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On-line prediction of cheese making indices using backscatter of near infrared light

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Abstract

The potential of a fibre optic sensor, detecting light backscatter in a cheese vat during coagulation and syneresis, to predict curd moisture, fat loses and curd yield was examined. Temperature, cutting time and calcium levels were varied to assess the strength of the predictions over a range of processing conditions. Equations were developed using a combination of independent variables, milk compositional and light backscatter parameters. Fat losses, curd yield and curd moisture content were predicted with a standard error of prediction (SEP) of $\pm 2.65\,\mathrm{g}\,100\,\mathrm{g}^{-1}$ ($R^2 = 0.93$), $\pm 0.95\%$ ($R^2 = 0.90$) and $\pm 1.43\%$ ($R^2 = 0.94$), respectively. These results were used to develop a model for predicting curd moisture as a function of time during syneresis (SEP $= \pm 1.72\%$; $R^2 = 0.95$). By monitoring coagulation and syneresis, this sensor technology could be employed to control curd moisture content, thereby improving process control during cheese manufacture.

Keywords: Syneresis; Curd moisture; Whey fat; Curd yield; Fibre optic; Optical sensor; Process control

1. Introduction

Barbano and Lynch (2006) stated that the development of new or improved methods of process control and product analysis in the dairy industry has been driven by consolidation and increased scale of dairy product manufacture. This has also been observed in the cheese manufacturing industry where an increasing degree of automation of the process is seen as highly desirable. Numerous studies have investigated the development of rapid and non-destructive techniques, often utilizing infrared technology, for monitoring unit operations within cheese manufacture. These have included determination of milk composition and quality (Biggs, 1967; Tsenkova et al., 2006), monitoring milk coagulation and predicting the optimum cutting time (Payne, Hicks, & Shen, 1993) as well as monitoring cheese ripening and quality (Fagan, Everard, O'Donnell, Downey, Sheehan et al., 2007; Irudayaraj, Chen, & McMahon, 1999).

Of the influential cheese making operations affecting cheese yield and quality that are under the control of the cheese maker, syneresis is probably the most important. A decrease in moisture content by as little as 1% translates into an important reduction in cheese yield and profits (Emmons, 1993). Inadequate curd moisture content also has a negative effect on cheese ripening and its final quality and price. The development of a monitoring and control technology for this operation has been generally overlooked.

Recently, a limited number of studies have investigated technologies with potential as syneresis monitoring and control technologies (Everard et al., 2007; Fagan, Leedy, et al., 2007; Taifi et al., 2006). Taifi et al. (2006) studied the potential of ultrasonic velocity and attenuation to determine the onset of syneresis in a milk gel. They stated that velocity evolution obtained at high ultrasonic frequency appeared to be an indicator of the occurrence of syneresis and that syneresis was also characterized by a large

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increase in attenuation. However, this study investigated the spontaneous onset of microsyneresis rather than syneresis as induced in industry by cutting a gel. Everard et al. (2007) proposed a method for monitoring syneresis based on changes in colour measurements occurring in a cheese vat. They found that a computer vision image analysis technique was capable of distinguishing the effects of pH and stirring speed and that with the inclusion of known factors and calibration to a range of operating conditions there is potential for predicting an endpoint of syneresis. However, a limitation of the technique was that images were obtained of the surface of the curd/whey mixture and stirring speed significantly affects the level of curd particles present at the surface. In fact, Everard et al. (2007) found that moisture content of the curd could only be predicted using this method at high stirring speeds. A method of monitoring syneresis utilizing the backscatter of near infrared light has also been developed (Fagan, Castillo, Payne, O'Donnell, Leedy et al., 2007; Fagan, Leedy et al., 2007). Fagan, Leedy et al. (2007) proposed that a sensor detecting near infrared light backscatter in a cheese vat with a large field of view (LFV) relative to curd particle size would have potential for monitoring both milk coagulation and curd syneresis. They found that the response of the prototype sensor was affected by temperature and that the sensor showed potential for predicting whey fat content, curd moisture content and curd yield (Fagan, Leedy et al., 2007). However, the preliminary predictions presented in that study were limited in their use due to the small data set used and the reduced strength of the predictions found. Fagan, Castillo, Payne, O'Donnell, Leedy et al. (2007) found that the LFV sensor was sensitive to both aggregation of casein micelles and development of curd firmness during milk coagulation and that the sensor response during syneresis was related to changes in curd moisture and whey fat content. The effect of temperature on the sensor response was also found to be consistent with the effect of temperature on the kinetics of both coagulation and syneresis. It is necessary to determine if the LFV sensor can be used to predict important cheese making indices. The first objective of this study was to develop equations to predict curd moisture content, whey fat and curd yield at the end of syneresis. The second objective was to predict curd moisture content as a function of processing time during syneresis, as this would facilitate process control and to determine if the technology has sufficient potential to warrant validation and scaling up.

