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Dynamic NIR Spectroscopy to Monitor Bread Dough Mixing: A Short Review

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ABSTRACT

Near infrared (NIR) spectroscopy has been recognized as a valuable tool for quality control in both industry and laboratories. The aim of this review is to describe the ability of the dynamic NIR spectroscopy to in-line monitor bread dough mixing. Dynamic NIR spectroscopy can be defined as the use of NIR spectroscopy methods as an in-line tool to monitor processing. Different configurations for probing dough mixer with the NIR spectrometer have been considered to continuously record NIR spectrum as a function of mixing time. More or less complex statistical methods of the NIR spectrum collection have been tested to construct NIR mixing curves, to determine optimum mixing times and to identify the relevant NIR wavelengths related to chemical interactions between the dough components (water, starch, protein and lipids). Analysis of NIR spectroscopy data give opportunities to complete the description of the physico-chemical mechanisms involved in bread dough development (hydration of starch and proteins and development of the gluten network during mixing).

Key words: Mixer, chemometrics, water, proteins, starch, lipids

INTRODUCTION

Near infrared (NIR) spectroscopy is a useful and cost effective method well adapted for wheat products, to analyze raw materials, ingredients and processes. The applications of NIR spectroscopy mainly concern three domains. (1) Rapid prediction of composition parameters and properties of raw materials using NIR databases. (2) Screening method in plant-breeding for the selection of cross-breeds with the desired qualities and in wheat grain diagnostics at the time of delivery. (3) In-line tool to monitor the molecular and structural changes of the wheat components during the processing stages for manufacture of the wheat based products.

Dynamic NIR spectroscopy can be defined as the use of NIR spectroscopy methods as an in-line tool to monitor processing (Kaddour *et al.*, 2007). Dynamic NIR spectroscopy provides information that is relevant to calculate the reaction rate constants for the process and to monitor the chemical changes of the wheat components and the physical changes in product structure. Dynamic NIR spectroscopy gives complementary information with those that can be obtained using classical analytical methods, such as rheology or chemical analysis. The potential applications of

dynamic NIR spectroscopy for cereal products concern in-line monitoring of unit operations involved in transformation of wheat flour to food products (flour agglomeration, dough mixing, pasta dough extrusion and sheeting, dough proofing, thermal treatment and storage). The NIR spectroscopy has been mainly studied at laboratory scale as an in-line method to monitor bread dough mixing. The most largely studied application concern the use of dynamic NIR spectroscopy to in-line monitor bread dough mixing.

The aim of this review is to describe the ability of the dynamic NIR spectroscopy to monitor bread dough mixing and to give original information related to the physico-chemical mechanisms at molecular and structural scales.

Dough mixing is an important stage in the bread making process, because the amount of mixing has a critical bearing upon final bread quality. Decisions with respect to adequacy of dough mixing are still partly based on operator experience. The physical and chemical reactions occurring during dough development are related to complex mechanisms involving the wheat proteins and water molecules. A number of analytical methods has been investigated to monitor dough development based on physical or chemical description of dough properties. The most popular in-line process measurements, based on changes in dough physical properties, are that of mixing torque or power consumption of the mixer. Dough development can also be measured using load cells that measures the force exerted by dough moving around the mixing bowl (Kilborn and Preston, 1981; Wilson and Newberry, 1995). At laboratory scale (using analytical methods after dough sampling), dough development has also been largely investigated by microscopy and chemical analysis (Graveland *et al.*, 1985; Amend and Belitz, 1990; Weegels *et al.*, 1996). While most of all the available in-line mixing measurements are based on changes in dough physical properties, most of the changes occurring during the dough mixing are related to chemical mechanisms.

NIR SPECTROMETERS AND DOUGH MIXERS

Wesley *et al.* (2002) patented original approach of NIR spectroscopy technique to monitor dough mixing. The development of fast diode array spectrometers enables NIR spectra to be recorded in a matter of seconds and offers the possibility of an online monitoring of dough development. The changes in NIR spectrum *versus* mixing time were considered to construct the NIR mixing curve and to determine the optimum mixing time. Several research groups in Europe (Alava *et al.*, 2001; Millar *et al.*, 2000; Kaddour *et al.*, 2007) and USA (Psotka *et al.*, 1999; Huang *et al.*, 2001) have confirmed the ability of NIR spectroscopy to monitor dough mixing and extended applications over different conditions.

