Modelling of acid coagulation data analysed by Formagraph and estimation of milk coagulation parameters

Isaya Appelesy Ketto, Siv B. Skeie, and Reidar Barfod Schüller

Department of Chemistry Biotechnology and Food Science, Norwegian University of Life Sciences, P.O Box 5003, 1432 Ås, Norway.

ABSTRACT

Milk acid coagulation data from a Formagraph have been modelled in order to determine the main parameters of the dynamic coagulation process i.e. Gel firmness at 60 min (CA), firming rate (CB) and delay time (CC). Traditional parameters (single point estimates) were gelation time (GT), gel firming rate (GFR) and final gel firmness (G60). Strong correlation was achieved between A *vs*. G60 and CC *vs*. GT (i.e. 0.97 and 0.93 respectively, while CB *vs*. GFR showed moderate correlation (0.40). CA and CC could be used in studying acid coagulation process of the milk, however the use CB needs further investigation.

INTRODUCTION

Acid coagulation properties of milk have gained significant concern for many years, this is because of their association with texture and consistency of milk protein gels of cultured milk products i.e. yoghurt gels. Caseins and whey proteins are the major proteins found in milk. In fresh milk, caseins (α_{s1}-, α_{S2}-, β- and κ-Casein) are organized in the form of colloidal aggregates known as casein micelles, while, whey proteins (β-lactoglobulin, α-lactalbumin) are globular in nature and are presented in the soluble phase of the milk. Casein micelles are covered with the hairy layer of κ-CN which provide steric stabilization against aggregation while the interior of micelle contains highly phosphorylated caseins (α_s-and β-CN), which participates in the formation of calcium phosphate nanocluster this provide colloidal stability to the casein micelles due to non-covalent crosslinkings[1].

Production of acid milk gels involve structural destabilization of the structure casein micelles through acidification by using acidulants (e.g. glucono-δ-lactone) or by lactic acid produced by starter cultures. Acidification of milk decreases the hydrophobicity of micelles through dissolution of colloidal calcium phosphate and neutralization of surface negative charges. This leads to the reduction in the colloidal stability and steric de-stabilization on the casein micelles, these events induce the aggregation of casein micelles[1].

For many years acid coagulation properties of milk have been analysed by low-amplitude oscillation rheometry, which is based on a non-destructive measurement[2, 3]. Recently, a new method for acid gel characterization, especially for a large number of samples have been established[4]. Traditional parameters obtained from the Formagraph print-out and coagulation pattern between two different samples are presented in Figure 1. There is a possibility of modelling the acid coagulation data retrieved from the Formagraph and estimate important acid coagulation parameters from the model by using all observations obtained from the computer storage, since the modelling of rennet coagulation data from Formagraph have already established[5-8], to our knowledge there is no information in the literature on the modelling of the acid coagulation properties measured by Formagraph. Hence, the current study was intended to model the acid coagulation data derived from Formagraph to estimate the main parameters derived from the dynamic coagulation process and compare them with traditional parameters.