2. Materials and methods

2.1. Experimental design

A three-factor, fully randomized, spherical, central composite design (CCD) was employed to assess the strength of predictions for several cheese making indices under a broad range of processing conditions. The experimental factors (temperature (T), calcium chloride ($CaCl_2$) addition level (CCAL) and cutting time level (β)), their selected levels and coded values are presented in Table 1. The CoAguLite (CL) sensor (model 5, Reflectronics Inc., Lexington, KY, USA) was employed to select the different experimental levels of cutting time as described below. The cutting times (t_{cut}) used in the experiment were determined relative to measurements of aggregation time based on light backscatter using the CL sensor. Thus, the CL sensor generated a real-time target value for t_{cut} for each experiment using the following equation proposed by Payne, Hicks, Madangopal, and Shearer (1993):

Table 1
The experimental factors and levels employed in the central composite rotatable experimental design

Factors (coded value)	Temperature (°C)	Added $CaCl_2$ (mM)	Cutting time (β) (dimensionless)[a]
−1.682	23.6	0.318	1.32
−1	27.0	1.00	1.80
0	32.0	2.00	2.50
1	37.0	3.00	3.20
1.682	40.4	3.68	3.68

[a]Experimental cutting time levels were selected as βt_{max}, where t_{max} was the time from enzyme addition to the inflection point of the light backscatter profile obtained using the CoAguLite™ sensor.

$$t_{cut} = \beta t_{max}, \quad (1)$$

where t_{max} was the time taken to reach the first maximum of the first derivative of the CL response, and β was a constant. Beta (β) values were obtained from the experimental design shown in Table 1 and were used to establish the range of target t_{cut} values for the experiment. Since changes in β represent changes in cutting time, during the discussion we will use the term cutting time (t_{cut}) instead of the less intuitive symbol β.

2.2. Milk preparation and compositional analysis

Unpasteurized unhomogenized milk was obtained from a local Kentucky milk processing plant (Winchester Farms Dairy, Winchester, KY, USA). Milk was analyzed using a MilkoScan FT 120 (Foss Electric, Hillerød, Denmark) and prepared for coagulation according to the procedure employed by Fagan, Leedy et al. (2007). The average composition of the milk fat, protein and total solids contents was $3.7 \pm 0.3\%$, $3.5 \pm 0.1\%$ and $12.2 \pm 0.3\%$, respectively.

2.3. Milk coagulation

Chymosin enzyme was used for milk coagulation at a level of $0.06\,mL\,kg^{-1}$ (CHY-MAX® Extra; Chr. Hansen Inc., Milwaukee, WI, USA). It had a relative milk-clotting activity test (REMCAT) strength of $643\,IMCU\,mL^{-1}$

(International milk-clotting units). Coagulation temperature was controlled in a 7-l cheese vat connected to a circulating water bath (Lauda, RM 20, Brinkman Instrument Inc., Westbury, NY, USA). Further details of the milk coagulation procedure are provided by Fagan, Leedy et al. (2007).

2.4. On-line light backscatter monitoring instrumentation

On-line, continuous monitoring of milk coagulation and curd syneresis was performed in the cheese vat using two different light backscatter sensor technologies, i.e. the CL and the LFV sensors. Light backscatter response from the two sensors was continuously monitored from the time of rennet addition (t_{c0}) to the end of syneresis (t_{s85}).

The CL sensor utilized near infrared light at 880 nm and consisted of two 600 μm diameter fibres. One fibre transmitted infrared radiation from a light source into the milk while the other fibre transmitted the radiation scattered by the milk particles to a silicon photo-detector. Further details on the CL sensor and data acquisition system were presented by Castillo, Payne, Hicks, and Lopez (2000).

The LFV sensor was a prototype designed at the University of Kentucky (Fig. 1). Further details of the LFV sensor and optical configuration have been presented by Fagan, Leedy et al. (2007). The sensor was connected to a miniature fibre optic spectrometer (model SD2000, Ocean Optics, Inc., Dunedin, FL, USA) which collected light backscatter over the range 300–1100 nm. It has been demonstrated that the LFV sensor signal at 980 nm incorporated less noise than at other wavelengths, while also being more sensitive to changes occurring in the vat during both milk coagulation and curd syneresis (Fagan, Leedy et al., 2007). Therefore, the LFV sensor response at 980 nm was selected for use in this study.

A number of optical parameters were derived from the LFV sensor response during coagulation and syneresis as outlined in Fagan, Leedy et al. (2007). These parameters are defined in Table 2.

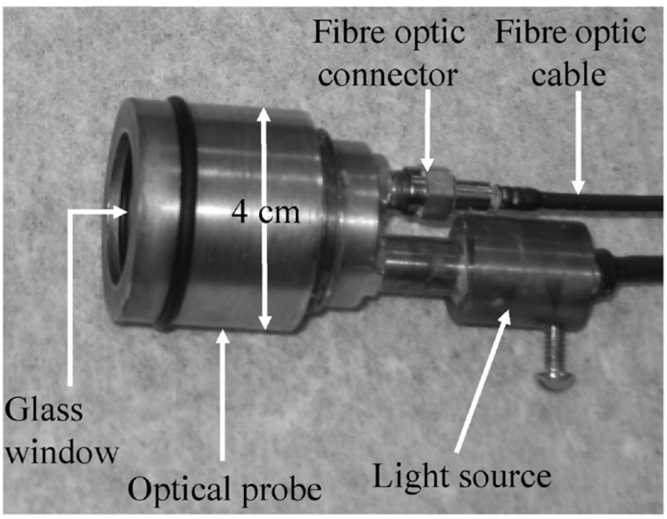

Fig. 1. Image of the prototype large field view sensor employed for on-line monitoring of milk coagulation and curd syneresis.