The in-line NIR description of dough mixing requires specific devices, able to continuously record NIR spectrum of the dough in the mixer tank without interference with the mobile shaft. Most of these systems have been designed as non invasive measurements, to record NIR spectrum without direct contact with the dough (Fig. 1). Wesley *et al.* (1998) designed a support frame which allowed the NIR spectrometer to be placed over the mixing bowl, with the dough at the nominal focal point of the instrument (Fig. 1a). Wesley *et al.* (1998) used also a fibre optic probe directly inside a pin mixer to make the measurement without interactions with the mobile shaft. Alava *et al.* (2001) included a holder for fibre optic probe inside the mixer tank. The probe was suspended 4 cm above the mean dough height as it mixed (Fig. 1b). have positioned the fibre optic probe beneath a glass window on the bottom of the mixing bowl (Fig. 1c). Kaddour *et al.* (2007) positioned the fibre optic probe directly in contact with the dough, at approximately 2 cm under the dough surface (Fig. 1d). According to specificities of the NIR spectrometers, different NIR

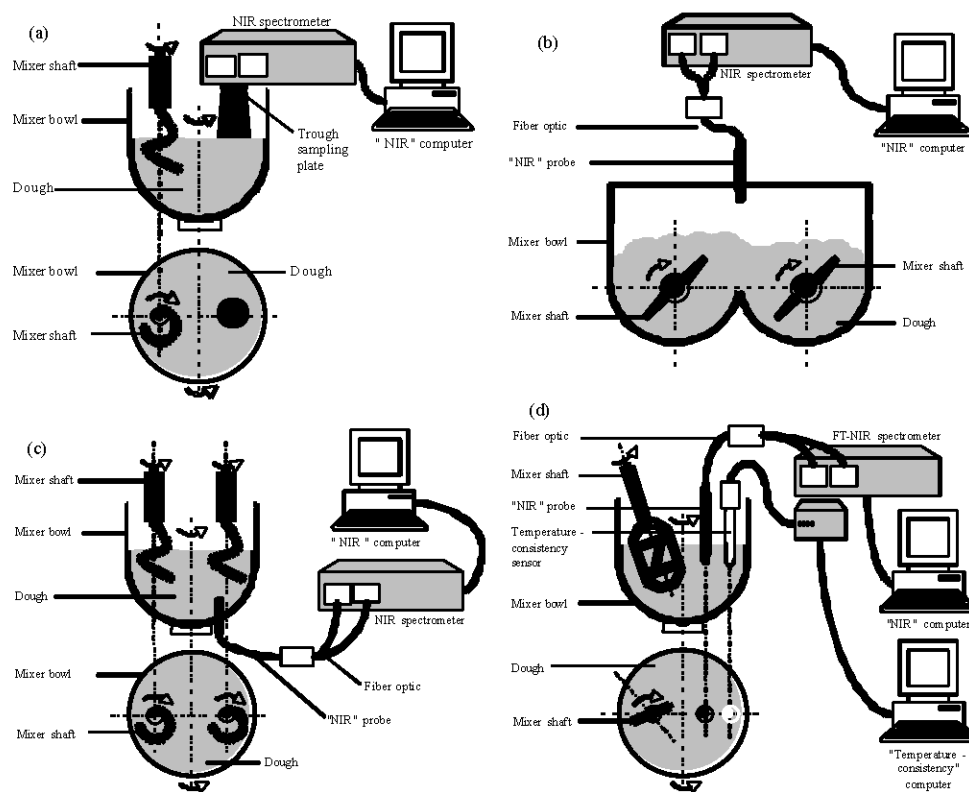


Fig. 1: Experimental devices proposed to in-line monitor dough mixing using NIR spectroscopy equipment. Adapted from (a) Wesley *et al.* (1998), (b) Alava *et al.* (2001), (c) Dempster *et al.* (2004) and (d) Kaddour *et al.* (2007)

wavelength regions have been considered to monitor dough mixing. Most of the studies have been conducted using NIR spectrometer that gathers spectral data over the 400-1700 nm range at 5 nm intervals (Wesley *et al.*, 1998; Alava *et al.*, 2001). Kaddour *et al.* (2007) tested a FT-NIR analyser to record NIR spectra over 1000-2500 nm range at 2 nm intervals.

