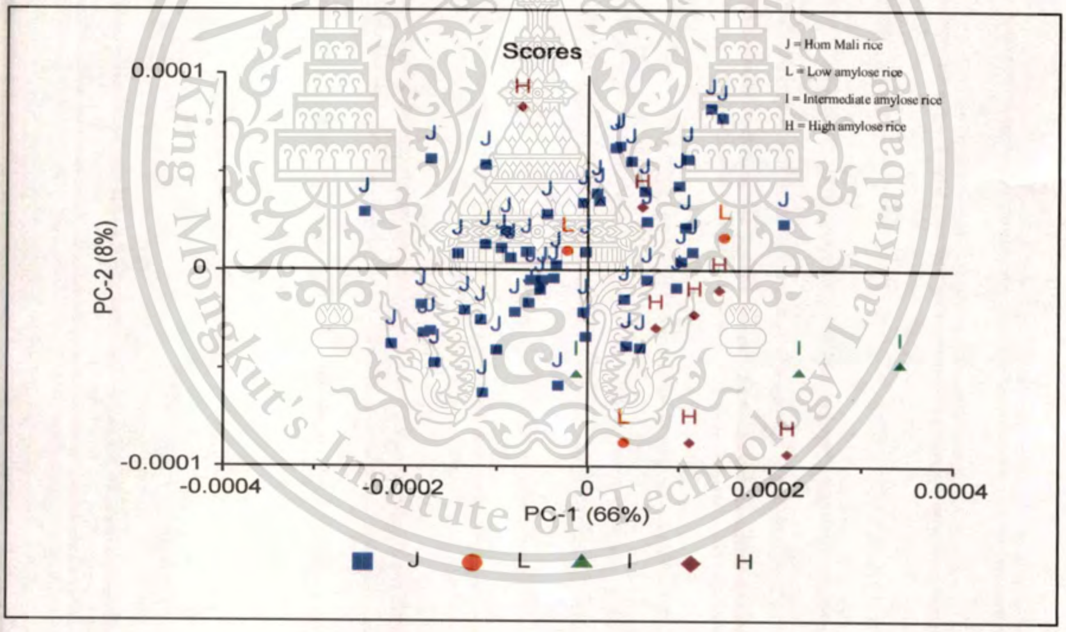


(B: MSC pre-processed NIR spectra of four rice groups)

Figure 3J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 5% degree of milling

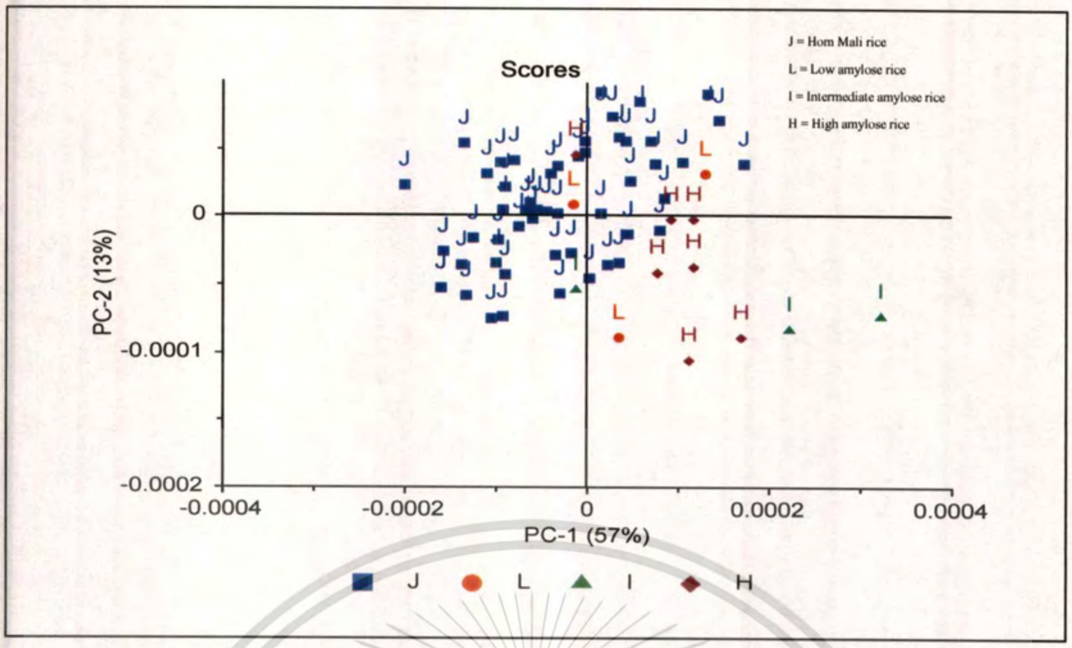


(C: SNV pre-processed NIR spectra of four rice groups)

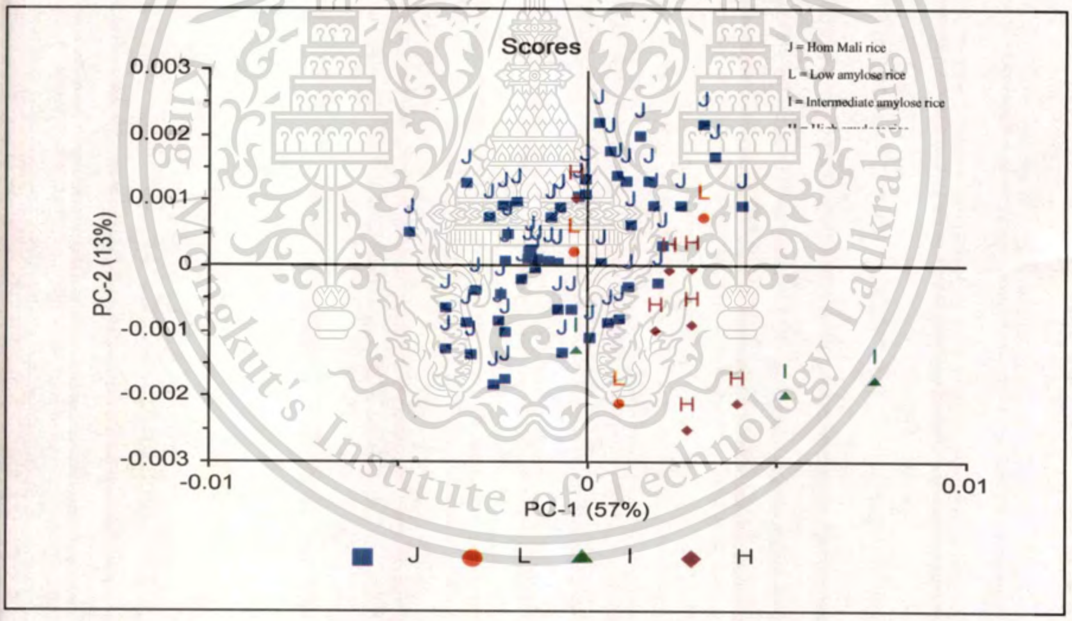


(D: Second derivative pre-processed NIR spectra of four rice groups)