Table 2
Definition of optical parameters derived from the light backscatter ratio profiles during coagulation and syneresis using the LFV sensor

Parameter	Units	Definition
t_{max}	min	Time to the first maximum of R'[b]
t_{cut}	min	Time to gel cutting
R_{max}	dimensionless	Value of R[a] at t_{max}
R_{cut}	dimensionless	Value of R at t_{cut}
R'_{max}	min^{-1}	Value of R' at t_{max}
ΔR_{syn}	%	Percent decrease in R from t_{s0}[c] to t_{s85}[d]

[a] R, light backscatter ratio, i.e., the LFV sensor response at any time relative to the average response obtained in the first 60 s of coagulation;
[b] R', first derivative of the light backscatter ratio;
[c] t_{s0}, start of syneresis;
[d] t_{s85}, end of syneresis.

2.5. Gel cutting and stirring procedure

The gel was cut when indicated by the CL data acquisition software using a specially designed, manual cutting system (Fagan, Leedy et al., 2007). The first recorded time point after t_{cut} is defined as the start of the syneresis process (t_{s0}), and time (t) is measured from t_{s0}. The curd was left to heal for 4.5 min before initiating stirring at 10 rpm (Servodyne mixer 50003-10, Cole Parmer Instrument Co., Vernon Hills, IL, USA). The stirring process continued at this speed up to 85 min (t_{s85}).

2.6. Curd and whey sampling and analysis procedure

Sampling and chemical composition analysis of the curd and whey were carried out according to the procedure provided by Fagan, Leedy et al. (2007). The curd yield on a wet basis (CY_{wb}) for each experiment and the total accumulated whey fat loss at the end of each experiment (WFL) were computed using the equations detailed in Fagan, Castillo, Payne, O'Donnell, and O'Callaghan (2007).

2.7. Syneresis kinetics

It is well documented that changes in curd moisture and whey fat content during syneresis follow first-order kinetics. Therefore, the experimental data obtained for curd moisture and whey fat content have been previously fitted to first-order equations (Fagan, Castillo, Payne, O'Donnell, Leedy et al., 2007).

Recently Fagan, Castillo, Payne, O'Donnell, Leedy et al. (2007) also fitted the LFV sensor response during syneresis to a first-order equation (Eq. (2)).

$$R_t = R_\infty + (R_0 - R_\infty)e^{-k_{LFV}t}, \tag{2}$$

where R_t was the light backscatter ratio during syneresis at time t (min), R_∞ was the light backscatter ratio at an infinite time, R_0 was the light backscatter ratio during syneresis at t_{s0}, and k_{LFV} was the kinetic rate constant (min^{-1}) for the LFV sensor response during syneresis.

2.8. Statistical analysis

The experimental data recorded for changes in curd moisture and whey fat content, and for the LFV sensor response as a function of time during syneresis were fitted to first order equations described above using the nonlinear procedure in SAS, to estimate kinetic parameters.

A number of different regression models for predicting whey fat content, curd yield, curd moisture content and the kinetic rate constants for curd moisture and whey fat content, which included independent and dependent variable were tested using the maximum R^2, regression and nonlinear procedures in the SAS statistical package (version 9.1, 2002–2003, SAS Institute, Cary, NC, USA).

3. Results and discussion

A critical step in developing the LFV sensor as a technology for monitoring syneresis is the development of models, which could be used to predict main syneresis indices, such as whey fat content, curd yield and curd moisture content. In this study, the initial database contained more than 40 parameters which may have potential to predict syneresis indices, some of which had a high degree of multi-collinearity. As our preference was to obtain simple prediction models that would be easy to implement and calibrate in the cheese plant, the maximum R^2 procedure was selected, rather than more complex modeling techniques such as grey box or hybrid modeling, as an exploratory method to reduce the number of parameters to a small number which would be most useful in predicting each variable. The selection of parameters was also based on scientific meaning of the parameters, the potential information they may carry, and on the practical in line application/calibration of the parameters. This predictive approach has been demonstrated over the years to be very effective for the development of simple and easy to implement on-line sensor technologies for milk processing automation (Castillo et al., 2000; Payne, Hicks, Madangopal et al., 1993; Payne, Hicks, & Shen, 1993).

The best four-parameter models for predicting accumulated total whey fat losses at t_{s85} (WFL) (g), curd moisture content at t_{s85} (CM_{85}) (%), the kinetic rate constants for changes in whey fat concentration and curd moisture content during syneresis (k_{WF}, k_{CM}) (min^{-1}), and curd yield on a wet basis CY_{wb} (%) were developed. The parameters incorporated into the models included the independent variable T, its quadratic term, milk composition, dependent variables derived from the LFV sensor response during coagulation and syneresis as defined in Table 2 and kinetic parameters, R_0, R_∞ and k_{LFV}, derived from the fitting of experimental data to Eq. (2).

