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MODELING THE RHEOLOGICAL BEHAVIOR OF GELATINIZING STARCH SOLUTIONS

Вy

Kirk David Dolan

A DISSERTATION

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

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ABSTRACT

MODELING THE RHEOLOGICAL BEHAVIOR OF GELATINIZING STARCH SOLUTIONS

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Kirk David Dolan

"Viscosity" of gelatinizing starch dispersions is used in quality control and process design around the world. A comprehensive model to predict viscosity for an arbitrary process has not been proposed in the published literature. The purpose of this study was to present a generalized mathematical scheme to identify and measure factors influencing viscosity development during gelatinization in food processing: shear rate, temperature, moisture content, temperature-time history, and strain history.. Back extrusion and mixer viscometry techniques were chosen to illustrate a general experimental technique, because variables were known and highly controlled. The results (within 10 % standard deviation of errors) suggested that, for larger processes, the limiting factor will be measurement accuracy rather than fit of experimental data in determining parameters.

A back extrusion technique was used to estimate effect of gelatinization only. An index of apparent viscosity of a 13.7% gelatinized cornstarch solution at constant shear rate and strain history was measured at 20 C. Activation energy of gelatinization was estimated as 210. kJ/mol over the range 81-95 C, and decreased in the range 95-105 C. A Brookfield RVTD mixer viscometer was used to gelatinize 5.5, 6.4, and 7.3% (d.b.) native corn starch dispersions. Torque response, the dependent variable, was used to estimate parameters in a generalized model. The independent variables were impeller speed, temperature, (50-95 C), moisture content, temperature-time history, and strain history. Predicted and experimental pasting curves were compared. A simplified and rapid procedure for estimating parameters from an arbitrary pasting curve was proposed, and applied to a bean starch dispersion.

Dispersions thickened with decreasing temperature and had an Arrhenius activation energy between 6.4 and 11.5 kJ/mol. There was no evidence that retrogradation caused this effect. Maximum viscosity depended on cook temperature, ranging from a 150- to a 220-fold increase at 85 and 95 C, respectively. First order reaction kinetics was accurate (9.8% standard deviation) in describing viscosity increase during gelatinization. Torque decayed exponentially after initial gelatinization. Comparison of relative effects showed a pasting curve could be predicted by knowing only the rate of gelatinization during heating rise, the rate and extent of breakdown during shear decay, and the torque response to temperature during cooling. To my father and mother, who introduced me to my Eternal Father, who has taught me,

"Let not the wise man boast of his wisdom or the strong man boast of his strength or the rich man boast of his riches,

but let him who boasts boast about this: that he understands and knows me, that I am the Lord, who exercises kindness, justice, and righteousness on earth, for in these I delight."

Jeremiah 9:23,24

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vi

TABLE OF CONTENTS

List of Tablesx	
List of Figuresx	i
Nomenclaturex	iv
1. Introduction	>
 Back extrusion used in modeling rheological behavior of starch solutions throughout gelatinization	
2.2.1 Rheological Models for Starch Solutions	
2.3. Modeling Approach.82.3.1. General Mathematical Model72.3.1.1. Shear rate effect12.3.1.2. Temperature effect12.3.1.3. Moisture content effect12.3.1.4. Temperature-time history effect12.3.1.5. Strain history effect12.3.2.1. Simplicity of form12.3.2.3. Generality12.3.2.4. Ease of measurement1	0 1 1 2 5 6 6 6 7 7
 2.3.3 Simplified Model for Starch Gelatinization	8 9 9 0 1 5
 2.5. Results	8 2 4
2.8. Summary and Conclusions	4

3.	Mixer viscometry used in modeling rheological
	behavior of gelatinizing starch solutions
	3.1. Abstract
	$\sim 3.2.$ Introduction
	3.3. Theoretical Considerations
	3.4. Practical Considerations
	3.5. Materials and Methods53
	3.5.1. Experimental plan
	3.5.2. Apparatus
	3.5.3. Procedure
	3.5.4. Analysis 65
	3.5.4.1. Analysis Involving All
	Parameters 65
	3542 Simplified Analysis 71
	3 6 Results 72
	3.7 Discussion 01
	3.7. Discussion of parameters with
	J. 7. 1. Comparison of parameters with
	$\begin{array}{c} 1110111101\cdots 191\\ 2 7 2 \\ \end{array}$
	2.7.2. Weistung content officers
	2.7.4 Temperature Effects
	3.7.4. Temperature Effects
	3.7.5. Strain history effects
	3.7.6. Predicted pasting curves
	3.7.6.1. Heating rise
	3.7.6.2. Shear decay
	3.7.6.3. Cooling
	3.7.6.4. Relative influences of
	independent variables
	3.7.6.5. Simplified Analysis
	3.8. Conclusions101
4.	Industrial applications of rheological modeling103
	4.1. Prediction of velocity profile103
	4.2. Rapid parameter estimation105
5.	Overall Summary and Conclusions108
6.	Suggestions for future research110
	6.1. Limitations of the model110
	6.2. Other applications111
7.	Bibliography
8.	Appendices
	8.1 Appendix A Parameter Estimation Analysis
	8.2 Appendix B Observed equilibrium torque of
	gelatinizing native corn starch to determine
	effects of moisture content and temperature-time
	history (corresponding to Table 3.2) 124
	8 3 Annendix C Time and temperature data 126
	8 3 1 Annendix C 1 Time and temperature data
	for each cample in Annendiv R 176
	8 3 2 Annendix C 2 Time and temperature data
	6. J. Z. Appendix C. Z fille and temperature data
	for each sample used in back extrusion145

-

8.4. Appendix D Computer programs (written by K.
Dolan unless otherwise indicated) to estimate k,
a, and DEg, from normalized torque versus
temperature-time history in Appendices B and C157
8.5. Appendix E. Calculated viscous activation
energy (ΔE_v) of gelatinized native corn starch to
determine effects of temperature (corresponding
to Table 3.3)173
8.6. Appendix F Observed equilibrium torque of
gelatinized native corn starch to determine effects
of shear rate (corresponding to Table 3.4)
8.7. Appendix G Calculated strain history parameters
of gelatinized native corn starch (corresponding
to Table 3.5)175
8.8. Appendix H Example of mathematical procedure
to correct and normalize raw torque during a
pasting curve to a reference temperature (60 C)
and reference temperature-time history (zero) at
10 s intervals176

LIST OF TABLES

Table 2.1	Physical meaning of terms in Eq. 2.29	
Table 3.1	Summary of studies reporting viscosities of gelatinized starch dispersions	3
Table 3.2	Experimental design for determining effects of moisture content and temperature-time history	5
Table 3.3	Experimental design for determining effects of temperature	5
Table 3.4	Experimental design for determining effects of shear rate	7
Table 3.5	Experimental design for determining effects of strain history	7
Table 3.6.	Experimental design to produce pasting curves	9
Table 3.7.	Procedure to estimate the parameters4	7
Table 3.7a	Analytical design and step-wise correction for Table 3.24	7
Table 3.7b.	Calculation steps4	7
Table 3.8	Comparison of parameter estimates to those in literature for native corn starch	4
Table 4.1	Procedure for rapid analysis of parameters using a tube viscometer	7

LIST OF FIGURES

Figure 2.1	Mechanism of starch gelatinization (from Remsen and Clark, 1978)
Figure 2.2	Typical force-penetration curve obtained from back extrusion testing at a constant plunger velocity
Figure 2.3	Schematic of test tube in plastic holder during back extrusion24
Figure 2.4	Use of temperature-time history to collapse a series of curves, each at constant temperature, to one curve
Figure 2.5	Average normalized viscosity versus time for 13.7% (d.b.) starch solutions at 20 C and constant shear rate after heating at 81, 84, 85, 91, 95 101, and 105 C
Figure 2.6	Figure 2.5 with the abscissa replaced by temperature-time history (Regression does not include values at 101 and 105 C.)
Figure 2.7	Residual (measured value-predicted value) versus temperature-time history for regression line in Figure 2.631
Figure 3.1a	Experimental apparatus of mixer viscometer and bath system
Figure 3.1b	Brookfield small sample adapter with flag impeller and copper-constantan thermocouple
Figure 3.1c	Flag impeller62
Figure 3.2	Equilibrium torque at 60 C versus time of heating at 85, 88, 92, and 95 C for 6.4% (d. b.) starch dispersions

Figure 3.3	Equilibrium torque at 60 C versus time of heating at 85, 92, and 95 C for 7.3% (d. b.) starch dispersions
Figure 3.4	Superposition of Figures 3.2 and 3.3, with torque normalized and time transformed to temperature-time history. Regression line corresponds to Eq. 3.3 (42 of 100 points)76
Figure 3.5	Experimental and predicted torque and temperature versus time for 6.4% (d.b.) cornstarch dispersion, using constant parameters for prediction
Figure 3.6	Pasting curve of Figure 3.5, using varying strain history and temperature parameters for prediction
Figure 3.7	Replicate of Figure 3.6, except final temperature is 60 C81
Figure 3.8	Pasting curve with all variables as in Figure 3.6, except heating time equal to 8 min82
Figure 3.9	Replicate of Figure 3.883
Figure 3.10	Pasting curve with all variables as in Figure 3.8, except cooling rate was increased
Figure 3.11	Pasting curve with all variables as in Figure 3.8, except starch concentration equals 6.4% (d.b.)
Figure 3.12	Pasting curve with all variables as in Figure 3.6, except rpm equals 50
Figure 3.13	Pasting curve with all variables as in Figure 3.6, except maximum temperature equals 85 C
Figure 3.14	Pasting curve of Figure 3.6, with four predicted curves: Curve 1, prediction without temperature and strain history terms; Curve 2, prediction without the temperature term; Curve 3, prediction without the strain history term; Curve 4, prediction with all terms
Figure 3.15	Pasting curve for 6% (d.b.) bean starch Phaseolus vulgaris var. seafarer90
Figure A.1	Sensitivity coefficients for Eq. 3.3120

Figure A.2	Ratio of X_2/X_3 versus k Ψ to determine extent
-	of linear dependence122

Nomenclature

- A relative amount of viscosity increase due to gelatinization (dimensionless)
- A3 material constant related to the effective molecular weight of the protein (dimensionless)
- a power law coefficient relating shear-rate effects on the molecular weight of denatured protein (dimensionless)
- B relative amount of viscosity reduction due to irreversible mechanical degradation (dimensionless)
- b exponent measuring the lubricating effects of moisture on dough viscosity (dimensionless)
- C dry weight of starch per unit weight of dispersion (decimal)
- C_p protein concentration, dry weight basis
- C₁ arbitrary constant (units depend on text definition)
- C₂ arbitrary constant (units depend on text definition)
- d parameter related to the rate of mechanical degradation (dimensionless)
- F_D maximum force for ideal back-extrusion, Figure 3.3 (N)
- g arbitrary constant
- K consistency coefficient (Pa sⁿ)
- K_r pseudo-consistency coefficient at reference temperature T_r and reference moisture content MC_r (N m minⁿ)
- k reaction transmission coefficient, affecting rate of gelatinization ([K s]⁻¹)
- L length of pipe over which pressure drop occurs (m)
- L_p distance traveled by plunger (m)
- M torque (N m)
- $M_{MC,Tm}$ torque corrected to reference values of moisture content and maximum temperature (N m)
- M_0 ungelatinized torque (at $\Psi=0$) (N m)

	Greek
у	normalized torque (dimensionless)
tf	total time of experiment (s)
t	time (s)
Tm	maximum temperature reached by a sample (K)
Tr	arbitrary reference temperature (K)
T ₀	initial temperature (K)
Τg	threshold temperature for gelatinization (K)
Т	absolute temperature (K)
R	universal gas constant (8.314 J/mol K or 1.986 cal/mol K), or radius of pipe (m) (Section 5.2)
Q	weight of swollen starch per unit weight of dry starch (decimal)
n	power law flow index (dimensionless)
Ν	impeller speed (revolutions per minute)
MCr	reference moisture content (dry basis, decimal)
МС	moisture content (dry basis, decimal)
M'∞	torque after shearing (as $\Phi \rightarrow \infty$) (N m)
M'0	torque before shearing (at $\Phi=0$) (N m)
M∞	fully gelatinized torque (as $\Psi \rightarrow \infty$) (N m)

- α exponent describing molecular weight effect on viscosity (dimensionless)
- α₀ intercept coefficient relating effect of denatured protein molecular structure on viscosity at low shear rates (s^a)
- β_r material constant related to the maximum viscosity increase due to protein gelation (dimensionless)
- $\dot{\gamma}$ viscometric shear (strain) rate (s⁻¹)

Ϋ́ average viscometric shear rate (s^{-1}) "activation energy" of gelatinization (J/mol) ΔE_g ΔEv viscous activation energy of temperature effects (J/mol) ΔΡ magnitude of pressure drop (Pa) Δt elapsed time (s) exponent relating effects of moisture level to the extent 3 of protein denaturation (dimensionless) apparent viscosity index (Pa s) η apparent viscosity at zero time (Pa s) η_0 ungelatinized apparent viscosity, equal to $\eta_0(Pa s)$ η_{ug} apparent viscosity as $\Psi \rightarrow \infty$, or $\Phi \rightarrow \infty$ (Pa s) η∞ $\eta_{\dot{\gamma},T,Tm,MC}$ apparent viscosity corrected to reference values of shear rate, temperature, maximum temperature, and moisture content. (Pa s) Heinz-Casson high-shear limiting viscosity at reference μ_r temperature T_r and reference moisture content MC_r (Pa s) Heinz-Casson yield stress at reference temperature T_r σr and reference moisture content MC_r (Pa) Ψ integral temperature-time history (K s) Ψ' $k\Psi$ (dimensionless) Ψ'r reference value of Ψ' (dimensionless) Ψ'' defined by Eq. A.5 (s) Φ integral strain history (dimensionless) ξ thermal diffusivity (m^2/s)

1. Introduction

Viscosity is an objective and convenient measure of the extent of gelatinization in starch dispersions. Numerous excellent studies have explained the effects of shear rate and starch concentration, but none of those reviewed suggested a comprehensive procedure for predicting viscosity. Furthermore, few studies have differentiated among the factors affecting gelatinization most. The purpose of this dissertation was to identify and quantify variables influencing starch viscosity development most, and determine relationships among the variables. The goal of this work was to test a comprehensive model in benchtop experiments, then in pilot plant conditions, and finally in full-scale processing. This dissertation presents results for benchtop experiments, and proposed a procedure for pilot-plant and industrial trials.

This work is composed, primarily, of two journal articles. The comprehensive model considered in both was based on the work of Morgan et al. (1989), where the rheological behavior of protein dough was modeled during extrusion cooking. The proposition was that starch viscosity could be described as a function of shear rate, temperature, moisture content, temperature-time history, and strain history. The variables had to be measurable during or before the process to use them for prediction. The first article investigated only the temperaturetime history effect, because that term had not previously been applied to starch. The work involved a back extrusion

technique to measure a "viscosity index" for 13.7% corn starch dispersions at 20 C.

The second article investigated all the terms and their interactions, but emphasis was placed on temperature-time history and strain history effects. Published literature indicated that strain history effects had not been previously quantified for starch solutions. A mixer viscometer was used to measure torque for 5.5-7.3% (d.b.) corn and 6% (d.b.) bean starch dispersions. The model is equipment-independent, so both devices were chosen to demonstrate how to apply the model to any system. The model was shown to accurately predict a typical industrial pasting curve.

The final section of this dissertation addresses an additional objective: to use the results of both articles to present a simple, generalized model and experimental design to evaluate starch gelatinization behavior for industrial applications.

2.1 Abstract

A generalized a priori theoretical model relating apparent viscosity of protein dough to several independent variables was used to model gelatinized starch dispersions. Independent variables in the original model were shear rate, temperature, moisture content, temperature-time history and strain history. The model is applied here to corn starch dispersions gelatinized using various temperature-time treatments. Apparent viscosity of a 13.7% gelatinized cornstarch solution at constant shear rate and constant strain history was measured at 20 C using a back extrusion technique. Activation energy of gelatinization was estimated as 210. kJ/mol (50. kcal/mol) over the range 81-95 C, and decreased in the range 95-105 C.

2.2 Introduction

The largest single food group in the human diet is cereal grains. Starch, the primary constituent of cereal grains, is used in different ways by the food industry (Lund, 1984). Foods containing starch are processed over a range of temperatures and concentrations. Among these products, in order of increasing concentration, are soups and gravies, puddings, custards and doughs. Starch is used as a thickening agent and as a processing aid, such as corn starch used to dust work surfaces or in-process material to prevent sticking (Whistler et al., 1984).

"Gelatinization" is typically defined as the physicochemical phenomenon of swelling of starch granules as they imbibe water at temperatures sufficient to destroy the birefringence of the granules.

The process occurs as the starch/liquid system is heated above a characteristic "gelatinization temperature." Below this temperature, birefringence of the starch granules is preserved. For a population sample of granules, gelatinization temperature usually varies over a 10° C temperature range, indicating distribution of different gelatinization temperatures. Viscosity of dilute starch suspensions in the early heating stages will increase mainly because amylose is released while, in later stages, viscosity increases further due to interaction of extragranular material and swelling of the granules (Lund, 1984).

Apparent viscosity can be used to quantify the thickening effect of starch. One application is the prediction of minimum pressure or minimum wall shear stress for flow of a processed fluid. This information can aid in preventing plugging, of pipes, a costly problem in industrial processing. Knowledge of the viscosity of starch-thickened foods is needed to design process systems with optimum operating performance as well as superior texture and product quality. Other applications include mixing systems, aseptic processing, and steam infusion.

2.2.1 Rheological Models for Starch Solutions

The Visco-Amylo-Graph (C.W. Brabender Instruments. Inc., 50 E. Wesley St., S. Hackensack, NJ 07606) is an empirical instrument used industrially to simulate effects of processing conditions on the rheological behavior of starch solutions. Thus, the ability of the instrument to predict flow properties depends upon the knowledge base of rheological behavior of solutions. This knowledge is usually

unavailable when new products are being developed which involve changes in formulation or process conditions.

Several authors have presented models of the apparent viscosity of starch solutions. Christianson and Bagley (1983) and Bagley and Christianson (1982) found for dilute (less than 26%, g starch/g soln) corn starch and wheat starch dispersions, apparent viscosity/(C*Q) exponentially increased with C*Q, where C*Q equals the grams of swollen starch per gram of dispersion. Q, the grams swollen starch per grams initial dry starch, increased non-linearly with increasing temperature, showing the dependence of viscosity on temperature.

Christianson Beckwith Bagley, and (1983) proposed an exponential dependence of intrinsic viscosity on the volume fraction of swollen corn and wheat starch granules for volume fraction between 0.6 and 1.0. Evans and Haisman (1979) suggested the viscosity was a function of volume fraction for gelatinized corn, potato, and tapioca starch solutions up to 10% starch.

A parameter related to apparent viscosity is yield stress. Bagley and Christianson (1983) found a yield stress existed for 11-13% gelatinized wheat starch dispersions measured at 23°C, and found no yield stress for 10-14% dispersions measured at 60°C. Christianson and Bagley (1984) reported yield stresses existed in 11 and 12% cornstarch solutions, and did not exist in 8 and 10% dispersions. They found that yield stress depended on temperature-time (T-t) history. Wong and Lelievre (1982) described yield stress of 1.6-8.2% wheat starch function of solutions starch concentration, swelling as а capacity, and the number fraction of large granules in the starch.

The dependence of viscosity and yield stress of starch

solutions on T-t history can be inferred from the data of Bagley and Christianson (1982) and Christianson and Bagley (1983, 1984). However, in none of the above-mentioned models was the T-t history explicitly included. Other models for food doughs, discussed in the next section, clearly separate the opposing effects of temperature and temperature-time history.

All of the previously mentioned studies modeled viscosity of starch based on variables measured at the end of the test, such as volume fraction and swelling capacity. The researchers did not correlate these variables with in-process conditions, such as temperature and The first-order modeling of Suzuki et al. (1976), Bakshi and time. and Kubota et al. (1979) is different because it Singh (1980) correlates end measurements to temperature and time during the test. Suzuki et al. (1976) reported ΔE_g for cooked rice as 80 and 37 kJ/mol for temperature ranges of 75-110 and 110-150 $^{\circ}$ C respectively. Kubota et al. (1979) found ΔE_{eq} equal to 59 kJ/mol between 70 and 85°C for rice **Bakshi and Singh (1980)** gave ΔE_g values of 78 and 44 kJ/mol starch. for rough rice in the ranges 50-85 C and 85-120 $^{\circ}$ C respectively, and ΔE_{π} equal to 100 and 40 kJ/mol for brown rice in the ranges 50-85 and 85-120°C respectively.

2.2.2 Other Rheological Models Applicable to Starch

The molecular mechanisms acting in starch systems with excess water and in those with limited water are different. In the first case dispersed starch undergoes gelatinization, swells, and forms a thicker dispersion. In the latter case, starch undergoes melting and granules seldom swell; the latter material resembles more a glass. whereas the

first system is a dispersion of deformable particles. Therefore the purpose of presenting dough viscosity models is not to suggest the phenomena are similar; rather, it is to propose that in both cases, temperature-time history and temperature may be treated as two separate independent process variables with opposite effects on viscosity.

Cuevas and Puche (1986) applied dimensional analysis to describe the apparent viscosity index (a relative indicator) and consistency of corn dough. They varied the speed and measuring temperature of a Brookfield viscometer, and the concentration of the corn dough (for 35 and 40% corn flour).

Harper et al. (1971) and Cervone and Harper (1978) predicted viscosity of cereal doughs and pregelatinized corn flour as a power law function of shear rate, an exponential function of 1/T and an exponential function of moisture content. Bloksma (1980) found that unless heating was "extremely slow," (less than .01 K/s) the viscosity of wheat flour doughs was a function of the actual temperature and thermal history.

the effect other variables, In comparison to of protein denaturation starch gelatinization drastically increase and solution viscosity. Both phenomena occur at temperatures above а certain level, and continue toward completion as long as that threshold is exceeded. Thus. there are two effects above the threshold: the "thinning effect" of higher temperatures which decreases viscosity, and the integral T-t kinetic history effect of gelatinization (or denaturation) which increases the viscosity.

Some researchers have separated these two opposite effects in their models. The development of Roller (1975) was used by Remsen and

Clark (1978), who tested 22-35% MC (wet basis) defatted soy flour doughs. Janssen (1984) expressed apparent viscosity of an extruded food containing starch or protein as a function of shear rate, temperature and T-t history. Harper et al. (1978) presented a model for apparent viscosity as a function of T-t history and moisture content of bovine plasma protein suspensions.

2.3 Modeling Approach

2.3.1 General Mathematical Model

Morgan et al. (1989) proposed a mathematical model describing apparent viscosity of denaturing protein doughs as a function of shear rate, temperature, moisture content, T-t history, and strain history

$$\eta(\dot{\gamma}, \mathsf{T}, \mathsf{MC}, \Psi, \Phi) = [(\tau_o/\dot{\gamma})^n + (\mu_r)^n]^{1/n} e^{[(\Delta \mathsf{E}_v/\mathsf{RT})(1/\mathsf{T}-1/\mathsf{T}_r) + b(\mathsf{MC}-\mathsf{MC}_r)]}$$

$$\{1+A^{\alpha}(1-e^{-k\Psi})^{\alpha}\}$$
 $\{1 - B(1-e^{-d\Phi})\}$ (2.1)

Eq. 2.1 was developed for this study by translating the approach of Morgan et al. (1989), from a protein denaturation-based phenomenon where water content is limiting (doughs) to a starch gelatinization model where excess water is available. Table 2.1 describes the analogy/physical meaning of each term in Eq. 2.1. Further explanation is reported in Morgan et al. (1989).

A number of assumptions were made in developing Eq. 2.1:

-No elastic effects,

-No compositional effects from materials other than starch and

Table 2.1. Physical meaning of terms in Eq. 2.1.

Term	Physical Meaning
$[(\tau_{o}/\gamma)^{n}+(\mu_{r})^{n}]^{1/n}$	shear rate effect
$e^{\left[\left(\Delta E_{v}/RT\right)\left(1/T-1/T_{r}\right)\right]}$	temperature effect
e ^{[b(MC-MC} r)]	moisture content effect
$(1+A^{\alpha}(1-e^{-k\Psi})^{\alpha})$	gelatinization (T-t history) effect
(1-B(1-e ^{-dΦ}))	strain history effect

4

•

moisture content,

-No dependence upon maximum shear rate

-No explicit volume fraction dependence,

-The effects of gelatinization on viscosity may be approximated by first-order reaction kinetics,

-Homogeneous, isotropic medium.

The similarities and differences in the model with respect to starch versus protein are discussed in the following sections. The use of a dough viscosity model for dilute systems has been justified by a review of literature for excess-water systems, not for water-starved systems. The objective of this study is to determine the feasibility of applying the approach presented by Morgan et al. (1989) to the gelatinization behavior of raw corn starch solutions.

2.3.1.1 Shear rate effect.

Christianson and Bagley (1983, 1984), Bagley and Christianson (1982), Wong and Lelievre (1982), Doublier (1981), and Evans and Haisman (1979) in separate studies investigated the effect of shear rate on the apparent viscosity of dilute wheat starch, corn starch. and tapioca starch solutions. All results showed shear-thinning behavior for the gelatinized solutions, but no attempt was made to quantify and/or correlate thermal history effects.

Christianson and Bagley (1984), Bagley and Christianson (1982), Lang and Rha (1981), and Evans and Haisman (1979) measured yield stresses of gelatinized corn and wheat starch dispersions in separate studies. Their findings indicate a model for starch dispersion viscosity must account for non-Newtonian behavior including the

presence of a yield stress. The Herschel-Bulkley model describes both phenomena. However, at high shear rates this model approaches infinite or zero viscosity depending on the power law index This behavior creates a problem if gelatinized starch solutions have a finite limiting viscosity, such as those experienced in high-shear processes. A simple model accounting for non-Newtonian behavior, yield stress, and finite limiting viscosity is the Heinz-Casson model, (Table 2.1, first term) used by Christianson and Bagley (1984), and selected for this study.

2.3.1.2 Temperature effect.

Within the starch literature reviewed, the work of Doublier (1981) with wheat starch pastes was the only one in which temperature effects were measured separately from thermal history effects, i.e. gelatinization was complete before measuring the change in viscosity with temperature. His plot of data shows adequate agreement (no measure of variance was given) with the viscosity model suggested by the Eyring kinetic theory (Eyring and Stern, 1939). The Eyring model is the second term in Table 2.1.

2.3.1.3 Moisture content effect.

Doublier (1981) used a power-law model to describe the dependence of apparent viscosity of 0.1 to 2.5% wheat starch solutions on moisture content. Harper et al. (1971) used an exponential model. Bagley and Christianson (1982, 1983) and Christianson and Bagley (1983) presented plots showing the effects of moisture content on the viscosity of wheat starch and corn starch dispersions. The

data suggest an exponential decrease of viscosity with increasing moisture content. Morgan et al. (1989) used the same assumption.

studies, excluding Morgan et al. The last three (1989). investigated dilute solutions. where water did not limit gelatinization. Thus, the moisture term in Eq. 2.1 (Table 2.1, third describes the lubricating effect of water between the term) starch If water were limiting (which may be the case with dough), granules. moisture content would have a reverse effect upon viscosity, because gelatinization would depend on moisture content.

2.3.1.4 Temperature-time history effect.

Thermal (T-t) history is distinguished from temperature in that the former depends upon the path. Thus, if the starch solution viscosity was dependent on only temperature, its value would be the same at 80 C, whether a sample had been brought to 80 C 30 seconds or in 5 minutes. In fact, the viscosity differs in according to the temperature exposure over time. Furthermore. T-t history and temperature have opposing effects on fluid viscosity. Greater T-t histories increase viscosity to a limit. Whereas greater temperatures decrease viscosity.

Remsen and Clark (1978) presented a simplified model of the gelatinization process (Figure 2.1). The fact that gelatinization begins with separate granules and ends with a network of linked particles suggests a "pseudo" polymerization. After exceeding a threshold temperature, the viscosity of starch solutions increases to a maximum over time as gelatinization occurs. Conversely. as shown by the second term in Table 2.1, an increase in temperature causes a



Raw starch granules made up of amylose (helix) and amylopectin (branched).

Addition of water breaks up amylose crystallinity granules and disrupts helices. Granules swell.

Addition of heat and more water causes more swelling. Amylose begins to diffuse out of granule.