NIR SPECTRUM AND NIR MIXING CURVES

Raw NIR spectra recorded during dough mixing were presented by different authors. The different dough spectra exhibited typical broad absorbance bands at 985, 1205, 1465, 1783 and 1940 nm (Psołka *et al.*, 1999; Kaddour *et al.*, 2007). The broad bands centred at 1460 and 1940 nm are probably due to water. The two small bands at 1200 and 1783 nm could be associated to C-H vibrations. Movement of the dough during mixing and therefore variation in the signal intensity produced a large degree of baseline variation of the raw NIR spectra. The raw NIR spectra also describe the evolution of the dough granularity, due to the scattering effect of the dough surface and to the diffusive effect of the dough.

Second derivative treatment of NIR spectra have been proposed to construct NIR mixing curves and to generate additional information about chemical reactions occurring during dough mixing (Wesley *et al.*, 1998; Alava *et al.*, 2001; Kaddour *et al.*, 2007). The use of second derivative treatment eliminates the baseline shifts between spectra caused both by the position of the dough

in the mixer and scattering effect, separates the overlapped absorbances and helps identify wavelengths related to reactive groups. The direct description of the second derivative NIR spectra indicates absorption features at 1385, 1413, 1436, 1466, 1900, 2173 and 2276 nm. The peaks can be associated to chemical changes of the dough components (Osborne and Fearn, 1986) and more particularly to starch vibrations (1900 and 1385 nm), to proteins vibrations (2173 and 2239 nm) and to C-H₂, CONH₂, H₂O, starch and CONHR vibrations (1401-1480 nm). Alava *et al.* (2001) reported the OH first overtone for water molecules (at 1450 nm), wheat lipids (at 1410 nm), wheat gluten (at 1460 nm) and wheat starch (at 1450 nm). Wesley *et al.* (1998) indicated that the water first overtone (at 1450 nm) is overlain with absorbance due to the NH first overtone and the first overtone of the CH combination bands and still remains relatively difficult to analyse.

The direct interpretation of the NIR spectra collection (wavelength×absorbances×mixing time) is difficult because of large number of NIR spectra (more than 500 spectra), broadness (in terms of bandwidth) and complexity of the absorbances. Thus, different methods were used to characterise the most important NIR bands variations in the NIR spectra collection.

From individual NIR absorbance values: Wesley *et al.* (1998) proposed a simple method to construct NIR mixing curves by plotting the changes in absorption values measured at 1160 or 1200 nm on the NIR spectra after second derivative treatment. The shape of the NIR mixing curves suggested that as mixing starts, less material which absorbs NIR radiation (at 1160 or 1200 nm) is present until a specific mixing time, called NIR mixing time. The NIR mixing time was found close to the time at optimum dough development. Psotka *et al.* (1999) constructed NIR mixing curves by only using the absorption value at 1380 nm from the raw NIR spectra. NIR mixing time was defined at the deflection point on the line configuration of the cumulative spectral data. High correlation coefficient ($r^2 = 0.89$) was found between the NIR mixing time and optimum dough development time when measured from torque values.

Identified two major NIR wavelengths (at 1205 and 1455 nm) that generate the maximum variability in the spectra throughout the mixing process. The NIR mixing curves have been constructed from plot of the mean centred ratio $\log(1/R)_{1455 \text{ nm}} / \log(1/R)_{1205 \text{ nm}}$ against mixing time. The NIR mixing time was identified at the top of the bell-shaped curve of the NIR mixing curves. Nearly the same time for dough development was found using NIR spectra, using torque measurements and from trained mixer operators (with a window of uncertainty of approximately one minute).

From NIR spectra: Alava *et al.* (2001) identified a restricted wavelength range (1125-1180 nm) over the raw NIR spectra to construct NIR mixing curves. Peak area (calculated by integration of the area under the spectral curve between 1125 and 1180 nm) was plotted as a function of mixing time. The NIR mixing curves showed a linear trend at short mixing times and when the dough was overmixed, with a change in gradient between. The turning point of the NIR curve (defined as NIR mixing time) was related to the peak power consumption point of the mixer, to changes in dough rheology and to bread loaf volume and crumb texture.