One drawback of these initial models was that R_0, R_∞ and k_{LFV} terms were derived by fitting R, from cutting the gel to the end of the syneresis process, to Eq. (2) and therefore these parameters would not be useful for on-line, real-time prediction of cheese making indices prior to whey drainage. In order to overcome this, a second set of predictive models was obtained where only the first 15 min of data recorded by the LFV sensor after cutting were fitted to Eq. (2). All parameters which were obtained using this procedure were denoted by the subscript "15", e.g., k_{LFV15}, R_{015} and $R_{\infty 15}$ variables. The maximum R^2 procedure in SAS was repeated using the kinetic parameters derived from fitting R during the first 15 min of syneresis to Eq. (2) and no significant difference was found between models that utilized k_{LFV15}, R_{015} and $R_{\infty 15}$ rather than k_{LFV}, R_0 and R_∞ terms. Therefore, the models developed using the k_{LFV15}, R_{015} and $R_{\infty 15}$ terms were selected for discussion.

These best four-parameter models for predicting WFL ($g\,100\,g^{-1}$), CY_{wb} (%), CM_{85} (%), k_{WF} and k_{CM} (min^{-1}), are shown in Table 3 as models I, II, III, IV and V, respectively. All models used a combination of independent variables, milk composition and LFV dependent variables. It should be noted that all the predictors used in models I to V and those used in successive models are known as early as 15 min after cutting the gel.

3.1. Prediction of final curd yield, whey fat loses and curd moisture content

Model I predicted WFL with a standard error of prediction (SEP) of $\pm 2.65\,g\,100\,g^{-1}$ with R^2 of 0.93 using three factors, i.e., temperature, milk protein content (P_m) and one optically determined parameter, the light backscatter ratio during syneresis at an infinite time ($R_{\infty 15}$), obtained from fitting the first 15 min of data of R to Eq. (2) (Fig. 2). These results indicate that, as was proposed by Fagan, Castillo, Payne, O'Donnell, Leedy et al. (2007), the LFV sensor response during syneresis is significantly related to changes in the fat content of the whey in the cheese vat.

Three individual parameters were used in model II to predict CY_{wb}, namely, temperature, milk total solids content (TS_m), and the light backscatter ratio during syneresis at t_{s0} (R_{015}) as determined by fitting the first 15 min of data of R to Eq. (2) (Table 3). It should be noted that R_0 would be a function of the gel properties at cutting. Model II predicted CY_{wb} with an SEP of $\pm 0.95\%$ and R^2 of 0.90 (Fig. 3).

The model developed to predict CM_{85}, model III, shown in Table 3, utilized one independent variable, i.e., temperature, and three other parameters, i.e., time to the first maximum of R' (t_{max}), milk fat content (F_m), and fat protein ratio of milk (FP_m). This model predicted CM_{85} with an SEP of 1.46% and R^2 of 0.94 (Fig. 4). The inclusion of coagulation parameters in the model for predicting CM_{85} highlights the importance of coagulation conditions in determining curd moisture content. Clearly, the LFV sensor response during syneresis is affected by

Table 3
Models for the prediction of final whey fat losses (WFL), curd moisture content (CM_{85}), curd yield on a wet basis CY_{wb}, and the kinetic rate constants for changes in whey fat and curd moisture content (k_{WF}, k_{CM}), using milk composition, independent variables and LFV light backscatter parameters[a]

Model		d.f.	β_0	β_1	β_2	β_3	β_4	R^2	SEP
I	$WFL = \beta_0+\beta_1 T+\beta_2 T^2+\beta_3 P_m+\beta_4 R_{\infty 15}$	56	181*	−13*	0.24*	7.4***	11*	0.93	2.65
II	$CY_{wb} = \beta_0+\beta_1 T+\beta_2 T^2+\beta_3 TS_m+\beta_4 R_{015}$	56	74***	−1.5**	0.01 ns	−1.1***	−3.2***	0.90	0.95
III	$CM_{85} = \beta_0+\beta_1 T+\beta_2 t_{max}+\beta_3 F_m+\beta_4 FP_m$	56	114*	−1.2*	0.26 ns	−11*	26*	0.94	1.43
IV	$k_{WF} = \beta_0+\beta_1 R_{max}+\beta_2 R'_{max}+\beta_3 t_{max}+\beta_4 R_{\infty 15}$	56	−0.23 ns	1.18***	−13.42*	−0.03**	−0.26*	0.54	0.074
V	$k_{CM} = \beta_1 T^2+\beta_2 t_{max}+\beta_3 k_{LFV15}$	57	—	0.00003*	−0.001**	3.61*	–	0.52	0.031

[a]Number of data points = 60; d.f., degrees of freedom; T, temperature (°C); P_m, milk protein (%); F_m, milk fat (%); TS_m, milk total solids (%); FP_m, milk fat protein ratio; $R_{\infty 15}$, light backscatter ratio (R) at an infinite time (Eq. (2)) obtained from the first 15 min of data; R_{015}, R at t_{s0} (Eq. (2)) obtained from the first 15 min of data; t_{max}, time to the first maximum of first derivative of the light backscatter ratio (R'); R_{max}, value of R at t_{max}; R'_{max}, value of R' at t_{max}; k_{LFV15}, kinetic rate constant for the LFV sensor response during the first 15 min of syneresis (Eq. (2)); β_0–β_4, regression coefficients.
*$P<0.05$.
**$P<0.01$.
***$P<0.001$.