Granules, now containing mostly amylopectin, have collapsed and are held in a matrix of amylose forming a gel.



decrease in viscosity, as expected for most fluids. Remsen and Clark (1978), Harper et al. (1978), Janssen (1984), and (1989) have modeled the T-t history effect on the Morgan et al. viscosity of cereal dough, bovine plasma, starch and protein foods, and defatted soy flour, respectively. Harper et al. (1978) and Morgan et al. (1988) assumed protein denaturation could be approximated by a "pseudo" first-order reaction, and made the process analogous to polymerization. Janssen (1984) assumed both protein denaturation and starch gelatinization could be approximated by first-order and Suzuki et al. (1976) proposed a first-order model for kinetics. the gelatinization of rice starch.

There is a major difference between protein denaturation and starch gelatinization. Denaturation is a chemical reaction, where a threedimensional structure is lost as hydrogen bonds are broken. Gelatinization is both a physical and chemical process. The physical process is hydration and swelling of granules, with leaching of amylose and amylopectin molecules into the solution. The physicochemical process is water breaking intermolecular hydrogen bonds and replacing them with water-polysaccharide hydrogen bonds. However, the overall effect of both processes is similar. Full denaturation results in unravelled aggregated protein, and gelatinization results in a loose matrix of granules and long chain molecules. In both cases the net effect is an increase in viscosity.

Therefore, the gross effect of starch gelatinization on viscosity was made analogous to that of a first-order condensation polymerization. The same assumption was made by Morgan et al. (1989) for protein denaturation (Table 2.1, fourth term).

2.3.1.5 Strain history effect.

Starch granules were assumed to undergo irreversible damage due to mechanical degradation, solubilization of granules, and depolymerization of starch. Any reversible degradation caused by breakdown of starch flocculates was not considered. The shear (also called strain) rate was used as a measure of the degradation and subsequent decrease in viscosity (thixotropy). The strain rate-time effect (strain history term in Table 2.1) is prominent in high shear processes.

Shear rate and strain history are two separate effects, similar to temperature and T-t history. A given strain rate produces an instantaneous stress response, as shown by a rheogram (stress versus shear rate). However, while undergoing shear, the viscosity of a fluid may decrease asymptotically to a limit (thixotropy), showing the effect of strain history. As an illustration, Wong and Lelievre (1982) made measurements as quickly as possible because the viscosity of their starch solutions at higher shear rates drifted down with time. There are few models of starch solution viscosity as a function of strain history. Diosady et al. (1985)proposed a describing intrinsic viscosity of raw starch solutions as a model function of the fraction of starch fully cooked and the product of stress and time.

Since both protein and starch solutions show an asymptotic decrease in apparent viscosity as strain is applied, the strain history term (Table 2.1) proposed by Morgan et al. (1989) is also appropriate for starch.

2.3.2 Advantages of the Model

2.3.2.1 Simplicity of form.

Albert Einstein once said, "Everything should be made as simple as possible, and no simpler." For example, a linear function to describe the temperature profile in unsteady-state heat transfer is simple but unacceptably inaccurate. A higher-order polynomial may be accurate but unwieldy. A compromise can be made by using the simplest form still retaining acceptable accuracy; in this case, perhaps a parabola or exponential. The model used in this work was developed under the same concept, that the best model is simple yet accurate.

2.3.2.2 Predictive nature.

A general type of model is $y_n - f(x_n)$, where y_n are dependent variables and x_n are independent variables. However, some models are of the form $y_1 - f(y_2)$. The difference in words is that y_1 in the second model cannot be predicted; that is, y_1 is known only after the test when y_2 is measured. The current work distinguishes the two models by referring to the first as "predictive" and to the second as "dependent." An example of the difference between the two models is the directions for cooking a cake. Typical instructions are "bake the cake for 40 min at 350°F, or until a knife placed into the center comes out clean." The time and temperature suggested are independent variables predicting the cleanliness of the knife (y_2) , which in turn predicts that the cake is done (y_1) . In this research, any independent variable which could not be measured before or during a process was

discounted.

An example of a dependent rheological model is that of Bagley and Christianson (1982) and Christianson and Bagley (1983). They proposed apparent viscosity (y_1) as a function of the amount of swollen starch per dry starch (y_2) of the final product. Another example is the intrinsic viscosity model of Diosady et al. (1985), where he uses the fraction of starch fully cooked as an independent variable.

2.3.2.3 Generality.

Independent variables with universally-recognized, objective definitions were used, rather than those created specifically for this work. For example, shear rate, temperature, time, and moisture content are used for any fluid and are strictly defined, whereas "degree of gelatinization" or "fraction fully cooked" (Diosady et al., 1985) are substance-specific and have various definitions.

2.3.2.4 Ease of measurement.

"Intensive" or "specific" properties (those independent of mass) were preferred over "extensive" properties (those dependent on mass), because measurement techniques were easier and more accurate for the former. The model also became more general because it was less substance-specific.

Shear rate, temperature, and time are intensive properties. Shear rate is calculated using the velocity profile of the substance. Temperature is measured by a thermocouple, and time by a clock. Although moisture content is an extensive property, it can be measured when formulating the sample. These measurement techniques of intensive variables are contrasted to those for extensive properties. The techniques for measuring volume fraction and swollen weight of starch seem to be more difficult (Bagley, Christianson and Beckwith, 1983).

2.3.3 Simplified Model for Starch Gelatinization

For this study all variables in Eq. 2.1 were constant except the T-t history. Therefore, the simplified form of Eq. 2.1 is

$$\eta - \eta_{ug} [1 + A^{\alpha} (1 - e^{-k\Psi})^{\alpha}]$$
 (2.2.0)

resulting in apparent viscosity as an exponential function of Ψ , where

$$\Psi - \int [T(t)exp(-\Delta E_g/RT(t)] dt \text{ if } T \ge T_g \\ 0$$

if

T<Tg

(2.2.1)

and

¥−0

and

$$\eta_{ug} = [(\tau_o/\hat{\gamma}_1)^n + (\mu_r)^n]^{1/n} e^{[(\Delta E_v/RT_1)(1/T_1 - 1/T_r) + b(MC_1 - MC_r)]} + (1 - B(1 - e^{-d\Phi_1}))$$
(2.2.2)

from Eq. 2.1, where γ_1, T_1, MC_1 , and Φ_1 are arbitrary. It is proposed that Eq. 2.2 be used to predict the relative increase in viscosity of a dilute starch solution at any point in the gelatinization process. There are three distinct features of Eq. 2.2:
- 1) The gelatinization effect is additive.
- 2) The value of the constant A is the relative increase in viscosity caused by gelatinization. For example, if A^{α} 1, the final viscosity (as Ψ goes to infinity) increases 100%, relative to the ungelatinized viscosity.
- 3) The gelatinization effect has an exponential dependence upon T-t history, which in turn has an exponential dependence upon inverse absolute temperature. This "double"-exponential dependence, similar to first-order Arrhenius kinetics, describes the drastic increase of viscosity during gelatinization.

The value of ungelatinized viscosity and A give a range of the physically possible viscosity values. The integral T-t function and its coefficient (k) characterize the extent of reaction. In this research, the viscosity of the cornstarch solution increased 80 times (A^{α} equal to 80 in Eq. 2.2) after complete gelatinization.

2.4 Materials and Methods

2.4.1 Choice of Variables

A parameter in a multi-variable model can be found by experimentally holding all variables constant except the one independent variable associated with the parameter. The dependent variable then varies and the parameter is fit statistically.

Eq.2.2 shows that k, α , and ΔE_{σ} are the parameters and apparent

viscosity is the dependent variable. However, the associated independent variable is not obvious because ΔE_g is within an integral (Eq. 2.2.1). Since an integral must be used for processes where temperature is a function of time, ΔE_g cannot be solved for explicitly, but is approximated by an iterative procedure. The parameter k is lumped with ΔE_g .

2.4.2 Experiments

Corn starch solutions varying from 13.2 to 13.7% starch were hand-mixed, to minimize strain history, using distilled water at 23 C. Moisture content was determined from sets of three 12 g samples oven-dried 24 hr at 105 C.

The gelatinization threshold temperature was approximated by 3 C per min. between parallel plates in a heating a sample at Rheometrics Fluid Spectrometer (Model 8400). The gap was 0.8 mm and the steady shear rate was 100 1/s. A 30-gauge thermocouple (Omega Engineering, One Omega Drive, P.O. Box 4047, Stamford. CT 06907) lead was attached to the top plate with tape (Scotch) to press the tip against the plate. Silicone grease was applied to the tip to assure contact to the top plate. Another thermocouple monitored bath temperature at the bottom plate. The gelatinization temperature Was approximated as a weighted average of the top plate temperature and bath temperature at the time when the viscosity began to increase continuously, as measured by the spectrometer. Based on an estimate of thermal resistance, the bath temperature was weighted twice as much as the top plate temperature.

The starch solution was subjected to different T-t histories.

on prior observations of the gelatinization and gelling Based phenomena, 125 x 13.5-mm (inner diameter) screw-top glass test tubes, one-third full of the solution were heated in an ethylene glycol/water bath (Aminco top-loading heating/cooling bath. Silver MD) at constant temperature. Seven temperatures were Springs. 81, 84, 85, 91, 95, 101, and 105 C . For each temperature, used: sets of two to three tubes were heated for various times ranging from 20 s to 20 min, depending upon the glycol bath temperature. The tubes were shaken in a container at at 250 rpm, a speed determined visually to prevent settling of starch granules. The temperature at the radial center of the solution and 12 mm below the solution surface was measured every 10 s by a needle-nose T-type thermocouple (Omega Engineering, one Omega Drive, P.O. Box 4047. Stamford, CT 06907) fixed in each of one to four representative tubes for each The average measured temperature at each time was bath temperature. used for T-t history calculations. At the prescribed cook time, the tubes were removed from the bath, and immediately placed in an ice bath at 0 C to reduce the temperature below T_{σ} within 30 seconds.

2.4.2.1 Apparent viscosity.

The solutions were allowed to gel at room temperature. from 18 to 22 C. The apparent viscosity of each tube was characterized using a back extrusion device (Figure 2.2), a technique described by Harper et al. (1978). A stainless steel plunger was forced through the gel at a constant rate of 50 mm/min over a distance of 25 mm. measured from the original surface of the gel. The force required to move the plunger was recorded graphically by an Instron (Model 4202)



Figure 2.2 Typical force-penetration curve obtained from back extrusion testing at a constant plunger velocity

23

Universal Testing Machine (Instron Corp., Canton, MA).

The area under each curve was used to convert it to a right triangle of equivalent area with the same travel distance Lp (Figure 2.3), thereby yielding a height equal to Fp, the maximum force. This procedure is a modification of that of Harper et al. (1978). The ratio of Fp to Lp times a constant was used as a relative value of viscosity (Hickson et al., 1982).

The dimensionless form of Eq. 2.2 is

$$\eta/\eta_{\rm ug} -1 = A^{\alpha} (1 - e^{-k\Psi})^{\alpha}$$
 (2.3)

As Ψ goes to infinity,

$$\eta_{\omega}/\eta_{\mu\sigma} - 1 = A^{\alpha}$$
 (2.4)

Dividing Eq. 2.3 by Eq. 2.4 yields

$$\frac{(\eta/\eta_{ug}) - 1}{(\eta_{\omega}/\eta_{ug}) - 1} = \frac{\eta - \eta_{ug}}{\eta_{\omega} - \eta_{ug}} = y - (1 - e^{-k\Psi})^{\alpha}$$
(2.5)

Eq. 2.5 was used for plotting the results. For each bath temperature, a curve of normalized viscosity $(\eta - \eta_0)/(\eta_{\infty} - \eta_0)$ versus time was fit. The multiplicative form of Eq. 2.1 allows the effects of a varying temperature of measurement and moisture content to be cancelled by using normalized viscosity.



Figure 2.3 Schematic of test tube in plastic holder during back extrusion

2.4.2.2 Temperature-time history.

According to Eq. 2.5, all y versus time curves at different temperatures can be converted to one master curve, y versus Ψ . (Figure 2.4), once the proper ΔE_{g} is determined. Because Ψ was an integral, the following iterative procedure was developed:

1) An estimate of ΔE_{σ} was made, based on values reported in literature.

2) By using the representative measured temperature-time history (T-t) and the estimate of ΔE_g , Ψ was calculated for each group of replicates taken out of the hot bath at a specific time and temperature.

First the "mass-average Ψ " value was calculated. The gelatinized starch inside the tube was treated as an infinite solid cylinder at uniform initial temperature T_o , subjected to two step changes in environment temperature: first, an increase to the hot bath temperature, and second, a decrease to the ice-bath temperature at 0°C. Heisler's chart (Holman 1976, Figure 4-13) was used to calculate temperature at 10 different radii as a function of the measured center temperature. The combined thermal resistance of the glass tube wall and the heat transfer coefficient between the tube wall and bath fluid was estimated as at least 20 times less than the internal gelatinized starch

resistance. Thus, at each time the mass average Ψ value

$$\frac{1}{mass av. \Psi = 2\int T(r)e^{(-\Delta E}g^{/(RT(r))}(r/R)d(r/R)}$$
(2.6)





was calculated by Simpson's rule (Hornbeck, 1975). Eq. 2.6 is the integration over volume. These values were integrated over time using the trapezoidal rule (Hornbeck, 1975),to obtain the integral temperature-time history Ψ (Eq. 2.2.1) for each replicate group. y versus. Ψ were then plotted as points for each replicate group for all bath temperatures, using one value of ΔE_p , estimated in 1.

3) Using a computer routine, ΔE_g was varied and the procedure outlined in step 2 was repeated for each change. The coefficient k was lumped with ΔE_g because k was not varied independently. but forced to change with the fit of the equation every time ΔE_g was changed. The agreement between y and Ψ was measured by a Marquardt nonlinear regression (Draper and Smith, 1981) of all points using the statistical computer routine Plot-it (Eisensmith, 1987). The ΔE_g yielding the greatest coefficient of determination (R²) was used, as was the corresponding k for the fit to Eq. 2.5. A linear transformation on Eq. 2.5 was rejected because the resulting variance of residuals increased dramatically with Ψ (discussed in Neter et al., 1985, p.467-469)

The effect of different heating bath temperatures was shown by regression on successively smaller sets of data: 1) all points, 2) all points except those at 105 C, and 3) all points except those at 101 and 105 C.

2.5 Results

Figure 2.5 shows the seven curves of average normalized viscosity versus time, and Figure 2.6 shows the same curves transformed to one curve (normalized viscosity versus integral T-t history). with the regression line and 95% confidence band. The coefficient of determination was 0.843 for the regression of all values except those for 101 and 105 C (Figure 2.6). The activation energy yielding the greatest coefficient of determination was ΔE_g equal to 210.kJ/mol (50.0 The coefficient of Ψ in Eq. 2.2.0, k. was equal to kcal/mol). 0.846×10^{26} (K s)⁻¹. The estimate of the exponent α was 0.494. Each point in Figure 2.6 represents an average of two or three viscosity The regressions on all points and values at the same Ψ value. on all points except those at 105 C gave lack-of-fit significances less than 0.0001. The regression on all points gave ΔE_g equal to 170 kJ/mol (40. kcal/mol) and a coefficient of determination of 0.755.

Figure 2.7 is a plot of residuals (measured value - predicted value) versus $\Psi \times 10^{26}$ for the regression line in Figure 2.6. There were two to three replicates in each of 31 sets, giving 87 total observations. The standard deviation and absolute mean of residuals was 0.09 (9.0% of full-scale) and 0.076, respectively. In addition, the F value for lack-of-fit was 0.76 at a significance of 78.2%.

The weighted average "threshold" gelatinization temperature was 65. C. The average moisture content of the raw starch varied from 8.0 to 12%. The average viscosity indexes at 99% gelatinization were estimated as 4300, 7300, 9600, and 7800 cp at 81. 85, 91, and 95 C, respectively.



.5 Average normalized viscosity versus time for 13.7% (d.b.) starch solutions at 20 C and constant shear rate after heating at 81, 84, 85, 91, 95 101, and 105 C





Residual (measured value-predicted value) versus temperature-time history for regression line in Figure 2.6.

2.6 Discussion

The regression on all point shows that Eq. 2.5 is inadequate to include the full range from 81 C to 105 C. A better fit for all temperatures may be found by expressing ΔE_g as a function of temperature, or as a different constant within certain temperature ranges (Suzuki et al. 1976, Kubota et al. 1979, Bakshi and Singh, 1980). This method is a concession for using first-order kinetics to describe what is probably a mixed-order reaction (Lund. 1984). The three separate regressions revealed ΔE_g decreased at higher temperatures, in agreement with Suzuki et al. (1976) and Bakshi and Singh (1980). Most likely a different level of gelatinization, having a lower activation energy, is triggered at higher temperatures.

The 0.843 coefficient of determination and 78.2% significance of F lack-of-fit (Figure 2.6) indicate the usefulness of the model form $y=(1-\exp(-k\Psi))^{\alpha}$ for the temperature range 81-95 C. However, the 0.98 rather than 1.0 coefficient in the regression line (Figure 2.6) indicates the difficulty of deciding what value of viscosity is the limiting value.

Data for 101 and 105 C (Figure 2.6) were not included in the regression, but were plotted to show how far they lay from the rest of the data. This excessive deviation may have been caused by the increased error at high temperatures, specifically in the calculation of T-t history. Errors in temperature measurement are magnified in Ψ as temperatures increase, because of the exponential dependence of Ψ on inverse temperature (Eq. 2.2.1).

At a given T-t history, the viscosity is lower when heated at higher temperatures (Figure 2.6). This result suggests there is a

limit to how quickly water can enter and hydrate the starch granules. Although the calculated T-t history may be greater, the diffusion of water in and the diffusion of amylose out cannot proceed any faster. Another limiting factor is the increased amount of water vapor produced as temperatures approach 100 C. Not only is heat lost to vaporize liquid water, but the vaporized water cannot enter and swell the granule as liquid water can.

In addition, the values at 101 and 105°C may have been affected by the more complete disintegration of granules and the increased solubility of the starch. Christianson and Bagley (1983) also mention the increased amount of solubles at temperatures greater than 94°C.

Figure 2.7 shows the residual for every observation in the Figure 2.6 regression. The standard assumptions (Beck and Arnold, 1977) are that errors are additive, have zero mean with constant variance, are uncorrelated, and have a normal probability distribution. Randomness and lack of trends (Figure 2.7) suggest that the errors are additive. An absolute mean of .068 does not seriously violate the assumption of zero mean, and the number of positive and negative residuals is 47 and 40, respectively. The "band" of residuals is approximately horizontal and of constant width, showing a constant variance with Ψ , unlike the results for the linear form of Eq. 2.5. The number of changes in sign (48) is more than half the total observations (87). According to Beck and Arnold (1977, p.409) the errors are uncorrelated. In summary, the standard assumptions for residuals are valid.

2.7 Problem for Calculating the Cook Time of a Steam Infusion Process.

The model developed in this study can be used to solve process engineering problems. One example is provided in this section. Assume that a steam-infusion process requires a final apparent viscosity (η) is 700 cp, and the material has an ungelatinized viscosity (η_{ug}) of 20 cp. The following fundamental information is provided from prior rheological measurements: $k = 2.3 \times 10^{19}$ (K min)⁻¹, $\Delta E_g = 150$. kJ/mol, α =1.0, and A = 49. Calculate the required cook time considering a sequence of steps:

- 1. Make sure desired η (700cp) is less than maximum $\eta_{\infty} = \eta_{ug}(1+A) = 20(1+49)=1000$ cp
- 2. Calculate the normalized viscosity (Eq. 2.5): y- (700-20)/(1000-20)=0.69
- 3. Rearranging Eq. 2.5,

 $(.69) = -\ln(1-y)/k = -\ln(1-.69)/(2.3 \times 10^{19}) = 5.1 \times 10^{-20}$

4. Calculate cook time for a constant cooking temperature 85 C = 358 K. Rearranging Eq. 2.2.1 $\Delta t = \Psi e^{(\Delta E_g/RT)}/T =$ (5.1 x 10⁻²⁰)K min exp[(15 x 10⁴ J/mol)/(8.314 J/mol K *358 K)]

/358 K -1.1 min= 66 sec= cook time

This type of analysis would be appropriate for steam infusion problems involving starch-thickened fluids, such as many baby food products.

2.8 Summary and Conclusions

A general model was used to simulate starch viscosity development during gelatinization. Only the thermal history effect of gelatinization was experimentally verified. However, the authors propose a comprehensive model, including independent variables of shear rate, temperature, moisture content, T-t history. and strain history, for describing viscosity of dilute starch solutions. The shear rate dependence is described by the Heinz-Casson model, including a yield stress and finite limiting viscosity at high shear. The temperature effect is modeled using the Arrhenius relationship, and the influence of moisture content is assumed to be exponential. The gross effect of gelatinization on viscosity is modeled using first-order kinetics, leading to a temperature-time history term. The effect of strain history is approximated as exponential.

Evaluation of the T-t history effect indicates the relative influence of gelatinization upon apparent viscosity can be modeled as a function of one parameter only, temperature-time history. Expression of "activation energy" as a functions of temperature will improve the model.

Unlike starch viscosity models in the literature, this model does not require measurement of the end product. The model is general in that it can be used for any system geometry, process. or equipment, and can predict apparent viscosity at high shear rates. The form of the model (Eq. 2.1) allows each term to represent the complete effect of one variable (Table 2.1). Therefore, any one term may be easily replaced by another suggested form. For example, the Heinz-Casson model can be directly replaced by the power-law form for apparent viscosity.

The model can be tested and modified by estimating the parameters for several types of starch. Future research should be directed towards a verification of each term to assess which are most influential and which may be neglected. The assumption of independence of variables should also be investigated. The model can then aid in full-scale simulations of the processing of any starch-thickened fluid, if gelatinization is the overriding cause of viscosity increase. 3. Mixer viscometry used in modeling rheological behavior of gelatinizing starch solutions.

3.1. Abstract

"Viscosity" of gelatinizing starch dispersions is used in quality control and process design around the world. A comprehensive model to predict viscosity for an arbitrary process has not been proposed in the published literature. The purpose of this study was to to present a generalized scheme to identify and measure factors influencing viscosity development during gelatinization in food processing. A mixer viscometer was selected to illustrate a general experimental technique, because variables were known and highly controlled. The results (within 10 % standard deviation) suggested that, for larger processes, the limiting factor will be measurement accuracy rather than fit of the model.

A Brookfield RVTD mixer viscometer was used to gelatinize 5.5, 6.4, and 7.3% (d. b.) native corn starch dispersions. Torque response, the dependent variable, was used to estimate parameters in a generalized model. The independent variables were impeller speed, temperature (50-95 C), moisture content, temperature-time history, and strain history. Predicted and experimental pasting curves were compared. A simplified and rapid procedure for estimating parameters from an arbitrary pasting curve was proposed, and applied to a bean starch dispersion.

Dispersions thickened with decreasing temperature and had an Arrhenius activation energy between 6.4 and 11.5 kJ/mol. There was no evidence that retrogradation caused this effect. Maximum viscosity depended on cook temperature, ranging from a 150- to a 220-fold increase at 85 and 95 C, respectively. First order reaction kinetics was accurate (9.8% standard deviation) in describing viscosity increase during gelatinization. Torque decayed exponentially after initial gelatinization. Comparison of relative effects showed a pasting curve could be predicted by knowing only the rate of gelatinization during heating rise, the rate and extent of breakdown during shear decay, and the torque response to temperature during cooling.

3.2. Introduction

Starch provides the major source of energy in the diet. Across the world, some cereal grain, usually rice, wheat, or corn, constitutes the major source of food, with starch comprising about 75% of the grain (Hodge and Osman, 1976). Whistler (1984) suggests why starch will continue to be a dominant industrial raw material: the birth of enzyme engineering allowing low cost conversion of starch to Dglucose; use of starch as a feedstock for alcohol and as an additive of tertiary oil recovery systems; and the growing world population .

Starch is consumed as part of the grain or is isolated as refined starch for use in foods, papers, adhesives, and textiles. For the refined starch applications, "gelatinized" starch is used. Atwell et al. (1988) presented definitions of "gelatinization," "pasting," and "retrogradation," based on a survey of 67 attendees of the Starch Science and Technology Conferences. They agreed upon the following definition of gelatinization:

Starch gelatinization is the collapse (disruption) of molecular orders within the starch granule manifested in irreversible changes in properties such as granular swelling, native crystallite [sic] melting, loss of birefringence, and starch solubilization. The point of initial gelatinization and the range over which it occurs is governed by starch concentration, method of observation, granule type, and heterogeneities within the granule population under observation. .

There are many ways to measure extent of gelatinization of starch. Qualitative methods include photography (scanning

electron microscopy) and measuring loss of birefringence, while quantitative methods include measurement of volume fraction and solubility. A macromolecular view can consider viscosity or gel formation, while a micromolecular view may consider glycosidic bonds or diffraction patterns. In spite of many analysis methods, the gelatinization process is still poorly understood (Lund, 1984)

For industrial use, one prefers to characterize starch gelatinization with an efficient and inexpensive method simulating process conditions. A tube viscometer identical in size to process equipment would be inexpensive, and would avoid the problems of scale-up. However, if all process conditions were tested, the method would be inefficient. "Obviously, starch products are pasted and used under a wide variety of conditions, and no standard cycle of cooking and cooling can be devised which will be generally representative of their diverse applications" (Mazurs et al., 1957) A more efficient procedure is to *model* all effects important in industrial processing, because the model can be used to interpolate more accurately.

None of the literature reviewed investigated a comprehensive model, but the tools to build one are found in the collective results. First, a quantitative, as opposed to qualitative approach, is more accurate and allows mathematical modeling. Secondly, a macro- as opposed to micromolecular method is usually simpler and is already used by industry in the Visco/amylo/Graph, which measures torque (viscosity) increase.

Published literature also provides enough data on starch viscosity to suggest a comprehensive model. Furthermore, fluid dynamics has already developed equations relating viscosity to temperature and velocity, two design criteria for food processing. In short, we already know how to apply viscosity; what is needed is a way to predict it.

A comprehensive model for protein doughs was proposed by Morgan et al. (1989). Dolan et al. (1989) applied only one term of the model to starch dispersions. The model may be directly applicable to a food process, but has not yet been thoroughly investigated. Processing conditions are difficult to control. Furthermore, some processes may mask the effects of less significant variables. Therefore, the present study required a device having highly controlled conditions, and showing the effects of all five variables: shear rate, temperature, moisture content, temperature-time history, and strain history. The Brookfield RVTD mixer viscometer was chosen because of its small sample size, constant shear rate, speed, simplicity, and reproducibility. Since the model is equipment-independent, it will work for any instrument, as long as the variables can be measured. Therefore, the current study used the Brookfield device as an example of how to estimate model parameters.

Other instruments were considered. In starch viscometry, the Brabender Visco/amylo/Graph (C. W. Brabender Instruments, South Hackensack, N.J.) is most frequently used. The Brabender instrument records, in arbitrary units, the torque required to balance the developing starch viscosity during a programmed heating and cooling cycle (Zobel, 1984). Shearing occurs between pins during cup rotation at constant speed. The Visco/amylo/Graph is accepted worldwide as the standard instrument to measure and record the gelatinizing properties of starches and starch-containing products as a function of time, temperature, and rate of shear (Shuey and Tipples, 1980).

An advantage of the Visco/amylo/Graph is that the effective shear rate is close to that in the mouth, which implies that rankings of viscosity derived from Brabender readings will agree with sensory consistency judgments (Wood and Goff, 1973). Another advantage is the large data base already existing for starches. A third advantage would be the constant rate of temperature change claimed by the manufacturer, but Osorio and Steffe (1988) showed the rate is not constant. The disadvantages of the instrument are a) multiple and varying shear rates around the pins; b) intermittent shearing action; c)measurement and control of starch temperature is at an arbitrary point and not at the location where the maximum temperature occurs; d) long testing times (between 45 and 120 min); e) large (500 ml) sample size (Voisey et al. 1976), f) lack of sensitivity., and g) lack of instrument-to-instrument reproducibility (Steffe et al., 1989).

Despite disadvantages a through d, the Visco/amylo/graph can be used as a quality control device. For example, incoming starch is accepted or rejected based on instrument standards. However, the fact that temperature and shear rate are unknown makes using the instrument for prediction of processing

conditions complicated and difficult. Many studies show correlation between the shearing action and the shear rate. By calibration with absolute devices, Wood and Goff (1973) determined effective shear rates of the Brabender Viscograph, an earlier model of the Visco/amylo/graph. Goodrich and Porter (1967), and Blyler and Daane (1967) estimated rheological parameters from a Brabender torque rheometer, an instrument having a complex shearing motion, as does the Visco/amylo/Graph. Lee and Purdon (1969) converted Brabender plastograph (an instrument giving relative readings) curves to Instron flow curves. In these studies, the shear rate was an "overall" shear rate, and the temperature was measured at only one location in the sample.