Figure 3J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 5% degree of milling (continued)

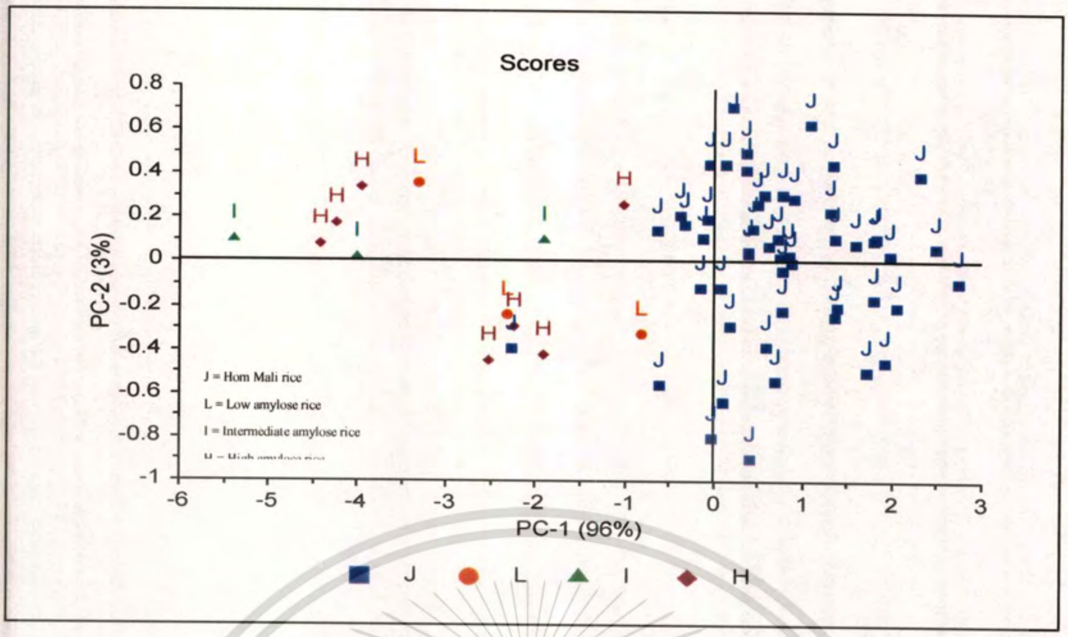


(E: MSC + Second derivative pre-processed NIR spectra of four rice groups)

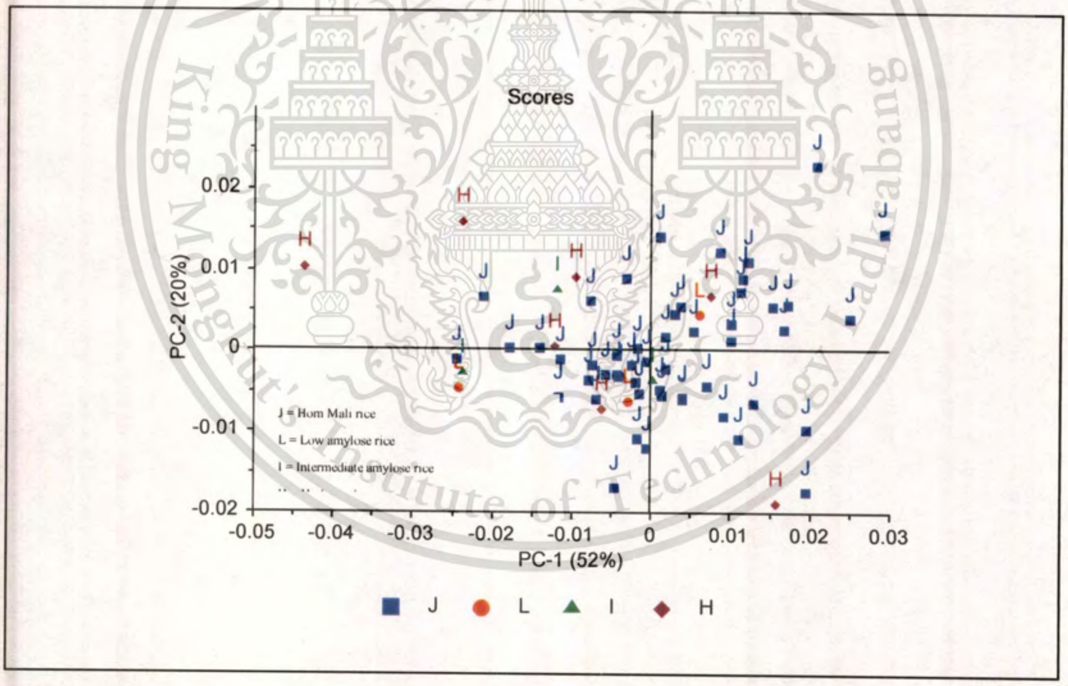


(F: SNV + Second derivative pre-processed NIR spectra of four rice groups)

Figure 3J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 5% degree of milling (continued)

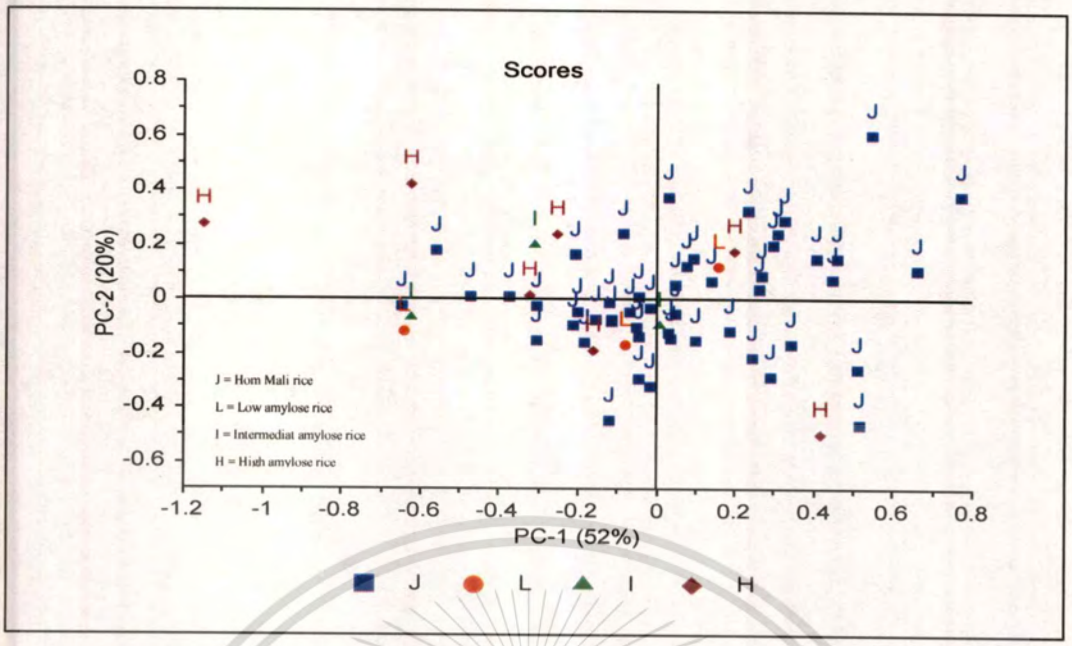


(A: Original spectra of four rice groups)