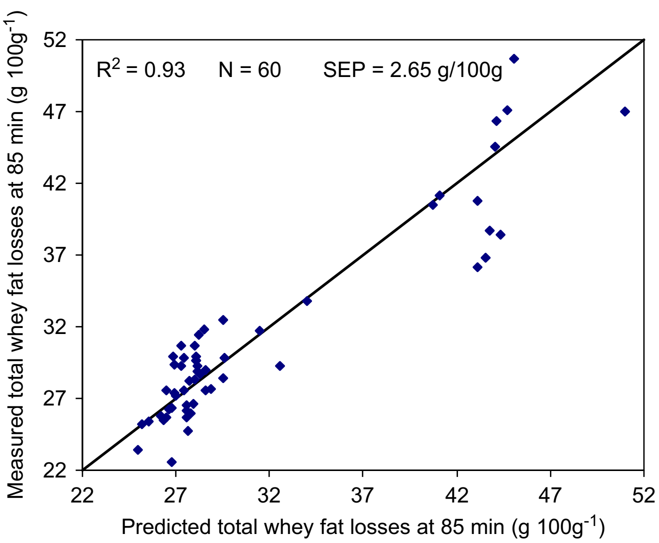

Fig. 2. Actual total whey fat losses at 85 min after cutting (WFL) versus prediction of WFL using model I ($WFL = \beta_0+\beta_1 T+\beta_2 T^2+\beta_3 P_m+\beta_4 R_{\infty 15}$). R^2, coefficient of determination; SEP, standard error of prediction; β_0 to β_4 are regression coefficients; T, temperature; P_m, milk protein content; $R_{\infty 15}$, light backscatter ratio during syneresis at an infinite time obtained by fitting the LFV sensor response during the first 15 min of syneresis to Eq. (2).

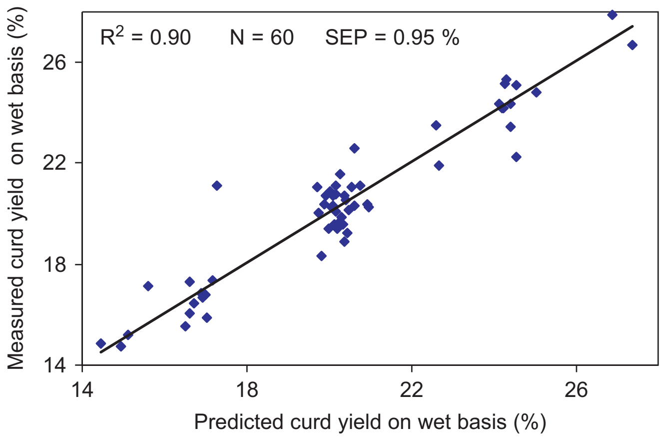

Fig. 3. Actual curd yield on a wet basis (CY_{wb}) versus prediction of CY_{wb} using model II ($CY_{wb} = \beta_0+\beta_1 T+\beta_2 T^2+\beta_3 TS_m+\beta_4 R_{015}$). R^2, coefficient of determination; SEP, standard error of prediction; β_0 to β_4 are regression coefficients; T, temperature; TS_m, milk total solids content; R_{015}, light backscatter ratio during syneresis at t_{s0} obtained by fitting the LFV sensor response during the first 15 min of syneresis to Eq. (2).

changes in curd moisture content as claimed by Fagan, Castillo, Payne, O'Donnell, Leedy et al. (2007).

The models presented for predicting WFL, CM_{85} and CY_{wb} are a significant improvement over the models previously presented by Fagan, Leedy et al. (2007) for the prediction of these parameters, which gave R^2 of 0.35, 0.34 and 0.75 for predicting WFL, CM_{85} and CY_{wb}, respectively. However, some relationships are observed between the parameters used in the models shown in Table 3 and those of Fagan, Leedy et al. (2007). In the model developed by Fagan, Leedy et al. (2007) for predicting WFL, t_{cut} and t_{max} were significant parameters. Temperature and P_m, which significantly affect coagulation rate and in turn t_{max} and t_{cut}, were highly significant in predicting WFL in model I (Table 3). The significance of these parameters in predicting whey fat content is due to the importance of the rheological properties of the gel at cutting and the temperature at which syneresis is carried out on the level of whey fat losses. The retention of fat is attributed to the relative rigidity and structure of the network at cutting (Johnson, Chen, & Jaeggi, 2001). At the lower temperatures of this study (below 30–32 °C), increasing the temperature increases the rate of curd firming. Therefore, gels formed at low temperatures if cut at short t_{cut} will be fragile, resulting in a fine curd and high fat losses. Lengthening t_{cut} at low temperatures will compensate for the slow firming rate and a stronger gel is formed and fat losses are reduced. However, at higher temperature (above 30–32 °C) coarsening of the milk gel occurs more rapidly, permeability of the gel will be greater and at longer aging times, microsyneresis can occur, all of which reduces the ability of the curd to retain fat. In this case, increasing