Thus, to estimate processing parameters, a device is needed that measures sample temperature throughout (or makes temperature gradient negligible) and keeps a constant shear rate. Lancaster (1964), Voisey et al. (1976) and Paton and Voisey (1977), Steffe et al. (1988), and Walker et al. (1988) presented instruments which meet these requirements, namely the Cooking Viscometer, the Ottawa Starch Viscometer, the Brookfield RVTD mixer viscometer, and the Rapid Visco-Analyzer. In addition. all these devices gave peak viscosity in 1-5 min, compared to 45 min for the Visco/amylo/Graph. Freeman and Verr (1972) also presented a rapid procedure to measure paste development with the Brookfield Syncro-Lectric viscometer. Bhattacharya and Sowbhagya (1981) presented a rapid Brabender viscograph test with a 50% saving in time and 20% saving in flour weight.

The present study also used a rapid mixer viscometry technique to measure torque, but results were given as estimated parameters (empirical coefficients) in a comprehensive model. Parameters are then used to <u>predict</u> a pasting curve as a function of temperature, temperature-time history, and strain history.

There is a need to remove equipment-dependence from rheological readings for starch: there is also a need for a comprehensive viscosity model. Janas and Tomasik (1986) concluded "more general description of properties of pastes ... can be achieved ... by means of a scope of parameters independent of measurement conditions [italics added]." Lund (1984) stated "studies on the kinetics of starch gelatinization are very limited." and "currently there is no definitive kinetic model for starch gelatinization." In the same work, Lund remarks "... it is highly questionable to develop a kinetic model for gelatinization...." because there are multiple-order reactions occurring (Lund, 1987). However, after the initial stage of gelatinization. a first-order model became more accurate (Lund. 1987). Janas and Tomasik (1986)wrote, "Due to lack of a precise theory and suitable devices as well as the nature of the material, results of rheological studies of starch pasting are deprived of any general meaning."

In light of the difficulties and yet the need for a partial solution, the objective of this work was to identify and measure factors influencing viscosity development during gelatinization.

3.3. Theoretical Considerations

Morgan et al. (1989) proposed a model for viscosity of protein doughs:

$$\eta(\dot{\gamma}, T, MC, \Psi, \Phi) = \left[\left(\frac{\sigma_{r}}{\dot{\gamma}} \right) + (\mu_{r})^{n} \right]^{\frac{1}{n}} e^{\left[\frac{\Delta E_{v}}{R} \left(\frac{1}{T} - \frac{1}{T_{r}} \right) + b \left(MC - MC_{r} \right) \right]}$$
$$* \left[1 + \beta_{r} \left[A_{3} \left(MC \right)^{\varepsilon} C_{p} \right]^{\alpha_{0} \dot{\gamma}^{a}} \left(1 - e^{-k\Psi} \right)^{\alpha_{0} \dot{\gamma}^{a}} \right] \left[1 - B \left(1 - e^{-d\Phi} \right) \right]$$

where

$$\Psi = \int_{0}^{t_{f}} T(t) e^{\left(\frac{-\Delta E_{g}}{RT(t)}\right)} dt \qquad T \ge T_{g}$$
$$= 0 \qquad T < T_{g}$$
$$(3.1.1)$$
$$\Phi = \int_{0}^{t_{f}} \overline{\dot{\gamma}} dt \qquad (3.1.2)$$

Simplifications were made in the gelatinization term of the Morgan et al. (1989) model. Only 100% corn and bean starch were used in the current study, so dry basis starch concentration (C_p) was 1.0. In an excess-water system, the molecular weight of gelatinized starch did not depend on moisture, so $\varepsilon = 0$. Although shear rate was varied, the dependence of α on shear rate was not investigated; therefore, β and A₃ were combined into one constant, A. The Morgan et al. (1989) generalized a priori model then becomes

$$\eta(\dot{\gamma}, T, MC, \Psi, \Phi) = \left[\left(\frac{\sigma_{r}}{\dot{\gamma}} \right) + \left(\mu_{r} \right)^{n} \right]^{\frac{1}{n}} e^{\left[\frac{\Delta E_{v}}{R} \left(\frac{1}{T} - \frac{1}{T_{r}} \right) + b \left(MC - MC_{r} \right) \right]} \\ \left[1 + A^{\alpha} \left(1 - e^{-k\Psi} \right)^{\alpha} \right] \left[1 - B \left(1 - e^{-d\Phi} \right) \right]$$

$$(3.1.4)$$

The application of the above model to starch dispersions is discussed in Chapter 2. Eq. 3.1 is assumed to be separable in all its variables; that is, each independent variable appears in a separate term, and the parameters are constant. The experimental design in this study was also set up to ensure this condition. There are at least two cases for which this assumption is inappropriate. The first is when parameters are functions of any independent variable. The other, a more serious situation, is for a term to vary in *form* as an independent variable changes.

Occurrence of the first kind does not invalidate the model; rather it requires that experiments are run over the range of the variable causing the violation. Then the functional form of the parameter can be substituted in Eq. 3.1. Both types of violations were investigated in the current study. The first kind occurred with temperature and strain history parameters; the second kind did not occur.

In this study, the yield stress was negligible. Therefore, the shear rate term (Heinz-Casson model) in Eq. 3.1.4 was replaced by the power law model, $\eta = K(\dot{\gamma})^{n-1}$ Eq. 3.1.4 was transformed

by the power law model, $\eta = K(\dot{\gamma})^{n-1}$ Eq. 3.1.4 was transformed by replacing η on the left side with torque (M) following two basic assumptions of mixer viscometry: shear stress is directly proportional to torque, and shear rate is directly proportional to impeller speed. Multiplying by $\dot{\gamma}$ and substituting N for $\dot{\gamma}$ yields

$$M(N, T, MC, \Psi', \Phi) = K_{r} N^{n} e^{\left[\frac{\Delta E_{v}}{R}\left(\frac{1}{T} - \frac{1}{T_{r}}\right) + b (MC - MC_{r})\right]}$$

$$*\left\{1 + A^{\alpha}\left(1 - e^{-\Psi'}\right)^{\alpha}\right\} \left\{1 - B (1 - e^{-d\Phi})\right\}$$

$$(3.2.0)$$

$$\Psi' = k \Psi = \int_{0}^{t_{f}} T(t) e^{\left(\frac{-\Delta E_{v}}{RT(t)} + \ln k\right)} dt$$

$$(3.2.1)$$

where K_r is a pseudo-consistency coefficient at reference temperature T_r and reference moisture content MC_r . Ψ' incorporates k with Ψ , to avoid large scaling factors caused by the exponential. Following the substitution of N for $\dot{\gamma}$, Eq. 3.1.2 now becomes

$$\Phi = \int_0^{t_{\rm f}} N \, \mathrm{dt} \tag{3.2.2}$$

The proportionality constants from mixer viscometry were absorbed into the parameters K_r and d. Eq. 3.2 is a more convenient form for use in the current work than Eq. 3.1.4. The two equations are, however, equivalent.

To predict a pasting curve, all parameters (a total of ten) of Eq. 3.1.1 and 3.2 must be known: For the N term, the parameters are K_r and n; for the T term, ΔE_v ; for the MC term, b; for the Ψ term, A, ΔE_g , k and α ; and for the Φ term, B and d. As explained in the experimental plan, each parameter or group of parameters was estimated by holding all but one independent variable constant during data collection. The difficulty with this approach is that interaction of variables forces one to take data outside the desired range, and then extrapolate back into the range. For example, one cannot measure the temperature effect above 75 C because gelatinization obscures it. Therefore, temperature effect was found in two ways : 1) by estimating the parameter below 75 C and then assuming it was accurate above 75 C; and 2) by estimating the parameter above 75 C after gelatinization was complete. Effects of temperature-time and strain histories had to be divorced from each other in the same way.

Thus, for parameter estimation, there were five simplified forms of Eq. 3.2, corresponding to the five independent variables. When only $\dot{\gamma}$, T, or MC was varied, the form of Eq. 3.2 was straightforward (Morgan et al., 1988). When only Ψ was varied, Eq. 3.2 collapses to an analog of Eq. 2.5

$$\frac{\mathbf{M} - \mathbf{M}_0}{\mathbf{M}_{\bullet\bullet} - \mathbf{M}_0} = \left(1 - \mathbf{e}^{-\Psi'}\right)^{\alpha} = \mathbf{y}_{\Psi}$$
(3.3)

where M_0 and M_{∞} are the ungelatinized and fully gelatinized torques, respectively.

Similarly, if only Φ is varied, Eq. 3.2 becomes

$$M = M_0 [1-B (1-e^{-d\Phi})]$$
 (3.4.0)

Letting $\Phi \rightarrow \infty$ gives

$$\dot{M}_{\infty} = \dot{M}_0 [1 - B]$$
 (3.4.1)

Eq. 3.4.1 provides a definition of B, so that Eq. 3.4.0 can be expressed in the form of Eq. 3.3

$$\frac{M - M_0}{M_{on} - M_0} = (1 - e^{-d\Phi}) = y_{\Phi}$$
(3.4.2)

where M'_0 and M'_{∞} are the torques before and after shearing. "d" indicates the rate at which torque decays. "B" is the relative amount of viscosity decrease caused by degradation. Both d and B may be functions of $\dot{\gamma}$, T, and Ψ , as already discussed. The experimental plan shows how d and B were estimated at different values of the three independent variables.

3.4. Practical Considerations

Dispersion concentrations of 5.5, 6.4, and 7.3% (g dry starch/g soln) were selected to correspond to the Amylograph standard concentration, 7% (g bone-dry starch/g soln), (Shuey and Tipples, 1980). The viscosity of these solutions was below the minimum necessary to register accurately during back extrusion with a 50-N load cell on the Instron Testing Machine, used by Dolan et al. (1988). Furthermore, the thickest dispersions, cooled to 25 C after 17 min at 95 C, were not solids. Using a flag impeller, the mixer viscometer (Brookfield RVTD) gave different torque readings at different axial distances along a culture tube. Therefore, 6-8% dispersions had to be mixed continuously to avoid concentration gradients.

Table 3.1 summarizes the literature reviewed reporting apparent viscosity of starch dispersions as a function of the independent variables in Eq. 3.1. Nine studies fit shear stress (τ) to shear rate ($\dot{\eta}$) with a shear-thinning model, and four of the studies included yield stress. The same nine studies presented viscosity varying with moisture content MC, but only two (5 and 7) fit the data to a model where MC was the only independent variable. In both studies, the model used was the power-law, $\eta = C_1(MC)$ ^g. Although there was no model for MC in the other studies (1-4 and 13-14), the viscosities presented suggested an exponential or power-law increase with starch concentration. Although there were five studies varying temperature, only Doublier (1981) used more than two

temperatures. He used the Arrhenius relationship (temperature term in Table 2.1), valid for most fluids. Nine studies varied the thermal history, but only studies 8-12 reported and quantified it, with a first-order kinetic model different from this study. The first four studies (1-4) did not report temperature as a function of time, so the absolute thermal history was unknown. Studies 8-12 used a first-order kinetic model, reported temperature over time, and estimated activation energies (ΔE_g). Only Doublier (1981, 1987) investigated timedependent behavior, though without a specific strain history function

Based on Table 3.1, the shear rate- and moisture contentdependence of starch dispersions has been well investigated and has shown consistent behavior. The temperature-dependence is less established, and may have to be assumed constant above gelatinization temperatures, when gelatinization interferes. The temperature-time history-dependence has been investigated five different ways, with five models based on first-order kinetics. The strain history-dependence is unknown other than that starch dispersions are thixotropic. Therefore, the experimental plan placed emphasis on varying thermal and strain history, while still varying shear rate, temperature, and moisture content to correct the data for use in the comprehensive model (Eq. 3 2).

Table 3.1. Summary of dispersions.	of studies	reporting	viscosities	of	gelatinized	starch
	τ_	.	.9			

Independent ^a										
Starch	Conc.		<u>variable</u>					Dependent		
type	% db	Method	Ŷ	T	MC	Ψ	Φ	variable Reference		
corn	5-26	concentric cylinder	x	x	x	xb		vol.frac., 1.Christianson& viscosity Bagley (1983)		
wheat	7-25	concentric cylinder	x	x	x	xb		vol. frac., 2.Bagley & Chris- viscosity tianson (1982)		
wheat	8-15	concentric cylinder	x	x	x	xb		yield 3. Bagley & Chris- stress tianson(1983)		
corn	8-14	concentric cylinder	x	x	x	xb		yield 4. Christianson & stress Bagley (1984)		
corn potato tapioca	up to 10	concentric cylinder	x		x			vol. frac., 5.Evans & Hais- viscosity, man (1979) yield stress		
wheat	1.6- 8.2	cone and plate	x	x	x			viscosity 6.Wong & yield stress Lelievre(1982)		
wheat	0.3-8	concentric cylinder	x	x	x		xc	viscosity 7.Doublier (1981)		
rice	excess water	plastomete	•			x		strain 8.Suzuki et al. (1976)		
rice potato	6 & 30	capill rheom				x		viscosity 9. Kubota et al. (1979)		
rice	excess water	iodine blue				x		enthalpy 10.Bakshi & Singh (1980)		
rice	excess water	DSC				x		enthalpy 11.Lund & Wirakar- takusumah(1984)		
potato	18	DSC				x		enthalpy 12.Pravisani et al. (1985)		
maize wheat	5-10	viscograph conc. cyl.	x		x		xc	viscosity 13. Doublier(1987)		
corn	3.3	conc. cyl	x		x			viscosity 14. Colas (1986)		
$a\dot{\gamma}$, shear rate; T, temperature; MC, moisture content; Ψ , temperature-time										
history; Φ, strain history										
bReport	^b Reported temperature and time separately; did not use a temperature-time									
function										

cReported shear rate and time separately; did not use a strain history function

3.5. Materials and Methods

3.5.1. Experimental plan

In all experiments, the dependent variable, torque was directly proportional to viscosity at constant shear. Independent variables were impeller speed (directly proportional to shear rate), moisture content, temperature, temperature-time history and strain history. For any given run, impeller speed and moisture content were constant. The assumption of a separable model (Eq. 3.2) was tested by conducting trials over a range of conditions. In the experimental design, there were five divisions--four for estimating the parameters, and one for testing the results obtained in the first four divisions.

One cannot always independently estimate all parameters (constants) of a given model. Clearly, parameters appearing in groups cannot be estimated, because any combination resulting in the same group value will work. Sometimes not even all these groups may be found (Beck and Arnold, 1977). Hence, before designing experiments, one should determine which parameters can be estimated (*identifiability*), and what ranges of independent variables give the most accurate estimate. Appendix A describes how to make both determinations for Eq. 3.2.

Table 3.2 shows the experimental design for determining effects of moisture content and thermal history. The 10 C temperature range was chosen to approximate the range of the Visco/amylo/graph where raw corn starch thickens most rapidly
	moisture	content and to	emperature-	time history ^a
Impeller speed (rp	Temp m) (C)	g starch/ g solution	Fluid Jack Temp(C)	et Heating time (min)
100	60	5.5	95 92 85	10,15 20,25 25,30
100	60	6.4	95 92 88 85	2,4,6,8,10,12 3,5,7,9,11,15 3,3.5,4,5,8,12,15 3,3.5,4,6,9,12,15
100	60	7.3	95 92 85	2,2.25,2.5,4,7,10 2.5,3,7,20,25 3,3.5,4.5,8,12
^a Experim	ents condu	cted in duplic	ate	

Table 3.2. Experimental design for determining effects of

Table 3.3. Experimental design for determining effects of temperature²

Impeller speed (ru	Temp om)Range(C)	g starch/ g solution	Fluid Jacker Temp (C)	t Heating time (min)		
100	50-70	6.4	95	3 b 4 b 5 b 6 b		
100	60-95	6.4	95	8 c		
^a ΔE _v was estimated from each run ^b Experiments conducted in duplicate ^c The cooling phase of Set 2.1 Table 3.5 (triplicate)						

Approximately equivalent ranges of Ψ were achieved by shortening heating times as glycol jacket temperatures were increased. Only equilibrium torque measurement $(M_{\Phi \to \infty})$ was used, and each trial was duplicated. The purpose of this design was to use the 6.4 and 7.3% results to estimate gelatinization parameters and the 5.5, 6.4, and 7.3% results to estimate the moisture content parameter.

Table 3.3 describes the experimental design for determining effects of temperature. ΔE_v was estimated for each test by varying temperature only, a procedure made possible by the small sample size. Different heating times were used to check the assumption that ΔE_v was independent of Ψ . With smaller heating times (Table 3.3), when the sample was incompletely gelatinized, the temperature range had to be less than T_g to avoid influence of gelatinization. For greater heating times, when gelatinization was complete, the torque was recorded as the sample was cooled, because temperature-time history and strain history effects had already reached a plateau.

In addition, the purpose of the experimental design for determining effects of shear rate (Table 3.4) was to estimate the shear index, n. The range of rpm was the operating range of the viscometer.

The experimental design for determining effects of strain history is given in Table 3.5. There were two divisions, Sets 1.1-1.3 (division 1) and Set 2.1 (division 2). In division 1, only strain history was varied in thixotropic (shear breakdown) studies. Torque over time was recorded at the specified

Impeller speed (rpm)	Temp (C)	g starch/ g solution	Fluid Jacket Temp (C)	Heating time (min)
0.5				
2.5	60	6.4	95	8 a
10 20				
50 <u>100</u>	· _ · _ · _ · _ · _ · _ ·			
$\begin{bmatrix} 0.5\\1\\2.5\end{bmatrix}$				
2.5 5	50	6.4	95	1 2 b
20				
100				
^a Experiments ^b From experi	conducte mental pa	ed in duplicate asting curve (7	; Fable 3.6)	

Table 3.4. Experimental design for determining effects of shear rate^a

Table 3.5. Experimental design for determining effects of strain history^a

		2			
Test Set	Impeller speed (rpm)	Temp (C)	g starch/ g solution	Fluid Jacket Temp (C)	Heating time(min)
1.1	100 50 20	60	6.4	95	12
1.2	100	60	6.4	95	8 4
1.3	100	50 95	6.4	95	12
2.1	100	82-95	6.4	95	3-8b
^a Expe ^b Expe	riments conc riments conc	lucted in d lucted in t	uplicate riplicate		

conditions. N, T, and Ψ were varied separately to check the assumption that d and B were constant over those ranges. All but one set of tests (Table 3.5) were at temperatures less than T_g (65 C) to avoid interference from gelatinization or thermal degradation. Each trial was duplicated. In division 2, strain history was allowed to vary simultaneously with T and Ψ . The purpose was to determine if strain history interacted with T or Ψ .

The experimental design to produce pasting curves (Table 3.6) to test the predictive ability of the model (Eq. 3.2). N, T, MC, Ψ , and Tm were varied separately to produce eight pasting curves. Torque and temperature were measured over all time. The curve of Set 1 was predicted first using a separable model, and then the curves of all sets were predicted using an inseparable model to find the improvement in fit. For the separable model, all parameters from the results of Tables 1-5 were held constant, and Eq. 3.2 was solved for M. For the inseparable model, shear rate, MC, and Ψ parameters were held constant, while the T and Φ parameters were allowed to vary according to the results of Table 3.3 and Set 2.1, Table 3.5, respectively. With the substitution of these functions for the T and Φ parameters, Eq. 3.2 was again used to predict M. The model was further tested by using bean starch and decreasing the final temperature to 5 C (Set 6, Table 3.6).

Test Set	speed (rpm)	Final Tem (C)	ip g starch/ g solution	Fluid Jacket Temp (C)	Heating time (min)	
1	100	50	6.4	95	12	
2	100	60	6.4	95	12	
					<u>8 a</u>	
<u>3</u>	100	<u> 60 </u>	<u> </u>	<u>95</u>	8	
4	50	50	6.4	95	<u>12b</u>	
5	100	50	6.4	85	12	
6	100	5	6	95	<u>23</u> c	
^a Experiments conducted in triplicate						
bUser	d to estimate	shear ind	ex (Table 3.	4)		
CPuri	fied bean star	rch Phase	olus vulgari	s var. seafare	r	

Table 3.6.Experimental design to produce pastingcurves

3.5.2. Apparatus

Figure 3.1 is a schematic of the experimental apparatus. The equipment and procedure in this work were a modification that used by Steffe et al. (1988). The difference was that in this study, three rather than two fluid baths were used, to gain more rapid temperature change. There were also three sets of two valves in this study, rather than multiple ports on two valves. The apparatus mixes continuously, makes continual temperature measurements, and produces peak viscosity for corn starch within five minutes. T-type (30-gauge) thermocouples were calibrated in boiling distilled water at known elevation and barometric pressure. Maximum error is 1.0 C (Omega Engineering, Stamford, CT). Two automatic timers (GraLab models 171 Timer and 625 Timer/Intervalometer, Dimco-Gray Co., Centerville, OH) were used to measure elapsed time and control the sequencing of the ethylene glycol to the jacket. Maximum error is 0.1 s. Torque was measured on an arbitrary 100-unit scale by a viscometer (Brookfield RVTD, Brookfield Engineering Laboratories, Inc., Stoughton, MA). Published accuracy and reproducibility are 1% of range in use and 0.2%, respectively. A visual record of torque over time was kept on an analog chart recorder (OmniScribe recorder, model B5217-5, Houston Instrument, Austin TX). In the strain history experiments only (Table 3.5), torque over time was recorded using a hand calculator (HP 41CX, Hewlett Packard, Corvallis, OR) to read (through an HP 3468A Multimeter) and print (to an



Experimental apparatus of mixer viscometer and bath system Figure 3. la



Figure 3.1b Brookfield small sample adapter with flag impeller and copper-constantan thermocouple.



:

Figure 3.1c Flag impeller.

HP 82162A Thermal Printer) the viscometer torque voltage. The torque and temperature over time for the pasting curves (Table 3.6) and experiments to determine temperature effects (Table 3.3) were recorded on a personalcomputer (Apple Macintosh SE, Apple Computer, Inc., Cupertino, CA) with a 16-bit data acquisition board and accompanying software (ACSE-16-8 board and Analog Connection WorkBench software, Strawberry Tree Computers, Inc., Sunnyvale, CA).

3.5.3. Procedure

Native corn starch, Melojel (National Starch and Chemical Corporation, Bridgewater, NJ), was used for all experiments. The material was received as a white powder with an equilibrium moisture content of 8.4%, measured by drying at 104 C for 48 hr. Chronological order and time duration of experiments were first the 6.4% dispersion, three weeks; followed by the 7.3%. one week; and finally the 5.5%, two days. Distilled water at 26 \pm 2 C was added to the corn starch to give a 50-g dispersion, with pH between 5.8 and 6.2. Each dispersion was mixed at approximately 800 rpm (Corning PC-351 Hot-Plate Stirrer) for two minutes. A pipette (Gilson pipetman, Rainin Instrument Co., Inc., Woburn, MA) was used to transfer 12 ml in 4 ml increments, to the Brookfield small sample adapter chamber. The chamber was immediately placed inside the water jacket and the impeller was turned on at 100 rpm to keep the starch solids from settling. No settling was observed. At the completion of each test, the base of the chamber was checked for settling of solids. Heating of the sample began within 15 s. Heating time

for any one sample varied between 2 and 25 min, depending on heating temperature, which varied between 85 and 95 C. Time to reach maximum temperature was about 8 min. Temperature was measured every 10 s by a voltmeter (HP 3497A Data Acquisition/Control Unit) and computer program (HP-85) Except for Sets 1-3 of the strain history tests, the impeller rotated continuously at 100 rpm. Excluding Set 2.1 of the strain history tests (Table 3.5), the impeller rotation speed was varied as follows: 100 rpm until torque was 10 (Brookfield units, full scale equals 100 or 7187.dyne cm), 50 rpm between torque equal to 10 and 15, 20 rpm between 15 and 20, and 0 rpm until heating and cooling were completed and measuring temperature was reached. This procedure gave minimum breakdown while still maintaining homogeneous mixtures. Then the viscometer was restarted at the appropriate rpm (20, 50, or 100) simultaneously with the calculator. Mechanical degradation was recorded as decreasing torque over time.

Temperature of the starch solution was calibrated with the chamber thermocouple temperature, to account for conduction along the sheath and thermocouple, and the lag time. Heating and cooling cycles were duplicated for each of the four target temperatures. The impeller was replaced by a 1.5 mm-outer diameter, 175 mm-long aluminum sheath rotated by hand between 50 and 70 rpm. Four T-type insulated thermocouples (30-gauge) were wound around the sheath. The soldered tip of each thermocouple was placed where the flags would sweep in the sample: two tips at 4 mm above the sample chamber base,

one at 19 mm, and one at 34 mm. Thus, temperatures of these four points in the starch and the chamber thermocouple were measured every 10 s during hand-mixed runs. Although heat was added at the chamber wall, the radial temperature gradient was insignificant due to thorough mixing.

3.5.4. Analysis

3.5.4.1. Analysis Involving All Parameters

In the gelatinization experiments (Table 3.2), the analytical procedure of Dolan et al. (1988) was used with modification. At each target temperature and moisture content, temperatures at three axial positions in the starch were correlated linearly to chamber thermocouple temperature. Two to three replications were used.

The procedure for estimating parameters is illustrated in Table 3.7. Table 3.7a shows the analytical design and stepwise correction for Table 3.2, while Table 3.7b shows the calculation steps for Tables 3.2-3.5. The third column of Table 3.7a is measured torque, M. The right margin shows which parameters were estimated from particular groups of data. Table 3.7a is interpreted as follows. There were five horizontal blocks. The MC parameter, b, was estimated from each of the first three blocks (yielding b₁, b₂, and b₃), because only MC was varied at three constant maximum temperature (Tm) values. The average b was used to correct all M to a common MC (M_{MC}, the second column). Now the only variable in the first three blocks was Tm. Therefore, A^{α} was estimated from M_{MC} in the first three blocks (see the right margin). A^{α} was used to

Table 3.7. Procedure to estimate the parameters

Table 3.7a Analytical design and step-wise correction for Table 3.2.



 $N_r = 100 \text{ rpm}$ $T_r = 60 \text{ C}$ $\Psi'_r \rightarrow \infty$ $\Phi_r \rightarrow \infty$

Table 3.7b. Calculation steps

Using data for gelatinization effect (Table 3.2) for each Tm, fit $\ln M = \ln C + b(MC) \rightarrow \underline{estimate} \underline{b}$ $use average b = (b_1 + b_2 + b_3)/3$ correct all M to $MC_r \rightarrow M_{MC} = M e^{b(MC_r - MC)}$ from a plot of $M_{MC,\infty}$ versus $Tm \rightarrow \underline{estimate} \underline{A}^{\alpha} = f(Tm)$ $normalize M_{MC} (Eq. 3.3) \rightarrow y\psi' = (M_{MC} - M_0)/(M_{MC,\infty} - M_0)$ fit $y\psi' = (1 - e^{-\psi'})^{\alpha} \rightarrow \underline{estimate} \underline{k} \underline{a} \underline{\Delta E}_{\underline{g}}$ Table 3.7b (Cont'd)

Using data for temperature effect (Table 3.3) for each experiment, use M (N,MC, Ψ', Φ_r) fit $\ln M = \ln C + \Delta E_v / (RT)$ \rightarrow estimate ΔE_v Using data for shear rate effect (Table 3.4) for each experiment, use M (N, T, MCr, Ψ' , Φ_r) $\ln M = \ln C + n \ln(N)$ fit →estimate_n Use previously determined parameters to estimate the final one $\rightarrow K_r = M_0 / (N_r)^n$ (3.6)Using data for strain history effect (Table 3.5 Sets 1.1-1.3) for each experiment, use $M(N,T,\Psi',Tm)$ $\ln(M - M_{\infty}) = \ln(M_0 - M_{\infty}) - d * N \Delta t$ fit \rightarrow estimate d. B for each data set where $B = (M_0 - M_\infty)/M_0$ Using data for strain history effect (Table 3.5 Set 2.1), find d

and B while T and Ψ vary simultaneously

fo	r each experiment, use	$M(N_r, T, MC_r, \Psi')$	Tm _r)
fit	$ln[(M/M_0) - (M_{\infty}/M_0)] =$	lnB-d*N∆t	(8.3)
	→estimate_"ov	erall" d. B	

correct all M_{MC} to a common Tm by normalizing to $y\psi'$ (first column). Since $y\psi'$ had now been corrected for MC and Tm, the only remaining variable in all five blocks was Ψ' . Therefore, k, α , and ΔE_g were estimated from all $y\psi'$ (right margin). The method for estimating b, M_{∞} , and A^{α} is straightforward. As $\Psi' \rightarrow \infty$, $A^{\alpha} = (M_{\infty} - M_0)/M_0$. The gelatinization parameters ΔE_g , k, and α (Eqs 3.1.1 and 3.3) were estimated by minimization of the sum of squares of residuals ([observed $y\psi'$]-[predicted $y\psi'$]) as follows: The optimal value of ΔE_g was found using a minimization routine (quadratic interpolation method, routine name UVMIF, Math Library, IMSL, Inc.); the initial guess of ΔE_g was based on reported values; for each iteration in this routine, ΔE_g was held constant, and k and α were estimated simultaneously by sequential nonlinear regression (Box-Kanemasu method, Beck and Arnold, 1977). The reported k and α are those corresponding to the optimal ΔE_g , to which the routine converged. Both the routine and the nonlinear regression package were written in Fortran 77, and were run on a VAX-11/750 VMS 4.7 computer. Average CPU execution time was 42 s. In summary, gelatinization tests (Table 3.2) provided five parameters: b, A, ΔE_g , k, and α

Table 3.7 shows how the temperature parameter ΔE_v and shear index n were estimated. The tenth parameter K_r was estimated at N_r, T_r, MC_r, $\Psi'=0$, and $\Phi=0$. Eq. 2 then reduces to

$$M_0 = K_r \left(N_r\right)^n \tag{3.5}$$

from which K_r can be obtained

$$K_r = M_0 / (N_r)^n$$
 (3.6)

All terms on the right side of Eq. 3.6 were known constants, yielding K_r.

