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Real-time modeling of milk coagulation using in-line near infrared spectroscopy

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ABSTRACT

This paper considers the extraction of meaningful information in real-time from near infrared (NIR) reflection measurements of coagulating milk. This information can be used for developing automatic cutting time determination. NIR spectra (1000–2500 nm) recorded during coagulation were compressed by principal component analysis. Using component scores as a function of time, two models are proposed for describing the three milk coagulation processes: κ-casein proteolysis, micelle aggregation, and network formation. A model for the entire coagulation process and a composite model for the three individual coagulation processes were established and tested on 12 cheese batches. Both models fitted very well ($R^2 > 0.99$) to the experimental NIR data. An algorithmic procedure is presented that is able to provide real-time parameter estimation for a semi-empirical model describing the kinetics of the milk coagulation processes as well as determining the transition times between the three different coagulation processes.

1. Introduction

The milk coagulation step in cheese manufacturing is terminated by cutting the formed milk gel, where timing of the cut affects final cheese yield and quality. Cutting at too low firmness (cutting too early) results in yield loss and cutting with too high firmness (cutting to late) results in high moisture cheese with undesirable properties (Johnson et al., 2001; Lucey, 2002; Payne et al., 1993). At today's cheese dairies, plant operators predominately do cutting time evaluation manually, which hinders process automation. Consequently, there is a need for automatic methods of optimized cutting time determination.

Rheological analytical methods can determine physical cheese gel characteristics, e.g. storage modulus G′ (Lucey et al., 2003), that cutting time is directly dependent on. These types of measurements are, however, not easily implemented as on-line, real-time process measurements. Reflection of near infrared (NIR) radiation is widely used in the food industry for on-line monitoring of food systems (Simpson, 2010) and NIR has been applied in several studies to detect the optimal gel cutting point (Castillo et al., 2003a; Mertens et al., 2002; Payne et al., 1993). There is however no direct dependency between cutting time and optical properties such as acquired by NIR reflection but rather a dependency to the timely development of NIR measurements. Therefore, the fundamental idea of predicting cutting time using NIR has in many studies been that the shape of the measurement profile over time (i.e. the kinetics) somehow contains information that the optimal cutting time is dependent on (Castillo et al., 2003a; Mertens et al., 2002; Payne et al., 1993). A prerequisite for this idea to work is that the variability of production factors which cutting time depends on (e.g. temperature and milk composition) is accounted for by variability in the shape of the measurement profile over time. This idea has been pursued previously by extracting a collection of parameters that are characteristic for the measurement profile such as maxima or time of maximum change and subsequently investigate if cutting time depends on these parameters. Two main approaches have been used to extract parameters from the measurement profile: (1) by extracting minima or maxima of the first or second derivative of the profile or (2) fitting a kinetic model to the measurement profile and subsequently extracting the model parameters.

The first approach which account for the majority of studies have extracted the measurement profile parameters by identifying time or NIR response at maxima or minima of the first or second derivative of the profile. Particularly, the process time at the maximum of the first derivative, referred to as the inflection-point, has been used. A cutting time prediction model (Eq. (1)) is then made by linear regression:

$$t_{cut} = a + bt_f \quad (1)$$

Where t_f is the time of inflection-point and a and b are parameters estimated by least squares based on a set of inflection-points and their corresponding optimal cutting times t_{cut} (Payne et al., 1993; Crofcheck et al., 1999; Castillo et al., 2003a). This prediction model has however proven to be too simplistic when protein content varies, because the profile variability at the inflection-point does not entirely account for the variability in cutting time that protein variations infer (Mertens et al., 2002). An improved cutting time model was then proposed with the addition of a protein term (Castillo et al., 2003a). It is however perhaps too difficult to

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implement a registration of milk protein content for every new batch in a production environment.

Another approach which has been little exploited is to first estimate the shape of the NIR measurement time profile by a kinetic model and secondly withdraw model parameters as input variables for prediction of optimal cutting time. The advantage of fitting a kinetic model is that more data from the profile is taken into account, when the parameters are extracted. In this way the coagulation is better described than only extracting e.g. maximum of the derivatives.

Previous studies have proved that kinetics models can describe the NIR measurement profile well (Mertens et al., 2002; Castillo et al., 2003b). However, these studies have not considered how such kinetic models could be exploited for real-time process control. Such real-time acquired information could potentially be used for more accurate cutting time prediction.

The objective of this study is (1) to provide meaningful information from near infrared (NIR) reflection measurements of coagulating milk by formulation and testing kinetic of models and (2) to demonstrated how kinetic models can be applied during the coagulation process i.e. in real-time. Experimentally the study is based on twelve experiments of milk coagulation measured by NIR reflection. Different kinetic models are formulated and evaluated regarding fit to NIR data and their robustness towards missing data.