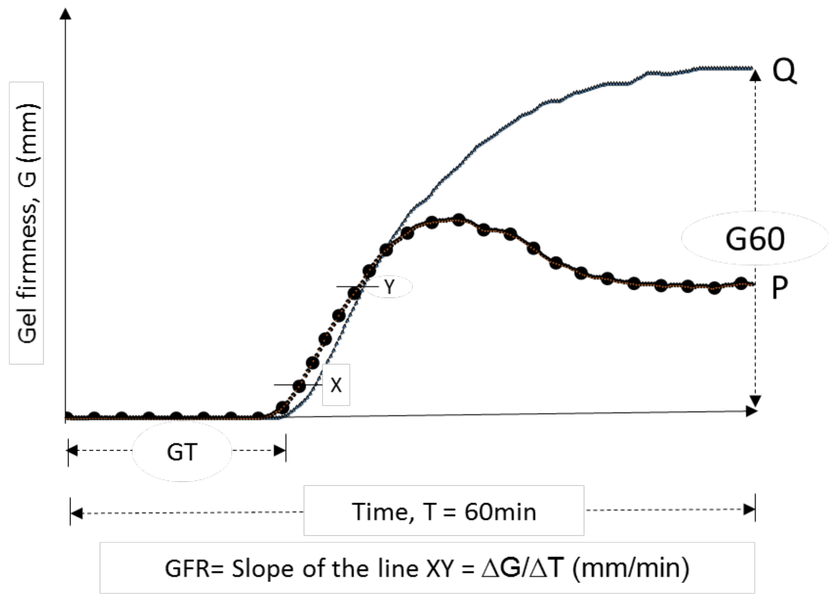

Figure 1: Parameters obtained from Formagraph output/single point estimates (GT=gelation time, GFR=gel firming rate and G60=final gel firmness at 60 minutes) between two different samples. Sample P showed gel shrinkage (Syneresis) at 60 minutes while sample Q showed continuous increase in gel firmness over time.

MATERIALS AND METHODS

Milk samples

Fresh milk samples from four (4) lactating cows were collected during the day from the Centre of Animal Research of Norwegian University of Life Sciences (SHF). Milk samples were cooled to 4°C immediately after sampling before transported to the Dairy technology laboratory and stored overnight at 4°C until the next day when the tests were done. At the dairy technology laboratory milk samples were analysed for fat, lactose, total protein and casein by MilkoScan FT1 (Foss Electric A/S, Hillerød, Denmark) and pH by pH meter (PHM61; Radiometer, Copenhagen, Denmark), before acidification.

Acid coagulation was monitored by Formagraph (LAT; Foss-Italia, Padova, Italy) for 60 minutes as described[4]. Acid coagulation parameters obtained were gelation time (GT, min; time taken from acid addition until the width of bifurcates were increased to 1.2 mm), gel firming rate (GFR, mm/min; the steepness of the curve) and final gel firmness (G60, mm; gel firmness at 60 minutes after acid addition). The model was fitted on the 4 samples (1×10 =10 equations/sample) except for one sample where only 9 parallels were made (= 39 model equations). All samples showed a continuous increase in the gel firmness over time as shown by sample Q in Figure 1.

Model description

A simple growth model was tested over 60 minutes after acid addition, the model was adopted from the model established by Bittante[5] and McMahon et al[8] on the rennet gels.

$$\hat{y} = A \times (1 - e^{-B*(x-C)}) \qquad \text{(Eq. 1)}$$

Where $\hat{y}$ is the gel firmness (mm) modelled against time (x, min); A is the asymptotical potential value at infinite time (mm); B is the time constant (mm/minutes) and C is the delay time (minutes).

By using the model described above it was possible to estimate the acid coagulation parameters i.e. acid gelation time (CC), gel firming rate (CB) and gel firmness at 60 minutes (CA).

Statistical analysis

Acid coagulation data were modelled by using MATLAB[9]. Standard deviation and coefficient of variation were estimated from each model parameter for all samples tested and compared with the traditional parameter estimates derived from the Formagraph output. Simple linear regression was used to determine the linear relationship between the parameters.

RESULTS AND DISCUSSION

Milk composition and pH

Table 1 presents the chemical composition and pH on the samples analysed. The content of fat and total protein had the largest variation between samples whereas the content of lactose and casein were more stable while the pH had little variation between the milk samples. Sample 5704 showed higher G60 compared to 6169, 5616 and 6114 (Figure 2).

Table 1: Chemical composition of the milk samples

Sample	pH	Lactose	Fat	Protein	Casein
5616	6.8	4.78	4.23	3.18	2.47
6169	6.72	4.63	4.05	3.6	2.73
6114	6.73	4.38	2.86	3.07	2.38
5704	6.74	4.54	4.34	3.62	2.71