In the strain history experiments assuming a separable model (Sets 1-3, Table 3.5), the only independent variable was Φ . Eq. 3.4.3 was rewritten as

$$M - M_{\infty} = (M_0 - M_{\infty}) e^{-d\Phi}$$
(3.7)

The thixotropic parameter "d" (Equation 5) was estimated by linear regression of $ln(M-M'_{\infty})$ versus (N Δt) during the first 15 min (Table 3.7). B (Eq. 3.4.1) was solved for in the same manner as was A, yielding B = $(M'_0-M_{\infty})/M'_0$. d and B were correlated to N, Ψ' , and T, in that order. Taking d as an example, d at Ψ'_r , T_r was correlated first to N, and then all d's were corrected to N_r. The procedure was repeated for correlation to Ψ' and finally to T.

With Set 2.1 in Table 3.5 (for testing whether d and B interacted with the independent variables), d and B were found by factoring out, from the torque data, all effects except strain history. Then Eq. 3.2 was solved for the strain history term:

$$\{1 - B(1 - e^{-d\Phi})\} = M \frac{\left[\frac{\Delta E_{v}}{R}\left(\frac{1}{T_{r}} - \frac{1}{T}\right) + b(MC_{r} - MC)\right]}{K_{r} N^{n} \left\{1 + A^{\alpha} \left(1 - e^{-\Psi'}\right)^{\alpha}\right\}} = \frac{M}{M_{0}}$$
(3.8.1)

M'₀ was calculated after all other parameters were known. Rearranging Eq. 3.6.1 yields

$$\frac{M}{M_0} = \{1 - B(1 - e^{-d\Phi})\} = (1 - B) + Be^{-d\Phi} = \frac{M_{ee}}{M_0} + Be^{-d\Phi}$$
(3.8.2)

Thus, the data for Set 2.1 were fit according to

$$\ln\left(\frac{M}{M_0} - \frac{M_{\infty}}{M_0}\right) = \ln B - d\Phi$$
(3.8.3)

This method is an "extraction" of parameters from a pasting curve, once all other parameters are already known. In summary, strain history tests provided two parameters, d and B.

3.5.4.2. Simplified Analysis

To test the fit of the model with a different material and a minimum of experiments, parameters for bean starch were estimated from one curve only. Since N and MC were constant for any one curve, only the T, Ψ' , and Φ parameters were estimated. The procedure involved three step-wise corrections of the data, corresponding to the three variables. A pasting curve was divided into three sections: 1) heating rise--from the beginning of temperature increase until peak torque; 2) shear decay--from peak torque until beginning of cooling; and 3) cooling--from beginning of temperature decrease until final torque. Results (from Table 3.6) show that cooling was the only region where a single variable, T, had a significant effect. The same results show that Ψ' and T were the only significant variables during heating rise, and that Φ parameters depended on T and Ψ' . Therefore, parameters were estimated for T (using cooling data only), Ψ' (using cooling and heating rise data only), and Φ (using all data), in that order, following the same type of sequential correction shown in Table 3.7a.

3.6. Results

The estimated parameters are listed in Table 3.8 and are compared to literature values when possible.

In gelatinization experiments (Table 3.2), coefficients of determination (\mathbb{R}^2) for the chamber thermocouple calibrations ranged from 0.94 to 0.99. During the most rapid heating (Tm=95 C), chamber thermocouple readings lagged average starch temperature by as much as 4 C. Average moisture content parameter b was equal to - 0.511 with an 15.% coefficient of variance, and the equation used for A was $A^{\alpha} = 6.80 e^{.0367Tm} - 1$, with $\mathbb{R}^2 = 0.90$. Average ungelatinized torque (M_0) was 0.2 / (7.19 x 10³) N m. Because published literature used a powerlaw rather than an exponential for the moisture content effect, the parameter (g) for the power law was estimated as -3.22 with a 15% coefficient of variance (Table 3.8). Both moisture content parameters (b and g) were greater in magnitude at lower temperatures.

Figures 3.2 and 3.3 show the increase of torque with time and temperature at constant rpm for the 6.4 and 7.3% dispersions. Figure 3.4 shows 42 of the same data, corrected to 6.4% starch concentration, with torque normalized (Eq. 3.3) and time transformed to Ψ' (Eq. 3.1.1). The 42 data chosen were those with y less than 0.95, because in this region the torque was most sensitive to the parameters (Appendix A). Parameter estimates were $\Delta E_g = 740$. kJ/mol, k = 2.36 (K s)⁻¹ (scaled to Ψ), and $\alpha = 0.310$. Although the regression converged, ΔE_g and k were correlated (a change in one caused a compensating

T.L. 20	Compari	son of parameter estim	ates to those in	literature for native corn starch
1 auto 0.0.			Value from	Value from
Variable	Parameter	Description	current study	literature
z	Kr	pseudo consistency coefficient	0.11 N m min ⁿ	specific for Brookfield
	Ľ	flow behavior	0.204	0.45, Colas (1986)
		Index		and Haisman (1979) 0.65, estimated from
f	ΛF	viscons activation	11.5 kJ/mol	Christianson and Bagley (1903) 21.5 kJ/mol wheat starch,
-	DEV	energy		Doublier (1981)
MC	ء م	dimensionless parameter	-0.511	not found
)	8	dimensionless parameter	-3.22	-2.5, Evans and Haisman (1979) -3.88, wheat starch, Doublier (1981)
÷	ΔE_{g}	starch gelatinization	740 kJ/mol	630 kJ/mol, estimated from Christianson and Bagley (1983)
	¥	reaction rate parameter	2.36(scaled to Y	<pre>/)2.08 x 10¹⁰ (K s)⁻¹ Eyring and Stearn (1939)</pre>
	8	dimensionless parameter	0.310	0.434 for defatted soy flour
				weight polystyrene, Collins and
				Bauer (1965) 100 250 Econd Unitation
	≺	relative increase in viscosity	222.	100-330, Evans and naisman (1979)
Ð	p	shear-decay rate	6.39 x 10 ⁻³	not found
	В	parameter dimensionless parameter	0.39	greater than 0.36 Paton (1977)
awhere n=1	η ₀ (MC) ^g			







change in the other). Standard deviation of the residuals was 9.8%.

In fitting the Arrhenius relationship for temperature effects, the lowest correlation for any sample was $R^2 = 0.92$. ΔE_v appeared to increase rapidly with Ψ' and then approach a limit, behavior similar to viscosity. The trend of ΔE_v was fit to two lines:

$$\Delta E_v/R = 92.13\Psi' + 600 \qquad \Psi' < 0.3216 R^2 = 0.77 \qquad (3.9.1)$$

$$\Delta E_v/R = 0.3770\Psi' + 765 \qquad \Psi' \ge 0.3216 R^2 = 0.58 \qquad (3.9.2)$$

where $0 \le \Psi' \le 300$

For shear effects, the average shear index was 0.204 with a standard deviation of 0.004. The lowest correlation for any sample was $R^2 = 0.94$. Parameter K_r was equal to 0.11 dyne cm (min)ⁿ x 7187. (Eq. 3.6).

For strain history effects with all other variables held constant (division 1, Table 3.5), the parameters d and B were correlated to N, Ψ' , and T as follows:

$d(N, \Psi'_r, T_r) = (58.3/N - 0.1385)/60,000$	$R^2 = 1.00$	(3.10.1)			
$d(N_r, \Psi', T_r) = (0.34 \exp(-0.0049 \Psi') + 0.4)/60,000$	$R^2 = 0.86$	(3.10.2)			
$d(N_r, \Psi'_r, T) = (0.043(T-273) - 2.1)/60,000$	$R^2 = 0.94$	(3.10.3)			
$B(N, \Psi'_r, T_r) = 0.001N + 0.19$	$R^2 = 0.70$	(3.11.1)			
$B(N_r, \Psi', T_r) = 0.012 exp(0.0051 \Psi') + 0.10$	$R^2 = 0.93$	(3.11.2)			
$B(N_r, \Psi'_r, T) = 0.0088(T-273) - 0.23$	$R^2 = 0.78$	(3.11.3)			
For curve fitting, the reference values used were $N_r = 100$, $T_r =$					
60 C, and a finite scaled value of $\Psi'_r = 1250$). The torqu	e			

decrease within the first minute was a more rapid decay than that of the remainder of the curve.

For the pasting curves of division 2, Table 3.5, after all effects except strain history had been factored out (Eq. 3.6), torque decay was noticeable only after peak torque. Average d and B for the three trials were 6.38 and 0.39, with coefficients of variance 20 and 5%, respectively. The average Ψ' when maximum torque occurred was 6.84. These results were used for predicting the final pasting curves (Table 3.6)

Figure 3.5 shows the predicted and experimental pasting curves (Table 3.6, Set 1), assuming the model is separable. The constant parameter values were b = -0.511, d = 0.425, B=0.280, and $\Delta E_v/R = 2200$ K. The remaining parameters were as listed in Table 3.8.

Figures 3.6-3.13 show the predicted curves (in the order of Table 3.6) using d and B extracted from real pasting curves (Set 2.1, Table 3.5). Shear rate, MC, and Ψ' parameters were set to the estimates from this study, and ΔE_v was varied according to Eq. 3.11. Φ parameters were varied as follows: d and B were





















Torque (dyne cm/7187.)

set to zero until $\Psi' = 6.84$, then held constant at 6.4*(100/N)(inverse proportionality suggested by Eq. 10.1) and 0.39, respectively, until beginning of cooling (Set 2.1, Table 3.5 results). During cooling, B was varied linearly with temperature from 0.39 at 95 C to 0.29 at 60 C, while d was varied according to Eq. 3.9.

The experimental curve of Figure 3.6, with three different predictions, each with different terms of Eq. 3.2 left out, is presented in Figure 3.14. Figure 3.15 shows the experimental and predicted torque for bean starch (Set 6, Table 3.6). The estimated parameters were, in order: for T, $\Delta E_v = 7.8$ kJ/mol; for Ψ , $\Delta E_g = 430$ kJ/mol, k = 0.48 (scaled to Ψ), $\alpha = 0.42$; and for Φ , d=2.1, B=0.16.






3.7. Discussion

3.7.1. Comparison of parameters with literature

 K_r (Table 3.8) was the only equipment-dependent parameter, because it is a scaling constant for the given system. In this work, there was no advantage to give it absolute significance by estimating $\overline{\dot{\gamma}}$ according to standard mixer viscometry techniques (Rao, 1975).

Parameters n, k, and ΔE_g (Table 3.8) did not compare well with those published in literature. The value of n in this study was for corn starch paste gelatinized at 95 C, whereas the maximum temperature in other studies was 90 C. Further study is needed to show how shear-thinning increases with maximum temperature. k and ΔE_g are discussed in the following section. All other parameters (Table 3.8) have absolute physical significance, but ΔE_v and α were not found for corn starch.

3.7.2. Gelatinization effects

Although the ΔE_g estimated in this study was more than six times greater than those reported for rice starch (References 8-12, Table 3.1) and potato starch (Reference 9, Table 3.1), the values cannot be compared because different mathematical models were considered. The primary reason is that unlike the standard equation for first-order kinetics, Eq. 3.3 has the exponent α . Another reason is that the current study used a different zero heating time reference viscosity. Other studies (References 8-12, Table 3.1) used a arbitrary point during early stages of gelatinization (Lund, 1984). This study used

ungelatinized viscosity, which was about equal to the viscosity of water. Furthermore, the cited researchers estimated ΔE_g from isothermal experiments; the temperature was varied in the current study. In addition, there were different combinations of ΔE_g and k with identical sum of squares (correlation). Therefore, the model (Eq. 3.2) predicted y accurately (9.8% standard deviation), but could not estimate a unique activation energy of gelatinization. Thus, the value of ΔE_g is not to be taken as an absolute physical parameter, nor was the purpose of this research to estimate the value; rather, the purpose was to estimate torque response, which was done with the combination of k and ΔE_g . To estimate ΔE_g , α must be set equal to 1.0 (the model of References 8-12, Table 3.1). If the values are still unusually high, additional isothermal experiments must be conducted.

3.7.3. Moisture content effects

There was no difference (15.% coefficient of variance) in the exponential model used in this study and the power-law model for moisture content. However, The moisture content range was not intended to differentiate between the two models. There was correlation between b and Tm (stronger MC effect at lower Tm), but the range of Tm (10 C) was small enough to accept an average b.

3.7.4. Temperature Effects

 ΔE_v increased with the extent of gelatinization (represented by Ψ' , Eq. 3.9). Physical chemistry predicts that the response of fluids to temperature depends on the molecular structure (Bird et al., 1960). Since gelatinizing starch is changing its "macromoelecular structure", a dependence of ΔE_v on Ψ' is expected. This dependence could be further investigated by comparing temperature response of starches with different ratios of amylose, a linear molecule, and amylopectin, a branched molecule. The ratio for native corn starch is approximately 1 amylose to 3 amylopectin.

3.7.5. Strain history effects

The rate and extent of breakdown should also depend on the molecular structure (size and shape). The network of macromolecules in gelatinizing starch changes as both T and Ψ' increase. Therefore, the dependence of B and d on T and Ψ' (Eq. 3.10.2, 3.10.3, 3.11.2, 3.11.3) confirms predictions from physical chemistry.

There were two divisions of strain history results. The first (Sets 1-3, Table 3.5) showed that Φ effects depend on Ψ' and T, in contrast to the assumption that Eq. 3.2 parameters were constant. Therefore, observations from division 1 are true only when all variables other than Φ are constant. The second (Set 2.1, Table 3.5) was an attempt to bypass this problem by estimating Φ parameters while Ψ' and T were increasing (during a pasting curve). This interference was unavoidable, because Ψ' could not be held constant at T greater than T_g . These two divisions will be discussed in order.

In division 1, the product d*N varied within 25% (Eq. 3.10.1). Therefore, the estimate of a constant d*N was used in predicting pasting curves (Table 3.6). The rate of breakdown was greater at lower thermal histories (Eq. 3.10.2) and at higher temperatures (Eq. 3.10.3), results consistent with intuition about thinner fluids. d was more dependent on T than on Ψ' (40% decrease compared to 400% increase, respectively). B, the relative amount of breakdown, was strongly influenced by Ψ' and T, but not by N (Eq. 3.11). Over the range of increasing Ψ' and T, B varied from 0.10 to 0.28 (Eq. 3.11.1), and from 0.30 to 0.60 (Eq. 3.11.2), respectively. This increase in susceptibility to breakdown was caused by the greater pliability of the swollen granules (Christianson and Bagley, 1983).

The rate of breakdown (d) experienced during pasting (d=0.0064, division 2) was two to three times greater than that (d=.00200 at 95 C) when Ψ ' and T were held constant (division 1, Eq. 3.10.3). During pasting, B reached its maximum value (at 95 C) more quickly than predicted (Eq. 3.11.2), implying B is less dependent on Ψ ' at higher temperatures. Therefore, results of division 1 were inaccurate for predicting pasting curves, as discussed in the following section.

3.7.6. Predicted pasting curves

The predictive ability of the model (Eq. 3.2) was tested by using the parameters estimated at constant conditions (Tables 3.2-3.5) to predict torque when T, Ψ' , and Φ varied simultaneously (Table 3.6). Figure 3.5 shows the prediction assuming all parameters are constant. The lack of a predicted shear decay indicated d was underestimated (division 1). The peak torque was underpredicted and the final torque at 50 C was

overpredicted because the temperature parameter (ΔE_v , Table 3.3) estimated at long cook times was too large. Therefore, the predictions of Figure 3.5 imply Eq. 3.2 would fit better if d, B, and ΔE_v were allowed to vary with Ψ' , in contrast to the the assumption that parameters were constant. Eq. 3.9 confirms the dependence of Arrhenius activation energy (ΔE_v) on extent of gelatinization. From beginning to end of the pasting process, ΔE_v doubled (Eq. 3.9). Therefore, errors in ΔE_v were magnified in predictions at longer cook times. At the beginning of gelatinization, the granules are rigid particles suspended in water. Viscosity is controlled by the water phase, whose viscosity change with temperature is negligible compared to that of the paste. As gelatinization progresses, the granules swell and form a network whose viscosity responds to temperature.

Figures 3.6-3.13 show the robustness of the model (Eq. 3.2) over the range of conditions in Table 3.6. For all parts except the cooling section of Figure 13, the predicted follows the trend of the experimental curve, with approximately a constant error magnitude. In Figures 3.6-3.13, T, Ψ' , and Φ are changing simultaneously within each figure.

The ability of the model to predict for different cooling temperature, heating time, cooling rate, moisture content, shear rate, and maximum temperature is shown separately in Figures 3.6 and 3.7, 3.8 and 3.9 (replicates), 3.10, 3.11, 3.12, and 3.13, respectively.

The qualitative and quantitative characteristics of each region of a pasting curve (heating rise, shear decay, and cooling) will be discussed in order.

3.7.6.1. Heating rise

The heating rise was overpredicted for all curves except Figure 3.11. The first-order kinetic model was least accurate during the beginning of gelatinization, where multiple-order reactions occur (Lund, 1984; Biliaderis, 1986). Although the rate of torque rise (governed by k and ΔE_g) was estimated from fully gelatinized torque measurements (Table 3.2), the results were also valid at the beginning of gelatinization. Therefore, there was negligible effect of strain history on gelatinization, because the time of initial torque rise did not shift by more than 5%.

3.7.6.2. Shear decay

At the beginning of shear decay, since d and B are "turned on" at a specific Ψ' value, there is some overprediction of the peak torque in Figs. 6-13. Using a step-change for d and B was chosen because the exponential decay model (Eq. 3.4) fit only the data after the peak. In the region near the peak, there is interaction of gelatinization and strain history. In Figures. 3.6-3.13, after the peak, the error magnitude was approximately constant (Figures. 3.8, 3.9, and 3.11), showing the rate parameter d was insensitive to the conditions varied. Figure 3.11 was the only prediction where shear decay began late, suggesting the onset of shear decay is dependent not only on Ψ' but also on the torque magnitude (Shuey and Tipples, 1980, p. 3). The assumption of a "time constant" = d*N (Figure 3.12) was reasonable, as shown by the prediction (since N had been halved, d was doubled). The error of Figure 3.12 resembled that of the other figures, showing the estimate of constant shear index n was valid over all temperatures considered.

3.7.6.3. Cooling

Cooling in Figures 3.6-3.12 began at different values of Ψ' , yet the cooling rise was predicted with a consistent trend. At lower Ψ' values (Figure 3.13, where maximum temperature was 85 C), the prediction did not follow the experimental trend. At this incomplete stage of gelatinization, change in starch viscosity caused by cooling from 85 to 50 C was undetectable. The Ψ' value at this point (700 s. at 85 C) was approximately equal to Ψ' after 180 s.at 95 C (Figures 3.6-3.12), suggesting temperature effects were negligible during heating rise. The granules at 85 C, unlike those at 95 C, had not swollen sufficiently to reveal any effect of temperature. **3.7.6.4. Relative influences of independent variables**

Figure 3.14 summarizes all the results by showing the relative influence of each term in Eq. 3.2 throughout the representative pasting process of Figure 3.6. The reference temperature was 95 C. There was less than 5% difference between Curve 1 and Curve 2 during heating rise (time less than 220 s), showing the overriding influence was gelatinization, with minimal contribution from temperature. Between peak torque (time equal to 220 s) and beginning of cooling (time equal to 730 s), temperature varied less than 5 C and gelatinization approached a limit, so strain history was the primary influence. In this shear decay region, Curve 2, prediction without temperature correction, was virtually identical to prediction with temperature correction (Figure 3.6), because the experimental temperature was within 2 C of 95 C. After cooling began, gelatinization ended and the rate of torque decay was negligible, so temperature was the only influence. Curve 3 shows the rise caused by cooling. Therefore, for any one pasting curve, there are at most two variables simultaneously causing torque to vary. In summary, Figure 3.14 shows that a corn starch pasting curve can be predicted by knowing only the rate of gelatinization during heating rise, the rate and extent of breakdown during shear decay, and the torque response to temperature during cooling.

The usual interpretation of set-back is that retrogradation, the association of swollen granules, causes the viscosity increase (Mazurs et al., 1957; Freeman and Verr, 1972; Shuey and Tipples, 1980). In this study, setback occurred in 20 s, too short a time for retrogradation to occur. Furthermore, for fully gelatinized and sheared pastes, a small as a 2 C decrease resulted in a reversible viscosity increase over 30 s. Cooling in the Brabender device occurs in 30 min., when retrogradation is just beginning. Therefore, what has been attributed to retrogradation is really a cooling effect.

3.7.6.5. Simplified Analysis

Figure 3.15 shows that Eq. 3.2 can be applied with a minimum of data. Although the shear decay region was not

visible (Figure 3.15), it was revealed when T and Ψ' effects were removed. The shear decay was one-third (d_{bean}/d_{corn}) as fast and four-tenths (B_{bean}/B_{corn}) as great as that for cornstarch, and was therefore obscured by gelatinization. ΔE_{ν} showed a distinct increase in the range 30-5 C, compared to 95-30 C, resulting in the underestimation at the end of cooling. Although activation energy for temperature effects depended on Ψ (Eq. 3.9), ΔE_{ν} can be set to a constant as long as all the data are corrected to a reference temperature. The estimated parameters for Ψ' and Φ changed to compensate for the inaccuracy of ΔE_{ν} at small Ψ' Therefore, all the parameters, not just those for Ψ' were correlated. This method can be used only if M is desired. For example, one cannot use the constant ΔE_{ν} to calculate the peak torque if T was equal to 70 C.

For corn and bean starch dispersions (Figures 3 6-3.15), the Brookfield RVTD viscometer gave more accurate data in less time (8 min. compared to 45 min.) than the Visco/amylo/Graph. The greater accuracy in measuring shear rate and temperature made the Brookfield a convenient tool for modeling. The results of the RVTD viscometer could be recorded as families of curves or as model parameters, which help explain the gelatinization process. Because of these advantages, the Brookfield device should be considered as a replacement or companion to the Brabender instrument.

This type of modeling (Eq. 3.2) is instructive, because it brings together present knowledge and takes a risk by assuming independent effects. The advantage is that if the assumption is correct, the experimental time will be decreased to a fraction of that required for a full factorial design. For example, even if the assumption is wrong for three variables, but correct for one, the number of experiments will be reduced from $(2x3)^4=1296$ to $(2x3)^3=216$, where 2x3 represents duplicates at three values of each independent variable. Therefore, this kind of modeling can benefit all kinds of experimental research.

3.8. Conclusions

- Each effect of shear rate, temperature, moisture content, temperature-time history, and strain history, as presented in the Morgan et al. (1988) model, was necessary to account for the torque response of pasted corn and bean starch dispersions. Having fit highly controlled experiments (5.5-7.3% d.b. corn starch dispersions at 50-95 C, and 6% bean starch at 5-95 C), the model can be applied next to pilot plant conditions.
- 2. Although each of the five variables affected viscosity, there was only one variable controlling torque response during each period of corn starch pasting: gelatinization during heating rise; strain history during shear degradation; and temperature during cooling.
- 3. The most significant interactions were between the temperature parameter and temperature-time history, and between strain history parameters and temperature-time history. However, there was no change in the form of the terms, only in the values of the regression parameters. Therefore, the model was not changed, but the parameters were estimated as functions of temperature-time history. Strain history parameters should always be estimated last, because they are the most sensitive.
- 4. Dispersions thickened with decreasing temperature, behaving as typical fluids. Arrhenius activation energy was between 6:4 and 11.5 kJ/mol. There was no evidence that

retrogradation caused this effect, because the cooling took place in 20 s.

5. The Brookfield RVTD viscometer gave more accurate data in less time (8 min. compared to 45 min.) than the Visco/amylo/Graph. The greater accuracy in measuring shear rate and temperature made the Brookfield a convenient tool for modeling. Because of these advantages, the Brookfield device should be considered as a replacement or companion to the Brabender instrument.

4. Industrial applications of rheological modeling

4.1. Prediction of velocity profile

Since there are already analytical solutions for velocity profiles of various non-Newtonian models, we wish to write Eq. 3.1 in the same form as these models. Replace the Heinz-Casson model in Eq. 3.1 with the Herschel-Bulkley model. All terms except the shear rate term are combined into the consistency coefficient K:

$$η(\dot{\gamma}, T, MC, \Psi, \Phi) = K(\dot{\gamma})^{n-1}$$
(4.1.0)

where

$$\begin{bmatrix} \frac{\Delta E_{\mathbf{v}}}{R} \left(\frac{1}{T} - \frac{1}{T_{r}}\right) + b \left(MC - MC_{r}\right) \end{bmatrix} \begin{bmatrix} 1 + A^{\alpha} \left(1 - e^{-k\Psi}\right)^{\alpha} \end{bmatrix} \begin{bmatrix} 1 - B(1 - e^{-d\Phi}) \end{bmatrix}$$

$$(4.1.1)$$

A starch-thickened fluid food gelatinizing at temperature T_1 is entering a holding tube at the same temperature. Assume radial velocity v_r and viscous dissipation are negligible. The velocity profile for a power-law fluid in laminar flow is

$$\mathbf{v}_{z}(\mathbf{r}) = \left(\frac{\Delta P}{2LK}\right)^{\frac{1}{n}} \left(\frac{n}{n+1}\right) \left(R^{\frac{n+1}{n}} - r^{\frac{n+1}{n}}\right)$$
(4.2)

Given a constant n, Eq. 4.2 indicates the velocity profile uniformly decreases as K increases during gelatinization. Since the flow rate is not varying, this behavior is not possible. Therefore, the pressure drop ($\Delta P/L$) must not be constant as the velocity decreases. The flow rate is

$$Q = \pi \left(\frac{\Delta P}{2LK}\right)^{\frac{1}{n}} R^{\frac{3n+1}{n}} \left(\frac{n}{3n+1}\right)$$
(4.3)

104

There are at least two ways to approach the problem. The first way is to assume n constant, divide the pipe into incremental lengths, solve for the pressure drop over a length using Eq. 4.3, and substitute it into Eq. 4.2 to solve for the velocity profile over that length. This method should give an "order of magnitude" estimate.

The second way is to assume the pressure drop is constant, and determine how n changes with K, through experiment. This method is more practical for a process engineer.

For non-isothermal flow, such as when a starch-thickened fluid begins to gelatinize in a heat exchanger, one may couple Eq. 4.2 with the energy equation:

$$\frac{\partial T}{\partial z} = \frac{\xi}{v_z(r)} \left(\frac{\partial^2 T}{\partial r^2} + \frac{1}{r} \frac{\partial T}{\partial r} \right)$$
(4.4)

At each time, a numerical scheme can be used to calculate the temperature profile, which is then substituted to find the velocity profile. For many industrial problems, the most important criterion is the maximum velocity to calculate the "worst-case" hold time of the fluid after it has reached a constant temperature. The assumption of negligible yield stress and the use of Eq. 4.2 and 3.14 should be sufficient for most processes.

4.2. Rapid parameter estimation

Based on the results of this work, the following experimental design and estimation procedure is suggested to characterize viscosity of a gelatinizing fluid (Table 4.1). Given the time restrictions of industry, we followed the principle of "getting the most from the least." See Dail et al. (1989) are designing a tube viscometer to find rheological properties under aseptic processing conditions.

The interpretation of Table 4.1 is similar to that of Table 3.7a. The analytical design is in the upper part of Table 4.1, and the calculation steps are the equations in the lower part. The fifth column, η , is measured viscosity. The first correction is made on this column and is placed in the column to the immediate left. The step-wise correction proceeds in this manner, with subsequent corrections moving towards the left. The correction equation for each column is given directly underneath the column.