Due to the large amount of spectral data collected during dough mixing, the construction of NIR mixing curves has also been investigated by using chemometrics tools. Principal Component Analysis (PCA) of the NIR spectra recorded *versus* time has been considered using either the raw or the second derivative NIR spectra (Alava *et al.*, 2001; Kaddour *et al.*, 2007). The Principal

Components (PC) scores were calculated to describe the total spectral variance from which changes in the dough could be monitored over time. Only the two first PC have been classically considered as accounting for most of the total spectral variance observed during mixing. The other principal components scores were too noisy. It is possible to identify the NIR mixing times from the plots of the PC versus mixing time, as they showed minima associated with, but not at, the peak torque or physico-chemical changes during mixing. The NIR mixing times when calculated after PCA of second derivative NIR spectra were found to be the closest time to the time at dough maximum consistency. On the other hand, the time to maximum consistency was significantly higher than the NIR mixing times when determined by PCA from raw NIR spectra (Kaddour *et al.*, 2007).

PHYSICO-CHEMICAL ANALYSIS OF NIR SPECTRA

The NIR spectroscopy has been considered to provide useful insights into both physical and chemical changes that occur during bread dough development. Different NIR regions were identified as relevant to describe dough mixing as a reactive system and to understand the underlying chemical changes.

The interpretation of data extracted from the raw NIR spectra recorded during mixing has been associated to changes in the dough movement, appearance and physical characteristics (Alava *et al.*, 2001; Kaddour *et al.*, 2007). Movement of the dough during mixing and therefore variation in the signal intensity produced a large degree of baseline variation. Changes in raw NIR spectra with mixing time describe changes in specular and diffusive properties of dough and baseline shift evolution caused by the dough macroscopic structure modification during mixing. It bears most of the physical changes involved in dough from a heterogeneous blend of ingredients to a smooth and finally sticky and filamentous dough.

Description of the second derivative NIR spectra was mainly considered in regards with changes in water interactions and chemical reactions between the wheat components. Specific wavelengths are directly identified from the description of the NIR spectra collection or using chemometrics methods, for instance from the spectral loading patterns calculated by PCA (Kaddour *et al.*, 2007).

To improve the spectral analysis of the NIR curves, Kaddour *et al.* (2008a) investigated the potential of generalized two-dimensional correlation spectroscopy (2D COS) as chemometric tool. The generalized 2D COS method can handle signals fluctuating as an arbitrary function of time, or any other physical variables such as temperature, pressure, or even concentration (Noda, 1993; Ozaki and Noda, 1996; Wang *et al.*, 1998). The 2D COS is a particularly powerful method in the NIR region where spectra are often greatly complicated due to the overlapping of overtones and combination modes (Noda, 1993; Ozaki *et al.*, 1999; Czarnik-Matusiewicz and Pilorz, 2006). The 2D COS method generates two kinds of correlation maps (synchronous and asynchronous maps) based on a set of dynamic spectra calculated from perturbation-induced dynamic fluctuations of spectroscopic signals. Changes in the intensity of the synchronous 2D correlation spectrum make it possible to identify wavelengths for which intensity simultaneously varied. The asynchronous 2D correlation spectrum allows the identification of wavelengths varying out of phase or sequentially (i.e., delayed or accelerated). This method allows identifying synchronous and asynchronous changes in signal intensities at specific wavelengths. A typical example, presented in the study of Kaddour *et al.* (2008a), shows contour maps of the synchronous and asynchronous 2D COS spectra that were constructed from raw NIR spectra. Changes along the diagonal line of the synchronous map were observed at 1890, 1940, 2150 and 2300 nm. Different cross-peaks were identified at the

spectral coordinates: 1460-1890, 1460-2150 and 1460-2300 nm. The positive synchronous values of the cross-peaks suggest that the absorption bands at 1460, 1890, 2150 and 2300 nm simultaneously increase or decrease during mixing. The asynchronous 2D NIR correlation spectrum based on raw NIR spectra presents two broad cross-peaks at 1400-1900 and 2000-2325 nm. These streaks in 2D NIR asynchronous spectrum indicate extensive baseline fluctuations that made the 2D map relatively difficult to analyse (Czarnecki, 1998).