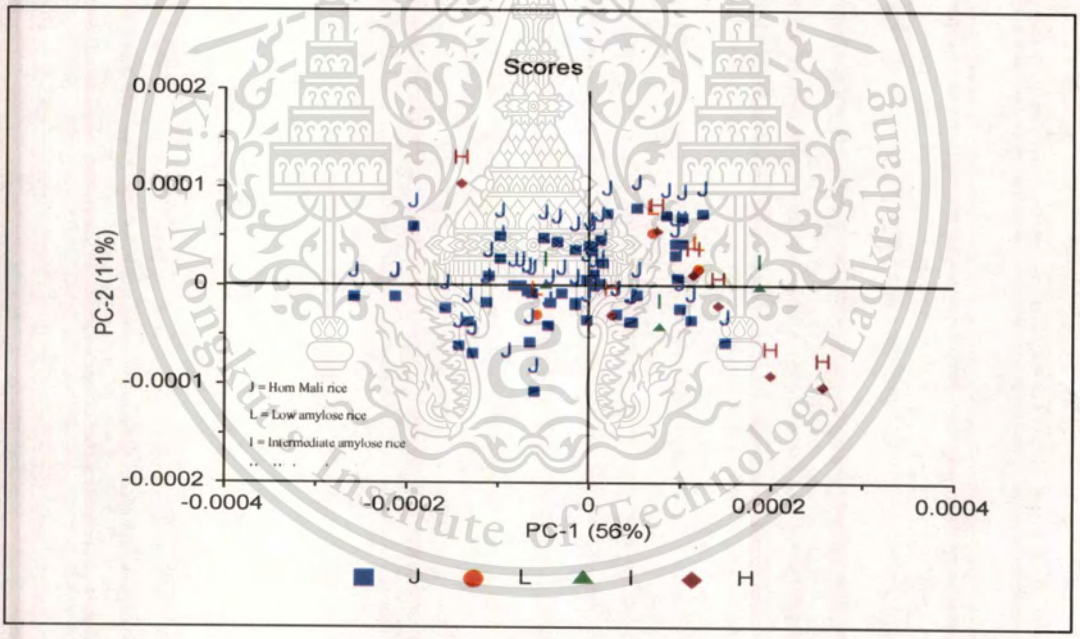


(B: MSC pre-processed NIR spectra of four rice groups)

Figure 3J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 10% degree of milling

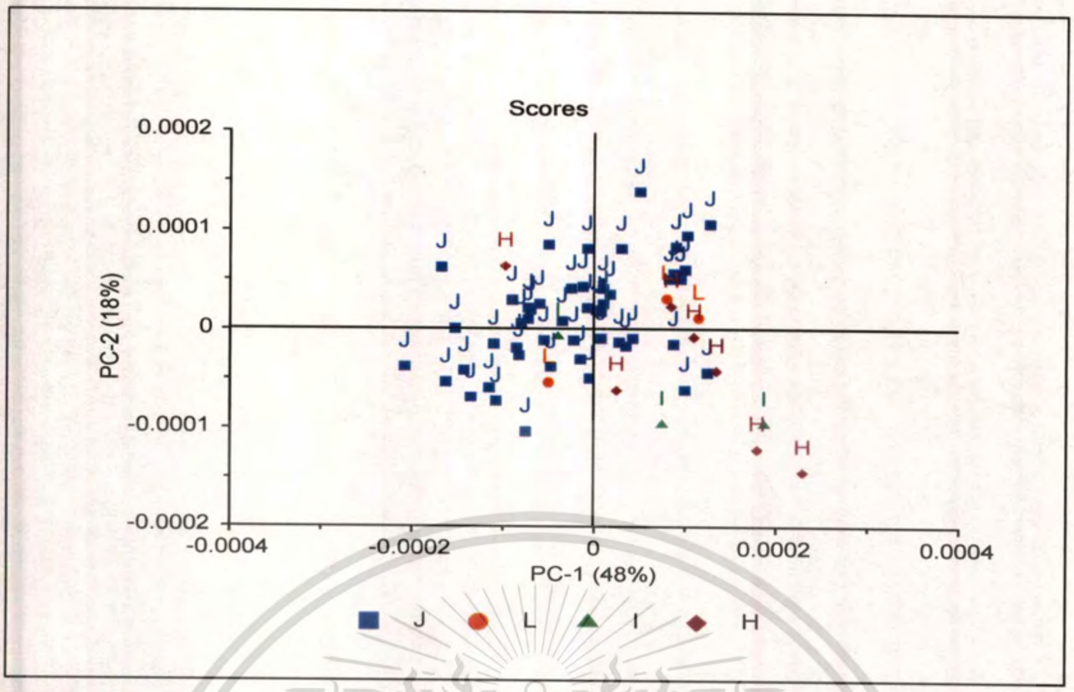


(C: SNV pre-processed NIR spectra of four rice groups)

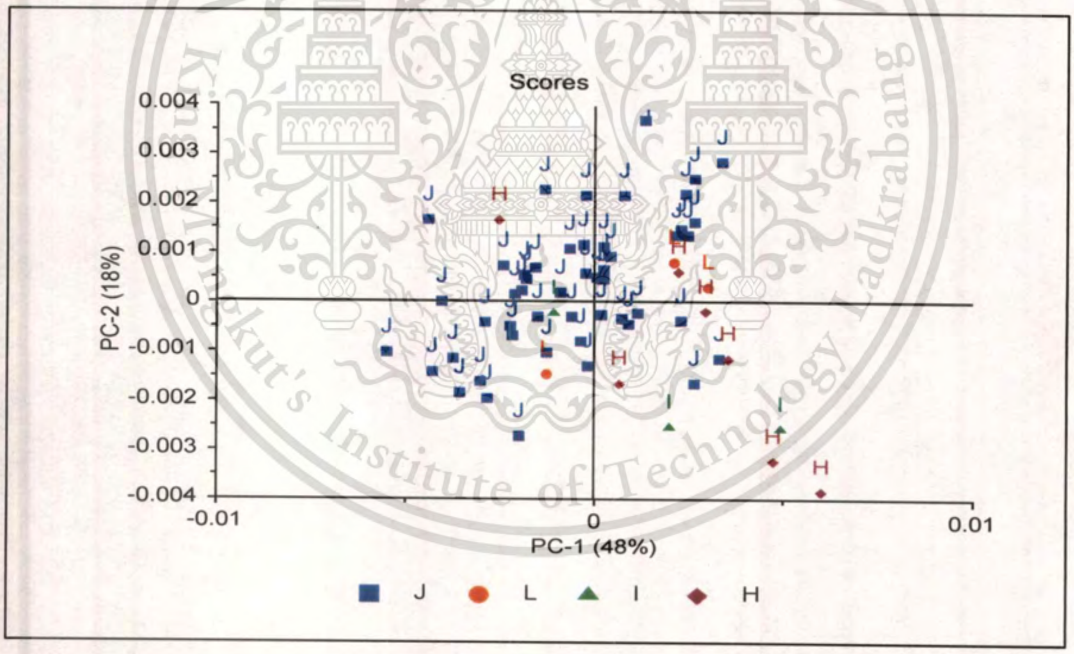


(D: Second derivative pre-processed NIR spectra of four rice groups)