The overall procedure is to hold all variables constant except one, and estimate the parameter for that variable. Then use that parameter to correct all η to a reference value of that variable, and repeat the entire process again. Therefore, the independent variables had to be selected such that each varied separately, with all others constant. Temperature must be varied below the gelatinization temperature, to keep gelatinization from obscuring the temperature effect. Therefore, T₁, T₂, and T₃ (all greater than T_g) are used to estimate maximum gelatinized η as a function of T, but T₄ and T₅ (below gelatinization) are

Table 4.1. Procedure for rapid analysis of parameters using a tube viscometer.



necessary to estimate the Arrhenius temperature effect, i.e. thinning at higher temperatures. The experiments at T_1 , T_4 , and T_5 are all gelatinized at T_1 (Table 4.1, Tm column), and then the last two are cooled in a second heat exchanger to T_4 and T_5 .

The order of analysis is as follows: estimate K and n from the enclosed η data, and correct all η to $\dot{\gamma}_r$; estimate ΔE_v from enclosed $\eta_{\dot{\gamma}_r}$ and correct all $\eta_{\dot{\gamma}_r}$ to T_r ; estimate dependence of maximum viscosity on Tm from enclosed $\eta_{\dot{\gamma},T}$, and correct all $\eta_{\dot{\gamma},T}$ to Tm_r; estimate b from enclosed $\eta_{\dot{\gamma},T,Tm}$, and correct all $\eta_{\dot{\gamma},T,Tm}$ to MC_r. If b fits poorly, check if it varies with Tm, and fit accordingly.

5. Overall Summary and Conclusions

This work brought together proven knowledge with hypothesis, and categorized objective, measurable variables affecting starch solution viscosity. The effects least investigated (temperature, temperature-time history, and strain history) in published literature were emphasized, and then combined with those most investigated (shear rate and moisture content).

The Morgan et al. (1988) model was applied to 5.5-7.3% and 13.7% native corn starch, and 6% bean starch dispersions, using two different methods: back extrusion and mixer viscometry. The independent variables influencing the dependent variable, viscosity, were shear rate, temperature, moisture content, temperature-time history, and strain history. Each of these five was varied individually with all others held constant to estimate the model parameters. The parameters were used to predict pasting curves in the mixer viscometer, where temperature, temperature-time history, and strain history changed simultaneously. Results showed that, except for temperature and strain history parameters, this experimental procedure yielded accurate results. Therefore, the temperature parameter was estimated at various temperature-time histories. Then, the strain history parameters were reestimated more accurately by allowing temperature and temperature-time history to change simultaneously. The final results indicated the model could apply to systems larger than the Brookfield viscometer

and Instron Testing machine, if the independent variables are measurable.

This type of modeling (Eq. 3.2) is instructive, because it brings together present knowledge and takes a risk by assuming independent effects. The advantage is that when the assumption is correct, even for only one of several variables, the experimental time will be decreased to a fraction of that required for a full factorial design. Therefore, this kind of modeling can benefit many different kinds of experimental research.

6. Suggestions for future research

6.1. Limitations of the model

The model (Eq. 3.2) is not invalidated if a different form for any one of the terms is found. Any of the terms can be replaced with the new form. The model is invalidated when enough interactions are shown to require factorial experiments. The value of the model is that it requires a minimum of experiments, while still explaining the physical process. In this work, the strain history parameters were estimated last, because they were highly dependent on Ψ' and T, and at short times, Ψ' could not be held constant at high T. If any other parameters were as dependent as these, the difficulty of estimation would probably make the model (from the practical standpoint) unacceptable. The complexity of the model increases if two or more independent variables change simultaneously. Future research on starches should estimate strain history parameters last, when other variables are changing.

The model does not account for ingredients, requiring new parameters for a new substance. The correlation of the MC parameter to Tm may cause problems over a large temperature range, but may also be insignificant at higher temperatures. The power-law relationship for MC ($M=C[MC]^b$)was valid in this work and preferred in published literature over the exponential (Eq. 3.2) form. The correlation of k and ΔE_g prevents finding their absolute value, if one wishes to compare activation energies in literature. Based on the sensitivity

coefficients, the following substitution to remove correlation was proposed by J.V. Beck (Mich. St. Univ, Mech. Eng. Dept., E. Lansing MI): define a new parameter $\beta_1 = \Delta E_g(k)^{1/100}$. Solve for ΔE_g in terms of k and β_1 , and substitute it into Eq. 3.3. y should become virtually insensitive to k over a 100-fold change, and β_1 can be estimated without correlation.

Another drawback of the model is that non-linear regression is required to estimate the three gelatinization parameters. Although a poorer fit will result, α can be set to one, and Eq. 3.3 can be manipulated to allow linear regression. This method can give a "first estimate."

6.2. Other applications

The present study intentionally used a device in which all five variables--shear rate, temperature, moisture content, temperature-time history, and strain history--affected response. For other situations, one should first judge which, if any, of the variables may be insignificant. For example, both history functions will probably be constant in aseptic food processing.

A more accurate method to estimate gelatinization effects is the DSC method of Lund and Wirakartakusumah (1984). However, this method may give parameters useless for process conditions, because there is no constant shearing.

Future research of starches should always include a complete history of temperature, rather than saying only that a "sample temperature was within 2 C of the target within 12-20 min." (Christianson and Bagley, 1983). Then the explanation of viscosity as a function of volume fraction (Christianson and Bagley, 1983) may be extended to viscosity as a function of temperature-time history.

Strain history has barely been investigated. For pipe flow, especially in aseptic conditions with long holding tubes, it is unknown whether strain history effect follows exponential decay as a function of average or wall shear rate. The exponential decay may be invalid at the high shear rates in pipe flow. For low shear rates, viscosity may be more influenced by the maximum shear rate than by strain history. A "spike" increase in shear rate could have a greater overall effect than the constant shearing. Extrusion provides this wide range of shear rates for doughs. During constant shearing, thermal degradation effects are difficult to separate from strain history effects. Back extrusion is one method to avoid shearing.

The elastic components of starch solutions may become important for smaller diameter pipes. Effects of α have not been measured. Theoretically, α represents the molecular weight effect on viscosity, and is a function of shear rate.

In addition to applying the model to a tube viscometer simulating process conditions (Sec. 4.2), one can apply it to a steam infusion or steam injection process. For any pipe flow, the minimum residence time can be estimated (Section 3.2.1), and possibly verified using phosphorescent particles. If the model fits small ranges of independent variables, the ranges should be extended to include several decades. Because of the model's generality, it can be applied to all kinds of gums, doughs, and starches, including modified starches, and mixtures containing starches which gelatinize only at higher temperatures. In this last case, the activation energy of gelatinization may have to be modeled as a function of temperature (Dolan et al., 1989). The strain history term has already been applied to pumping of time-dependent materials, such as mayonnaise. If the model is valid for homogeneous foods, one may attempt to apply it to foods with particulates. Finally, the procedure of collecting into one expression known terms, and assuming separable variables, can be applied to many materials and many variables other than viscosity.

7. Bibliography

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8. Appendices

8.1. Appendix A. Parameter Estimation Analysis

The model for gelatinization effects on torque (Eqs. 3 and 1.1) show that two parameters, k and ΔE_g , appear as a group, although ΔE_g is in an exponential and an integral. Therefore, these parameters may be linearly dependent. The sensitivity coefficients for Eq. 3.3 are

$$X_{1} = \frac{\partial y}{\partial \alpha} = \alpha \left(1 - e^{-k\Psi}\right)^{\alpha} \ln \left(1 - e^{-k\Psi}\right)$$

$$X_{2} = \frac{\partial y}{\partial k} = \alpha e^{-k\Psi} \left(1 - e^{-k\Psi}\right)^{\alpha - 1} \int_{0}^{t_{r}} T(t) e^{\left(\frac{-\Delta E_{g}}{RT(t)}\right)} dt$$

$$X_{3} = \frac{\partial y}{\partial(\Delta E_{g})} = -k \alpha e^{-k\Psi} \left(1 - e^{-k\Psi}\right)^{\alpha - 1} \left(\frac{1}{R}\right) \int_{0}^{t_{r}} e^{\left(\frac{-\Delta E_{g}}{RT(t)}\right)} dt$$
(A.1)
(A.1)
(A.2)
(A.2)

Figure A.1 is a plot of these sensitivity coefficients, using parameters values from Dolan et al. (1988). X_1 is obviously not linearly dependent, but X_2 and X_3 appear to have proportional magnitudes over the entire range.

To find whether X_2 and X_3 are linearly dependent, divide Eq. A.2 by Eq. A.3





$$\frac{X_2}{X_3} = -\frac{R}{k} \frac{\int_0^{t_f} T(t) e^{\left(\frac{-\Delta E_g}{RT(t)}\right)}}{\int_0^{t_f} \left(\frac{-\Delta E_g}{RT(t)}\right)} = -\frac{R}{k} \frac{\Psi}{\Psi''}$$
where
$$\Psi'' = \int_0^{t_f} e^{\left(\frac{-\Delta E_g}{RT(t)}\right)} dt$$
(A.4)

(A.5)

Since R and k are constants, Eq. A.4 shows that for constant T, X_2 and X_3 are linearly dependent, because $X_2/X_3 = -RT/k$. For time-varying temperature, k and ΔE_g will be more difficult to estimate unambiguously as the ratio Ψ/Ψ' approaches a constant.

Figure A.2 shows Ψ/Ψ'' versus $k\Psi$ for a typical thermal history in this work. Between k Ψ equal to 0.1 and 2.0, Ψ/Ψ'' varied more at the higher ΔE_g (12% decrease) than at the lower (approximately 5%). This small (5%) change explains why we cannot visually detect the linear independence in Figure A.1. According to Figure A.2, k and ΔE_g can be estimated independently at least between $k\Psi$ equal to 0 and 1, and we expect more accuracy with greater values of ΔE_g . According to Figure A.1, y (portion gelatinized) is most sensitive to all parameters in the range $k\Psi$ equal to 0 to 1 (0-37% gelatinized). At k Ψ greater than 2 (86% gelatinized), values of y have less and less influence on the estimates (Figure 3.17). Therefore, the majority of the data used to estimate gelatinization parameters were at y less than 80% gelatinized. The values near



Ratio of X_2/X_3 versus k Ψ to determine extent of linear dependence.

100% gelatinization were used to calculate the maximum torque $(M_{\infty}, Eq. 3.3)$.

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124 APPENDIX B

8.2.Appendix B Observed equilibrium torque of gelatinizing native corn starch to determine effects of moisture content and temperature-time history (corresponding to Table 3.2)

Impeller			Fluid	Heating	5	Equil.
speed	Temp	g starch/	Jacket	time	Sample	torque
(rpm)	(C) ⁻	g soln	Temp(C)	(min)	number(s	s)(Brkfld units)
			95	10	95	30.1
				15	96	29.6
100	60	5.5	92	20	97	26.3
				25	98	25.3
			85	25	99	19.1
				30	100	18.3
				2	1	6.9
				4	2,3	35,36.8
				6	4,5,6	42.7,38.3,41.1
100	60	6.4	95	8	7,8	41.1,41.3
				10	9,10	42.5,42.0
				12	11,12	44.0,42.0
				14	13,14	43.0,44.2
				16	15.16.17	46.0.47.0.39.1
				3	18	21.6
				5	22,23,24	35.5,35.3,35.0
				7	25,26,27	32.0.38.2.38.5
100	60	6.4	92	9	28,29	39.5.38.5
				11	30,31	39.4.39.5
				15	32,33	40.4.42.3
				20	34	42.8
				25	35	42.3
				3	36.37	8.3.9.9
				3.5	38.39	17.0.17.5
				4	40.41	27.4.30.6
				5	42,43,44	27.6.32.7.32.3
100	60	6.4	88	8	45.46	33.8.31.7
				12	47.48	34.1.33.3
				15	50.51	32.8.34.0
				25	49	34.4
				3	52.53	2.1.3.2
				3.5	54.55	8.2.6.9
				4	56.57	12.4.11.5
100	60	6.4	85	6	58.59	22.4.24.9
				9	60.61	29.3.30.2
				12	62.63	33.3.31.9
				15	64	32.8
				25	65,66	34.4,33.6
				23	05,00	54.4,55.0

Append	ix B (C	Cont'd)				
100	60	7.3	95	2 2.25 2.5 4 7 10 15	67 68,69 70,71 72,73 74,75 76 77	$13.2 \\ 27.7, 28.6 \\ 36.8, 39.3 \\ 52.4, 50.7 \\ 63.9, 65.6 \\ 61.6 \\ 60.6 \\ 100000000000000000000000000000000000$
100	60	7.3	92	2.5 3 7 20 25	78,79 80,81 82,83 84 85	25.5,17.3 42.5,42.0 58.0,61.3 64.6 63.6
100	60	7.3	85	3 3.5 4.5 8 12 25	86 87,88 89,90 91,92 93 94	13.3 15.2,21.1 34.1,37.9 49.2,52.2 52.5 51.6
126 APPENDIX C

8.3.Appendix C Time and temperature data

8.3.1.Appendix C.1 Time and temperature data for each sample in Appendix B.

Format (for entering computer program in Appendix D):

- 7 starch concentration ("6" means 5.5%, "7" means 6.4%, "8" means 7.3%)
- 0 0 indicates new sample
- 92 fluid jacket temperature
- 76 sample number

 T_2

t2

- 34.2 torque (Brookfield units (full scale=100), corresponding to Appendix B)
- T₁ t₁ Temperature (C) time (s)
- $\begin{bmatrix} I \\ T_n \\ t_n \end{bmatrix}$ last data for this sample 0 0 start with new sample

7		5.5		ê1	220
0	0	55		61 E	220
85	•	0.7		61.5	230
52		67.7	70	81.9	240
2.1		03.8	80	82.2	250
	20	71.8	90	82.5	260
40 3	70	73.2	100	82.8	270
	80	74.2	110	83	280
/0.3	90	75.2	120	83.1	290
71.5	100	76.4	130	83.3	300
72.6	110	77.2	140	83.5	310
73.5	120	77.9	150	83.5	320
74.5	130	78.5	160	83.7	330
75.4	140	78 9	170	83.7	340
76.2	150	70.7	190		350
76.8	160	/9.3	190	03.0	330
77.4	170	80.1	190	83.3	300
77 0	100	80.6	200	83.4	370
77 6	100	81.3	210	80	380
//.0	190	81.1	220	74	390
12.7	200	76.3	230	68.6	400
65	210	68.1	240	65.4	410
0	0	0	0	0	0
85		85	-	85	
53		56		59	
3.2		12 4		24.9	
67.3	70	48 3	60	67 9	70
69.3	80	99.4	00	70.3	
71.4	90	68	70	/0.3	
77 8	100	70	80	/1.9	90
72 0	100	71.8	90	73.1	100
/3.7	110	73	100	74.1	110
75	120	74.3	110	75.4	120
76.1	130	75.3	120	76.6	130
76.9	140	76.3	130	77.5	140
77.7	150	77.2	140	78.2	150
78.4	160	78	150	78.9	160
78.9	170	78.5	160	79.4	170
79.5	180	79	170	80	180
79.4	190	75 6	190	80.7	190
75.7	200	/9.6	190	41 3	190
70.3	210	80.2	190	6.10 01 0	200
66 6	220	80.8	200	81.8	210
~	440	81.4	210	82.3	220
	0	81.9	220	82.7	230
65		82.4	230	83	240
54		82.7	240	83.2	250
8.2		82.5	250	83.5	260
65.2	50	78.4	260	83.7	270
68.2	60	70	270	83.9	280
69.5	70	64.2	280	84	290
71.6	80		100	84.1	300
72.8	90	ů E	Ŭ	84.2	310
73.7	100	63		64.4 64.4	310
74.9	110	36		34.4	340
76 2	120	22.4		34.4	330
77 3	120	67.2	70	84.5	340
//.3	130	69.2	80	84.6	350
78.1	140	71.3	90	84.7	360
78.8	150	72.8	100	84.3	370
79.3	160	73.9	110	80.6	380
79.6	170	74.8	120	72.3	390
79.9	180	78.9	130	64.9	400
80.6	190	75.0	140		0
81.2	200	/4.8	740		J
81.1	210	//.8	120	63	
77.2	220	/8.3	160	60	
70 3	44U	78.8	170	29.3	
/U.J	230	79.3	180	66.2	70
94.0	240	79.7	190	68.3	80
0	0	80.1	200	70.4	90
85		80.6	210	71.8	100

72.7	110	80.7	230	84.3	340
73.7	120	81.3	240	84.3	350
74.5	130	81.7	250	84.4	360
75.4	140	82.2	260	84.5	370
76.2	150	82.6	270	84.6	380
77	160	82.9	280	84.6	390
78.1	180	63.1 83.4	290	84.7	410
78.6	190	83.6	310	84.8	420
79.1	200	83.7	320	84.8	430
79.7	210	83.9	330	84.8	440
80.2	220	84	340	84.9	450
80.8	230	84.1	350	85	460
81.3	240	84.3	360	85	500
82.2	250	54.J 84.A	370	50.1 26.1	510
82.6	270	84.5	390	85.2	550
82.9	280	84.6	400	85.2	600
83.2	290	84.6	410	0	0
83.4	300	84.7	420	85	
83.6	310	84.7	430	63	
83.8	320	84.8	440	31.9	
8J.Y	330	84.8	450	67 68 2	70
84.2	350	64.7 84.9	400	70.9	90
84.3	360	85	480	72.1	100
84.4	370	85	490	73	110
84.5	380	85	500	73.9	120
84.6	390	85.1	510	75.1	130
84.6	400	85.1	550	76.1	140
84.7	410	85.2	560	76.9	150
84.8	420	60.1 81.1	570	78.2	170
84.9	440	76.7	590	78.8	180
84.9	450	68.8	600	79.5	190
85	460	0	0	80.1	200
85	470	85		80.7	210
85.1	480	62		81.4	220
85.1	490	33.3	70	81.9	230
88.1	500	0/.4 40 s	70	64.J 82.6	240
85.2	520	71.2	90	82.9	260
85.2	530	72.4	100	83.2	270
85.2	540	73.5	110	83.4	280
84.8	550	74.6	120	83.6	290
81.2	560	75.7	130	83.7	300
74	570	76.7	140	83.9	310
07	560	//.4	180	85 1. 12	320
28	v	78.5 78.5	170	84.2	340
61		79.1	180	84.3	350
30.2		79.7	190	84.3	360
68.5	90	80.2	200	84.5	370
68.2	100	80.8	210	84.5	380
70.6	110	81.4	220	84.5	390
/1.0 79 4	120	81.9	230	54.5	400
73.8	140	94+9 82-7	250	54./ 84.7	410
75.1	150	83	260	84.8	430
76.2	160	83.3	270	84.8	440
77.1	170	83.5	280	84.8	450
77.9	180	83.7	290	84.9	460
78.5	190	83.8	300	84.9	470
79 7≙ ▲	200	83.9	310	84.9	480
/7.4	210	84.1	320	85	490 E10
av	24V	99.4	JJV	93	970

85.1	520	65		a 1 a	220
85.1	580	34.4		81.8	220
85.2	590	67.7	70	82.3	230
AE 2	600	69 3	/0	82.7	240
	730	07.J 71 g	80	83	250
78 3	730	71.3	50	83.3	260
70.3	740	/2.3	100	83.5	270
/0.2	/50	/*	110	83.7	280
03.7	760	75	120	83.9	290
0	0	76	130	84.1	300
85		76.9	140	84.2	310
64		77.7	150	84.3	320
32.8		78.3	160	84.4	330
67.6	80	78.8	170	84.5	340
69.9	90	79.3	180	84.6	350
71.3	100	79.7	190	84.7	360
72.3	110	80.2	200	84.8	370
73.3	120	80.8	210	84.8	380
74.7	130	81.4	220	84.9	390
75.9	140	81.8	230	AK	400
76.8	150	82.2	240		410
77.6	160	82.6	250	SS 85 1	420
78.3	170	82.9	260	99.2	430
78.9	180	83.1	270	93.4 Ar 9	430
79.4	190	83.4	280	GJ.4 Ag 3	440
79.9	200	83.5	290	63.4	450
80 6	210	81.7	200	63.2	460
91 2	220	83.9	310	85.3	470
01.2	220	43.6	370	85.3	490
01.0	230	6J.7 6A	320	85.4	500
94.3	240	64 64 1	330	85.4	550
94./	250	•••.1	340	85.5	560
83	260	64.2	350	85.5	600
83.3	270	54.3	360	85.8	1490
83.5	280	84.4	370	85.8	1500
83.8	290	84.4	380	85	1510
84	300	84.5	390	80.4	1520
84.1	310	84.6	400	72.5	1530
84.2	320	84.6	410	66	1540
84.4	330	84.7	420	0	0
84.5	340	84.7	430	88	
84.6	350	84.8	440	36	
84.7	360	84.8	450	8.3	
84.7	370	84.9	460	61.3	50
84.8	380	84.9	470	65.5	60
84.9	390	84.9	480	68.3	70
85	400	85	490	70.7	80
85.1	410	85	600	72.3	90
85.1	420	0	0	73.5	100
85.1	430	85	•	75.5	110
85.2	440	66		75.0	120
85.2	450	33.6		73.3	120
85.2	460	66.6	60	/0.3	140
85.3	470	63	70	77.7	140
86.3	490	70.8	80	/8.3	150
86.4	400	70.0		/8.9	160
	500	73	100	79.6	170
0J.4	500	73	100	80.4	180
93.4 98 e	210 210	/4•4 78 3	110	80.6	190
03.3 02 -	74U 840	/3.3	120	76.3	200
03.3	3 0 U	/8.2	130	68.5	210
03.0	570	77	140	63.4	220
53.6	600	11.7	150	61.1	230
45	910	78.3	160	0	0
80.1	920	78.8	170	88	
72.2	930	79.4	180	37	
65.5	940	80	190	9.9	
0	0	80.6	200	61.5	50
85		81.2	210	65.6	60

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68.6	70	71.6	240	P. 83	70
71.2	80	63.8	250	71.3	80
72.9	90	0	0	72.6	90
74.2	100	88		73.9	100
75.4	110	40		75.1	110
76.8	120	27.4		76.3	120
77.7	130	60.2	60	77.3	130
78.3	140	64.9	70	78	140
78.9	150	68.1	80	78.6	150
79.6	160	70.8	90	79.4	160
80.4	170	72.6	100	80.3	170
81.3	180	73.8	110	81.3	180
81.6	190	75.3	120	82.3	190
77.6	200	76.8	130	82.9	200
69.3	210	77.9	140	83.5	210
63.9	220	78.8	150	84.1	220
0	0	79.5	160	84.4	230
88		80.3	170	84.8	240
38		81.3	180	84.6	250
17		4 2.3	190	82.2	260
61.8	50	55 67	200	79.5	270
66.1	60	6J.3	220	78.7	280
68.8	70	59.1 84 E	220	79.3	290
71.3	80	•••.3	230	80.5	300
73.1	90	99.7	240	81.8	310
74.5	100	99.4 82 c	230	81.6	320
75.7	110		270	76.9	330
77	120	77.3	280	67.9	340
77.7	130	68.6	290	60	350
78.4	140	62.3	300	0	0
79	150	0	0	88	
/9.5	160	88	•	4) 30 7	
6 U.2	170	41		36./ 48 7	50
91.1	190	30.6			50
82.5	200	63.6	50	71.6	70
83 3	210	67.4	60	72.9	70
83.1	220	70.2	70	74.1	
79.9	230	72	80	75.4	100
72.3	240	73.3	90	76.5	110
65.9	250	74.7	100	77.5	120
62.6	260	76	110	78.1	130
61.2	270	77.1	120	78.7	140
0	0	77.8	130	79.5	150
88		78.5	140	80.4	160
39		79.3	150	81.5	170
17.5		80.3	160	82.3	180
62.5	50	81.4	170	83.1	190
66.7	60	82.4	180	83.6	200
69.1	70	83.1	190	84.1	210
71.5	80	83.7	200	84.5	220
73.2	90	84.2	210	84.9	230
74.4	100	54.5 68	220	85.2	240
75.7	110	53	230	85.4	250
76.9	120	67.J 84 A	490 380	85.6	260
77.7	130	97.7 20 G	230	85.8	270
78.4	140	5 0.3 73 1	270	86.1	280
79	150	13.1 KR.4	280	86.1	290
79.6	160	60.5	290	85.6	300
80.3	170	0		81.5	310
81.2	180	88	•	/3.4	320
82	730	42			J
94./	200	27.6			
03.J 82 1	220	62.3	50	20 2 99	
	44V			36.3	

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68.9	70	87.1	410	34.1	
71.3	80	87.2	420	66.5	60
72.7	90	87.2	430	69	70
/3.8	100	87.3	440	71.2	80
76.6	120	87.3	450	74.3	100
77.6	130	87.4	470	75.6	120
78.3	140	87.4	480	76.8	130
79.1	150	86.8	490	77.7	140
79.9	160	82.8	500	78.3	150
80.7	170	75.6	510	79	160
81.6 82 E	180	65. 3	520	79.6	170
83.1	200	88	U	81.2	190
83.7	210	46		82.1	200
84.2	220	31.7		82.8	210
84.6	230	66.8	50	83.4	220
85	240	69.3	60	83.9	230
85.3	250	71.8	70	84.4	240
85.5	260	73.4	80	84.8	250
03.0 AA	270	75.9	100	07.1 26.4	200
86.2	290	77.1	110	85.6	280
86.3	300	78	120	85.8	290
85.9	310	78.6	130	86	300
81.7	320	79.2	140	86.2	310
73.5	330	79.9	150	86.3	320
0	0	5U.0 81 A	160	86.4	330
46		82.3	180	60.J 86.6	350
33.8		83	190	86.7	360
65.8	60	83.7	200	86.8	370
68.9	70	84.1	210	86.8	380
71.2	80	84.6	220	86.9	390
72.8	90	85	230	86.9	400
74.1	100	60.J 45 s	240	87	410
75.5	120		250	66.3 87	430
77.4	130	86	270	87.1	440
78.1	140	86.1	280	87.1	450
78.7	150	86.3	290	87.2	460
79.4	160	86.5	300	87.2	470
80.2	170	86.6	310	87.2	480
81 0	180	30./	320	87.3	470 630
82.6	200	86.9	340	87.4	540
83.3	210	87	350	87.4	600
83.8	220	87.1	360	87.5	720
84.3	230	87.2	370	86.7	730
84.7	240	87.3	380	82.4	740
85	250	87.3	390	75.2	750
03.J 98 g	260	87.4 87.4	400	68.4	/00
85.7	280	87.5	420	88	•
85.9	290	87.5	430	48	
86.1	300	87.6	440	33.3	
86.2	310	87.6	450	66.6	60
86.3	320	87.6	460	69	70
86.5	330	87.7	470	71.6	80
50.5 84 4	340	87	480	73.2	100
86.9	350	GJ 75.8	500	/4./ 75.A	110
86.8	370	68.4	510	,3.8 77	120
86.9	380	0	0	77.9	130
87	390	88		78.6	140
87	400	47		79.1	150

79.8	160	84.4	240	96. 3	320
80.5	170	84.9	240	80.2	320
81.3	180	85.1	250	80.4 86 E	330
82.2	190	88.3	200	89.3	340
82.9	200	85.6	280	80.0	360
83.4	210	85.8	200	86.7	370
83.9	220	85.9	300	66 D	380
84.3	230	86.1	310	99.3 27	390
84.7	240	86.2	320	87.1	400
85	250	86.3	330	87.1	410
85.3	260	86.5	340	87.2	420
85.4	270	86.6	350	87.3	430
85.6	280	86.7	360	87.3	440
85.8	290	86.8	370	87.4	450
85.9	300	86.9	380	87.4	470
86.1	310	86.9	390	87.5	480
86.2	320	87	400	87.5	490
86.3	330	87.1	410	87.6	500
86.4	340	87.1	420	87.6	530
86.4	350	87.2	430	87.7	540
86.5	360	87.2	440	87.7	580
86.5	370	87.3	450	87.8	590
86.6	380	87.3	480	87.8	600
88.7	390	87.4	490	71.9	935
80.7	400	87.4	500	65.9	945
30.8	410	87.4	510	0	0
69.8 84 0	420	87.5	520	92	
88.9 86 0	430	87.5	580	18	
99.7	440	87.6	590	21.6	
00.J 17	450	87.6	600	62.1	50
87	400	87.9	1480	66.5	60
\$7.1	480	87.9	1490	69.5	70
87.1	510	87.9	1500	72.1	80
87.2	520	87	1510	73.8	90
87.2	570	82.7	1520	75.2	100
87.3	580	/3.3	1530	76.5	110
87.3	590	99.3	1240	77.5	120
87.3	600		U	78.3	130
87.4	715	50		/7.4	150
87.2	725	32.8			160
84.3	735	67.8	70	91.7 92 6	170
78.1	745	70.1	80	83.4	180
71.3	755	71.6	90	81.6	190
66.1	765	72.9	100	80.5	200
0	0	74.2	110	75	210
88		75.5	120	69.7	220
49		76.5	130	66.4	230
34.4		77.3	140	64.7	240
68.3	70	77.9	150	63.8	250
70.6	80	78.7	160	63.2	260
72.4	90	78.5	170	62.7	270
73.8	100	80.3	180	62.2	280
75	110	81.2	190	0	0
76.3	120	81.9	200	92	
/7.3	130	82.6	210	19	
78	140	83.2	220	28.1	
/8.0	150	83.7	230	64.1	50
7.3	190	84.2	240	68.1	60
20	170	84.6	250	71	70
0U.0 1 7	100	84.9	260	72.8	80
91./ 83 e	730	85.2	270	74.3	90
82 1	200	85.5	280	75.9	100
83.4	220	85.7	290	77.5	110
AA 1	220	85.9	300	78	120
	6JV	86.1	310	78.9	130

