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# A GENERALIZED VISCOSITY MODEL FOR THE COOKING EXTRUSION OF STARCH BASED PRODUCTS

By

Kevin Lewis Mackey

## A DISSERTATION

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

## DOCTOR OF PHILOSOPHY

Department of Food Science and Human Nutrition

#### ABSTRACT

# A GENERALIZED VISCOSITY MODEL FOR THE COOKING EXTRUSION OF STARCH BASED PRODUCTS

#### By

#### Kevin Lewis Mackey

A generalized model has been developed for predicting the extrudate viscosity of low to intermediate moisture content starch based products during cooking extrusion. The model incorporates the effects of shear rate, temperature, moisture content, timetemperature history and strain history.

The model was tested using doughs of potato flour, corn starch and whole wheat flour. Equipment used included an Instron Capillary Rheometer attached to a Model 4202 Instron Universal Testing Machine and an APV Baker MPF 50 D/25 co-rotating twin screw extruder. Die lengths of the capillary rheometer were  $6.35 \times 10^3$  m and  $2.54 \times 10^{-2}$  m while the diameters were  $3.18 \times 10^{-3}$  m and  $1.59 \times 10^{-3}$  m. Extruder dies of  $6.35 \times 10^{-3}$  m in length and diameters of  $2.54 \times 10^{-2}$  m and  $3.18 \times 10^{-3}$  m were used.

Experiments with potato flour were conducted at temperatures of 25, 50, 65, and 95°C. Cook times within the capillary rheometer were 0 to 12 minutes after compression. Moisture contents of 0.282, 0.507, and 0.772 g water per g solids (22.0%, 33.7%, and 43.6% wb, respectively) were used in the capillary rheometer, while the moisture contents in the extruder were 0.67 and 1.0 g water per g solids (40% and 50% wb). Shear rates ranged from 1-10000 s<sup>-1</sup>.

In potato dough, shear rate was described by the power law model. Timetemperature history and strain history did not influence viscosity. The final predictive model incorporates shear rate, temperature and moisture content and yielded an  $R^2$  of 0.951. Corn starch dough moisture contents were 0.359, 0.476, and 0.572 g water per g starch (26.4%, 32.0%, and 36.4% wb, respectively) for capillary rheometer tests and 0.5 and 0.6 g water per g starch (33.0% and 37.5% wb) for extrusion tests. In the capillary rheometer, barrel temperatures were held at 50, 55, 60, 75, 85, 95, and 110°C at cook times of 1, 2, 3, 6, 12, and 24 minutes.

In corn starch dough, slip analysis was inconclusive. Shear rate was modelled by the equation proposed by Ofoli et al. (1988). Viscosity was found to be a function of cook temperature and moisture content, but not cook time. Observed versus predicted viscosities gave an  $R^2$  of 0.95 after accounting for shear rate, temperature, moisture contents and time-temperature history in the capillary rheometer. Contrary to tests for potato doughs, extrusion tests indicated that strain history was important for highly puffed corn starch extrudates ( $R^2$ =0.79 before strain history correction). Strain history was modelled as a function of mechanical energy input (shaft work). After correction for strain history, the fit of the model improved to an  $R^2$  of 0.85.

Whole wheat flour tests were conducted at the same temperature and cook times as those for corn starch, but at moisture contents of 0.333, 0.337, 0.385, and 0.426 g water per g solids (25.0%, 25.2%, and 29.9% wb, respectively). As obseved for corn starch slip correction gave inconclusive results. Shear rate was best modelled by the Herschel-Bulkley model. Overall fit of the model steadily improved with corrections for temperature, moisture content and time-temperature history. Viscosity of cooked doughs were found to be a function of moisture content, cook time and temperature. The fit ( $R^2$ =0.56) was not as good for whole wheat flour as was observed for corn starch ( $R^2$ =0.95) and potato flour ( $R^2$ =0.95). The lower  $R^2$  may have been due to the presence of flour components such as bran, gluten (protein) viscoelastic effects and lipids which were not accounted for by the model. Incorporation of gelatinization kinetics alone in the time-temperature effects was inadequate to totally model the viscosity.

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#### Preface

This dissertation was written in an alternative format to aid the author in preparing portions of the dissertation for publication. The first three chapters feature an introduction, literature review and the model development. Chapters 4, 5, and 6 consist of three papers to be submitted for publication while chapters 7 and 8 are the conclusions and suggestions for future research. I hope that writing the dissertation in this format will not confuse the reader and will, perhaps, allow the reader to understand and apply the information in an easier manner.