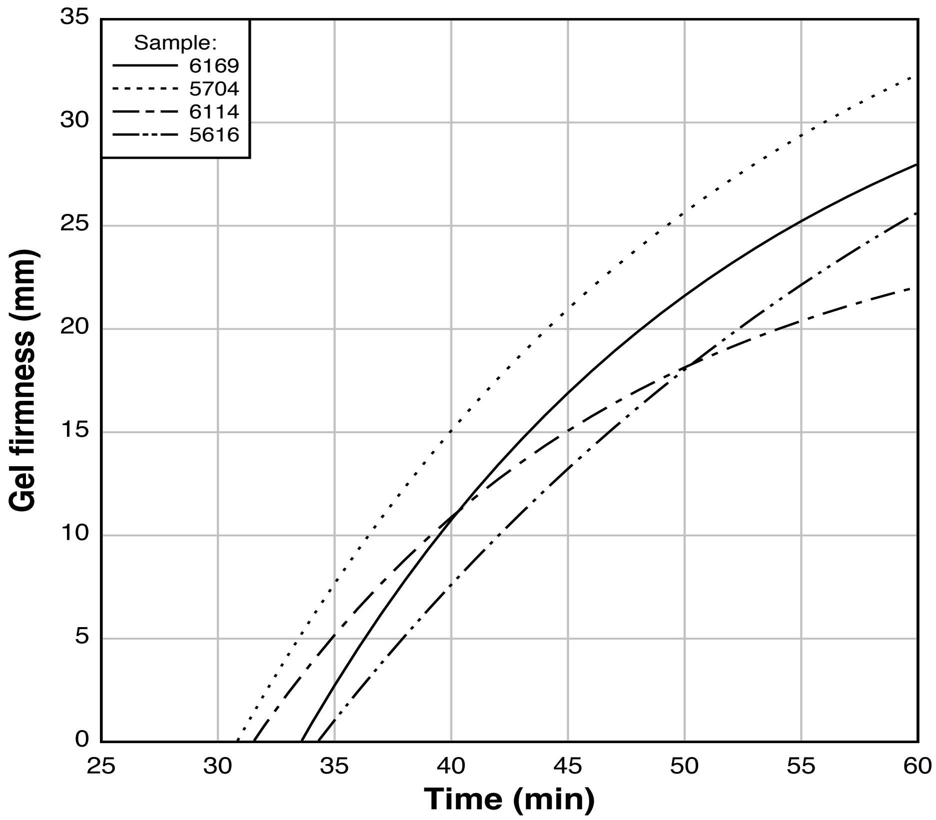

Figure 2: Modelled curves between the samples (average of the parallels)

Descriptive statistics

Table 2 shows the descriptive statistics for the traditional and the model parameters. Good repeatability was achieved model parameters compared to single point estimates, especially in CB showed low standard deviation within the parallels compared CA. In traditional estimates, GT showed good repeatability compared to GFR and G60. Samples expressed weaker gel showed poor repeatability on the single point estimate (G60) compared to the samples with strong gel. This could be explained by the fact that a stronger gel gives a constant movement of the Formagraph pendulum loop with less gel destruction compared with a weaker gel which most probably gives an irregular movement of the pendulum loop. The weaker gel most probably results in the loss of intimate contact between the loop and the gel[8]. Perhaps this effect would be less pronounced in conventional rheometry analysis because the analysis are made within the linear visco-elastic range (LVR).

Table 2: Descriptive statistics for the parameters within the samples between model parameters ad traditional parameters

Sample	Model parameters	n	Mean	SD	CV (%)	Model parameters	Mean	SD	CV (%)
5616	GT	10	35.29	1.5	4.25	CC	34.27	1.51	4.41
	G60	10	22.99	1.56	6.79	CA	23.79	1.22	5.14
	GFR	10	1.16	0.09	7.76	CB	1.58	0.08	5.34
6114	GT	9	32.37	1.12	3.46	CC	31.51	0.99	3.14
	G60	9	20.05	2.07	10.32	CA	20.67	1.65	7.99
	GFR	9	1.2	0.17	14.17	CB	0.73	0.06	7.73
6169	GT	10	34.06	0.56	1.64	CC	33.56	0.56	1.67
	G60	10	26.37	1.93	7.32	CA	27.43	1.84	7.99
	GFR	10	1.62	0.14	8.64	CB	1.04	0.06	5.36
5704	GT	10	31.17	1.04	3.34	CC	30.81	1.17	3.80
	G60	10	29.72	2.03	6.81	CA	30.86	1.72	5.54
	GFR	10	1.58	0.08	5.06	CB	1.06	0.03	3.12

Relationship between model parameters *vs.* single point estimates.