2. Materials and methods

2.1. Experimental procedure

To mimic production in an industrial setting twelve milk coagulation experiments (with similar parameter settings) were performed simulating Normal Operating Condition (NOC) batches. Preparation of reconstituted milk from skim milk powder followed the procedure of Hansen et al. (2010). Five liter of reconstituted milk was transferred to a 6 L cheese vat, which was inserted in a water bath for pre-conditioning to 32.0 °C, approximately 10 min before rennet addition. Chy-Max Plus rennet with 190 international milk clotting units IMCU mL^{-1} was used (Chr. Hansen A/S, Hørsholm, Denmark). A diluted rennet solution made within 3 min before experiment initialization was added to the milk resulting in a final concentration of 0.066 IMCU mL^{-1} of milk. The milk was stirred (18 rpm) for thirty seconds after rennet addition to ensure homogenous distribution.

NIR measurements were carried out using the Antaris MX FT-NIR Process Analyzer from Thermo Scientific (MA, USA) with a reflectance probe with SMA fiber connection. The spectrometer is self-referenced, so stability is ensured by collecting background spectra simultaneously with the sample measurements using an internal integrating sphere. To account for optical changes in the fibers cables connecting the probe to the spectrometer, a background spectrum was taken approximately 10 min prior to each batch run using a built-in reflectance standard (99% reflectance) in the instrument. In the NIR range 10,001–4000 cm^{-1} (corresponding to 1000–2500 nm) 1557 frequencies (ν) were measured equidistant with $\Delta\nu = 3.8569\ cm^{-1}$. A total of 32 averaged scans were found to provide an adequate *signal-to-noise* ratio. This resulted in an acquisition time of 36 s. Spectra were recorded as expressed in Eq. (2):

$$\log_{10}\left(\frac{1}{R}\right) = -\log_{10}\left(\frac{I}{I_0}\right) \tag{2}$$

Where I is intensity of the light beam striking the detector after being reflected from the sample and I_0 is the intensity of the light beam after being reflected from the built-in 99% reflectance standard. In this way, I/I_0 is the fraction of light being reflected by the coagulating milk. The spectral range 1000–1850 nm, with a total of 1200 variables was use for modeling.

2.2. Coagulation models and real-time application

2.2.1. Model for entire coagulation progress

Initial evaluation of NIR spectra revealed that main spectral development during coagulation was baseline changes (Fig. 1). Further evaluation of vibrational band specific changes due to coagulation is not done here but Dahm et al. (2010) provides details on this topic. Most previous studies (Castillo et al., 2003a; Mertens et al., 2002; Payne et al., 1993) in this specific field, select a single NIR wavelength for further analysis. Instead principal component analysis (PCA; Wold et al., 1987) was applied to transform the multivariate response into a single variable referred to as the first principal component (PC1), which account for of the main variability in the spectra. The advantage of using the time profile of PC-scores opposed to the profile of single wavelength NIR variables is due to the first order advantage which utilizes the covariation between spectral variables to provide robust estimates of spectral features and to strongly improve the signal to-noise-ratio (Bro, 2003).

There seems to be consensus in literature that the build-up of a rennet induced milk gel is the result of three underlying stages with different mechanisms: (*I*) initial enzymatic proteolysis of κ-casein after which the altered casein micelles are referred to as paracasein; (II) a subsequent aggregation of paracasein, where the aggregation rate depends on the concentration of free paracasein sites, implying that this stage is dependent on rate and degree of κ-casein proteolysis; (III) gelation, formation of polymer networks where aggregated micelle strands are cross-linking, also referred to as gel firming (Storry and Ford, 1982; McMahon et al., 1984; Carlson et al., 1987; Castillo et al., 2003b). The transition between stages is not easy to detect, because head-and-tail of the successive stage overlap to some extend in the process.

A kinetic model was applied (Eq. (3)) with seven parameters fitted by non-linear least squares using a Gauss–Newton algorithm with Levenberg–Marquardt regularization (Seber and Wild, 2003) to approximate the observed score-values coagulation profile $x(t)$. This model is a slight modification of the model proposed by Mertens et al. (2002):

$$x(t) = \frac{\alpha_1}{1 + \exp\left(-k_{\text{aggre}}(t - t_{\max})\right)} + \alpha_2 \exp\left(-k_{\text{network}}(t - t_{\text{network}})\right) + \alpha_3 \tag{3}$$

This model is composed of three terms: the logistic equation (also known from autocatalytic processes e.g. microbial growth, epidemics), an exponential term (also known from first order reactions) and an offset term. The logistic equation is a model of the initial s-shaped part of the profile where casein micelle aggregation occurs. The exponential term is a model of the later stage where micelle network formation takes place. Parameters α_1, α_2, and α_3 are related to the magnitudes in the profile; parameters k_{aggre} and k_{network} are rate constants related to the speed of micelle aggregation and network formation, respectively. Parameters $t_{\max}$ and t_{network} are concerned with the location of the s-shape and the exponential along the time-axis. More specifically, $t_{\max}$ is the time of maximum slope in the s-shape, which is the modeling counterpart for inflection point as determined by the maximum of first derivative (see Eq. (1)); t_{network} is likewise the time of maximum slope in the exponential shape, which in this time profile is the located at the onset of the exponential and thereby related to the onset of network formation. Table 1 provides an overview of the model parameters used in the present study.

2.2.2. Models for individual coagulation phase

Fitting a model for the entire coagulation progress, if only the first part of the process has run could potentially lead to unstable fitting (ill-conditioned solution). As a more robust model for