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79.9	140	71.8	80	35	
80.9	150	73.3	90	63	40
82.2	160	75	100	67.2	50
83.2	170	76.3	110	70.4	60
84	180	77.3	120	72.4	/0
84.8	200	/8.4 79.2	130	75.7	90
81.7	210	80.2	150	76.9	100
74.5	220	80.7	160	77.8	110
67.6	230	81.9	170	78.8	120
0	0	82.6	180	79.8	130
92		83.3	190	81	140
20		84.1	200	82.4	150
33.9		84.7	210	83.5	160
03.0	30	83.2	220	54.J 85	180
72	40 60	67.0 26.0	230	85.8	190
73.6	60	86.6	250	86.4	200
75.2	70	86.9	260	86.9	210
76.9	80	87.1	270	87.4	220
78	90	87.3	280	87.7	230
79	100	87.6	290	88.1	240
80.1	110	87.7	300	55.4	250
81.2	120	87.4	310	35.0	200
83.7	140	5 4 •▲ 77.2	320	89	280
84.5	150	71.1	340	89.1	290
85.3	160	66.9	350	88.6	300
86.1	170	0	0	84.5	310
86.8	180	92		77.3	320
86.9	190	23		70.9	330
83.6	200	35.3		00.3	340
71 9	220	47 3	40	92	v
67.8	230	70.5	50 60	25	
65.5	240	72.5	70	32	
64.2	250	74.1	80	63.7	50
0	0	75.7	90	67.7	60
92		76.9	100	71	70
21		77.7	110	/3 74 7	80
62.5	50	/0.3 70.5	120	76.4	100
66.8	60	80.7	140	77.6	110
69.5	70	82.2	150	78.4	120
72	80	83.3	160	79.3	130
73.5	90	84	170	80.3	140
74.8	100	84.7	180	81.3	150
70.2	110	35.4	190	04.0 83 7	170
77.9	130	50 2 2 2	200	84.4	180
78.8	140	87	220	85.2	190
79.7	150	87.5	230	85.8	200
80.8	160	87.8	240	86.4	210
82.1	170	88.1	250	87	220
83.1	180	88.4	260	87.4	230
53.1 76 =	190	88.5	270	57.3 28 3	240
72.K	210	5.5 2 2	280	30.2 88.5	260
66.5	220	88.2	300	88.7	270
0	0	83.4	310	88.9	280
92	-	76.4	320	89	290
22		70.5	330	89.1	300
35.5	• •	66.5	340	0	0
02.6	50	0	0	92	
70	70	92 34		38.2	
	, v	47			

63.2	50	88.1	240	90.4	440
67.6	60	88.4	250	90.5	450
71.1	70	88.7	260	90.6	460
72.8	80	88.9	270	90.6	500
74.2	90	89	280	90.7	510
73.9	100	89.3	290	90.7	540
17 0	110	89.5	300	90.1	550
78 9	120	67.J 40.7	320	63./ 76 1	500
79.9	130	97./ 89.9	320	/0.1 66 1	5/0
81.1	150	89.9	340		500
82.5	160	90.1	350	92	•
83.5	170	90.2	360	29	
84.3	180	90.2	370	38.5	
85	190	90.3	380	62.2	50
85.7	200	90.4	390	67.1	60
86.4	210	90.4	400	70.3	70
86.9	220	90.5	410	72.6	80
87.4	230	90.6	420	74	90
87.8	240	59 .7	430	75.7	100
5 5. 1	250	53.1 75 g	440	77.1	110
	260	/3.8 67 A	450	/7.9	120
88.8	270	97.4	400	78.9	140
89	290	92	v	/9.9 81	150
89.2	300	28		82.3	160
89.3	310	39.5		83.4	170
89.5	320	64.6	50	84.1	180
89.6	330	68.5	60	84.8	190
89.7	340	71.5	70	85.5	200
89.8	350	73.6	80	86.1	210
89.9	360	75.3	90	86.5	220
90	370	76.7	100	87.1	230
90	380	77.7	110	87.6	240
90.1	390	78.7	120	87.9	250
90.2	400	/7.8	130	5.35	200
A9 .2	410	82.3	160		280
84.1	440	83.5	160	91.00 AQ	290
75.5	450	84.2	170	89.1	300
67.8	460	84.9	180	89.3	310
62.7	470	85.7	190	89.5	320
60.7	480	86.4	200	89.6	330
0	0	86.9	210	89.7	340
92		87.4	220	89.8	350
27		87.8	230	89.9	360
38.5		88.2	240	90	370
0J.Y	50	38.3	250	90.1	380
71.1		55.7 22 A	200	30.1	700
73.1	70	99.7 89.1	270	90.2	A10
74.7	90	89.2	200	90.2	420
76.3	100	89.4	300	90.3	430
77.3	110	89.6	310	90.4	440
78.3	120	89.6	320	90.4	470
79.3	130	89.8	330	90.5	480
80.3	140	89.9	340	90.5	540
81.6	150	89.9	350	90.1	550
82.9	160	90	360	86.1	560
83.9	170	90.1	370	7 7	570
84.7	180	90.2	380	67.3	580
85.4	190	90.2	390	0	٥
36.1	200	90.3	400	92	
30.8	210	90.4	410	30	
57.2 67 7	220	70.4	420	39.4	E 4
9/./	230	70.5	430	60	20

68.8	60	76 7			
71.8	70	/0./ 77 A	120	87	210
73.9	80	78.2	140	67.5 AR	230
75.5	90	79.2	150	88.3	240
7.	100	80.3	160	88.6	250
78.8	110	81.6	170	88.8	260
79.7	130	82.7	180	89.1	270
80.8	140	83.4	190	89.3	280
82	150	84	200	89.4	290
83.1	160	84.7	210	89.6	300
84	170	63.4 98.0	220	87.8	310
84.7	180	86.3	230	6 9 .9	320
85.4	190	86.6	250	90.1	340
86.1	200	87	260	90.1	350
89.0	210	87.5	270	90.3	360
97.6	220	87.8	280	90.3	370
87.9	230	88.2	290	90.4	380
88.3	250	88.5	300	90,4	390
88.6	260	88.8	310	90.5	400
88.8	270	89.1	320	90.5	410
89	280	67.J 90.4	330	90.6	420
89.2	290	89.7	340	90.8	450
89.4	300	89.9	360	90.6	400
89.5	310	90	370	90.6	630
89.7	320	90.2	380	90.7	640
07.5 10 g	330	90.3	390	90.6	650
90.1	340	90.4	400	90.7	660
90.1	360	90.5	410	90.7	840
90.2	370	90.6	420	90.8	850
90.3	380	90.7	430	90.7	860
90.3	390	90.8	440	90. /	870
90.4	400	90.9	450	90.8	900
90.5	410	90	470	89.9	910
90.5	430	91	480	85.1	920
7U.0	440	91	490	75.1	930
90.5	460	91.1	500	65.9	940
90.6	500	91.2	510	0	0
90.5	510	91.2	530	92	
90.5	560	91.3	540	33	
90.6	570	91.3	570	94.3	50
90.5	580	91.4	600	67.9	50
90.6	590	0	0	70.6	70
90.6	620	92	-	72.7	80
90.4	060	32		74.4	90
90.7	660	40.4		75.9	100
90.7	660	60.9	40	77.1	110
89.8	670	66.2	50	78.1	120
85	680	07.7	60 20	79	130
75.4	690	73 74 9	70	81	140
65.9	700	76.2	90	82.3	160
0	0	77.6	100	83.4	170
72		78.5	110	84.2	180
20 E		79.4	120	84.9	190
60.9	50	80.5	130	85.5	200
65.4	60	81.6	140	86.1	210
68.5	70	82.9	150	86.7	220
71.1	80	83.9	160	87.3	230
72.7	90	34.6 28 3	170	57.7 20 1	240
74	100	60.5 Ar	190	66.1 20.5	23U 260
75.5	110	86.6	200	88.8	270

89	280	90.6	380	91.2	500
89.3	290	90.6	390	91.2	520
89.4	300	90.7	400	91.3	530
87.6	310	90.8	410	91.3	500
89.9	330	90.9	420	91.4	600
90.1	340	91.1	440	0	0
90.2	350	91.1	460	95	·
90.3	360	91.2	470	1	
90.4	370	91.3	480	6.9 47	60
90.6	390	91.J 91 A	500	73	70
90.7	400	91.4	530	75	90
90.8	410	91.5	540	76	100
90.9	420	91.5	580	77	110
90.9	430	91.6	590	78	120
91	450	91.6	600	95	
91.1	460	92	•	2	
91.1	470	35		35	
91.2	480	42.3		67	60
91.2	500	63.8	40	73	90
91.2	520	67.7 70.8	50	76	100
91.3	530	73	70	77	110
91.3	550	74.5	80	78	120
91.4	560	75.9	90	79	130
91.4 01 E	590	77.1	100	80	160
71.3	0	77.9	120	83	160
92	•	79.6	130	84	170
34		80.7	140	85	180
42.8		\$1.9	150	86	190
61.5	50	82.9	160	87	210
69.4	70	83.7	170	88	240
71.7	80	85	190	0	0
73.8	90	85.6	200	95	
75.3	100	86.2	210	3	
76.6	110	86.6	220	36.8	60
78.2	130	57.1 97 K	230	73	70
79.2	140	87.9	250	75	90
80.2	150	88.2	260	76	100
81.2	160	88.5	270	77	110
82.4	170	88.7	280	78	130
84	190	89 2 88	290	80	140
84.6	200	89.4	310	82	150
86.3	210	89.7	320	83	160
85.9	220	89.8	330	84	170
86.4	230	90	340	85	180
17 .3	250	90.1	350	87	210
87.8	260	90.4	370	88	230
88.2	270	90.5	380	88	240
88.5	280	90.6	390	0	0
58.9	290	90.7	400	95	
89.A	300	90.7	410	● ▲2 . 7	
89.6	320	90,0 70.8	430	67	60
89.8	330	90.9	440	73	70
90	340	91	450	75	90
90.2	350	91	460	76	100
90.3 90 4	360	91.1	470	77 79	120
3 V • 4	3/0	91.1	470	/0	

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70	110			77	110
	130	90.4	290		100
	140	90.8	300	/8	120
82	150	91.2	310	79	130
83	160	61 E	320	80	140
84	170	71.3	320	82	150
	100	91.8	330		160
•3	190	92.1	340	63	100
86	190	92.3	350	84	170
87	210	62 E	360	85	180
88	220	72.3	500 0	86	190
	220	0	0		210
	230	95		0/	220
89	250	7		88	230
90	270	41.1		89	250
91	300	49	40	90	270
42	330	0/	80	91	300
74	330	73	70	70	220
92.5	360	75	90	92	330
0	0	76	100	93	400
95			110	93.7	480
8		11	110	94.2	600
J		78	120	74.8	0
38.3		79	130	U .	v
67	60	80	140	95	
73	70		150	10	
78	90	04	130	42	
73	90	83	160	49	60
76	100	84	170	07	90
77	110	85	180	73	70
78	120		190	75	90
70	130	00	190	76	100
/ 5	130	87	210	77	110
80	140	88	230	11	100
82	150	89	260	78	120
83	160	90	270	79	130
84	170	30	270	80	140
		91	300		160
99	180	92	330	04	100
86	190	93	400	83	100
87	210	93.7	480	84	170
88	230	73.7	460	85	180
		0	0	96	190
87	250	95		04	220
90	270	8		87	210
91	300	41.3		88	220
92	330	44.5	4 0	89	250
02 E	360	0/	60	90	270
74.3	300	73	70	50	300
0	0	75	90	91	300
95		76	100	92	330
6		77	110	93	400
A1 1		//	110	93.7	480
41.1		78	120	04 7	600
07.8	60	79	130	79.4	
69.9	70	80	140	0	U
72	80	82	150	95	
73.7	90			11	
78 1	100	83	100		
/3.1	100	84	170		60
76.5	110	85	180	67	
77.7	120	86	190	73	70
78.9	130	47	210	75	90
80 1	140	87	110	74	100
an 1	740	88	230	/ •	110
41.4	150	89	260	77	110
93.7	160	90	270	78	120
83.4	170	01	300	79	130
94 A	100	21	300	90	140
94.4	190	92	330		1 80
85.1	190	93	400	52	130
85.9	200	97 7	480	83	160
86.6	210	· · · ·		84	170
97 1		U	U	96	180
0/.1	440	95		03	100
87.7	230	9		30	130
88.2	240	42. E		87	210
88.7	250	45.5	60	88	230
99 1	260	0/	3 U	AD	250
37.1	40U	73	70		280
87.5	270	75	90	90	200
90	280	76	100	91	310

92	350	60	140		
93	400	5U £2	140	74.2	130
93.7	480	83	160	75.3	140
94.2	600	84	170	76	150
94.4	720	85	180	70.4	170
U 95	0	86	190	78.4	180
12		88	230	79.3	190
42		89	250	80	200
69	60	90	270	80.6	210
72	70	92	300	81.2	220
74	80	93	400	81.4	230
75	90	94	520	78.3	240
76	100	94.4	840	,0.7	230
/8 70	110	0	8	85	•
80	140	85		89	
82	150	56		34.1	
83	160	13.3 68 8	60	65.4	70
84	170	68.3	70	67.8	80
85	180	70.3	80	69.8	90
86	190	71.5	90	70.3	110
87	210	72.8	100	73.2	120
88 80	230	74.1	110	74.2	130
90	230	75.1	120	74.9	140
91	300	75.5	130	75.6	150
92	340	75.9	140	76.4	160
93	400	77.7	160	77.2	170
94	470	78.6	170	77.9	180
94.4	720	79.5	180	/8./	200
0	0	79.8	190	80	210
73		76.7	200	80.7	220
43		69.7	210	81.3	230
66	50	64.9	220	\$1.7	240
70	60	0	0	82.1	250
73	70	63 87		82.5	260
74	80	15.2		82.7	270
76	90	66.7	70	82.3	280
77	100	68.9	80	71.4	300
78	110	70.9	90	65.1	310
/ 7 80	120	72	100	0	0
83	150	73.2	110	85	
85	170	74.4	120	90	
86	190	/J.J 78 g	130	37.9	
87	200	73.J 76_6	150	65	110
80	220	77.5	160	68	120
90	270	78.4	170	0 7. 2 70 g	140
71	300	79.1	180	70.9	150
77	J70	79.7	190	73.5	160
94	400	80.4	200	74.5	170
94.4	840	81	210	75.5	180
0	0	80.8	220	76	190
95	-	/0.0 Kr 3	230	76.4	200
14		0 0	490	77.3	210
44.2		85	v	78.3	220
68	60	88		/7.1 70 0	230
/1	70	21.1		AO - 5	250
/ J 78	80	67.4	80	81.1	260
76	100	68.7	90	81.6	270
77	110	70.3	100	82.1	280
78	120	71.6	110	82.4	290
		73.1	120	82.7	300

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83	310	75.3	150	84.1	310
83.2	320	76.2	160	84.2	320
76.9	330	77	170	84.3	330
69.5	350	77.9	180	84.5	340
0	0	78.6	190	84.5	350
85	·	79.3	200	84.6	360
91		80 5	220	54.7 AA A	370
49.2		81.1	230	84.8	390
65	60	81.5	240	84.9	400
70 2	70	82	250	85	410
71.5	80 90	82.4	260	85	420
72.7	100	82.7	270	85.1	430
74	110	83	280	85.1	440
75	120	83.A	290	68.3	450
75.8	130	83.6	310	85.2	400
76.6	140	83.8	320	85.2	480
77.6	150	83.9	330	85.3	490
79.3	170	84.1	340	85.3	540
80	180	84.2	350	85.4	550
80.6	190	84.3	360	85.4	600
81.2	200	34.4 84.5	370	Ŭ	0
81.8	210	84.6	390	65 A 9	
82.3	220	84.6	400	51.6	
82.7	230	84.7	410	67.2	60
83	240	84.7	420	68.9	70
83.5	230	84.8	430	70.7	80
83.7	270	84.9	440	71.7	90
83.8	280	84.9	450	73	100
84	290	65	460	74.2	110
84.2	300	60 85.1	480	/3 75.7	130
84.3	310	84.4	490	76.5	140
84.4	320	80.4	500	77.5	150
84.5	330	73.2	510	78.4	160
84.7	340	66.7	520	79.2	170
84.8	360	0	0	79.9	180
84.8	370	55		80.6	190
84.9	380	73 82 6		81.1	200
85	390	67.2	70	82	220
85	400	69.3	80	82.4	230
85.1	410	70.9	90	82.7	240
03.1 85 7	420	71.9	100	83	250
85.2	430	73.1	110	83.2	260
85.3	470	74.2	120	83.4	270
85.3	480	75	130	83.6	280
85	490	/3.5	140	0J.0 93.0	290
82.1	500	77.8	160	84	310
75.2	510	78.6	170	84.1	320
68.2	520	79.3	180	84.2	330
	0	80	190	84.3	340
92		80.7	200	84.4	350
52.2		81.2	210	84.5	360
65.6	70	81.8	220	84.6	370
67.7	80	52.2 87 e	230	54.0 24 7	79C
69.9	90	82.9	250	97./ AA_A	400
70.8	100	83.2	260	84.8	410
71.8	110	83.4	270	84.8	420
14.9	120	83.7	280	84.9	430
13.9 74.6	140	83.8	290	84.9	450
	7.4A	83.9	300	85	460

86	490			71 7	80
85.1	500	71	80	73	90.
85.1	600	72.4	90	74.3	100
85.3	1505	73.0	100	75.5	110
83.5	1515	74.0	110	76.7	120
77.9	1525	77 3	120	77.8	130
69.9	1535	77.3	140	79.3	140
0	0	80.2	160	80.7	150
92		81.5	140	81.8	160
78		\$2.5	170	82.8	170
25.5		83.4	180	83.7	180
66.8	60	83.8	190	84.5	190
69.6	70	81.2	200	85.2	200
71.3	80	73.7	210	85.8	210
72.7	90	66.5	220	86.2	220
73.9	100	0	0	86.7	230
75.1	110	92	•	87.2	240
76.4	120	82		87.6	250
77.5	130	58		88	260
78.7	140	66.3	60	88.4	270
80.3	150	69.1	70	88.7	280
81	160	71.2	80	89.1	290
77.9	170	72.5	90	89.5	300
70.2	180	73.7	100	89.7	310
0	0	74.9	110	90.3	320
92		76.2	120	90.3	330
79		77.4	130	90.4	340
17.3		78.6	140	90.6	350
67.6	60	80.1	150	90.8	300
70.2	70	81.5	160	90.9	370
71.6	80	82.5	170	91	380
72.6	90	83.4	180	91.1	390
73.9	100	84.2	190	91.1	410
75.4	110	85	200	91.2	410
70.8	120	85.6	210	91.2	420
77.9	130	86.2	220	91.7	430
/9.3	140	86.7	230	84./	450
-0.3	150	87.2	240		460
70.3	100	87.7	250	64. 0	
/0.0	170	88.1	260	U 92	•
0 2	0	88.5	270	74	
90		88.8	280	54 6	
42 E		89.2	290	67 8	70
48.3	60	89.5	300	70.3	80
70.5	70	89.7	310	71.5	90
71.7	80	90	320	73	100
73	90	90.2	330	74.3	110
74.3	100	YU.4	340	75.4	120
75.6	110	90.6	350	76.5	130
76.8	120	90.8	360	77.8	140
78	130	30.9	370	79.2	150
79.5	140	74.4	380	80.4	160
81	150	24·4 61 3	390	81.4	170
82.1	160	74.J Q1 4	410	82.4	180
83.1	170	71.4 Q1 A	420	83.1	190
84	180	74·4 61.2	440	83.9	200
84.2	190	71.4 94. E	430	84.5	210
80	200	99.3 78.4	440	85.1	220
71	210	A7.9	450	85.6	230
0	0	0,,		86.1	240
92		92	v	86.5	250
81		24 83		86.9	260
42		61.3		87.3	270
66.4	60	68.3	60	87.7	280
69.2	70	70.4	70	88.1	290