The 2D COS method has also been applied using second derivative NIR spectra. The synchronous 2D NIR correlation spectrum presented two groups of peaks close to the diagonal line and located around 1900 and 2250 nm. The asynchronous 2D correlation spectra showed a so-called butterfly pattern around 1900 nm, that was generated from an absorption band undergoing a wavelength position shift (Czarnecki, 1998; Morita *et al.*, 2006). Taking both the synchronous and asynchronous spectra into account, the bands shift and intensity variation around 1900 nm were believed to occur after changes at 2280, 2238, 2015, 1967, 1780 and 1438 nm. The absorption bands at 2015, 1967 and 1780 nm were not reported in the literature and could not be associated to particular molecular vibration.

An overview of the main NIR wavelengths associated to the specific chemical reactions occurring during dough mixing is presented:

1160 nm: Wesley *et al.* (1998) associated the systematic variation in the peak areas at 1160 nm during dough mixing with water molecules and their interactions with proteins and starch. Experiment with D₂O confirmed that absorbance at 1160 nm is due exclusively to water. The absorbance at 1160 nm is an O-H stretch-bend combination band and is considerably weaker than the first overtone absorption at 1450 nm. Any change in the environment of the water is likely to affect the fundamental frequency of the stretching and bending absorbances at 1160 nm, which will affect the intensity of the combination band. Alava *et al.* (2001) also supposed that the changes in peak area at 1125-1180 nm relates to the hydration of the flour. Belton (2005) considered this hypothesis as reasonable since there may be as little as 6 water molecules per amino acid residue present in gluten and changes might occur on mixing due to proteins hydration. However, the assignment of the 1160 nm peak solely to water is not certain. Any exchangeable groups and other possible causes contributing to the changes in intensity of the 1160 nm band would also be considered, such as temperature rise (Belton, 2005).

1200 nm: Wesley *et al.* (1998) considered that the systematic variation in the peak area at 1200 nm during dough mixing could be associated to a moderate starch absorption. The 1200 nm absorbance peak can be related to the 2nd overtone C-H vibration of the gluten and starch fractions (Law and Tkachuk, 1977). The spectrum of freeze-dried powdered gluten and starch shows absorbances at 1200 and 1185 nm, respectively. In dough, these absorbances combine into one envelope centered on 1200 nm. Wesley *et al.* (1998) indicated that experiments using a starch-water mixture showed neither any variation in Log (1/R) in the NIR. They suggested that water absorption only by starch does not contribute directly to the NIR mixing curve. Changes in protein structure (glutenin macropolymer and extractable gliadin) during mixing may greatly contribute to the variation in the NIR data. From rheological measurements, Alava *et al.* (2001) suggested that the NIR mixing time is associated to the time point at which the gluten network started to breakdown.

1352-1525 nm: Alava *et al.* (2001) identified the region 1375-1525 nm as a main wavelength contributor to describe dough mixing. The 1375-1525 nm region of the NIR spectrum has been associated with the O-H first overtone and could describe the changes in H-bond density between the wheat components and water molecules (Wesley *et al.*, 1998) indicated that the first overtone absorption at 1450 nm is overlain with absorbance due to the first overtones of N-H and C-H combination bands. assigned the band located at 1455 nm to protein and water absorption. Kaddour *et al.* (2007) associated the peaks at 1373 and 1401-1480 nm with the interaction of water molecules with the flour components and more particularly with the CH vibration of the starch molecules with water molecules (Law and Tkachuk, 1977; Osborne and Fearn, 1986).