The current results showed stronger linear relationship (R^2=0.93, Figure 3) between gelation time (GT) as a single estimate parameter and delay time (CC) of the model estimate , similar to Bittante[5] who reported similar values between model estimates and single point estimates.

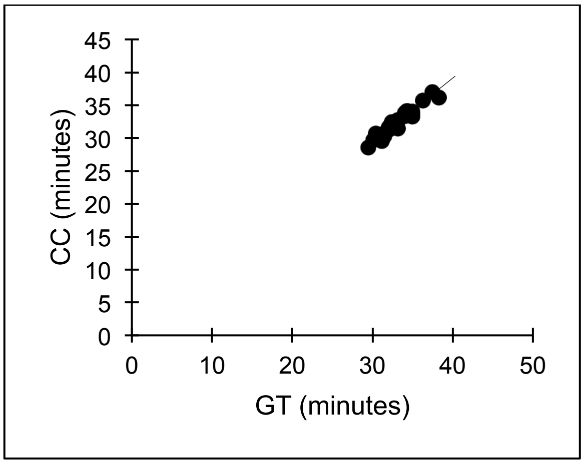

Figure 3: Correlation between delay time (C) and traditional gelation time (GT) (R^2=0.93, CC=0.987*GT)

The relationship between the estimated gel firming rate (CB) and the traditional gel firming rate (GFR) is presented in Figure 4. The two parameters showed moderate correlation (R^2 =0.40).

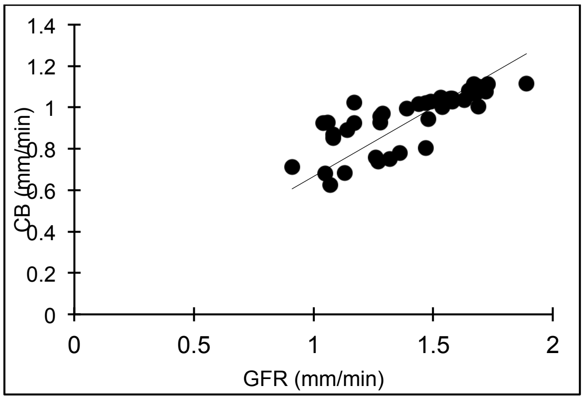

Figure 4: Correlation between model time constant (CB) and traditional gel firming rate (R^2 =0.40, CB=0.667* GFR)

Gel firmness at 60 minutes estimated from the model (CA) and observed final gel firmness (G60) showed stronger linear relationship (R^2 = 0.97, Figure 5), similar to Bittante[5].

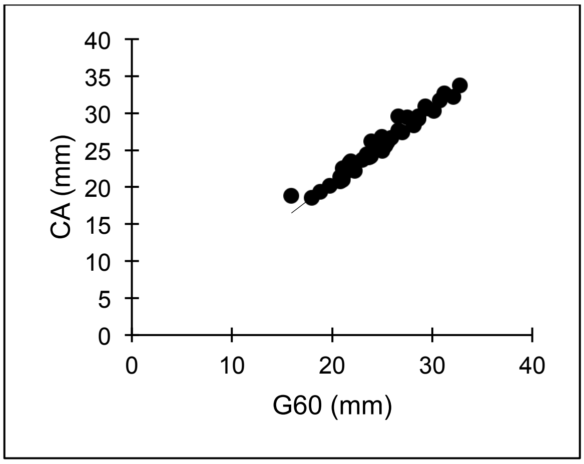

Figure 5: Correlation final gel firmness and traditional final gel firmness (R^2=0.97, CA= 1.035*G60)

CONCLUSION

Good repeatability was achieved the model parameters compared to single point estimates. CC *vs.* GT and CA vs G60 showed stronger linear relationship. This implies that gelation time and final gel firmness at 60 minutes can be estimated from the model and used in studying acid coagulation properties of milk by Formagraph, since they showed good repeatability in all samples tested. The use of estimated gel firming rate needs further investigation.

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