Kevin L. Mackey December, 1988

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# NOMENCLATURE

A, A', material constant describing effects of cook temperature and product moisture content on viscosity at  $\Psi = \infty$ , dimensionless A. rate constant of effect of moisture content on viscosity, dimensionless b Ср protein concentration, decimal dry basis CR capillary rheometer starch concentration, wet basis decimal Cs d rate constant of effect of strain history ( $\phi$ ) on viscosity, s D capillary diameter, m mechanical energy supplied by the extruder, Jm<sup>-3</sup> Es h Planck's constant. K consistency coefficient, Pa s K. consistency coefficient (Mizrahi-Berk), Pa<sup>0.5</sup> s<sup>m</sup> reaction transmission coefficient, s<sup>-1</sup> •K<sup>-1</sup> k, Boltzman's constant. k, transmission coefficient. k, L capillary length, m power index (Mizrahi-Berk), dimensionless m MC moisture content, dry basis decimal MC. reference moisture content, dry basis, decimal power indices, dimensionless ni volumetric flow rate,  $m^3/s$ Q R universal gas constant, 1.987 cal/g mole R, capillary radius, m

- t time, s
- T temperature, <sup>•</sup>K
- T, reference temperature, 'K
- TSE twin screw extruder
- $\alpha$  material constant describing polymer entanglement, dimensionless
- $\beta$  material constant describing effect of strain history on viscosity at  $\phi = \infty$ , dimensionless
- $\beta_{o},\beta_{r}$  material constant describing effects of temperature on gelatinization, dimensionless
- ε material exponent for describing effect of moisture content on protein denaturation, dimensionless
- $\dot{\gamma}$  shear rate, s<sup>-1</sup>
- $\dot{\gamma}_{w}$  shear rate at the wall, s<sup>-1</sup>
- $\Delta E_{v}$  free energy of activation, kcal/g mole
- $\Delta E_s$  energy of gelatinization, kcal/g mole
- $\Delta P$  pressure drop, Pa
- $\eta$  apparent viscosity, Pa s
- $\eta_a$  normalized apparent viscosity ratio, dimensionless
- v time-temperature history, s 'K
- φ strain history, dimensionless
- $\sigma$  shear stress, Pa
- $\tau_{\omega}$  shear stress at wall, Pa
- $\sigma_o$  yield stress, Pa
- $\tau_o$  yield stress, Pa

K	yield stress-related	parameter	(Mizrahi-Berk),	, Pa <sup>0.5</sup>
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- μ Newtonian viscosity, Pa s
- $\mu_{-}$  high shear limiting viscosity, Pa s
- $\eta_{-}^{\bullet}$  change in apparent viscosity due to gelatinization at  $\psi = \infty$ , Pa s
- $\mu_o$  high shear limiting viscosity (Bingham plastic), Pa s

# Subscripts of $\eta$

Ϋ́	apparent viscosity corrected for shear rate, Pa s
G	contribution to viscosity by gelatinization
pre	predicted apparent viscosity, Pa s
<b>00</b>	viscosity at $\psi = \infty$ , Pa s
<i>γ,</i> Τ, <i>M</i> C	apparent viscosity before gelatinization, Pa s
φ	apparent viscosity at $\phi = \infty$ , Pa s
γ, T	apparent viscosity corrected for shear rate and temperature, Pa s
Ϋ́,Τ,MC	apparent viscosity corrected for shear rate, temperture and moisture con- tent, Pa s
<i>γ,Τ,Μ</i> Ϲ,Ψ	apparent viscosity corrected for shear rate, temperture, moisture content and time-temperature history, Pa s
<i>Ϋ,Τ,Μ</i> Ϲ,Ψ,Φ	apparent viscosity corrected for shear rate, temperture, moisture content, time-temperature history and strain history, Pa s

# **CHAPTER 1 INTRODUCTION AND OBJECTIVES**

#### **1.1. Introduction.**

The predominant ingredient in extruded snack and ready to eat (RTE) cereals is starch (Harper, 1986). Many of these products do not use purified starch but rather degermed cereal grits which also contain some protein, fat, and fiber. The starch granule can undergo many changes leading to increased molecular rearrangement during extrusion, including loss of crystallinity, degradation and formation of amylose lipid complexes. These changes almost always will significantly affect viscosity. Therefore, temperature, moisture, shear, and feed composition are important factors accounting for changes in starch structure during extrusion (Harper, 1986).

Extrusion cooking of starch based foods is increasing each year due to the versatility, high productivity, low production costs, high product quality, increased energy efficiency and lack of product effluent of extrusion processes (Harper, 1981). However, the full economic exploitation of extrusion is currently constrained by a lack of understanding of the effects of ingredients and process conditions on product quality, and difficulties in process design and scale-up.

A general viscosity model would be useful for process engineering analyses. Harper (1986) states that there is no single model that incorporates starch gelatinization, viscoelastic behavior, density and thermal properties as functions of time, temperature, shear rate, and moisture content. Modeling in cooking extrusion needs more research, since models can be used to simplify complex processes in a cooking extruder, predict changes in product quality, and obtain a basis for new product development (Janssen, 1986). Most models proposed so far are empirical and limited to observed experimental conditions.

# 1.2. Objectives.

The overall goal of this research is to obtain an understanding of the interactions of shear rate, temperature, moisture content, time-temperature history and strain history on the viscosity of extruded starch-based doughs. To achieve this goal, the specific objectives of the study are to:

1. Develop a generalized viscosity model incorporating effects of time-temperature history, moisture content, temperature, strain history, and shear rate during extrusion of low moisture starch based foods.

2. Evaluate the model with data obtained from capillary viscometry and twin screw extrusion for three dough systems: corn starch, potato flour and wheat flour.