1778-2052 nm: Kaddour *et al.* (2007) associated the 1778-2052 nm wavelength range, to the hydrogen bond vibrations. The bands identified on the loading spectra associated to PC₂ were reflecting OH, H₂O and starch-water interaction vibrations. The band identified at 1890 nm probably described the hydration of starch during mixing. The NIR region around 1940 nm mainly assigned to a combination band of water molecules, could also be associated to C=O stretching second overtone of -CONH (1920 nm) and -COOR (1950 nm) or to -CONH₂ (asymmetric stretching of the N-H bond + amide II vibration) groups (Law and Tkachuk, 1977; Osborne and Fearn, 1986). Using the 2D COS method, Kaddour *et al.* (2008a) described peaks at 1900 nm that formed an elongated and symmetric positive pattern flanked by two negative fields. This so-called four-leaf-clover pattern was associated either to a band position shift or to intensity changes in highly overlapping bands (Czarnecki, 1998; Morita *et al.*, 2006). The four-leaf-clover pattern in the synchronous spectrum was composed of two auto-peaks at 1870 and 1910 nm. The presence of negative cross-peaks at the spectral coordinates 1870-1910 nm reveals that the changes are correlated, but occur in opposite directions (increase versus decrease). This suggests that the wavelength shift is concomitant with a decrease in the peak intensity at 1900 nm. The pattern close to the diagonal line at 1900 nm can be associated to water molecule vibrations. The peak shift and intensity modification could be associated to the hydration of flour components that causes a decrease of free water (Delwiche *et al.*, 1991).

2109-2325 nm: Different NIR absorption bands located at 2182, 2205, 2231, 2268 and 2282 nm, associated with the protein vibrations, can be related to changes in the protein structure during dough mixing (Kaddour *et al.*, 2007). Sefara *et al.* (1997) demonstrated that the 2255-2290 nm spectral range can be associated to proteins secondary structure modifications. Robert *et al.* (1999) identified two groups of spectral bands located at 2056, 2172, 2289 nm and at 2205, 2264, 2313 nm associated to α -helix and β -sheet structure, respectively. Using the 2D COS method, Kaddour *et al.* (2008a) indicated that negative sign of the cross-peaks between 2238 and 2280 nm revealed changes occurring at 2238 and 2280 nm were correlated and occurred in opposite directions (increase versus decrease). The absence of asynchronous peaks at these two wavelengths suggested that the absorption bands highly overlapped (Morita *et al.*, 2006). While the NIR absorption band at 2238 nm has been assigned to protein or starch structures (Fox *et al.*, 2002; Zardetto, 2005) the band located at 2280 nm was identified as a gluten/hydration sensitive band (Gottlieb *et al.*, 2004).

To explore the time dependence of NIR spectral responses during dough mixing, Kaddour *et al.* (2008a) investigated the potential of the moving window two-dimensional correlation spectroscopy (MW2D) as a chemometric tool. The 2D maps were calculated after partitioning the

entire NIR data matrix into a series of smaller matrices, called window matrices, containing restricted set of successive NIR spectra. The generalized 2D COS method was then used to calculate the autocorrelation intensities for the windowed matrix. These autocorrelation intensities represent the spectral variations in an average window mixing time. The 2D maps for dough mixing were produced by plotting the autocorrelation intensities as a function of the window mixing time. A typical example of MW2D correlation spectra is given in the study of Kaddour *et al.* (2008a). The MW2D correlation spectra calculated from raw NIR spectra revealed that dough mixing could be divided in two main steps according to time at optimum dough consistency. Four absorption bands varying in intensity were observed around 1460, 1890, 2050 and 2300 nm before the optimum dough consistency. Past the optimum dough consistency, only one important NIR band at 1940 nm varied in intensity. The results suggested that the first phenomenon observed during mixing deals with hydration of flour components (1460 nm) and modifications of protein structure (2050-2150 and 2300 nm). After the optimum dough consistency, the second phenomenon seems to involve principally water molecules vibrations (band at 1940 nm).

The application of the MW2D to second derivative NIR spectra indicated a shift of absorption bands to smaller wavelengths. Two correlation peaks along the wavelength axis corresponding to two distinct variations are observed in the MW2D correlation map, respectively at 1890 and 1930 nm. Those wavelength bands are associated to starch and water respectively (Law and Tkachuk, 1977; Osborne and Fearn, 1986). While the absorbance above 1930 nm decreased, that below 1890 nm increased before the optimum dough consistency was attained. Past the optimum dough consistency, peaks intensities varied in a similar way. Hydrogen bonding between water molecules and flour component therefore developed during mixing. One correlation valley bottom between 1890 and 1930 nm is observed, implying spectral intensity variation in that spectral variable range is smaller than that located above 1930 nm and below 1890 nm. Spectral variation between 1890 and 1930 nm can be supposed smaller than that between 1880-1890 and 1930-1935 nm. Kaddour *et al.* (2008a) demonstrated that the 2D methods show that the bands shift and/or intensity variation identified around 1900 nm are occurring after the absorption changes at 1967, 1780 and 1438 nm. The band located at 1438 nm was associated principally to water and starch vibrations (Osborne and Douglas, 1981) and described the hydration of starch during the first stage of mixing. The NIR spectral changes around 1900 nm were correlated with an increase in absorbance at 2238 nm and a decrease in absorbance at 2280 nm. The changes at 1900 nm described the hydration behavior of flour component in term of a decrease of free water. Changes at 2280 nm described modifications in gluten structure. The modification can concern the α -helix structure and the increase of the β -sheet structure of gluten during hydration and dough mixing in agreement with Belton *et al.* (1995) and Gregorski *et al.* (2001). The 2238 nm band associated to protein and starch increases during mixing. This band could be supposed to probably describe the entanglement of the gluten network around the starch granules (Kuktaite *et al.*, 2005; Peighambardoust *et al.*, 2005, 2006).