88.4	300	91	440	70	70
88.8	310	91	450	71.8	80
89.1	320	91.1	460	73.1	90
89.4	330	91.1	470	74.5	100
07.0 Ag.a	340	91.2	480	75.8	120
90.1	360	91.3	510	77.2	110
90.2	370	91.3	560	80.4	140
90.4	380	91.4	570	81.8	150
90.5	390	91.4	600	82.3	160
90.6	400	91.7	1500	79.3	170
90.9	410	71.3	1510	73.6	180
90.9	430	76.2	1530	99.4 0	130
91.1	440	68.7	1540	95	•
91.1	460	0	0	71	
91.2	470	95		39.3	
91.3	480	67		68.4	60
91.4	490 500	13·4 66-2	60	70.9	70
91.5	510	69.1	70	/6•4 73.8	90
91.5	530	70.8	80	75.2	100
91.6	540	72.1	90	76.6	110
91.6	550	73.	100	78	120
91.7	560	74.9	110	79.7	130
71./ 91.8	580	76.2	120	81.4	140
91.8	590	73	140	52.6	150
92.1	1200	66.5	150	80.1	170
91.4	1210	0	0	73.7	180
85	1220	95		67.4	190
75.6	1230	68		. 0	0
68.2	1240	27.7		95	
62	0	67.6 70 1	60 70	72	
85		71.6	80	54.9	60
63.6		73	90	71.1	70
81.8	150	74.4	100	72.5	80
82.8	160	75.8	110	73.9	90
83.7	170	77.2	120	75.4	100
54.0 96 A	180	78.8	130	76.8	110
86	200	79.8	150	78.2	120
86.6	210	74.4	160	/7.7	140
87.1	220	68.2	170	82.8	150
87.6	230	0	0	83.9	160
88.1	240	95		84.8	170
88.5	250	69		85.7	180
89.1	200	40.0	70	86.3	190
89.4	280	70	80	50.7 47 £	200
89.6	290	71.5	90	88.1	220
89.8	300	72.9	100	88.7	230
89.9	310	74.4	110	89.2	240
90.1	320	75.8	120	89	250
90.J	330	77.2	130	84.8	260
90.5	360	/0./ 80.K	160	76.6	270
90.6	360	80.8	160	07.4 0	200
90.7	370	76.4	170	95	•
90.7	380	68.7	180	73	
90.8	390	0	0	50.7	
90.8	400	95		68.3	60
90.9	410	70		70.8	70
91	430	JU.U 67.5	60	72.2	00
-			~~~	/3.0	20

74.9	100	05		90.2	220
76.3	110	73		90.7	230
77.6	120	/J 48.6		91	240
79.2	130		60	91.4	250
A1	140	76.3	30	91.7	260
82.2	150	/0./	70	92.1	270
83.3	160	73 A	80	92.4	280
84.3	170	73.9	100	92.7	290
85.2	180	74.0	110	93	300
85.9	190	70.1 77 A	120	93.2	310
86.5	200	78 9	120	93.4	320
87.1	210	80.7	140	93.6	330
87.7	220	82	150	93.7	340
88.2	230	83 .1	160	93.8	350
88.8	240	84.1	170	93.9	360
88.7	250	84.9	180	94	370
84.5	260	85.6	190	94	400
77.1	270	86.2	200	94.1	410
69.5	280	86.8	210	94.1	420
0	0	87.4	220	94.2	430
95		87.9	230	94.2	450
74		88.4	240	94.3	460
63.9		88.9	250	94.3	480
68.4	60	89.3	260	94.4	490
70.8	70	89.8	270	94.4	530
72.3	80	90.2	280	94.5	540
73.6	90	90.6	290	94.5	600
75	100	91	300	93.2	610
76.4	110	91.3	310	85.9	620
77.8	120	91.6	320	78.4	630
79.3	130	91.9	330	71.2	640
81.1	140	92.2	340	65.5	650
82.4	150	92.5	350	0	0
83.4	160	92.7	360	95	
84.4	170	92.9	370	. 77	
85.3	180	93	380	60.6	
85.9	190	93.1	390	67.3	50
86.5	200	93.2	400	70.2	80
87.1	210	93.3	410	72.2	/0
87.7	220	93.4	420	73.8	80
88.2	230	92.7	430	/3.4	100
88.0	240	86.5	440	70 7	110
89.1	250	75.8	450	/6./	120
87.0	200	72.1	460	5V.7 47 5	130
90	270	00.4	470	61 9	140
30.9 QA 4	40V 20A	0	0	9,50 28	150
91.1	300	73		25 86_1	160
91.A	310			A6_9	170
91.7	320	51.0 51.0	FA	87-6	180
91.9	330	99.J 71 1	3U 60	88.2	190
92.2	340	/▲•▲ 79 B	70	88.9	200
92.5	350	74.3	70	89.4	210
92.7	360	76.3	90	90	220
92.9	370	77.9	100	90.4	230
93.1	380	AO - 1	110	90.7	240
93.2	390	A1_A	120	91.2	250
93.2	400	A3.1	130	91.5	260
93.3	410	84.3	140	91.6	270
93.4	420	85.4	150	91.9	280
92.6	430	86.4	160	92.2	290
86.5	440	87.2	170	92.4	300
79.2	450	87.8	180	92.7	310
72.5	460	88.5	190	92.9	320
66.8	470	89.1	200	93.1	330
0	0	89.7	210	93.2	340

93.4	350	84.8			
93.5	360	8. 8	440	26.3	
93.7	370	84.9	430	69.7	70
93.8	380	94.5	400	71.9	80
93.8	390	63 92	470	73.5	90
93.9	400	65 88 1	490	75.1	100
93.9	410	03.1 Ar 1	500	76.5	110
93.8	420	93+1 95 7	510	77.8	120
93.8	450	93.4 88 3	540	78.8	130
93.9	460	95.4 95.2	340	79.5	140
93.9	480	03.J 88 3	550	80.3	150
94	490	93.J 98 A	570	81.1	160
94	510	3 .4	000	82	170
94.1	520	95	0	\$2.9	180
94.1	550	03		83.7	190
94.2	560	100		84.4	200
94.2	600	10.3		85	210
94.4	900		60	85.5	220
92.9	910		70	86.1	230
86.2	920	70.5	80	86.5	240
79.4	930	/1.8	90	87	250
74	940	/3	100	87.4	260
70.3	950	/4.1	110	87.8	270
68	960	/3.1	120	88.2	280
66.4	970	76.1	130	88.5	290
65.4	980	76.9	140	88.8	300
0	6	77.6	150	89	310
	J	78.2	160	89.2	320
99		78.8	170	89.4	330
19.1		79.4	180	89.6	340
67 A	70	79.8	190	89.7	350
69.1		80.2	200	89.9	360
70 7		80.7	210	90	370
71 .	100	81.1	220	90.1	380
72 0	110	81.5	230	90.2	390
72 7	120	81.9	240	90.3	400
74 7	120	82.3	250	90.4	410
78 8	140	82.6	260	90.5	420
76 2	150	82.9	270	90.6	430
77.8	140	83.1	280	90.7	440
78 1	170	83.4	290	90.7	450
78 7	100	83.6	300	90.8	460
79.1	190	83.8	310	90.8	470
79 6	210	83.9	320	90.9	480
79.0	220	84.1	330	90.9	490
17.7	220	84.3	340	91	500
90.3	230	84.4	350	91.1	510
	240	84.5	360	91.1	550
01.1	230	84.6	370	91.2	560
01.4	200	84.6	380	91.2	580
01.8 01.8	270	84.7	390	91.3	590
04.4	280	84.8	400	91.3	600
02.3	290	84.8	410	91.7	1200
04.8	300	84.9	420	90.1	1210
63	310	84.9	430	83.7	1220
83.3	320	85	440	74.4	1230
3J.3 	330	85	45(66.2	1240
83.7	340	85	46(0	~~~~
83.8	350	85.1	47(92	J
84	360	85.1	51(76 Qp	
84.1	370	85.2	521	20 28 2	
84.3	380	85.2	56	43.3 KQ Q	70
84.4	390	85.3	57	73 1	/U
84.5	400	85.3	60	/ 6 • £ 73 9	80
84.6	410	0	0	75.3	30
84.6	420	92		7 J + J 7 K K	110
84.7	430	97		79.9	120
		5.		/0	120

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78.9	130	86	190	89	240
79.6	140	86.6	200	89.3	250
80.4	150	87.1	210	90	260
81.2	160	87.5	220	90.3	270
82	170	88	230	90.7	280
82.8	180	88.4	240	91	290
83.7	190	88.9	250	91.3	300
84.4	200	89.4	260	91.7	310
85	210	90.2	270	92	320
85.5	220	90.6	280	92.3	340
86	230	91	290	92.5	350
86.5	240	91.3	300	92.7	360
87	250	91.6	310	92.9	370
87.4	260	91.9	320	93	380
87.8	270	92.1	330	93.1	390
88.2	280	92.3	340	93.3	400
88.5	290	92.4	350	93.4	410
88.8	300	92.5	360	93.5	420
89	310	92.7	370	93.6	430
89.2	320	92.8	380	93.6	450
89.5	330	92.9	390	93.7	460
89.6	340	93	400	93.7	480
89.8	350	93.1	410	93.8	490
89.9	360	93.3	420	93.8	510
90	370	93.4	430	93.9	520
90.1	380	93.4	450	93.9	540
90.2	390	93.4	460	94	550
90.2	400	93.5	470	94	600
90.3	410	93.6	480	94.1	610
90.4	420	93.6	490	94.1	650
90.5	430	93.7	500	94.2	660
90.5	440	93.7	530	94.2	700
90.6	450	93.8	540	94.3	900
90.7	460	93.8	570	93.6	910
90.7	470	93.9	580	87.2	920
90.7	480	93.9	600	80	930
90.8	490	93	615	74.1	940
90.8	510	89	620	69.6	950
90.9	520	86	625	66.7	900
90.9	530	82	630	0 0	1
91	540	78	635	0	
91	580	74	645	0	
91.1	590	71	650	0	
91.1	600	69	660	-1 -	•1
91.7	1502	0	0		
89.2	1512	95			
82.3	1522	96			
73.6	1532	29.6			
66.4	1542	69	60		
0	0	72.2	70		
95		74.6	80		
95		76.3	90		
30.1		77.8	100		
68.2	60	79.1	110		
71.5	70	80.1	120		
74	80	81	130		
75.8	90	82	140		
77.3	100	83	150		
78.9	110	84.1	160		
79.9	120	85.1	170		
80.7	130	85.8	180		
81.7	140	86.4	190		
82.6	150	87	200		
83.8	160	87.5	210		
84.8	170		220		
85.5	180	8 8. 5	230		

8.3.2. Appendix C.2 Time and temperature data for each sample used in back extrusion
Order of data is from least to greatest bath temperature: 81, 84,85,91,95,101, and 105 C.
Format:

heating temp
ηA, ηB,...ηlast
number of samples

sample letter time Temperature

new sample number

81	.99	.952	. 906	. 73	. 62	. 429	.164	0	0	0	0	0	
			115								-	-	
	λ	100	66.6										
	À	110	67.9										
	À	120	68.9										
	A .	130	07.8										
	2	150	72.3										
	Ä	160	73.5										
	Ä	170	74.5										
	λ	180	75.4										
	λ	190	76.2										
	λ	200	76.9										
	λ	210	77.4										
	À	220	77.8										
		230	78.1										
	-	240	/8.3									•	
	2	260	79.0										
	2	270	79.2										
	Ä	280	79.4										
	λ	290	79.5										
	λ	300	79.6										
	λ	310	79.6										
	2	320	79.6										
	2	330	79.6										
	À	340	79.6										
	A	350	79.7										
		300	79.7										
	<u>.</u>	370	79.7										
	~	300	79.7										
	2	400	79.7										
	Ä	410	79.7										
	λ	420	79.7										
	λ	430	79.8										
	λ	440	79.8										
	λ	450	79.8										
	À	460	79.8										
	À	470	79.8										
	~	480	79.8										
	-	500	79.8										
	ĩ	510	79.9										
	Ä	520	79.9										
	λ	530	79.9										
	λ	540	79.9										
	2	550	79.9										
	À	560	79.9										
	Ä	570	79.9										
	*	580	79.9										
	*	370	80.0										
	5	610	80.0										
	Ā	620	80.0										
	λ	630	80.0										
	λ	640	80.0										
	λ	650	80.0										
	λ	660	80.0										
	λ	670	80.0										
	A	680	80.1										
	λ	690	80.1										
	X	700	80.1										
	A >	710	80.1										
	*	720	80.1										
		130	00.1										

λ	740	80.1	3	240	78.5	B	900	80.3
λ	750	80.1	3	250	78.7	8	910	79.0
λ	760	80.2	8	260	79.0	8	920	73.8
λ	770	80.2	3	270	79.2	8	930	66.2
λ	780	80.2	B	280	79.4			57
λ	790	80.2	3	290	79.5	С	100	66.6
λ	800	80.2	B	300	79.6	C	110	67.9
λ	810	80.2	8	310	79.6	C	120	68.9
λ	820	80.2	B	320	79.6	C	130	69.8
λ	830	80.2	B	330	79.6	C	140	71.1
λ	840	80.3	3	340	79.6	C	150	72.3
λ	850	80.3	3	350	79.7	C	160	73.5
λ	860	80.3	B	360	79.7	C	170	74.5
λ	870	80.3	B	370	79.7	C	180	75.4
λ	880	80.3	B	380	7 9.7	C	190	76.2
λ	890	80.3	8	390	79.7	C	200	76.9
λ	900	80.3	8	400	79.7	С	210	77.4
λ	910	80.3	3	410	79.7	C	220	77.8
λ	920	80.3	3	420	79.7	С	230	78.1
λ	930	80.4	3	430	79.8	С	240	78.5
λ	940	80.4	8	440	79.8	C	250	78.7
λ	950	80.4	8	450	79.8	С	260	79.0
λ	960	80.4	8	460	79.8	С	270	79.2
λ	970	80.4	3	470	79.8	С	280	79.4
λ	980	80.4	3	480	79.8	C	290	79.5
λ	990	80.4	8	490	79.8	C	300	79.6
λ	1000	80.4		500	79.8	С	310	7 ?9.6
λ	1010	80.5	3	510	79.9	С	320	79.6
λ	1020	80.5		520	79.9	С	330	79.6
λ	1030	80.5		530	79.9	С	340	79.6
λ	1040	80.5		540	79.9	С	350	79.7
λ	1050	80.5		550	79.9	C	360	79.7
λ	1060	80.5		560	79.9	C	370	79.7
λ	1070	80.5		570	79.9	C	380	79.7
λ	1080	80.5		580	79.9	С	390	79.7
λ	1090	80.€		590	80.0	C	400	79.7
λ	1100	80.E		600	80.0	С	410	79.7
λ	1110	80.(610	80.0	С	420	79.7
λ	1120	80.ť		620	80.0	C	430	79.8
λ	1130	80.1	5	630	80.0	C	440	79.8
λ	1140	80.(5	040	80.0	C	450	79.8
λ	1150	80.(5	050	80.0	C	460	79.8
λ	1160	80.1		600	80.0	C	470	79.8
λ	1170	80.1		670	80.0	C	480	79.8
A	1180	80.'		680	80.1	C	490	79.8
λ	1190	80.'		200	80.1	C	500	/9.8
λ	1200	80.'		710	a0.1	C	210	70 0
A	1210	80.		720	90.1	C	520	77.7
À	1220	79.:		730	80.1	C	530	70.7
X	1230	74.1	Ĩ	740	90.1	6	344	70 0
A	1240	66.		750	AO 1		334	700
_		84		760	20.2	6	500	700
	100	66.	R	770	80.2		570	79.9
	110	67.	B	780	80.2		500	
	120	68.		790	80.2		600	80.0
	130	69.	B	800	80.2		610	80.0
	140	71.	A	810	80.2		620	80.0
	150	72.	2 R	820	80.2		230	
	160	73.	8	830	80.2			, , 78 8
	170	74.	B	840	80.3	6	68/	, , , , , , , , , , , , , , , , , , ,
8	180	75.	R	850	80.3		660	66.0
8	190	76.	B	860	80.3	U	001	39
	200	76.	8	870	80.3	n	100	66.6
	10	17.	B	880	80.3	כ	110	67.9
	220	77.	B	890	80.3	2	120	68.9
	230	/8.	-					

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D		
	130	69.8
D	140	71.1
	160	74.4
-	190	12.3
D	160	73.5
D	170	74.5
ñ	100	78 4
-	100	/3.4
D	190	76.2
D	200	76.9
	210	77 4
	410	//
D	220	77.8
D	230	78.1
	240	
D	24U	78.5
D	250	78.7
D	260	79.0
	220	70.0
U	270	/9.2
D	280	79.4
D	290	79.5
	200	70 4
U	300	79.0
D	310	79.6
D	320	79 6
-		
U	330	79.6
D	340	79.6
D	350	79.7
-		/3./
D	360	79.7
D	370	79.7
D	380	70 7
-		/3./
D	390	7 9.7
D	400	79.7
D	A10	79 7
-	440	/3./
D	420	79.7
D	430	79.8
n	440	70.0
-	440	/7.8
D	450	79.8
D	460	78.6
	470	73 4
	4/0	/3.4
D	480	65.8
		27
-	100	
-	100	00.0
E .	110	67.9
-	120	68.9
-	1 10	
1	130	69.8
	130 140	69.8 71.1
	130 140 150	69.8 71.1 72.3
	130 140 150	69.8 71.1 72.3
	130 140 150 160	69.8 71.1 72.3 73.5
	130 140 150 160 170	69.8 71.1 72.3 73.5 74.5
	130 140 150 160 170 180	69.8 71.1 72.3 73.5 74.5 75.4
	130 140 150 160 170 180	69.8 71.1 72.3 73.5 74.5 75.4 76.2
	130 140 150 160 170 180 190	69.8 71.1 72.3 73.5 74.5 75.4 76.2
	130 140 150 160 170 180 190 200	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9
	130 140 150 160 170 180 190 200 210	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4
	130 140 150 160 170 180 190 200 210 220	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8
	130 140 150 160 170 180 190 200 210 220	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8
	130 140 150 160 170 180 190 200 210 220 230	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1
	130 140 150 160 170 180 190 200 210 220 230 240	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5
	130 140 150 160 170 180 200 210 220 230 240 250	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.1 78.5 78.7
	130 140 150 160 170 180 200 210 220 230 240 250 250	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 78.7
	130 140 150 160 170 180 200 210 220 230 240 250 260	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0
	130 140 150 160 170 200 210 220 230 240 250 260 270	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0 79.2
	130 140 150 160 170 200 210 220 230 240 250 260 270 280	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0 79.2 79.4
	130 140 150 160 170 200 210 220 230 240 250 260 270 280	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0 79.2 79.4 79.4
	130 140 150 160 170 200 210 220 230 240 250 260 270 280 290	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0 79.2 79.4 79.5
	130 140 150 160 170 200 210 220 230 240 250 260 270 280 290 300	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.1 78.5 78.7 79.0 79.2 79.4 79.5 79.6
	130 140 150 160 170 180 200 210 220 230 240 250 260 250 260 270 280 290 310	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0 79.2 79.4 79.5 79.6 79.6
	130 140 150 160 170 200 210 220 230 240 250 260 270 280 290 300 310	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0 79.2 79.4 79.5 79.6 79.6 79.6
	130 140 150 160 170 200 210 220 230 240 250 260 250 260 250 250 250 300 310 320	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0 79.2 79.4 79.5 79.6 79.6 79.6
	130 140 150 160 170 200 210 220 230 240 250 260 270 280 290 300 310 320 330	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.1 78.5 78.7 79.0 79.2 79.4 79.5 79.6 79.6 79.6
	130 140 150 160 170 180 200 210 220 230 240 250 260 270 280 290 310 320 330 340	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0 79.2 79.4 79.5 79.6 79.6 79.6 79.6 78.2
	130 140 150 160 170 200 210 220 230 240 250 260 270 280 290 300 310 320 330	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.7 79.0 79.2 79.4 79.5 79.6 79.6 79.6 79.6 79.6 79.6 79.6
	130 140 150 160 170 200 210 220 230 240 250 260 250 260 250 260 250 250 300 310 320 330 340 350	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.1 79.0 79.2 79.4 79.5 79.6 79.6 79.6 79.6 79.6 79.6 79.6
	130 140 150 160 170 200 210 220 230 240 250 260 270 280 290 300 310 320 330 340 350 360	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 78.1 78.5 78.7 79.0 79.2 79.4 79.5 79.6 79.6 79.6 79.6 79.6 79.6 79.6 79.6
	130 140 150 160 170 180 200 210 220 230 240 250 260 270 280 310 310 320 330 340 350 360	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 78.1 78.5 78.1 78.5 79.0 79.4 79.5 79.6 79.6 79.6 73.0 65.4 11
	130 140 150 160 170 200 210 220 230 240 250 260 270 280 290 300 310 320 320 330 340 350 360	69.8 71.1 72.3 73.5 74.5 75.4 76.2 76.9 77.4 77.8 78.1 78.5 79.0 79.2 79.4 79.5 79.6 79.6 79.6 79.6 79.6 79.6 73.0 65.4 11 66.6

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8 4	,99	.975	.934	.837	.741	.591	.466	0	0	0	0	0
	λ	70	71.0)								
	λ	80	71.9									
	λ	90	72.9									
	λ	100	74.2	2								
	λ	110	75.	5								
	λ	120	76.7	7								
	λ	130	77.6	5								
	λ	140	78.4	•								
	λ	150	79.1	L								
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1	160	79.7	C	310	83.7
1	170	80.3	C	320	83.8
8	180	80.7	С	330	83.9
8	190	81.1	С	340	83.9
8	200	81.5	C	350	84.0
B	210	81.8	C	360	84.1
8	220	82.2	C	370	84.1
3	230	82.4	C	380	84.2
3	240	82.6	C	390	84.2
8	250	82.9	C	400	84.3
3	260	83.0	C	410	84.3
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8	410	84.3	D	170	80.3
8	420	84.3	D	180	80.7
8	430	84.3	D	190	81.1
8	440	84.3	D	200	81.5
8	450	84.3	D	210	81.8
B	460	84.3	D	220	82.2
8	470	84.3	D	230	82.4
B	480	84.3	D	240	82.6
B	490	84.4	D	250	82.9
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С	140	78.4	I	140	78.4
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C	160	79.	I	160	79.7
C	170	80.	I	170	80.3
C	180	80.	2	180	80.7
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	λ	140	79.7				200		-	340	04.4
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	A	160	80.8		1	8	220	83.0	C	350	84.4
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	λ	240	83.4				300	94 2	5		72 2
	λ	250	83.6				300	04.3		U 0	/3.4
		260	A3 A				310	84.3	D	90	74.5
	~	200	83.8		1	•	320	84.4	D	100	75.8
	A	270	83.9		1	R	330	84.4	n	110	77.0
	λ	280	84.0				340			100	70.0
		290	84 1				340	54.4	D	120	19.7
	-	300	04.1		1	8	350	84.4	D	130	79.0
		300	84.3		1		360	84.5	D	140	79.7
	λ	310	84.3		1		370	84. E	5	180	80 1
	λ	320	84.4							130	00.3
	1	330	A A				380	84.5	D	100	80.8
	7	330	04.4		1	B	390	84.6	D	170	81.2
	A	340	84.4		1	1	400	84.6	D	180	81.6
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	λ	360	84. E				410	04.0	U	130	82.0
		370				5	420	84.7	D	200	82.4
		3/0	84.3		1	8	430	84.7	D	210	82.7
	A	380	84.5		1		440	84.7	n	220	83.0
	λ	390	84.6				440				00.0
		400	94 4			5	430	84.7	D	230	83.2
	~		04.0		1		460	84.8	D	240	83.4
	A	410	84.6		1	8	470	84.8	D	250	83.0
	λ	420	84.7		1		480	94 9	5	260	79 0
	λ	430	84.7				100	04.0		200	/8.0
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	λ	470	84.9				320	03.0			
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	~	480	84.8		1	B	540	85.0			
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	C	130	73.	.1		
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	λ	80	75.1						D	60	73.6
	λ	90	76.6						D	70	74.1
	λ	100	78.1						D	80	75.1
	λ	110	79.5						D	90	76.6
	Ä	120	80.8						D	100	78.1
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	λ	220	87.6							50	68.6
	λ	230	87.9						2	60	73.6
	λ	240	88.2						2	70	74.1
	λ	250	87.7							80	75.1
	λ	260	83.9						1	90	76.6
	λ	270	76.4						2	100	78.1
	λ	280	67.6						3	110	79.5
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	-	120	03.0							110	/8.3
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		180	83.8						-		7
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		200	86.8						Ģ	60	73.6
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	3	220	85.7						G	80	75.1
	3	230	81.9						G	90	76.6
	8	240	74.4						G	100	76.1
	3	250	65.6						G	110	72.3
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	C	50	68.6						H	50	68.6
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	С	90	76.6						H	90	74.6
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	λ	100	81.1									
	λ	110	82.8									
	λ	120	84.3									
	λ	130	85.6									
	λ	140	86.8									
	λ	150	87.7									
	λ	160	88.6									
	λ	170	87.0									
	λ	180	81.2									
	λ	190	72.7									
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	8	70	74.5									
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156

APPENDIX D

8.4.Appendix D. Computer programs (written by K. Dolan unless otherwise indicated) to estimate k, α , and ΔE_g , from normalized torque versus temperature-time history in Appendices B and C

Figure D.1 Flow diagram of computer programs

Must compile all programs with REAL*8 using "fortran filename.for/g_floating" to allow numbers greater than 10^{28}

On VAX, use LINK MINUVB, INITB, SETUPB, FPSIUV, NLINB, MODSENSUV, IMSL/ LIB

MINUVB

Call INITE Call UVMIF Write minimum sum of squares and corresponding value of ΔE_g END

INITB

Read time and Temperature Calculate calibrated Temperature (TT,TM,TB) along small sample adapter axis END

UVMIF IMSL generic minimization routine, given f(x) over a range

Repeat Use RNLINA(ΔE_g) Until a tolerance (x<tol) is met END

 $RNLINA(\Delta E_g)$

Call SETUPUV(ΔE_g) Estimate k and α for a given ΔE_g , by using MODSENSUV(ΔE_g) END

157

SETUPUV (ΔE_g) sets up Ψ $\Psi = FPSI2(\Delta E_g)$ Scale Ψ between 0 and 11.0 END

 $MODSENSUV(\Delta E_g)$

Calculate sensitivity coefficients END

FPSIUV

Calculate Ψ END

```
MINUVB
         INTEGER MAXEN, NOUT
         REAL BOUND, F, FX, STEP, X, XACC, XGUESS, E
         EXTERNAL RNLINA, UMACH, UVMIF, INIT
         CALL INIT
OPEN(70,FILE='E',STATUS='UNKNOWN')
         READ(70, *) XGUESS, STEP, XACC
         CLOSE (70)
         BOUND=20.0
         MAXFN=50
         CALL UVMIF(RNLINA, XGUESS, STEP, BOUND, XACC, MAXFN, E)
         WRITE(7,*)'IER=',IER
         FX=RNLINA(E)
         CALL UMACH(2, NOUT)
         WRITE(7,99999)E*83130.,FX
FORMAT(' THE minimum is at ',7x,fl4.2,//,'
, 'value is ', fl4.11)
99999
                                                                   The function '
      S.
         end
```

"INITD" С for UVMIN AND NLIBO with 2 parameters AND ALL DATA(6,7,8%) 0000000 BATCH JOB! THIS PROGRAM READS TEMPERATURES AND TIMES FROM ONE FILE, THEN CALCULATES AND STORES TT(), TM(), AND TB(), AND TIME() FOR PSI SCALING, MUST SET UP TE DATA FILE WITH LAST VALUE HAVING GREATEST PSI INPUT: TEMP, TIME, Y(SAMPLE) OUTPUT: TEMP SPLIT INTO TT, TM, TB; TIME, AND Y(MAX SAMPLE TEMP), SENT TO FUNCTION FPSI С SUBROUTINE INIT DIMENSION TEMP(100,60) DIMENSION PS(5,5),T(100,5),Y(100),SIG2(100),B(5),Z(5),A(5), P(5,5), BS(5), VINV(5,5) S DOUBLE PRECISION P, PS, T PARAMETER (UR=83130.) COMMON T,Z,BS,I,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NP COMMON/TITEM/ TT(100,60),TM(100,60),TB(100,60),TIME(100,60) COMMON/NUM/ NPT(100), ISAM COMMON/SS/SYP, SLEAST COMMON/FILE/DFILE COMMON/CORR/TORQ(100), CTORQ(100), NUMSAM(100), TMAX(100) CHARACTER *14 FNMR, FNMW, DFILE, OUTFIL INTEGER TARGT(100), CONC(100) REAL ETAINF, M BQ(TMP)=.511 С С INITIALIZE SUM OF SQUARES, RUNNING VALUE OF LEAST SS SYP=-1 SLEAST=100 С WRITE(*,*)'ENTER FILENAME FOR READING TT DATA' C OPEN(45, FILE='NAME', STATUS='UNKNOWN') READ(45, 10)FNMR***OPEN INPUT AND OUTPUT FOR BECK C C WRITE(*,*)'ENTER THE NAME OF THE INPUT BECK DATA FILE' READ(45, '(A40)') DFILE C WRITE(*,*)'ENTER THE NAME OF THE OUTPUT FILE' READ(45, '(A40)') OUTFIL OPEN(7, FILE=OUTFIL, STATUS='NEW') CLOSE(45) 10 FORMAT(A) OPEN(10, FILE=FNMR, STATUS='UNKNOWN') ***L IS SAMPLE #, N IS # OF TIME INTERVALS WITHIN A SAMPLE C L=1 N-1 NUMSAM(1)=0С READ(10, *) IFLAG READ(10, *) TEMP(L, N), TIME(L, N) С WHILE TEMP IS > 0 DO READ TEMP AND TIME 30 IF(TEMP(L,N).GE.0)THEN ***NEW CONCENTRATION? STORE IT UNTIL CALCULATIONS PERFORMED С IF(INT(TEMP(L,N)).EQ. 0.AND.TIME(L,N).GT.0)THEN IFLAG=INT(TIME(L,N)) ENDIF С ***NEW SAMPLE? IF(INT(TEMP(L,N)).EQ. 0)THEN

С ***SAMPLE# > 1? IF (NUMSAM(L).GE.1) THEN С ***MAX # OF PTS FOR LAST SAMPLE NPT(L)-N-1 С С ***MAX TEMP. FOR THIS SAMPLE? J=NPT(L) IF(TEMP(L,J).GE.TEMP(L,J-1))THEN 60 TMAX(L) - TEMP(L, J) ***SLOPE FOR RAPID COOLING CURVE С $M=.0771 \times TMAX(L) - 5.7$ $TEMP(L, J+1) = TMAX(L) - M \times 10$ TEMP(L, J+2) = TMAX(L) - M * 20TIME(L,J+1) = TIME(L,J)+10TIME(L,J+2) = TIME(L,J)+20NPT(L)=J+2ELSE J=J-1 GO TO 60 ENDIF С С С ***INCREASE SAMPLE # L=L+1ENDIF С ***END 'SAMPLE >1' IF LOOP READ(10, *) TARGT(L) READ(10, *)NUMSAM(L) $READ(10, \star)TORQ(L)$ CONC(L) = IFLAG N=0 ENDIF ***END 'EQUAL TO ZERO' IF LOOP С N=N+1 READ(10, *) TEMP(L,N), TIME(L,N) GO TO 30 END IF ***END READING ALL SAMPLES LOOP С С ***MAX # OF PTS FOR LAST SAMPLE do 150 i=1,L-1 WRITE(*,*)'I=',I,' NPT=',NPT(I) С 150 CONTINUE С ***CALCULATE TT, TM, TB ACCORDING TO TARGET TEMP. С ISAM IS NUMBER OF SAMPLES С ISAM=L-1 WRITE(*,*)'ISAM=',ISAM С DO 50 I=1, ISAM IHEAT=NPT(I)-2 ***COOLING TEMPS NOT CALIBRATED С DO 65 K=IHEAT+1, IHEAT+2 TB(I,K) = TEMP(I,K) + 273.15TM(I,K) = TEMP(I,K) + 273.15TT(I,K) = TEMP(I,K) + 273.15CONTINUE 65 IF(TARGT(I).EQ.95.AND.CONC(I).EQ.7)THEN DO 70 K=1, IHEAT TB(I,K)=.819*TEMP(I,K)+18.66+273.15-1.45 TM(I,K) = .981 * TEMP(I,K) + 2.83 + 273.15 - 1.45TT(I,K)=.990*TEMP(I,K)+1.44+ 273.15-1.45
70	CONTINUE
	TMAX(I)=(TB(I, IHEAT)+2*TM(I, IHEAT)+TT(I, IHEAT))/4-273.15 ELSEIF(TARGT(I).EQ.95)THEN DO 80 K=1.IHEAT
	TB(I,K) = .834 * (TEMP(I,K) - 1.45) + 16.72 + 273.15
2.0	$T(I,K) = .725 \times (TEMP(I,K) - 1.45) + 27.86 + 273.15$
80	CONTINUE TMAX(I)=(TB(I, IHEAT)+2*TM(I, IHEAT)+TT(I, IHEAT))/4-273.15 ELSEIF(TARGT(I).EQ.92)THEN
	DO 90 K=1, IHEAT TB(I,K)=.836*(TEMP(I,K)=1.45)+16.47+273.15
	TM(I,K) = .823 * (TEMP(I,K) - 1.45) + 19.1 + 273.15 TT(I,K) = .853 * (TEMP(I,K) - 1.45) + 16.26 + 273.15
90	CONTINUE
	TMAX(I)=(TB(I,IHEAT)+2*TM(I,IHEAT)+TT(I,IHEAT))/4-273.15 ELSEIF(TARGT(I).EQ.88)THEN DO 100 K-1,IHEAT
	TB(I,K) = .807 * (TEMP(I,K) - 1.45) + 18.43 + 273.15
	TM(1,K)=.865*(TEMP(1,K)-1.45)+14.75+273.15 TT(1,K)=.886*(TEMP(1,K)-1.45)+12.83+273.15
100	
	ELSEIF(TARGT(I).EQ.85)THEN DO 110 K=1.IHEAT
	TB(I,K)=.871*(TEMP(I,K)-1.45)+12.01+273.15
	TM(1,K)=./84*(TEMP(1,K)-1.45)+19.96+273.15 TT(1,K)=.738*(TEMP(1,K)-1.45)+23.47+273.15
110	CONTINUE
	TMAX(1)=(TB(1, IHEAT)+2*TM(1, IHEAT)+TT(1, IHEAT))/4-2/3.15 ELSE WRITE(7,*)'YOU BOOFED ON ME! NO MATCH FOR TARGET TEMPS!'
	STOP
50	CONTINUE
2	DO 137 L-1, ISAM TC-TMAX(L)
	IF(CONC(L).EQ.6)THEN
	CTORQ(L) = TORQ(L) * EXP(BQ(TC) * .9)
	CTORQ(L) = TORQ(L)
	ELSEIF(CONC(L).EQ.8)THEN CTORO(L) = TORO(L) * EXP(BO(TC) * - 9)
	ENDIF
с	ETAINF=1.359*EXP(.036716*TC) WRITE(*,*)'ETA INFINITY='.ETAINF.'TMAX='.TC
c	***SCALE Y ACCORDING TO MAX VISC.
с	Y(L)=(CTORQ(L)2)/(ETAINF2) WRITE(*,*)'SAMPLE #='.NUMSAM(L).' TOTAL='.1.' Y='.Y(L)
C 137	CONTINUE
3	
~	CLOSE(10) RETURN END

С "SETUPUV" SUBROUTINE for UVMIN WITHIN NLIBO.FOR FOR 2 parameters THIS PROGRAM KEEPS TRACK OF SUM OF SQUARES AND E, CALCULATES 0000000 AND SCALES PSI AFTER NEW E INPUT FOR PSI SCALING, MUST SET UP TE DATA FILE WITH LAST VALUE HAVING GREATEST PSI INPUT: TT, TM, TB, E, TIME OUTPUT: SCALED PSI SUBROUTINE SETUP(E) REAL*8 FPSI, T, Q, SCLB, J DIMENSION TEMP(100,60) DIMENSION PS(5,5),T(100,5),y(100),SIG2(100),B(5),Z(5),A(5), Ş P(5,5),BS(5),VINV(5,5) DOUBLE PRECISION P, PS PARAMETER (UR=83130.) COMMON T, Z, BS, I, ETA, PS, P, B, A, y, SIG2, MODL, VINV, NP COMMON/TITEM/ TT(100,60), TM(100,60), TB(100,60), TIME(100,60) COMMON/NUM/ NPT(100), ISAM COMMON/SS/SYP, SLEAST С С ***WRITE THE SUM OF SQUARES OF RESIDUALS/SIGMA WRITE(7,*)'OLD SYP=',OLDSYP,' NEW SYP=',SYP
WRITE(7,*)'OLD/NEW=',OLDSYP/SYP,'LEAST/NEW=',SLEAST/SYP OLDSYP-SYP С ***KEEP RUNNING VALUE OF LEAST SS C IF(SYP.LT.SLEAST.AND.SYP.GT.0)THEN SLEAST=SYP END IF С ***WRITE WHAT E IS С WRITE(7,'(/'' J/mol'','' E/R1E4='',F8.3)')E*UR,E E='',F11.2,'' С ***CALCULATE NEW PSI C DO 50 I-1, ISAM T(I,1) = FPSI(E)CONTINUE 50 ***SCALE ALL PSI'S C j=0 q=T(ISAM,1) IF(q.GT.1.1 .AND.q .LE. 11) THEN RETURN ELSEIF(q.LE.1.1)THEN 300 IF(q.LE.1.1)THEN q=q*10 j=int(j+1.1) GO TO 300 ENDIF ELSEIF(q.GT.11)THEN 400 IF(q.GT.11)THEN q=q/10 j=int(j-1.1) GO TO 400 ENDIF ENDIF sclb=10.0**J DO 500 I=1, ISAM T(I,1)=T(I,1)*sclb 500 CONTINUE

WRITE(7,*)'SCALING FACTOR= 10 TO THE',27+J,' POWER' RETURN END

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"FPSI2.FOR" for NLIBO.FOR with 2 parameters
С
        calculates psi by trapezoidal rule integration over space
and then time for small sample adapter
C
С
        REAL*8 FUNCTION FPSI(E)
        REAL*8 dpsi(60), ar(60), art, arm, arb, ul, u2, u3, t
        REAL top, mid, bot
        DIMENSION ps(5,5),t(100,5),Y(100),sig2(100),b(5),
     S
                   z(5), a(5), p(5,5), bs(5), vinv(5,5)
        DOUBLE PRECISION p,ps
        PARAMETER (R=8.313, scl=le27, scl2=le4)
        COMMON t,z,bs,i,eta,ps,p,b,a,y,sig2,modl,vinv,np
        COMMON/TITEM/ tt(100,60),tm(100,60),tb(100,60), time(100,60)
        COMMON/NUM/ NPT(100), ISAM
С
        initialize
С
        FPSI=0
        n=1
        nmax=npt(I)
С
      ***calculate psi for ETA
C
С
        ***WHILE 'this sample' DO 'integration'
           DO 100 n=1, nmax
                 top=tt(1,n)
                 mid=tm(i,n)
                 bot=tb(1,n)
С
               ***don't calculate exponents less than -88
                 ul=E*scl2/top
                 u2=E*scl2/mid
                 u3=E*scl2/bot
                 art=0
                 arm=0
                 arb=0
С
С
               ***integrate over DISTANCE (axially)
С
               ***individual integrands
                     art=top*exp(-ul)*scl
                     arm=mid*exp(-u2)*scl
                     arb=bot*exp(-u3)*scl
С
               ***weight each integrand
                 ar(n)=(art+2*arm+arb)/4.0
                 write(*,*)'ar=',ar(n)/scl
С
                 write(*,*)'top=',top-273.15,'mid=',mid-273.15,'bot=',bot-273.15
С
С
C
               ***integrate over TIME
                  IF(n.gt.1)THEN
                    dpsi(n)=(time(i,n)-time(i,n-1))*(ar(n)+ar(n-1))*0.5
                   FPSI=FPSI+dpsi(n)
                 ENDIF
100
             CONTINUE
С
         RETURN
         END
```