3. Assess the effects of starch gelatinization during extrusion on rheological properties.

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#### **CHAPTER 2 LITERATURE REVIEW**

#### 2.1 Starch

#### **2.1.1. Introduction**

Starch is the major storage form of glucose (energy) in plants. In cereal grains, starch contents range from 60 to 70% of the weight of the grain (Hoseney, 1986). Besides being an excellent source of energy for plants and animals, starch also provides important physical properties to foods. Properties that are most important to the food scientist include gelling of puddings, thickening of gravies, setting of cakes, breads and other baked goods, and as a source of glucose for many sweeteners.

In higher plants (eg. cereal grains), starch is formed in the plastids. All starch is stored in the form of granules. Starch granules made in the chloroplasts of leaves are considered transitory because at nightfall, the granule is broken up and the glucose is transferred to other portions of the plant. Reserve starch granules are usually formed in amyloplasts, though starch can be formed in chloroplasts which have lost their lamellar structure and therefore begin to produce large amounts of storage starch (Shannon and Garwood, 1984). In general, one plastid produces one starch granule except for rice and oat plants which produce compound granules (Hoseney, 1986).

If examined under polarized light, intact starch granules show a distinct birefringence pattern consisting of a Maltese cross. The presence of birefringence is an indication of a high degree of order within the granule. Gelatinization is often defined as the loss of birefringence.

Starch granules are also made up of semicrystalline materials as indicated by the classical studies of Katz (1928) and his co-workers using X-ray diffraction. Katz (1928) showed that intact starch granules gave three types of X-ray diffraction patterns (A, B, or C) depending on the source. Cereal starches (i.e corn, wheat, barley) give the A pattern,

tuberous starches (potato) give the B pattern and smooth starches (pea and bean) give the C pattern. The C pattern is thought to be a mixture of both A and B patterns. Gelatinization of starches result in a loss of crystallinity and the appearance of the V type X-ray diffraction.

Starch consists mainly of two large polysaccharride molecules, amylose and amylopectin, consisting of long chains of glucose. Amylose is considered to be primarily a linear  $\alpha$ -(1-4) glucan with a molecular weight of 150,000-1,000,000 depending upon the source. Early research indicated that amylose was linear, as determined by enzyme studies ( $\beta$ -amylase) but later research indicates that the  $\beta$ -amylase used contained some  $\alpha$ -amylase and/or debranching enzymes. Present research indicates that some limited branching is present in the amylose molecule (Banks and Greenwood, 1975). Amylose content ranges from 20-30% among biological sources (Table 2.1.), however, there are genetic hybrids in which there is an increase or decrease of the amylose content available.

Amylopectin differs from amylose in both its molecular weight and its highly branched structure. The amylopectin molecule is made up of glucose units with  $\alpha$ -(1-4) glycosidic,  $\alpha$ -(1-6) glycosidic or both  $\alpha$ -(1-4) and  $\alpha$ -(1-6) glycosidic bonds. The average chain length is 20-25 glucose units and random branches give this molecule its high molecular weight. Evidence is mounting that amylopectin is the principal crystalline component of the starch granule (Lineback, 1984). Birefringence and X-ray diffraction patterns of waxy maize starches containing no amylose are similar to those of normal maize starch. High amylose maize starches are less birefringent and show less crystallinity than normal starches. Lineback (1984) also suggests that amylopectin is responsible for the crystalline structure, because amylose is released into solution when starches are exposed to gelatinization temperatures while amylopectin is not.

Table 2.1. Properties of whole granular starches.;				
Source	Gelatinization Temperature range	Granule shape	Granule Size	Amylose Content
	(*C)		(nm)	(%)
Barley	51-60	round or elliptical	20-25 2-6	22
Triticale	55-62	round	19	23-24
Wheat	58-64	lenticular or round	20-35 2-10	26(23-27)
Rye	57-60	round or lenticular	28	27
Oats	53-59	polyhedral	3-10	23-24
Potato	59-68	oval	40(15-100)	23
Corn	62-72	round or polyhedral	15	28
Waxy maize	63-72	round	15(5-15)	1
Broad bean	64-67	oval	30	24
Sorghum	68-78	round	35	25(23-28)
Rice	68-78	polygonal	3-8	17-19
High-	67-90	round	25	52
amylose		irregular		
maize		-		

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Source: Lineback (1984).

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#### **2.1.2.Structure of the starch granule**

#### **2.1.2.1. External structure of the starch granule.**

Starch granules from different plant sources have different morphologies (Table 2.1). The morphology depends on the structure and biochemistry of the starch producing chloroplast or amyloplast (Badenhuizen, 1969). These differences enable trained personnel to determine which plant produced the starch.

The granule grows via apposition, i.e., addition of material to the outer layers. This growth gives the characteristic ring structures seen in potato starch. These growth rings can also be seen in other starches after acid treatment of the starch granules. Scanning electron microscopy indicates that undamaged, unmodified granules have relatively smooth surfaces free of pores, cracks or fissures (Whistler et al. 1984).

#### **2.1.2.2.** Internal structure of the starch granule.

While the use of optical and scanning electron microscopy has enabled researchers to determine the general surface morphology of starch granules, the internal structure has been much more difficult to determine. The development and use of transmission electron microscopy (TEM) has provided researchers with greater resolution. Acid treatment (7% HCl for 35 days) has shown corn and waxy maize starch granules to have similar well-defined lamellar structures with alternating concentric electron-dense and electrontransparent rings (Mussulman and Wagoner, 1968). Rings occur at irregular intervals of 1200-4000 Å and suggest that the overall length of individual amylopectin molecules are of this length (Yamaguchi et al. 1979). Yamaguchi et al. (1979) proposed that a single amylopectin molecule starts at one growth ring and finishes at the next, with each molecule made up of many 70 Å clusters. It is interesting to note that high amylose corn starches do not reveal ring structures after acid or enzyme treatment, but instead show a heterogeneous internal structure.