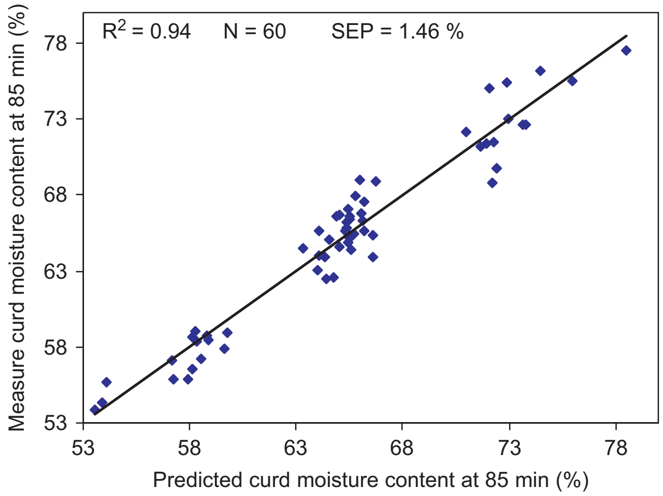

Fig. 4. Actual curd moisture content at the end of syneresis (CM_{85}) versus prediction of CM_{85} using model III ($CM_{85} = \beta_0 + \beta_1 T + \beta_2 t_{max} + \beta_3 F_m + \beta_4 FP_m$). R^2, coefficient of determination; SEP, standard error of prediction; β_0 to β_4 are regression coefficients; T, temperature; t_{max}, time to the first maximum of the first derivative of the light backscatter ratio (R'); F_m, milk fat content; FP_m, milk fat protein ratio.

t_{cut} will exacerbate these processes hence at high temperatures increasing t_{cut} results in greater fat losses (Fagan, Castillo, Payne, O'Donnell, and O'Callaghan, 2007). The P_m will also affect the rheological properties of the milk gel at cutting, which will therefore affect the fat retention capacity of the gel. Castillo, Payne, Hicks, Laencina, and Lopez (2003) stated that increasing the protein content of milk decreased the relative distance between time-based parameters t_{max} and t_{cut} measured as $(t_{cut} - t_{max})/t_{max}$, while Dalgleish (1980) found that increasing the casein concentration by ultrafiltration resulted in a firmer final curd. The basis for the inclusion of $R_{\infty 15}$ is that it has been previously demonstrated that there is a strong significant relationship between R and both curd moisture and whey fat content (Fagan, Castillo, Payne, O'Donnell, Leedy et al., 2007).

Fagan, Leedy et al. (2007) found also that t_{max} was significant in predicting CM_{85}, which was also observed in model III (Table 3) for CM_{85}. In that study, temperature primarily affected t_{max} and increasing temperature (decreasing t_{max}) increased the rate and extent of syneresis (Fagan, Castillo, Payne, O'Donnell, and O'Callaghan, 2007). Syneresis is also dependent on milk composition. Pearse and Mackinlay (1989) noted that an increase in F_m or P_m will decrease syneresis which accounts for the inclusion of F_m and FP_m terms in the CM_{85} prediction model (model III, Table 3). The CY_{wb} is primarily determined by curd moisture content but also to some extent on total solids retained in the curd. Factors which affect the rate and extent of syneresis as well as retention of solids, such as temperature and TS_m were important in predicting CY_{wb} (model II, Table 3). These similarities were observed in the CY_{wb} model presented by Fagan, Leedy et al. (2007) with CCAL, t_{max} and ΔR_{syn} found to be most significant. Indeed increasing temperature, reflected in a smaller t_{max}, will decrease final curd moisture as gels formed at higher temperatures have a greater permeability which results in a faster rate of syneresis and a larger amount of whey separation (Castillo, Lucey, Wang, & Payne, 2006). The effect of varying temperature and TS_m on CY_{wb} can be explained through the retention of casein and total solids as well as moisture. The LFV response parameter, R_{015}, is included in the CY_{wb} model (model II, Table 3) as it reflects the rheological properties of the milk gel at cutting, which as mentioned previously affects both expulsion of whey and retention of total solids.

3.2. *Prediction of the kinetic rate constants for changes in whey fat and curd moisture during syneresis*

It has been extensively documented by many authors that the kinetics of whey separation (Marshall, 1982) as well as the kinetics of curd shrinkage (Castillo et al., 2006), and fat globule dilution (Castillo, Payne, Lopez, Ferrandini, & Laencina, 2005; Fagan, Castillo, Payne, O'Donnell, Leedy et al., 2007) follow a first-order reaction. Recently, Fagan, Castillo, Payne, O'Donnell, Leedy et al. (2007) showed that changes in the light backscatter ratio response, R, during syneresis at different temperatures, are a result of curd shrinkage or compositional changes in whey fat content. Therefore, if R is related to changes occurring during syneresis it should most likely follow first-order kinetics and optical parameters obtained might allow the prediction of the syneresis kinetic rate constant.