Based on those different results some physical and chemical description of the reactions occurring during dough mixing can be proposed (Fig. 2). The first stage of bread dough mixing was associated to the hydration of flour constituents. The most important constituent identified by NIR spectroscopy as being hydrated are the starch granules, maybe due to their abundance on dough composition. This hydration causes a decrease of free water. After, the proteins seemed to be involved by a modification of their secondary structure. The protein structure modifications seem

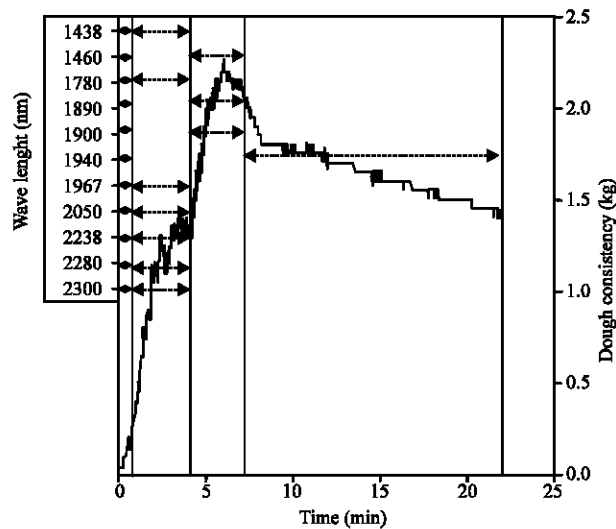


Fig. 2: Higher wavelength variation identified for each mixing step on a curve dough consistency

to be synchronous with the modification of the interaction between starch and protein. Those observations could describe the entanglement of the starch granule by the gluten network formation. After the optimum dough consistency only the water molecules seemed to be involved in the evolution of the NIR signal suggesting that the dough over-mixing stage is principally governed by a modification of dough-water interaction. This can confirm one of the most likely hypothesis suggesting that during over-mixing the water undergoes redistribution, thus altering the hydration state of the gluten phase that causes the stickiness of bread dough.

IMPACT OF FORMULATION AND MIXING CONDITIONS

The potential of NIR spectroscopy to provide a mean of non-invasively probing chemical changes occurring during dough mixing has been explored over a large range of wheat flour types, dough ingredient and mixer types. The studies were conducted with a view to extend the use of the NIR spectroscopy technique to different mixers and mixing conditions.

Impact of mixer type: The ability of NIR spectroscopy to monitor dough mixing has been investigated over different mixers (simple spiral, Z-arm, Pin, double spiral, double Z-arm and oblique fork mixers). The NIR spectroscopy response has been found to partly depend on mixer type. Different relationships were found between optimal mixing time for dough development (from torque measurement or best quality for end products) and NIR mixing times. This may reflect the differences between kinetics of physical mechanisms and of chemical reactions occurring during the dough development, as a function of mixer types.