FUNCTION RNLINA(E) CCCCCCCCC PROGRAM DESCRIPTION CCCCC С С С WRITTEN BY JAMES V. BECK С С NOVEMBER 1985 С C*************************** *C C C CVCCCCCCC VARIABLE IDENTIFICATION CCCCCCCC С С С С *C С С DIMENSION BLOCK 000000000 BLOCK 0000 C C С С REAL Y(100), SIG2(100), B(5), Z(5), A(5), BS(5), VINV(5,5) REAL BSS(5), CG(5), BSV(5), R(5,5), TORQ(100), CTORQ(100), TMAX(100) REAL*8 PS(5,5),P(5,5),PSV(5,5),SUMP,PSQ1,PSQ2,PSQ,T(100,5) INTEGER NUMSAM(100) CHARACTER*40 DFILE, OUTFIL, GFILE C С C** *********************************** *C С С coccccccc COMMON BLOCK BLOCK 0100 С С COMMON T,Z,BS,I,ETA,PS,P,B,A,Y,SIG2,MODL,VINV,NP COMMON/SS/SYP, SLEAST COMMON/FILE/DFILE COMMON/CORR/TORQ, CTORQ, NUMSAM, TMAX С С С С C* ******************************* *C С C CACCCCCCC DATA BLOCK BLOCK 0200 С С DATA EPS, EPSS, IIN, IOUT/1.0E-30, 0.0001, 5, 7/ С C *C С С CICCCCCCC INITIALIZATION BLOCK BLOCK 0400 C CHANGE DOLAN 88/9/12 C OPEN(5, FILE=DFILE, STATUS='OLD') С С C********************************* *C С С CPCCCCCCCC PROCESS BLOCK BLOCK 0500 С С --- START INPUT С С 88/8/2 addition Dolan CALL SETUP(E) 200 READ(5,*) N, NP, NT, ITMAX, MODL, IOPT, IPRINT FORMAT(1X, 'NO DATA POINTS IN FILE !!!') IF(N.LE.O) THEN 60 WRITE(7,60) STOP ENDIF С WRITE(*,'(/,9X,''N'',8X,''MP'',8X,''NT'',5X,''ITMAX'',5X,''MODE WRITE(*, (/, 34, ', 44, ', 104, ', 114, ' С С WRITE(7, '(/,9X, 'N'',8X, 'MP'',3X, 'NT'',5X, 'ITMAX'',5X, 'MODE

```
+L'',6X,''IOPT'',4X,''IPRINT'')')
      WRITE(7, '(7110, 4F10.4)') N, NP, NT, ITMAX, MODL, IOPT, IPRINT
C --- IF IOPT-0 THEN ON THE 2ED AND SUCEEDING STACKED CASES, THE DATA IS
C --- NOT REPRINTED.
С
 --- IF IPRINT-1, EXTRA PRINT OUT OF ETA, RESIDUALS B(1),... ARE GIVEN.
      READ(5,*)(B(I),I=1,NP)
      WRITE(7,'(10X,''B('',I1,'') = '',F16.5)') (I,B(I),I=1,NP)
С
      DO 150 J1=2,5
        BS(J1) = 0
150
       CONTINUE
C
      IF(IOPT.LE.0) THEN
        WRITE(7,'(/,6X,''J'',5X,''SAMP #'',6X''Y(J)'',3X,''TORQUE(J)''
     +, 3X, ''CORR.TORQ(J)'', 5X, ''T(J,1)'', 4X, ''TMAX'')')
         DO 10 12-1,N
           READ(5,*)J,SIG2(J)
           WRITE(7, '(218, 6F12.5)') J, NUMSAM(J), Y(J), TORQ(J), CTORQ(J)
           , (T(J,KT),KT=1,NT),TMAX(J)
           SIG2(J) = SIG2(J) * SIG2(J)
10
      CONTINUE
      END IF
С
313
      DO 2 IP-1,NP
         DO 2 KP-1,NP
           PS(KP, IP) = 0
           P(KP, IP) = 0
2
      CONTINUE
     WRITE(7,'(/,5X,''P(1,KP)'',9X,''P(2,KP)'',9X,''P(3,KP)'',9X,
+''P(4,KP)'',9X,''P(5,KP)'')')
      DO 6 IP-1,NP
         READ(5, *)(PS(IP,KP),KP=1,NP)
         WRITE(7, '(5D16.5)') (PS(IP,KP), KP=1, NP)
6
      CONTINUE
         ADDITION DOLAN 88/9/8
С
         CLOSE(5)
С
С
  --- ADD BLANK CARD AFTER LAST INPUT CARD
С
  ---END INPUT
С
      DO 18 IL=1,NP
         BS(IL)=B(IL)
        CG(IL) = 0
18
      CONTINUE
      DO 19 IP-1,NP
         DO 19 KP-1,NP
           P(KP, IP) = PS(KP, IP)
19
      CONTINUE
      I = 0
      MAX = 0
С
99
      MAX = MAX + 1
  --- START BASIC LOOP GIVES B(I) AND SY
С
С
       SY = 0
       DO 100 I3-1,N
         I = I3
         CALL SENS(E)
         CALL MODEL(E)
         RISD = Y(I)-ETA
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SY = SY + RISD \times RISD / SIG2(I)
        SUM = 0
        DO 20 K=1,NP
          DO 20 L=1,NP
            SUM = SUM + Z(L) * P(K,L) * Z(K)
20
       CONTINUE
        DELTA = SIG2(I) + SUM
        DO 29 JJ=1,NP
          A(JJ) = 0
29
       CONTINUE
        DO 30 JA=1,NP
          DO 30 KA-1,NP
            A(JA) = A(JA) + Z(KA) * P(JA, KA)
30
        CONTINUE
        CS = 0
        DO 40 JC-1,NP
          CS = CS + Z(JC) * (B(JC) - BS(JC))
          CG(JC) = CG(JC) + Z(JC) * RISD/SIG2(I)
40
        CONTINUE
        C = Y(I) - CS - ETA
        DO 50 IB-1,NP
          B(IB) = B(IB) + (A(IB) * C) / DELTA
50
       CONTINUE
        DO 41 ISV-1,NP
          DO 41 JSV=1,NP
            PSV(JSV, ISV) = P(JSV, ISV)
41
        CONTINUE
       DO 52 IV-1,NP
          DO 52 IU-IV, NP
            SUMP = 0
            DO 51 KP-1,NP
              DO 51 JP=1,NP
                 IF(KP-IV.EQ.0.OR.JP-IU.EQ.0) GOTO 51
                 PSQ1 = PSV(KP,JP)*PSV(IU,IV)
                 PSQ2 = PSV(IU,KP)*PSV(IV,JP)
                 PSQ = PSQ1 - PSQ2
            IF(DABS(PSQ1)+DABS(PSQ2).LT.1.E-15) THEN
              RP = PSQ * 1.E15
              ELSE
                 RP = PSQ / (DABS(PSQ1)+DABS(PSQ2))
            END IF
                 RP = ABS(RP)
                 RPP = RP - 1.0E - 12
                 IF(RPP.LE.0.0) THEN
                   PSQ = 0
                 END IF
                 SUMP = SUMP + Z(JP) * Z(KP) * PSQ
51
            CONTINUE
            P(IU, IV) = (PSV(IU, IV) * SIG2(I) + SUMP)/DELTA
52
        CONTINUE
        DO 53 IV=2,NP
          IVM = IV - 1
          DO 53 IU - 1, IVM
            P(IU, IV) = P(IV, IU)
53
        CONTINUE
        IF(IPRINT.GT.0) THEN
           IF(I.EQ.1) THEN
           WRITE(7,'(//,8X,''I'',9X,''ETA'',8X,''RESIDUALS'',6X,''B(
     [])'',11X,''B(2)'',11X,''B(3)'',11X,''B(4)'',11X,''B(5)'')
          END IF
```

WRITE(7, '(110,7E15.7)') I, ETA, RISD, (B(JC), JC=1, NP) END IF 100 CONTINUE C --- END BASIC LOOP, GIVES B(I) AND SY C --- START BOX-KANEMASU MODIFICATION С С START BOX-KANEMASU MODIFICATION IF(MAX-1)104,104,103 SS=SY/2.0 103 IF(SS-SYP)104,104,105 DO 210 IBS=1,NP 105 B(IBS) = BSV(IBS) 210 CONTINUE WRITE(IOUT, 212) FORMAT(7X, 'USE BSV(IBS)') 212 GOTO 211 104 CONTINUE DO 102 IBS=1,NP BSS(IBS) = BS(IBS) 102 CONTINUE ALPHA= 2.0 AA- 1.1 ALPHA- ALPHA/2.0 110 DO 116 IBS=1.NP BS(IBS) = BSS(IBS) + ALPHA*(B(IBS)-BSS(IBS)) BSV(IBS) = BS(IBS) 116 CONTINUE INDEX=0 G= 0.0 DO 115 IP=1,NP DELB- BS(IP)-BSS(IP) $G = G + DELB \star CG(IP)$ RATIO= DELB/(BSS(IP)+EPS) RATIO- ABS(RATIO) IF(RATIO-EPSS)113,113,114 113 INDEX- INDEX+1 WRITE(IOUT, 314) FORMAT(7X, 'MAX', 8X, 'NP', 5X, 'INDEX', 8X, 'IP') 314 WRITE(7, '(7110, 4F10.4)') MAX, NP, INDEX, IP 114 CONTINUE WRITE(7,122) I,Y(I), ETA, RISD, Z(IP), XYP, DELB, SIG2(I) C 115 CONTINUE SYP= 0.0 DO 117 I3=1,N I-I3 CALL MODEL(E) RISD- Y(I)-ETA SYP= SYP + RISD*RISD/SIG2(I) 117 CONTINUE IF(NP-INDEX)106,106,107 106 H=1.0 GOTO 132 107 CONTINUE SYN= SYP*0.999 IF(SYN-SY)112,112,111 111 IF(ALPHA-0.01)109,109,110 109 WRITE(7,108) ALPHA, SYP, SY FORMAT(3X, 'ALPHA TOO SMALL, ALPHA=', F12.6, 2X, 'SYP=', E15.6, 2X, 108 f'SY',E15.6) WRITE(7,1001)

101 133 134 1000	M-ITMAX IF(MAX-M)99,99 CONTINUE IF(IPRINT)133, IPRINT-IPRINT+ GOTO 99 CONTINUE RNLINA-SYP RETURN CONTINUE	,101 133,134 1			
C C****	CLOSE(IIN) CLOSE(IOUT)	****	****	*****	C ****C
CECCC		ERROR MESSAGES		BLOCK	0900 C C
CFCCC	ccccc	FORMAT STATEMENTS		BLOCK	0000 9000 C
C	STOP END	~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~ ~	*****		· · · · · ·

.

1001 FORMAT(10X, 'Z(1)', 12X, 'Z(2)', 12X, 'Z(3)', 12X, 'Z(4)', 12X, 'Z(5)') 1002 FORMAT(6E16.5) DO 1003 J-1,N CALL SENS(E) WRITE(7,1002) (Z(I), I=1, NP) 1003 CONTINUE C CHANGE DOLAN 88/9/12 RNLINA=SYP RETURN 112 CONTINUE SKSUM= SY - ALPHA*G*(2.0-1.0/AA) IF(SYP-SKSUM)131,131,130 130 H= ALPHA * ALPHA*G/(SYP-SY+2.0*ALPHA*G) GOTO 132 131 CONTINUE H= ALPHA*AA CONTINUE 132 DO 118 IBN- 1,NP B(IBN) = BSS(IBN) + H * (B(IBN)-BSS(IBN)) 118 CONTINUE 211 CONTINUE WRITE(IOUT, 121) 121 FORMAT(7X, 'MAX', 12X, 'H', 14X, 'G', 13X, f'SY',12X,'SYP') WRITE(7,122) MAX, H, G, SY, SYP 122 FORMAT(I10,1F15.8,4E15.7) WRITE(7, '(10X, ''B('', I1, '') = '', F16.5)') (I, B(I), I=1, NP) С END BOX-KANEMASU MODIFICATION WRITE(7,'(/,5X,''P(1,KP)'',9X,''P(2,KP)'',9X,''P(3,KP)'',9X, @''P(4,KP)'',9X,''P(5,KP)'') DO 206 IP=1,NP WRITE(7,207) (P(IP,KP),KP=1,NP) 206 CONTINUE 207 FORMAT(5D15.7) WRITE(7,135) 135 FORMAT(5X, 'CORRELATION MATRIX') DO 136 IR-1,NP DO 136 IR2=1,IR AR = P(IR, IR) * P(IR2, IR2)R(IR, IR2) = P(IR, IR2)/SQRT(AR) 136 CONTINUE DO 137 IR=1,NP WRITE(7,'(7E15.7)') (R(IR,III),III=1,IR) 137 CONTINUE DO 126 IPS-1,NP PS(IPS, IPS) = (1.0E+7) * P(IPS, IPS)CONTINUE 126 127 FORMAT(3X, 'IPS=', I4, 3X, 'PS(IPS, IPS)=', D15.8) DO 119 IP-1,NP DO 119 KP=1,NP P(IP,KP)= PS(IP,KP) 119 CONTINUE DO 120 IP=1,NP BS(IP) = B(IP)CG(IP) = 0.0120 CONTINUE WRITE(7,314) WRITE(7, '(7110, 4F10.4)') MAX, NP, INDEX, IP IF(NP-INDEX)101,101,123 123 · CONTINUE

"MODSENSUV.FOR" for NLIBO.FOR with 3 parameters subroutine model(E) dimension ps(5,5),t(100,5), y(100), sig2(100),b(5),z(5),a(5), S p(5,5), bs(5), vinv(5,5) double precision p,ps,psi,t common t,z,bs,i,eta,ps,p,b,a,y,sig2,modl,vinv,np psi=t(i,l) IF (bs(1).LT.0)THEN bs(1) = -bs(1)ENDIF IF (bs(2).LT.0)THEN bs(2) = -bs(2)ENDIF eta=(l-exp(-bs(l)*psi))**bs(2) return end subroutine sens(E) dimension ps(5,5),t(100,5),y(100),sig2(100),b(5),z(5),a(5), p(5,5),bs(5),vinv(5,5) Ş common t, z, bs, i, eta, ps, p, b, a, y, sig2, mod1, vinv, np double precision p,ps,psi,t parameter(R=8.313) iflag=1 means psi/T(t), =0 means psi psi=t(1,1) IF (bs(1).LT.0)THEN bs(1) = -bs(1)ENDIF IF (bs(2).LT.0)THEN bs(2)=-bs(2). ENDIF

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с
с
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С

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d=exp(-bs(l)*psi)

f=g**(bs(2)-1.0)

z(3)=g**bs(2)

Z(1)=bs(2)*d*psi*f
Z(2)=f*g*alog(g)

sensitivity coefficients

q=1-d

return end

C c

173 . APPENDIX E

8.5.Appendix E. Calculated viscous activation energy (ΔE_v) of gelatinized native corn starch to determine effects of temperature (corresponding to Table 3.3)							
Impelle	rTemp		Fluid	Heating	g Calculate	d Calculated	
speed	Rangeg	starch/	Jacket	time	Ψ , scaled	ΔE_v	
(rpm)	(0)	g soin	1emp(C)	<u>(min)</u>	<u>(KS)</u>	<u>(K)</u>	
100	50-70	6.4	95	3 4 5 6	0.836,0.322 0.188,0.154 3.5,3.8,4 60.2,50	2 787,614 4 909,1178 707,641,584 1088,926	
	60-95	<u></u>		8	567 452 446	1176 998 1408	

174 Appendix f

8.6. Appen	dix F.	Obse gelat deter	rved equi inized nat mine effe	librium t ive corn cts of sh	orque of starch to ear rate
		<u> </u>	esponding	to Table	2.3.4)
Impeller	Temp		Fluid	Heating	Equil.
speed	Range	g starch/	Jacket	time	torque
(rpm)	(C)	g soln	Temp(C)	(min)	(Brkfld units)
0.5 1 2.5 5 10 20 50 100	60	6.4	95	8	14.8 15.2 16.8 18.8 21.8 26.2 34.7 44.1
0.5 1 2.5 5 10 20 50 100	60	6.4	95	8	15.3 15.7 17.1 19.1 22.0 26.3 34.7 43.9
0.5 1 2.5 5 10 20 50 100	50	6.4	95	12	18.6 19.1 21.5 23.9 27.5 32.7 42.7 53.7

175 APPENDIX G

8.7.Appendix		G.	Calcula	ited sti	rain histo	ry param	eters of
			gelatini	ized na	itive cori	n starch	
	•		(corres	ponding	to Tab	le 3.5)	
Impeller			Fluid	Heating	Calculated		
speed	Temp	g starch	/Jacket	time	Ψ , scaled		
(rpm)	(C)	g soln	Temp(C)	(min)	(K s)	-d*1000	В
100					740	0.498	0.276
					936	0.352	0.312
50	60	6.4	95	12	303	0.992	0.230
					407	1.115	0.203
20					335	2.775	0.235
					449	<u> 2.765 </u>	<u> 0.203 </u>
				8	117	0.644	0.107
					100	0.555	0.111
100	60	6.4	95		104	0.669	0.121
				4	2.9	0.757	0.149
					4.3	0.712	0.121
			50	12	556	0.407	0.268
100	60	6.4			518	0.331	0.283
			95	8	195	2.2	0.330
					329	1.19	0.32

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176 APPENDIX H

Appendix H. Example of mathematical procedure to correct and normalize raw torque during a pasting curve to a reference temperature (60 C) and reference temperature-time history (zero) at 10 s intervals.

Temp. correction factor = $e^{\left(\frac{\Delta f_v}{R}\right) \left(\frac{1}{T_r} - \frac{1}{T}\right)}$ $\frac{\Delta E_v}{R} = 217 * \psi + 600$ $t \psi = 1 + A^* (1 - e^{(-k^*\psi)})$

temp correction factor= $e^{(217*\psi+600)*(\frac{1}{(60+272\cdot15)}-\frac{1}{(7+272\cdot15)})}$

 ψ correction factor= $\frac{1}{t_{\Psi}}$

normalizing factor $(1/K_r)=(1+219.8)^*(1-0.2864)/44.16$

starch Temp	Ψ	temp. correction factor	tψ	Experi mental torque	torque corrected to 60 C	torque corrected to 60 C, u=0	torque corrected to 60 C, $\psi=0$, normalized
С	K-s			N-m	N-m	N-m	N-m
C 58.7 65 70.2 73.9 75.9 78.1 78.7 80.6 81.5 82.4 82.8 83.9 84.4 84.8 83.9 84.4 84.8 85.7 86.5 87	K-s 0.000 0.000 0.000 0.000 0.000 0.001 0.003 0.003 0.003 0.003 0.003 0.017 0.029 0.052 0.086 0.13 0.208 0.305 0.305 0.424 0.598	1.007 0.974 0.948 0.93 0.921 0.911 0.909 0.896 0.892 0.896 0.892 0.89 0.885 0.881 0.878 0.869 0.866 0.858 0.848	1.041 1.234 1.984 3.804 6.35 10.715 14.756 21.636 29.576 38.791 47.722 60.175 72.304 83.869 101.179 113.315 125.993 139.28	N-m 0.17 0.15 0.15 0.17 0.24 0.35 0.55 0.8 1.32 2.57 5.01 8.05 11.15 14.81 18.34 22.05 25.79 29.22	N-m 0.169 0.154 0.158 0.183 0.261 0.384 0.605 0.889 1.473 2.881 5.630 9.102 12.656 16.877 21.100 25.445 30.055 34.435	N-m 0.162 0.125 0.080 0.048 0.041 0.036 0.041 0.041 0.050 0.074 0.118 0.151 0.175 0.201 0.209 0.225 0.239 0.247	N-m 0.579 0.445 0.285 0.171 0.146 0.128 0.146 0.147 0.178 0.265 0.421 0.540 0.625 0.718 0.744 0.801 0.851 0.882
87.8 86.8 87.6 87.9 88.2 89.1	0.398 0.788 1.02 1.34 1.72 2.29	0.848 0.842 0.83 0.828 0.827 0.822	139.28 147.466 157.146 164.625 170.346 178.746	29.22 32 34.7 36.96 38.63 39.72	34.435 37.902 41.298 44.070 46.149 47.712	0.247 0.257 0.263 0.268 0.271 0.267	0.882 0.917 0.938 0.955 0.967 0.952
88.9 89.7 89.9 90 90.3 91 91.3 91.2	2.99 3.84 4.86 6.13 7.56 9.52 12.1 14.9	0.823 0.819 0.817 0.817 0.815 0.811 0.81 0.81 0.809	180.173 184.345 186.203 186.757 188.721 193.014 195.037 195.037	40.4 40.75 40.91 40.79 40.54 40.2 39.76 39.26	48.484 49.149 49.326 49.136 48.960 48.557 47.970	0.269 0.267 0.265 0.264 0.260 0.254 0.249 0.246 0.238	0.960 0.951 0.947 0.942 0.929 0.905 0.888 0.878 0.849

Appendix H. (Cont'd).

91.9	22.6	0.805	199.529	38.07	46.847	0.235	0.838	
92.2	27.3	0.802	201.675	37.51	46.324	0.230	0.820	
92.6	33.1	0.8	204.124	36.86	45.734	0.224	0.799	
92.9	40.1	0.797	206.038	36.25	45.182	0.219	0.782	
93.2	48.5	0.794	208.254	35.64	44.650	0.214	0.765	
93.1	57.6	0.793	208.254	35.05	44.043	0.211	0.755	
931	66.6	0.792	208.254	34.53	43.545	0.209	0.746	
63 3	76 1	0 789	209 343	33.98	43 067	0.206	0734	
94 1	891	0 783	214 754	33.5	42 894	0.200	0713	
63 3	102	0 785	214 754	33.07	42 348	0.197	0 704	
94	115	0.78	214.754	32.66	42 231	0.197	0 702	
94 i	130	0 777	215.049	32.27	42.007	0 195	0.697	
937	145	0 777	215.049	31.89	41 654	0 194	0.691	
94 2	160	0 772	215 581	31.56	41 61 1	0 193	0.689	
Q4 4'	178	0.768	217.065	31 17	41 454	0 191	0.681	
94.5	198	0 764	217 961	30.88	41 431	0 190	0.678	
94 1	217	0.763	217 961	30.61	41 270	0 189	0.676	
04 A	235	0.759	217 961	30 3	41 239	0 189	0.675	
04 1	252	0.758	217 961	30.06	41 105	0.189	0.673	
94.6	272	0.750	2191	29.82	41 261	0.188	0.672	
94 1	292	0751	2191	29.69	41 260	0 188	0.672	
94.6	311	0 746	2191	29 57	41 570	0 190	0.677	
94 1	330	0 746	2191	29.35	41 418	0 189	0.674	
94 5	348	0 741	2191	29 18	41611	0 190	0.678	
94 3	368	0739	2191	29.03	41 667	0.190	0.679	
94 3	386	0.736	219.1	28.87	41.741	0 191	0.680	
94.6	407	0.731	219.1	28.73	41.998	0.192	0.684	
93.9	426	0.733	219.1	28.6	41.884	0.191	0.682	
94.2	441	0.729	219.1	28.97	42.792	0.195	0.697	
91	451	0.747	219.1	29.91	43.140	0.197	0.703	
87.3	452	0.771	219.1	30.73	42.905	0.196	0.699	`
83.3	452	0.799	219.1	31.5	42.411	0.194	0.691	
79	452	0.831	219.1	32.29	41.771	0.191	0.680	
76.5	452	0.851	219.1	33.1	41.817	0.191	0. 681	
73.7	452	0.873	219.1	33.97	41.775	0.191	0.680	
71.9	452	0.888	219.1	35.1	42.414	0.194	0.691	
70.1	452	0.904	219.1	36.43	43.276	0.198	0.705	
68.2	452	0.921	219.1	37.96	43.690	0.199	0.711	
67.2	452	0.93	219.1	39.51	44.718	0.204	0.728	
65.6	452	0.945	219.1	40.63	44.758	0.204	0.729	
64.8	452	0.953	219.1	41.61	45.217	0.206	0.7 36	
63.8	452	0.962	219.1	42.4	45.293	0.207	0.738	
63.1	452	0.969	219.1	43.03	45.416	0.207	0.7 40	
62.5	452	0.975	219.1	43.54	45.480	0.208	0.741	
62.4	452	0.975	219.1	43.98	45.860	0.209	0.747	
61.4	452	0.985	219.1	44.32	45.419	0.207	0.7 40	
61.1	452	0.988	219.1	44.62	45.488	0.208	0.741	
60.8	452	0.992	219.1	44.92	45.554	0.208	0.742	
60.3	452	0.997	219.1	45.18	45.419	0.207	0.740	
59.8	452	1.003	219.1	45.41	45.251	0.207	0.737	
59.6	452	1.004	219.1	45.64	45.320	0.207	0.738	
59.3	452	1.007	219.1	45.8	45.239	0.206	0.737	
58.6	452	1.014	219.1	45.95	44.829	0.205	0.730	

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