Hood (1982) states that the molecular structure of starch corresponds with the crystalline structure of the starch, and that it is well accepted that starch molecules are radially oriented within the granule. Pairs of the outer chains of amylopectin can form double helices which also contribute to the crystalline properties (Kainuma and French, 1972). Kassenbeck (1978) used TEM and ultrathin sections of starch granules to present further evidence that radial orientation of amylopectin molecules exists. He also presented three possible types of molecular organization: (1) a radially aligned, fibrillar arrangement of amylose in ordered regions; (2) amylose in amorphous regions where the amylose was degraded by the preparative method and appears in the form of precipitates;, and (3) an arrangement of amylopectin in crystalline regions where it appears as periodically arranged block-like areas in radial sections, with crystallites in tangential lamellae.

French (1984) states that there is no sharp line separating the crystalline and amorphous sections of the starch granules and that some or all of the starch molecular chains continuously change from one phase to another. He also states that there is no definite evidence that amylose contributes to the crystalline structure of the starch granule. Amylose not contributing to crystallinity would explain why amylose molecules are seen outside the granule early in the gelatinization process and amylopectin molecules are not.

# 2.1.3. Physical and Chemical Changes

Increase in viscosity of dilute solutions of starch and water is attributed to the starch granule taking up water and a concurrent swelling of the granule (Hoseney, 1986). As the granule swells, starch molecules are leached out causing further increases in viscosity.

Gelatinization minimally entails (1) loss of crystallinity of the granule as measured by loss of birefringence and its X-ray diffraction patterns; (2) an uptake of heat as the

conformation of starch changes; and (3) hydration of starch accompanied with granule swelling (Donovan, 1979). A more detailed summary of gelatinization is given by Olkku and Rha (1978) and is presented as follows:

(1) Granules hydrate and swell to several times their original size.

(2) Granules lose their birefringence.

(3) Clarity of the mixture increases.

(4) Marked, rapid increase in consistency occurs and reaches a peak.

(5) Linear molecules dissolve and diffuse from ruptured granules.

(6) Mixture retrogrades to a paste-like mass or gel.

Atwell et al. (1988) recently proposed the following definition of starch gelatiniza-

tion:

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 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.

This definition best describes what is occurring during the process of gelatinization and will be used in this work.

#### **2.1.3.1.** Physical changes

In the presence of sufficient water and at temperatures below gelatinization, water is slowly and reversibly taken up by the granule (Olkku and Rha, 1978). Once gelatinization temperatures are reached, the granules begin to swell and become distorted (Sterling, 1978; Christianson et al., 1982). The granule's ability to polarize light and diffract X-rays is lost at this time (Sterling, 1978; Hoseney, 1986; Olkku and Rha, 1978; Donovan, 1979). Sterling (1978) reports that a three to six fold increase in volume is seen when starch granules begin to gelatinize. This increase is confirmed by Christianson et al. (1982), where a three and a half fold increase in corn starch granule size was seen. The starch granule swells in a tangential direction during the gelatinization process. When temperatures increase beyond gelatinization temperatures, the granule continues to swell and may increase up to 25-30 fold, followed by a gradual collapse (Sterling, 1978).

Christianson et al. (1982) presented excellent SEM photographs of corn starch granules at various stages of gelatinization. As the temperature increases, the granules begin to swell radially (65°C), ridges are formed at the surface (67°C), the granules become more angular in structure (70°C) and, at higher temperatures, the granules melt into thin flat disks. Different sections of the granule appear to swell at different times, and Sterling (1978) postulated that differences in molecular structure cause this phenomenon. Christianson et al. (1982) confirmed this when the amorphous regions were seen to swell at lower temperatures than the regions of the more highly ordered portion of the granule.

Along with this swelling, solubilization of starch molecules is occurring and by the time a temperature of 70°C has been attained, approximately 10% of the starch has left the corn starch granule (Christianson et al., 1982). The granules seem to pass a transition at 80°C where melting or softening of the granule occurs (Christianson et al., 1982). Twenty per cent of the starch is soluble at 85°C and the granule appears smooth and more fluid than what is seen at lower temperatures. Wheat starch granules show a more ordered swelling as described by both Bowles et al. (1980) and Miller et al. (1973).

It is interesting that both Miller et al. (1973) (wheat starch) and Christianson et al. (1982) (corn starch) have reported that maximum viscosity of starch suspensions heated

in the presence of excess water occurs after the majority of granule swelling has stopped. This is an indication that granule swelling is not the only reason an increase in viscosity is seen.

Christianson et al. (1982) also compared viscosity data and SEM micrographs of starch dispersions of varying concentration and exposure to different temperatures. At 65°C and under low shear, granules swelled but retained birefringence and exhibited dilatant behavior. When exposed to high shear, shear thinning occurred. After loss of birefringence (67-70°C) softening of the granules occurred so that shear thinning occurred at all shear rates.