Figure 3J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 10% degree of milling (continued)

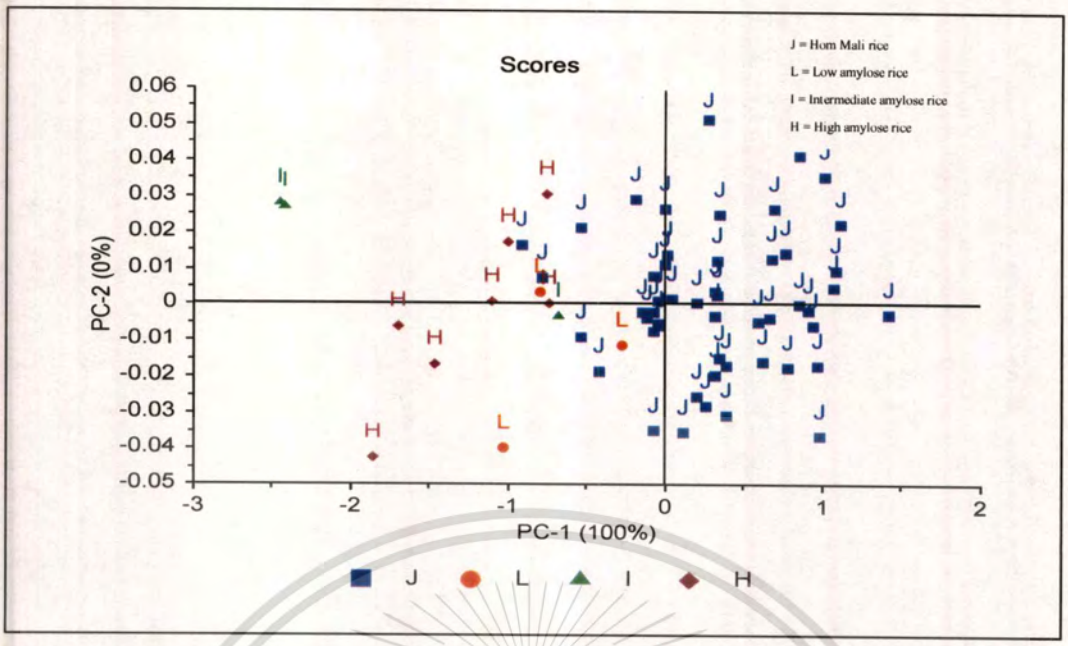


(E: MSC + Second derivative pre-processed NIR spectra of four rice groups)

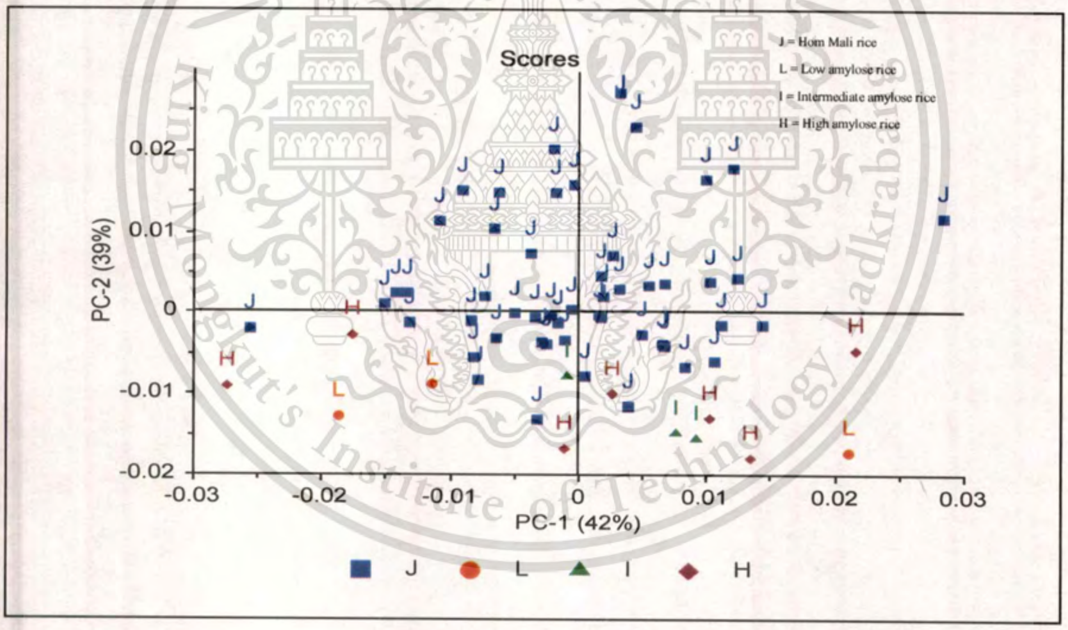


(F: SNV + Second derivative pre-processed NIR spectra of four rice groups)

Figure 3J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 10% degree of milling (continued)

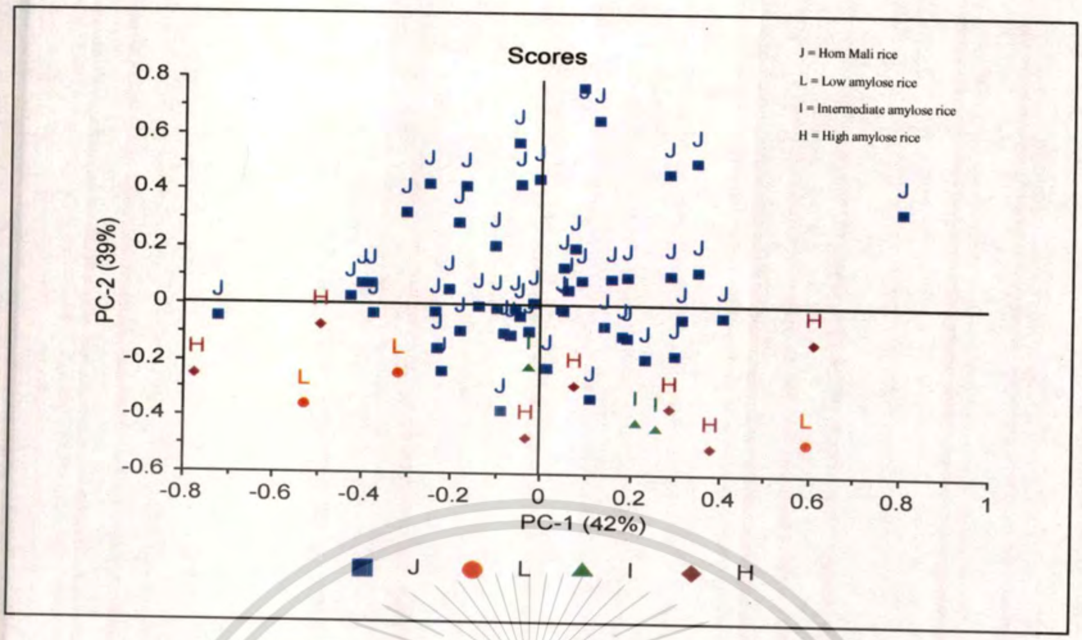


(A: Original spectra of four rice groups)