It was found that the ability of the models to predict k_{CM} and k_{WF} was somewhat limited (Table 3). The k_{WF} (model IV), which utilized, R_{max}, R'_{max}, t_{max} and $R_{\infty 15}$ had an SEP of $\pm 0.074\,\text{min}^{-1}$ and R^2 of 0.54, leaving 46% of the variation unexplained. The inclusion of the three coagulation parameters, R_{max}, R'_{max} and t_{max}, confirms the findings of the WFL model (model I, Table 3). It was noted from model I that the coagulation rate is affecting both the rheological properties of the gel at cutting and the rate of gel firming, both of which significantly impact the level of WFL. The weakness of the k_{WF} model may be due to the complex effect of temperature on fat release and the resulting inability of the LFV kinetic parameters to account for the behavior of R resulting from the behavior of whey fat kinetics at the highest temperatures in the study, i.e. 37.0 and 40.4 °C. It has previously been documented that the decrease in R during syneresis occurred more rapidly at higher temperatures, however at the higher temperatures in this study (37.0 and 40.4 °C) at approximately 20 min after cutting R increased slightly prior to leveling off (Fagan, Castillo, Payne, O'Donnell, Leedy et al., 2007). This was attributed to the constant release of fat at these temperatures throughout syneresis. Therefore, at high temperatures fitting R to a first-order equation cannot fully explain the LFV response, hence the limitations in using parameters derived in this manner to predict k_{WF}. Model V for the prediction of k_{CM} was also weaker than models for predicting WFL, CY_{wb} or CM_{85}.

This model, utilizing temperature, t_{max}, and k_{LVF15}, predicted k_{CM} with an SEP of $\pm 0.031\,min^{-1}$ and R^2 of 0.52, leaving almost half of the variation unexplained. Yet, it will be shown later that this model is still useful. It has already been noted in the CM_{85} model (model III, Table 3) that temperature will significantly affect the rate and extent of syneresis. It is also interesting to note that t_{max} reflects the rate of coagulation and primarily the rate of aggregation, while k_{LVF15} reflects the initial rate of syneresis. Therefore, as expected, the k_{CM} model incorporates parameters which either impact or reflect the rate of syneresis.

3.3. Practical utility of the prediction models

The range error ratio (RER) was used to assess the practical utility of the models (Williams, 2001). This ratio is calculated by dividing the range of a given parameter by the prediction error for that parameter. The RER is a method of standardizing the prediction error by relating it to the range of the reference data. An RER value of less than 6 indicates very poor classification and is not recommended for any application. An RER of 7–20 indicates that the model classification is poor to fair and could be used in a screening application. Finally, a model which has an RER of 21–30 would illustrate good classification suggesting a role in a quality control application.

The RER was highest for WFL, CY_{wb} and CM_{85} models (models I, II and III) with RER values of 16–17, indicating fair prediction models. The k_{WF} and k_{CM} models (models IV and V) were deemed to have a poor utility value (RER = 7–8).

3.4. Dynamic prediction of curd moisture content as a function of processing time

As stated in the introduction, a decrease in moisture by just 1% will have a detrimental impact on cheese yield and profits. Therefore, an on-line sensor, such as the LFV, which could be employed to monitor coagulation, predict cutting time (Fagan, Leedy et al., 2007) and detect changes in curd moisture and whey fat during syneresis, combined with a precise, real-time model for predicting curd moisture content at any given time during syneresis would be of great interest. Such a combination could enhance the overall control of curd moisture content during cheese making.

It has already been shown that changes in curd moisture content during syneresis follow first-order kinetics and that, under specific processing conditions, i.e., when the syneresis time is long enough to allow the maximum whey removal under these conditions, the final curd moisture only seems to depend on milk composition, gel properties and temperature (Table 3). It is noted that in model I, for predicting WFL, $R_{\infty 15}$ remained significant, in model II, for predicting CY_{wb}, R_{015} remained significant while in model III, for predicting CM_{85}, no kinetic parameter derived from the LFV sensor during syneresis remained significant. Therefore, it should be possible to adapt the first-order decreasing kinetic equation proposed by Fagan, Castillo, Payne, O'Donnell, Leedy et al. (2007) in order to predict curd moisture content during syneresis. In such a first-order equation there would be only two unknown terms, CM_∞ and k_{CM}. Therefore, it is proposed to combine the first-order kinetic equation describing the decrease in moisture content during syneresis with a prediction model for k_{CM} (model V, Table 3; using T^2, a LFV coagulation rate factor, t_{max} and a LFV syneresis rate factor k_{LFV15} as predictors) and a prediction model for CM_∞ (model III—CM_{85}—Table 3; using T, t_{max}, F_m and FP_m) in order to predict curd moisture content as a function of processing time from cutting. Thus the following equation, denoted model VI, for predicting curd moisture during syneresis is obtained:

$$CM_t = CM_{85} + (CM_0 - CM_{85})e^{-k_{CM}t} \tag{3}$$

where CM_t is the curd moisture (%) during syneresis at time t (min), CM_0 is the curd moisture content (%) at the beginning of syneresis, t_{s0}, i.e. the milk moisture content, CM_{85} was estimated using model III (Table 3) and k_{CM} was estimated using model V (Table 3). Model VI (Eq. (3)) was used to predict curd moisture at 10 min intervals between t_{s5} and t_{s85} ($n = 540$; 9 time points per experiment × 60 experiments) (Fig. 5) giving an SEP of ±1.72% and R^2 of 0.95, i.e. only 5% of variation was unexplained. The RER for this model is 23 indicating a good utility value and a role in process control. Further, it should be noted that all