In their review on the gelatinization of starch, Olkku and Rha (1978) discussed the effects of various ingredients on gelatinization. Proteins are believed to inhibit escape of soluble portions from the granule but do not appear to affect swelling. The same conclusion is drawn for the effects of oils and surface active agents. Pentosans are thought to compete for water and therefore inhibit gelatinization and granule swelling. Addition of salt can increase the granule's ability to swell, while addition of sucrose retards hydration of the starch granule (Olkku and Rha, 1978; Bean and Yamazaki, 1978).

#### **2.1.3.2.** Chemical changes

Along with the physical changes occurring in the starch granule, the chemical structure is also changing during the gelatinization process. The intramolecular hydrogen bonds are disrupted upon heating and the structural integrity of the granule is lost. Once disruption of hydrogen bonds occur, the amorphous regions of the granule are the first to hydrate (Hood, 1982). This swelling of the amorphous phase can contribute to the disruption of crystalline regions by pulling molecules away from the crystals (French, 1984). Blanshard (1979) proposed that in addition to diffusion of water and swelling, a hydration-facilitated helix-coil transition which is a melting process also occurs.

Miller et al. (1973) showed that amylose leached from the granule during heating and formed an extra granular network which contributed to increased viscosity. Approximately 10% of the starch has been solubilized at 70°C and by 80°C, 20% of the starch has been solubilized (Christianson et al., 1982). Using proton magnetic resonance (PMR) Jaska (1971) found water mobility to reversibly decrease with increased temperature until gelatinization temperatures are attained. This decrease in mobility indicates adsorption of water to starch molecules. When gelatinization occurs, an increase in water mobilization occurs which indicates a transfer of soluble starch (about 90% of total) into solution (Jaska, 1971). Jaska (1971) concluded that some of the starch is in solution inside the granule before it leaves the granule and that soluble starch solubilizes over a narrow temperature range.

Various methods of thermal analysis have been used to study starch gelatinization (Hoseney, 1984; Nakazawa et al. 1984; Wootton and Bamunuarachchi, 1979a; Wootton and Bamunuarachchi, 1979b; Stevens and Elton, 1971; Biliaderis et al., 1980; Ghiasi et al., 1982a; Donovan, 1979), the effects of low moisture conditions (Wootton and Bamunuarachchi, 1979; Takahashi, et al., 1982; Burt and Russell, 1983; Sweat et al. 1984; Eliasson, 1980; Collison and Chilton 1974; Biliaderis et al., 1986), protein concentration (Eliasson, 1983), lipid and lipid-like substances (Harbitz, 1982; Kugimiya et al., 1980; Ghiasi et al. 1982b), and solute concentration on gelatinization (Ghiasi et al., 1983; Spies and Hoseney, 1982; Evans and Haisman, 1982; Oosten, 1982). These methods of thermal analysis include differential thermal analysis, differential scanning calorimetry, and thermal mechanical analysis.

When gelatinization of starch is measured by differential scanning calorimetry (DSC) under low moisture conditions, two endotherms are observed. When excess water is present, the DSC curve shows only one endotherm indicating that water content

directly affects gelatinization kinetics. Various models have been proposed for this phenomenon. Donovan (1979) suggests that upon hydration/swelling of the amorphous portions of the granule and due to coupling with crystallites, melting of the latter occurs as long as water is present in excess. He postulated that when the amount of water is insufficient for complete melting, the remaining crystallites melt at a higher temperature and thus support the second DSC peak.

Another hypothesis for starch gelatinization at low to intermediate moisture contents is proposed by Evans and Haisman (1982). They propose that two endothermic peaks reflected two types of melting: granules containing less stable crystallinity melt first; upon melting, the polysaccharride chains absorb more water making less water available for the remaining ungelatinized granules, causing these granules to melt at higher temperatures.

Biliaderis et al. (1986) have proposed a third explanation for starch gelatinization under low to intermediate moisture conditions. They postulate that the DSC curve is not representative of the initial crystallite profile, but rather the composite thermal effect of several processes that occur simultaneously during heating: melting, annealing and crystallization. They proposed that the order-disorder phase transitions of starch-water mixes are analogous to those of semicrystalline synthetic polymers. The thermomechanical properties of starch polymers can be altered by the presence of small amounts of water as a plasticizer. In the presence of a plasticizer, the glass transition temperatures of the granule's amorphous portion are decreased which in turn facilitates melting or reorganization of the starch crystallite and the amylose-lipid complexes to occur at lower temperatures.

Wootton and Bamunuarachchi (1979b) and Eliasson (1980) report a linear relationship between moisture content and enthalpy of gelatinization when measured with a DSC. This change in enthalpy may be caused by a change in entropy and not in the

energy of activation, in accordance with the proposed mechanism of gelatinization by Biliaderis et al. (1986). Eyring and Stearn (1939) also report that the change in enthalpy seen at different moisture contents of protein materials was due to differences in entropy and not due to a change in activation energy. Eliasson (1980) also reports that the temperature of the first endotherm does not vary significantly with water content.