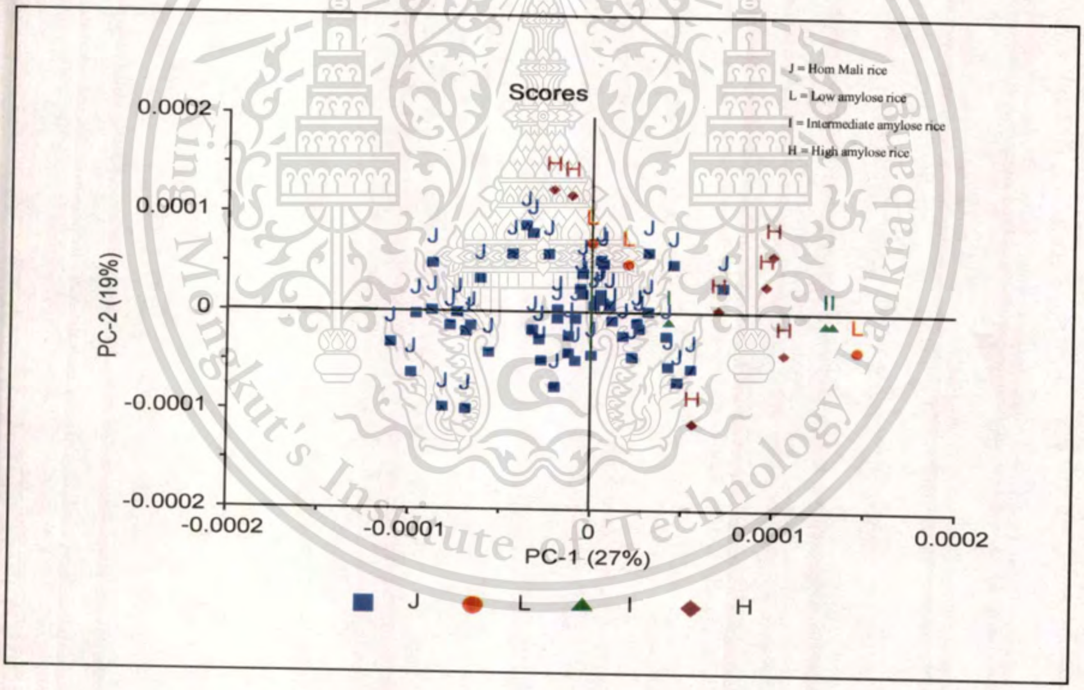


(B: MSC pre-processed NIR spectra of four rice groups)

Figure 4J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 15% degree of milling

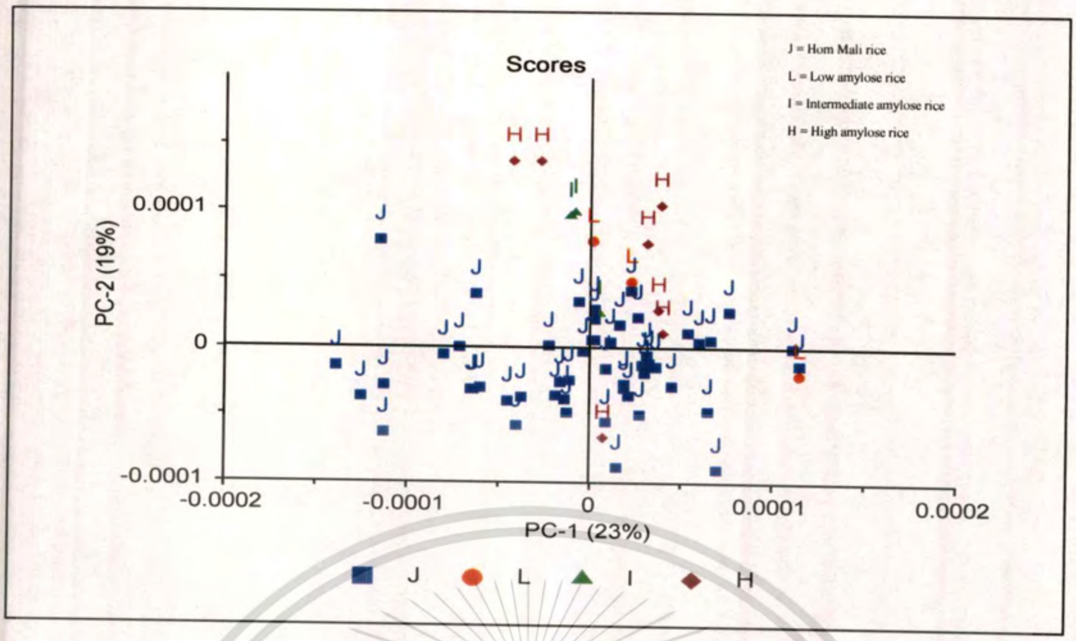


(C: SNV pre-processed NIR spectra of four rice groups)

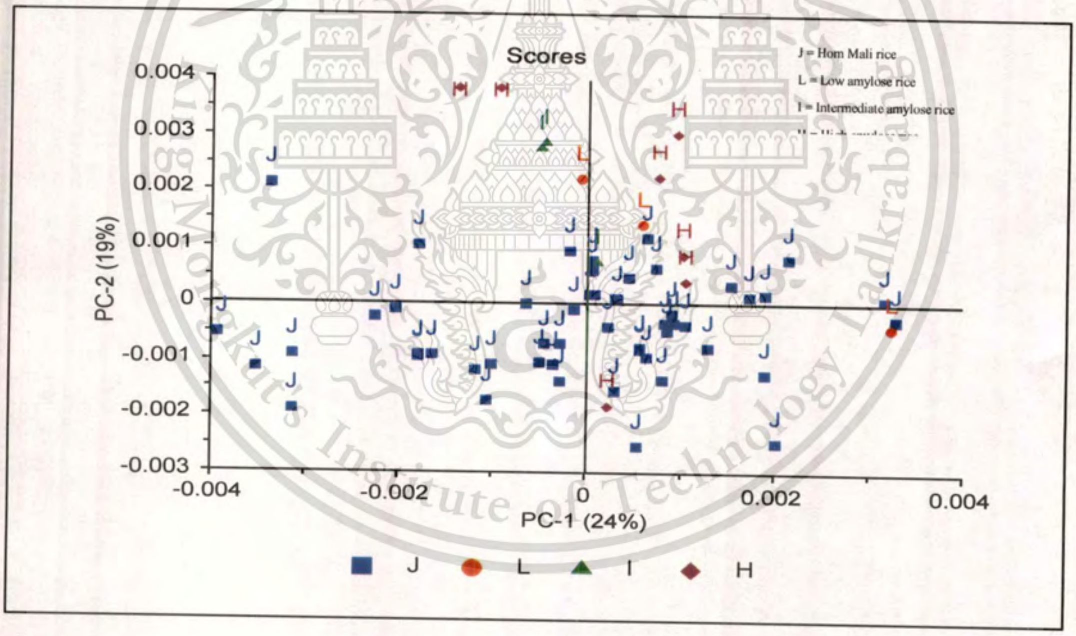


(D: Second derivative pre-processed NIR spectra of four rice groups)