Using a laboratory spiral mixer, Wesley *et al.* (1998) demonstrated that NIR mixing curves indicated almost similar values for NIR mixing times than the time at maximum power consumption (for two different flours). Using a laboratory Z-arm mixer and a laboratory pin mixer, Wesley *et al.* (1998) found that the NIR measurement predicts a slightly longer mixing time than the power consumption curve. The time difference may be due to the power consumption measurement giving an artificially low value because of lubrication of the dough and the dough becoming wrapped around the mixer blades. Using a Hobart Mixer having a double helical agitator, produced results

indicating nearly the same time for dough development between NIR measurement and torque measurement. Correlation was found ($r^2 = 0.89$) between NIR mixing times and maximum torque times (Psotka *et al.*, 1999). Using double Z-arm mixer, Alava *et al.* (2001) reported higher NIR mixing times for dough development compared to the times to maximum torque (for five different flours). Using an oblique fork mixer (Mahot mixer) equipped with a rotating bowl and an oblique shaft, Kaddour *et al.* (2007) reported similar mixing time values for the NIR mixing times and the times to maximum consistency.

Impact of wheat flour characteristics: The ability of NIR spectroscopy to monitor dough mixing has been demonstrated using wheat flours from different origins or types (Wesley *et al.*, 1998). The variation in the NIR mixing times is consistent with the variation in power consumption. Kaddour *et al.* (2007) indicated that NIR spectroscopy differentiated industrial wheat flours in a similar way than the torques measurements. Alava *et al.* (2001) also demonstrated that differences between wheat varieties differing in protein strength induced differences in NIR mixing curves and torques measurements. Whatever the flour strength, the NIR measurement predicts a slightly longer mixing time than the power input measurements. Alava *et al.* (2001) also compared the NIR mixing times to rheological properties of the gel-protein fraction for a wide range of single variety flours. High correlations ($r^2 = 0.85$) were found between measurements derived from NIR mixing curves and the elastic modulus (G') of the flour gel protein fraction.

Impact of dough ingredients: Wesley *et al.* (1998) indicated that consistent results were obtained for different un-yeasted and full formula wheat flour doughs. Millar *et al.* (2001) evaluated the impact of different ingredients levels (water, oxidizing agent, reducing agent, emulsifier and enzyme) on the NIR mixing curves. Multiple bread dough formulations have been tested by Huang *et al.* (2001). Huang *et al.* (2001) indicated that NIR mixing curves can be used to describe the changes in rheological and chemical mechanisms of bread dough during mixing, generated by the addition of the different ingredients and additives. tested 32 different dough formulations to determine if the changes could be detected using NIR spectroscopy.

Application to diluted dough: Kaddour *et al.* (2008b) demonstrated that NIR spectroscopy can also be useful to in line describe the physical and chemical modifications that occur during mixing of diluted dough. Diluted dough is usually considered to separate wheat flour into gluten and starch. Using the batter process, flour and water are mixed (water-to-flour ratio of 0.7-1.8) to form a slack dough which is mechanically broken up with additional water. Starch and gluten then separated from the slurry by sieving or centrifugation (Frederix *et al.*, 2004). Almost similar physical (i.e., torque changes) and chemical mechanisms (i.e., protein network development) have been supposed to occur during diluted dough development than those associated with bread dough development (Robertson *et al.*, 2006). The main specificities of diluted dough concern the delaying effect of high water contents on the physical and chemical mechanisms inducing longer dough development time. Using a classical dough mixer (with rotating bowl and oblique shaft) and fiber optic probe, Kaddour *et al.* (2008b) recorded almost similar NIR spectra during diluted dough mixing, than those associated to bread dough. For the diluted dough, it is possible to construct NIR mixing curves and to predict the time to maximum consistency from NIR spectra using PCA method. The analysis of NIR spectra using chemometrics methods (PCA, 2D COS and MW2D) allowed to propose a description of the physical and chemical mechanisms involved in diluted dough during

mixing, in accordance with the changes in physical properties (i.e., dough consistancy) and chemical reactions (i.e., glutenin depolymerisation).

CONCLUSION

The NIR spectroscopy has the potential to provide a mean of invasively or non-invasively probing chemical changes that occur during dough development, because the absorbances in the spectra can be directly related to the chemical dough components (water, starch, protein and fat). Principle of the NIR method is based on monitoring a plurality of specific NIR absorbances that exhibit a change as dough mixing progresses, reaching a minimum or maximum at optimum dough development and a change in the opposite direction as the dough mixing continues. Using the NIR technology in breadmaking laboratories studies is very challenging to generate relevant information to monitor dough mixing because, it is the least perturbing method of exploring molecular changes during the input of mechanical energy.

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