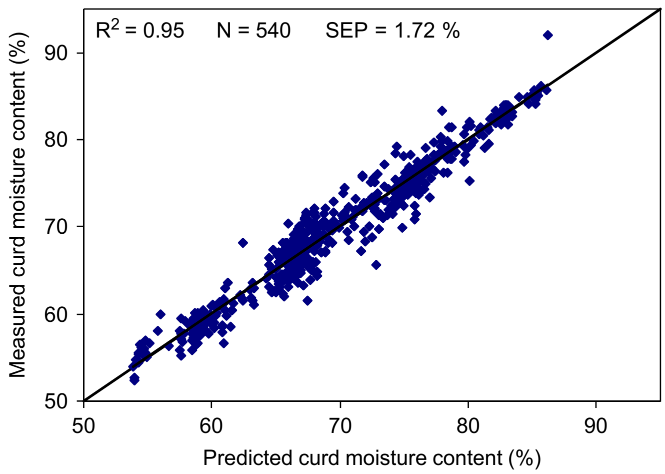

Fig. 5. Actual curd moisture content at time t during syneresis (CM_t) versus prediction of CM_t obtained using model VI ($CM_t = CM_{85} + (CM_0 - CM_{85})e^{-k_{CM}t}$; where $CM_{85} = \beta_0 + \beta_1 T + \beta_2 t_{max} + \beta_3 F_m + \beta_4 FP_m$ and $k_{CM} = \beta_1 T^2 + \beta_2 t_{max} + \beta_3 k_{LFV15}$). R^2, coefficient of determination; SEP, standard error of prediction; CM_{85}, curd moisture content at the end of syneresis (t_{s85}); k_{CM}, kinetic rate constants for changes in curd moisture content during syneresis; β_0 to β_4 are regression coefficients; T, temperature; t_{max}, time to the first maximum of the first derivative of the light backscatter ratio (R'); F_m, milk fat content; FP_m, milk fat protein ratio; k_{LFV15}, kinetic rate constant for the LFV sensor response during the first 15 min of syneresis (Eq. (2)).

the predictors used in model VI are known as early as 15 min after cutting of the gel.

The wide range over which the prediction equation was tested (50–90% curd moisture content) suggests that this technology should be applicable to the control of curd moisture during the manufacture of a wide range of cheese varieties. This technology should also provide a number of additional advantages for the processor which would result in greater consistency and efficiency during production. It should assist in optimizing the manufacturing process as milk composition varies over the year. The gel cutting protocol may be varied in different seasons by the cheese maker in order to account for variations in total solids content of milk that modifies curd firming, affecting fat and moisture retention. Therefore, employing this technology may assist the cheese maker in optimizing curd particle size.

Bacteriophage infections of starter lactic acid bacteria constitute a major problem in the industrial production of cheese. Phage infection can lead to slow lactic acid production which results in a high pH and high moisture cheese (del Rio et al., 2007). The associated economic losses due to downgrading can be substantial. The application of this optical sensor technology would facilitate real-time action in order to obtain a desired curd moisture content in the event of a slow starter due to phage infection or other issues, prior to the problem being resolved and would also draw attention to such a problem upon its occurrence. This technology should also assist in reducing energy costs, and could potentially increase production, by maintaining the syneresis process to the shortest time required.

The LFV optical sensor technology should assist the control of curd moisture content during cheese manufacturing over a broad range of cheese processing conditions which are generally applicable to the manufacture of most cheese types. However, further adaptation of the LFV sensor technology will be required to account for specific variations in cheese making procedures used in the cheese industry. For example, the LFV sensor will need to be adapted to take account of variations in procedures such as cooking operations, cyclical stirring, curd washing, etc. This study clearly shows that the LFV sensor can be used in combination with a real-time model to predict curd moisture as a function of time after k_{LFV15} is determined, within a wide range of gel cutting time levels, processing temperatures and calcium chloride concentrations. The results of this study show that the sensor has a great deal of potential and further investigation is warranted. This includes validation of the technology and models, addressing the sensitivity of the prediction algorithm to error, scaling up the technique, as well determining a design control strategy.

4. Conclusion

A novel optical sensor technology that can be employed to monitor both milk coagulation and curd syneresis in a stirred cheese vat using a single sensor has been developed to predict important indices during cheese making. The new syneresis technology consists of a unique LFV optical sensor that provides the information on gel assembly and curd shrinkage kinetics required for whey fat losses, curd yield and curd moisture content prediction. These syneresis indices were successfully predicted using a combination of independent variables, milk compositional parameters and LFV light backscatter parameters. This study has demonstrated the excellent potential of an on-line optical light backscatter sensor to monitor curd syneresis. Validation and up scaling of the technology is warranted.

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