Thermal analysis of starch-water mixtures with varying levels of solute concentrations (salt or sucrose) shows increased thermal transition temperatures and a narrowing of the gelatinization temperature range. It is believed that these constituents compete with starch for water and therefore make water unavailable for gelatinization (Ghiasi et al., 1983; Spies and Hoseney, 1982; Evans and Haisman, 1982; Oosten, 1982). Eliasson (1983) indicates that increased levels of gluten lowered the gelatinization enthalpy and increased the gelatinization temperature. This is similar to results reported by Ghiasi et al. (1982a). It is believed that protein inhibits migration of water into the starch granule. Gelatinization of starch in the presence of lipids or surfactants indicate a lowering of gelatinization temperatures and increase in gel strength (Harbitz, 1983; Kugimiya et al., 1980; Ghiasi et al. 1982b). This is most likely due to the formation of an amylose lipid complex.

#### **2.1.4. Measurement Methods**

Many methods of measuring starch gelatinization are discussed in the literature. These methods include light microscopy, polarized light microscopy, electron microscopy, viscosity changes, X-ray diffraction, thermal analysis, and enzymatic methods.

# **2.1.4.1. Light Microscopy**

The use of a microscope allows the researcher to observe swelling duration, degree of swelling, swollen granule integrity and size (Zobel, 1984). Freke (1971), Collison and Chilton (1974) and Bean and Yamazaki (1978) all utilized a microscope to study starch

gelatinization. Both Freke (1971) and Bean and Yamazaki (1978) used a microscope equipped with a stage heater and a camera loaded with high contrast black and white film, while Collison and Chilton (1974) exposed the starch solution to heat and then observed the results under a microscope. When heating on a microscope, care must be taken to prevent dehydration. This can be done by sealing the cover slop with mineral oil (Bean and Yamazaki, 1978) or silicone grease (Freke, 1971). Starch concentration of less than 1% were used by Freke (1971) and Bean and Yamazaki (1978) to reduce the number of granules in the field of observation. Snyder (1984) discussed the use of various stains (iodine, methylene blue, etc.) to aid in the determination of granule morphology. Chlorazol violet R on heat treated starch was used by Collison and Chilton (1974) to aid in determining damaged starch granules. Bean and Yamazaki (1978) also measured granule swelling by photographing a scale and then superimposing this scale.

#### **2.1.4.2.** Polarized Light Microscopy

As previously mentioned, ungelatinized starch granules exhibit birefringence (a Maltese cross) when viewed under polarized light. Use of a polarized microscope to determine gelatinization is described by Snyder (1984), Burt and Russell (1983), Ghiasi et al. (1982a), Bean and Yamazaki (1978), Lelievre (1973) and Miller et al. (1973).

Two methods are discussed: (1) use of a stage heater with the microscope while taking pictures at selected temperature intervals (Bean and Yamazaki, 1978; Lelievre, 1973) and (2) controlled heating of the starch to a desired temperature, rapid cooling and then observation under a microscope (Ghiasi et al. 1982a; Burt and Russell, 1983; Miller et al. 1973). Heating rates from 1°C per 30 min (Lelievre, 1973), to 1°C per min (Bean and Yamazaki, 1978) to 10°C per min (Burt and Russell, 1983, Ghiasi et al. 1982a) have been used. As in unpolarized high microscopy the attachment of a camera and use of high contrast black and white film aid in the analysis.

# 2.1.4.3. Electron Microscopy

Use of electron microscopy to study changes in granule structure during gelatinization has advantages over light microscopy techniques. These advantages include a greater depth of field and a higher resolution (about 70 A). Two types of electron microscopy have been used in observing starch granules: (1) Scanning (SEM) and (2) Transmission (TEM). SEM has been used to observe surface changes during gelatinization and TEM has been utilized to help discern the internal structure of the starch granule.

# **2.1.4.3.1. Scanning Electron Microscopy (SEM)**

Preparation of the samples for study by SEM is very important. The samples must be dry to enable coating of the surface with a heavy metal (usually a 60:40 mix of goldpalladium). Gelatinized or partially gelatinized starch samples have been prepared in an amylograph (Holmes and Soeldner, 1981; Hill and Dronzak, 1973; Miller et al., 1973; Christianson et al., 1982) or similar instrument, or by gently stirring (100 RPM) in a water bath (Varriano-Marston et al., 1985).

Freeze drying the samples after heat treatment has been used extensively; however, the methods of preparation vary widely. Some authors directly froze the starch pastes in liquid nitrogen (Holmes and Soeldner, 1981; Miller et al. 1973) while others centrifuged the paste and decanted the supernate (Christianson et al., 1982; Varriano-Marston et al., 1985). Christianson et al. (1982) washed these pastes several times to remove minor amounts of exudate.

Freeze-drying methods also vary from freezing inside a round-bottom flask using an ethanol-dry ice bath (Christianson et al., 1982) and freezing in a -20°C freezer, to immersion in liquid nitrogen or liquid isopentane (Varriano-Marston et al., 1985). Varriano-Marston et al. (1985) report that rapid freezing followed by rapid freeze drying caused more damage than slow or rapid freezing and slow freeze drying.

Upon drying, starch granules are then placed on double stick tape and coated with a gold or gold:palladium (60:40) mix to a thickness of 200-300 A. The coated samples are then placed in the SEM and pictures are taken following the manufacturer's instructions.