Figure 4J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 15% degree of milling (continued)



(E: MSC + Second derivative pre-processed NIR spectra of four rice groups)



(F: SNV + Second derivative pre-processed NIR spectra of four rice groups)

Figure 4J Score plot of PC_1 and PC_2 based on NIR spectra of four rice groups of Hom Mali rice, low, intermediate and high amylose rice group of milled rice at 15% degree of milling (continued)

Appendix K

PLS score plot of the best model of Hom Mali rice and the aromatic and non-aromatic rice samples using PLS-DA model

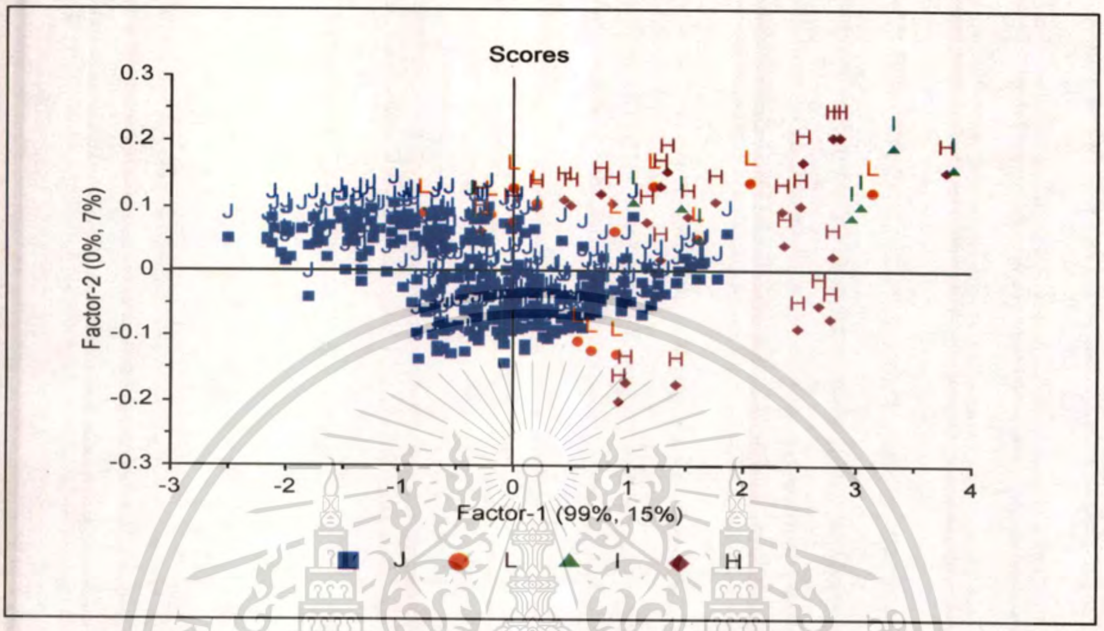


Figure 1K PLS score plot of all degree of milling of Hom Mali rice (J), low (L), intermediate (I), and high (H) using NIR spectra (no pre-processing) for the calibration set

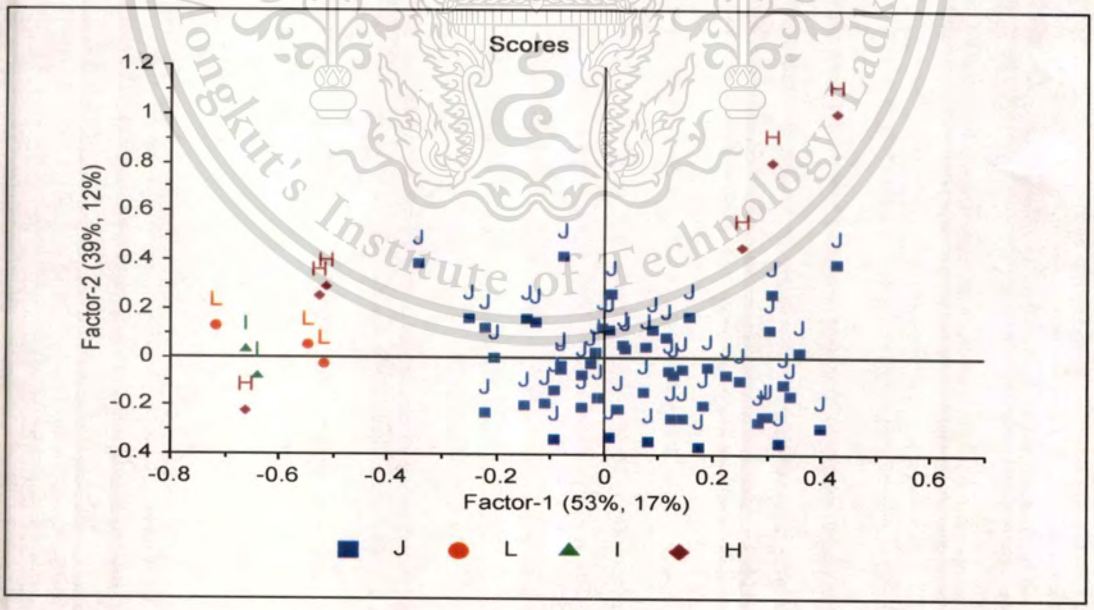


Figure 2K PLS score plot of brown Hom Mali rice (J), low (L), intermediate (I), and high (H) using NIR spectra performed with SNV for the calibration set

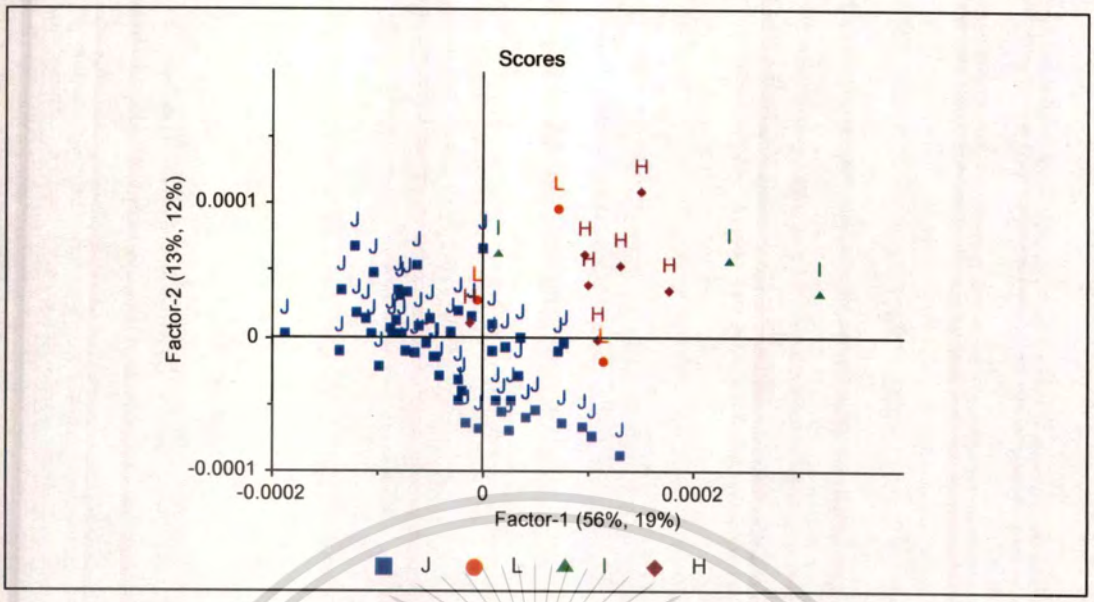


Figure 3K PLS score plot of milled rice at 5% degree of milling of Hom Mali rice (J), low (L), intermediate (I), and high (H) using NIR spectra performed with MSC + second derivative for the calibration set

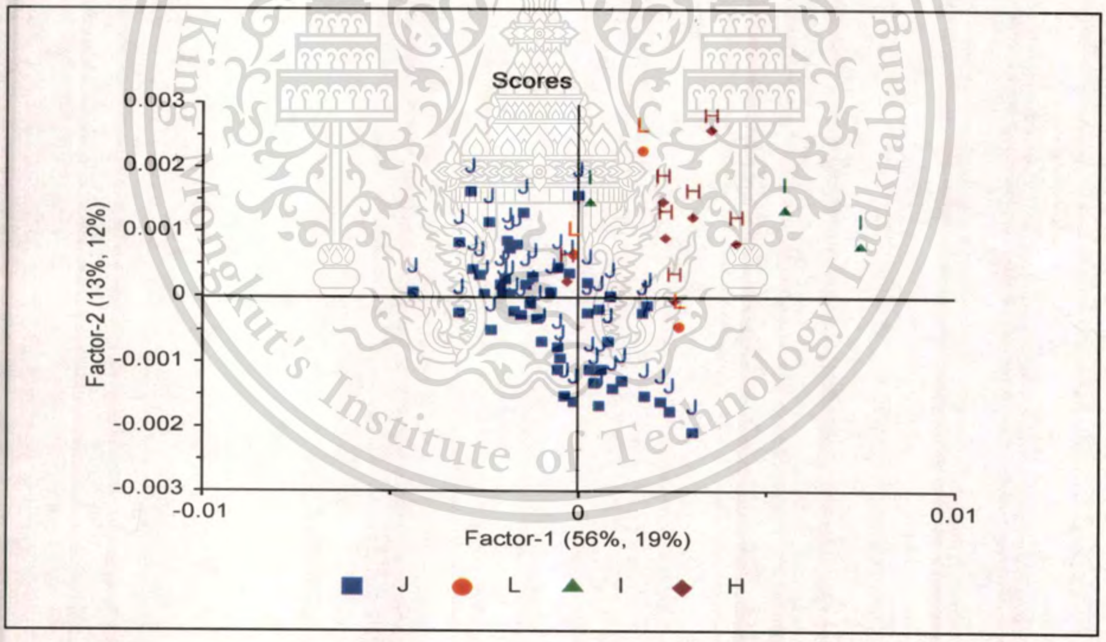


Figure 4K PLS score plot of milled rice at 5% degree of milling of Hom Mali rice (J), low (L), intermediate (I), and high (H) using NIR spectra performed with SNV + second derivative for the calibration set

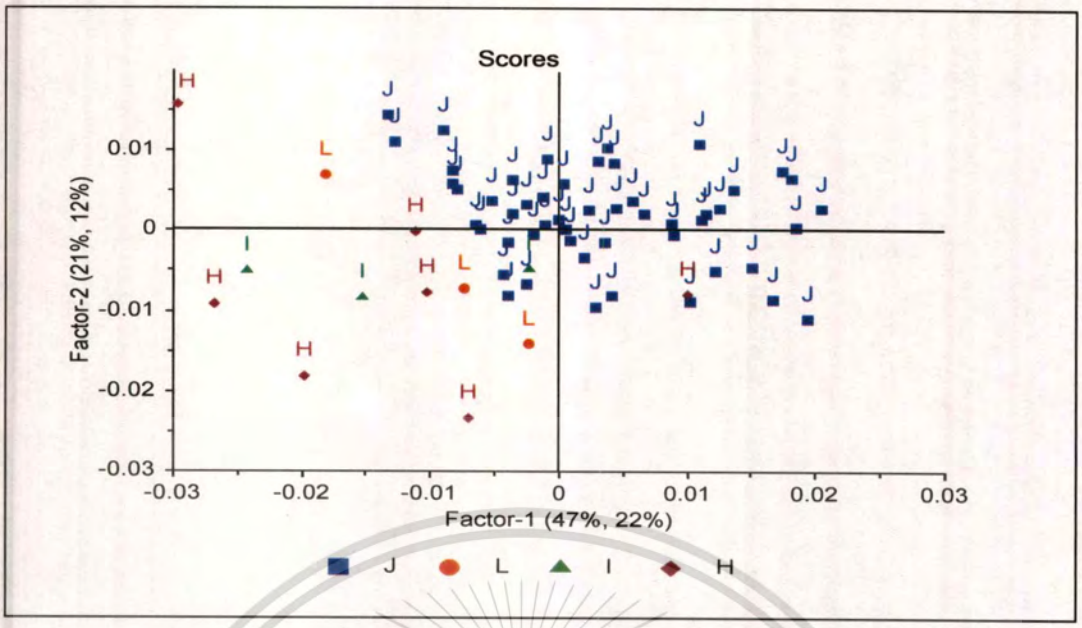


Figure 5K PLS score plot of milled rice at 10% degree of milling of Hom Mali rice (J), low (L), intermediate (I), and high (H) using NIR spectra performed with MSC for the calibration set