#### 2.1.4.3.2. Transmission Electron Microscopy (TEM)

While giving higher resolution capabilities, sample preparation for TEM is much more difficult and can yield artifacts resulting in atypical morphologies. This occurs because the granules are not easily infiltrated by the embedding media (Lineback, 1984). Because of these difficulties, partial degradation of the granules using acid or enzymes, staining, or freeze fracturing have been used (Mussulman and Wagoner, 1968; Chabot et al. 1978; French, 1984).

Stains that react specifically with certain components of the granule are called positive stains while those that provide an electron-dense outline of an otherwise electrontransparent object are called negative stains. These stains must be of high electron density and they must be non-crystalline (phosphotungstic acid or uranyl acetate) in order to be usable.

Freeze fracture consists of rapidly freezing the sample in liquid nitrogen and then impact fracturing and evaporation at low temperatures. Coating of freeze fractured samples is done first with carbon and metal. The carbon and metal films are cleaned by destroying the original object by chromic acid.

#### 2.1.4.4. Viscometers

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Gelatinization of starches and effects of different treatments on starch or the presence of various food ingredients (eg. fats, protein, sugar, salt) on gelatinization can be measured by changes in viscosity. The use of the Brabender Viscoamylograph is a traditional method for measuring starch gelatinization. Steffe et al. (1988) have proposed an alternative to the Brabender Viscoamylograph using a Brookfield viscometer with a small sample adapter, mixer paddle, and two water baths. This alternate method gave similar curves compared to the Viscoamylograph but required significantly lower sample sizes and data collections.

Amylograph procedures are described extensively in the Amylograph Handbook (Shuey and Tipples, 1980). Briefly, the amylograph measures the torque required to balance the viscosity that is developed when a starch slurry is exposed to a programmed heating and cooling cycle. Depending on the type of starch, a known weight (eg. 40 g wheat, 15 g potato) is added to 500 ml of water and placed in the amylograph.

The slurry is equilibrated to 50°C and then the heating cycle is started. The sample is heated at 1.5°C/min to 95°C, held at 95°C for 1 hour and then cooled at 1.5°C/min to 50°C. From this curve, the gelatinization temperature, pasting (i.e. maximum viscosity) peaks, ability to withstand shear (shear thinning) and extent of setback or gel formation upon cooling can be quantified. Addition of carboxymethylcellulose to the starch slurry permits detection of initial gelatinization temperatures which are difficult to see in some starch slurries.

Viscosity of starch pastes using standard concentric cylinder, cone and plate, and parallel plate geometries have been reported by DeKee et al. (1980), Christianson and Bagley (1983), Christianson and Bagley (1984), Evans and Haisman (1979) and many others. Generally, the starches are gelatinized in other apparatus and placed in the viscometer to measure the viscosity.

#### **2.1.4.5.** Thermal Analysis

Use of thermal analysis to study gelatinization has become increasingly popular in the last ten years, primarily because small sample sizes are required and gelatinization temperatures and enthalpies of transition can be determined easily.

#### **2.1.4.5.1.** Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) has been used by numerous authors to study the effects of moisture levels, protein content, salt (NaCl) content, sucrose content, and lipids or surfactants on gelatinization (Eliasson, 1983; Lund, 1983; Lelievre, 1976; Donovan, 1979; Nakazawa et al., 1984; Wootton and Bamunuarachchi, 1979a; Stevens and Elton, 1971; Biliaderis et al. 1980; Wootton and Bamunuarachchi, 1979b; Sweat et al., 1984; Eliasson, 1980; Biliaderis et al., 1986; Evans and Haisman, 1982; Ghiasi et al., 1982b; Spies and Hoseney, 1982; Kugimiya et al., 1980; Harbitz, 1983; Colonna and Mercier, 1985; Hoseney, 1984).

Approximately 20 mg of a starch-water solution is placed in a tared DSC pan. The starch may be input dry and water added with a syringe, or a starch slurry may be used. The pans are then hermetically sealed and equilibration is allowed to occur, usually over one hour. A DSC scan is then performed using an empty pan as reference at the rate of 10°C per min from 20°C to a maximum of 150°C. Temperatures greater than 150°C require a pressurized system because of the possibility of pan failure. Once the endotherm is obtained, the peak corresponding to gelatinization (50-85°C) is then integrated to give the enthalpy of the transition.

# **2.1.4.5.2.** Thermal Mechanical Analysis (TMA)

Thermal mechanical analysis (TMA) measures the volume expansion of materials as they are heated at a certain rate. Biliarderis et al. (1986) used TMA to examine the expansion of 50% starch-water mixtures. Two hundred and fifty milligrams of rice starch were firmly packed in the TMA's quartz cell and covered with a thin layer of sandparaffin oil (5:1, w/w) and placed in the TMA. A heating rate of 2°C per min was used over a temperature range of 25 to 97°C. Weight loss due to evaporation of water and normalization to a standard weight were then performed using the TMA's software. TMA indicated a two-stage swelling pattern, the first associated with the onset of gelatinization, the second with the melting of starch crystals.

#### 2.1.4.6. Others

Other important, but relatively minor methods (in terms of use) have also been used to measure starch gelatinization. These include X- ray diffraction, Nuclear magnetic resonance (NMR), and enzyme digestibility. X-ray diffraction and NMR are used infrequently because of the cost of equipment and difficulty of use. Enzyme digestibility can be used to quantify starch gelatinization, but it gives little information about the exact structural and physical changes occurring.