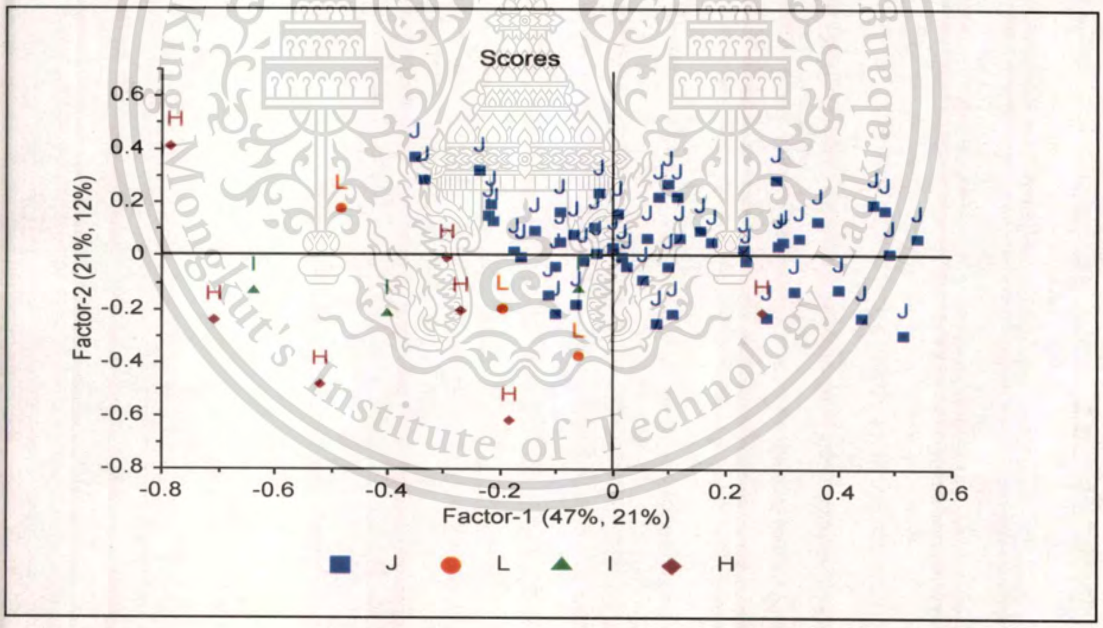


Figure 6K PLS score plot of milled rice at 10% degree of milling of Hom Mali rice (J), low (L), intermediate (I), and high (H) using NIR spectra performed with SNV for the calibration set

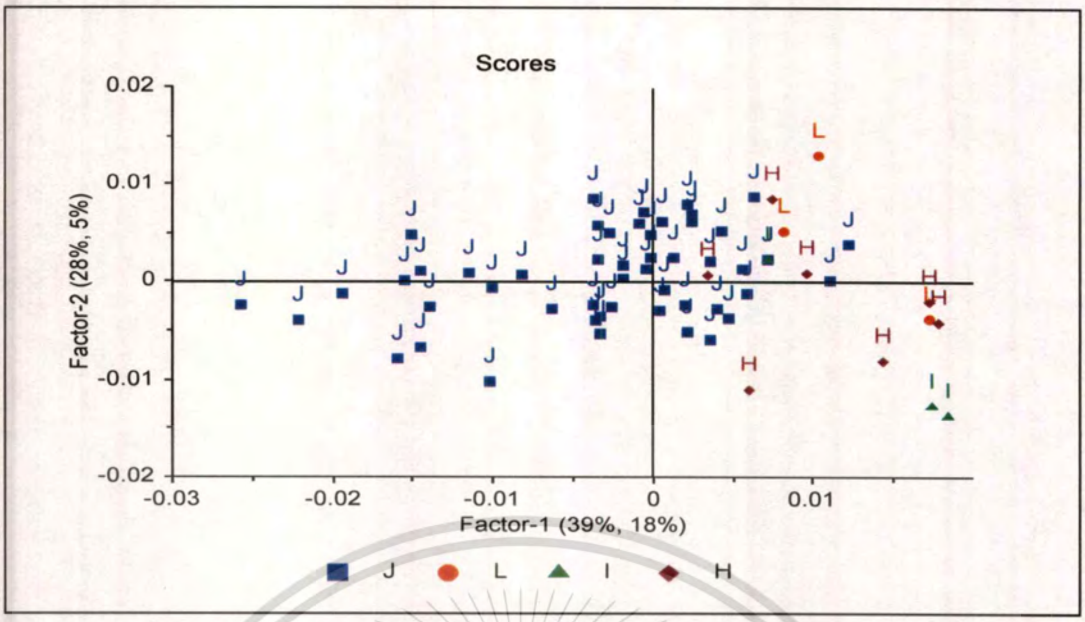


Figure 7K PLS score plot of milled rice at 15% degree of milling of Hom Mali rice (J), low (L), intermediate (I), and high (H) using NIR spectra performed with MSC for the calibration set

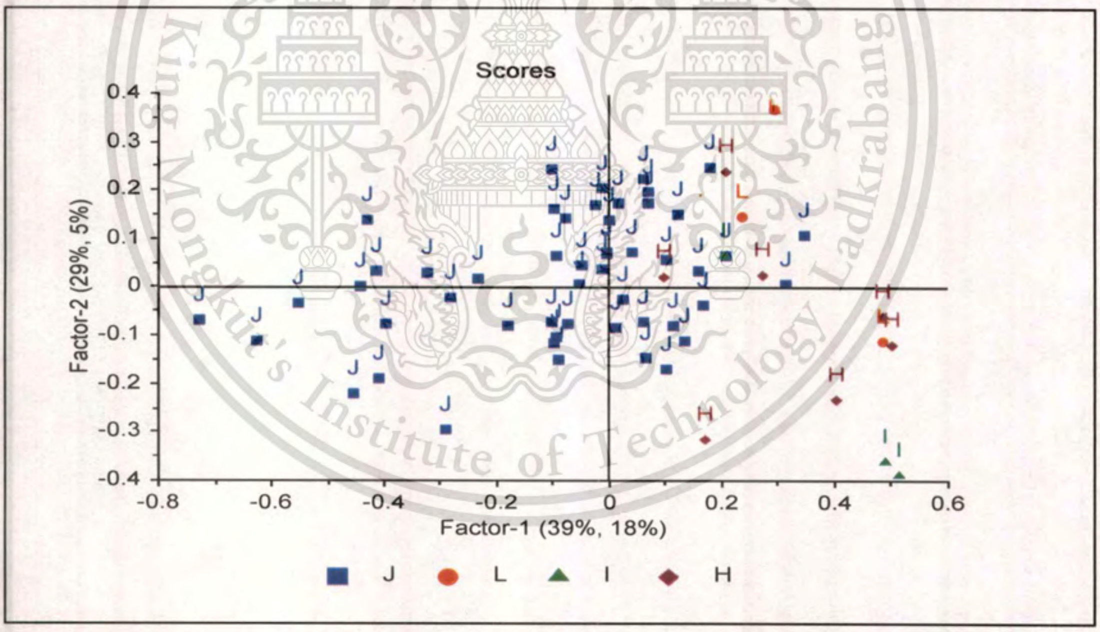


Figure 8K PLS score plot of milled rice at 15% degree of milling of Hom Mali rice (J), low (L), intermediate (I), and high (H) using NIR spectra performed with SNV for the calibration set

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Imsil, A., Sirisomboon, P., Rittiron, R. and Areekul, V. 2012. "Prediction of the physicochemical properties of rice with different degrees of milling using FT-NIR spectroscopy." The 3rd Asian Near InfraredSymposium, Bangkok, Thailand.

Imsil, A., Rittiron, R., Sirisomboon, P. and Areekul, V. 2011. "Classification of Hom Mali rice with different degrees of milling based on physicochemical measurements by principal component analysis." **Kasetsart J. (Nat. Sci.)**. 45(5) : 863-873.