#### 2.1.4.6.1. Enzyme

Chiang and Johnson (1977a, 1977b) report a method used to quantify the amount of gelatinized starch in flour or starch containing foods. Based on the fact that digestion of starch is easily performed by the enzyme glucoamylase to form glucose, this method uses spectrophotometric methods to determine the total and gelatinized starch.

The method is as follows: 1) disperse 20 mg of the sample in a 50 ml centrifuge tube and 3-5 ml water, 2) add 25 ml of glucoamylase solution and incubate 30 minutes at 40°C, 3) add 2 ml of 25% trichloracetic acid to inactivate the enzyme and precipitate proteins, 4) centrifuge for 5 minutes (16000 X g's), 5) place 0.5 ml in test tubes containing 4.5 ml 0-toluidine reagent, 6) boil for 10 minutes then cool, 7) add 5 ml of glacial acetic acid and measure absorbance at 630 nm. Other methods are reported by Zobel (1984) and will not be discussed here.

#### **2.1.4.6.2.** X-ray diffraction

X-ray diffraction was first used by Katz (1928) to measure changes of starch from native to gelatinized to retrograded forms. Hellman et al. (1954) and Yang et al. (1985)
have also used X-ray diffraction to measure changes in the starch granules. By exposing starch granules and starch gels to X-rays, the researcher can determine the crystalline structure of the material. Yang et al. (1985) used small angle X-ray scattering to measure changes in birefringence of starch granules during heating, cooling and storage. French (1984) also lists many researchers who utilized X-ray diffraction and their findings about the native starch granules.

# 2.1.4.6.3. Nuclear Magnetic Resonance

Nuclear magnetic resonance (NMR) measures starch gelatinization at a molecular level using either high-resolution or wide-line proton magnetic techniques. Jaska (1971) followed the hydration and solubilization of starches using wide-line techniques. Lelievre (1975) used pulsed NMR to measure water mobility during gelatinization. It was determined that mobility decreased as hydration of the starch occurred at the onset of gelatinization, and as heating progressed beyond gelatinization temperatures, the starch chain mobility increased. Both of these studies suggest that gelatinization is a melting process. Actual procedures depend upon the equipment being used.

#### 2.2. Rheology

# 2.2.1. Introduction

Rheology is the study of deformation and flow of matter (New American Heritage Dictionary, 1982). Measurement of rheological properties for food products is important because they can be used to describe basic physical properties of the food material, therefore eliminating subjective terms such as gumminess or crunchiness, and enabling better process and quality control. Szczesniak (1987) stresses that the measurement of rheological properties should be performed in an instrument where the nature and magnitude of the acting forces and the sample dimensions are well known, and the results can be expressed in fundamental units.

#### **2.2.2. Models For Rheological Modelling of Food**

In an ideal system, there would be just two types of materials: solids and liquids. The solids would follow Hooke's law when stress is applied, and liquids would follow Newton's law of constant viscosity. However, many food materials exhibit properties of both solids and liquids, making it difficult to measure rheological properties of foods. Foods can be either viscoelastic solids, elastico-viscous (elastic) liquids or inelastic fluids.

Walters (1975) defines viscoelastic solids as materials that do not continually change their shape when subjected to stresses, and elastic liquids as those which change their shape continually when subjected to stress, irrespective of how small the stress may be. Prentice (1984) expands Walters' (1975) definitions by defining viscoelastic foods as those which behave as if they had a solid structure (i.e. elastic), but whose deformation is modified by viscous behavior; and elastico-viscous foods as those which show some kind of elastic behavior (such as recoil) when flow ceases. There are many models used to describe viscosity of fluid and semi-fluid foods. The simplest model which describes viscosity is Newton's law (Table 2.2.1). However, there are very few foods which exhibit Newtonian behavior (among them fluid milk, and dilute corn syrup solutions); therefore more complex models are necessary.

Common rheological models which are used to describe viscosity of fluid foods are the power law or Ostwald-de Waele (Reiner, 1949), Casson (Casson, 1959), Bingham (Bingham, 1922) and Herschel-Bulkley (Herschel and Bulkley, 1926). Of these, the model that is most widely used is the power law model because of its simplicity and ease of parameter estimation. Simple log-log transformation of shear stress and shear rate data allows one to estimate the parameters via linear regression provided a value for yield stress is given. The power law model has some drawbacks, however. First, as shear rate increases towards infinity, viscosity approaches a value of zero. A second drawback is that as shear rate approaches zero the viscosity becomes infinite. However, within these limitations the power law has been found to adequately describe many food products.

Food products may exhibit a yield stress. Yield stress is defined as the minimum stress that must be applied to initiate flow. Barnes and Walters (1985) recently questioned if there was a yield stress or whether it is the inability of the instrumentation to measure flow. However, over the short time frame a producer or consumer is concerned with, many foods do exhibit a yield stress (eg. Mayonnaise, ketchup, molten chocolate).

The simplest model which includes a yield stress is the Bingham model (Bingham, 1922). This model assumes that once the yield stress has been exceeded, normal Newtonian behavior occurs. Butter and margarine are examples of Bingham foods, but in general the Bingham model is of little use because very few foods behave this simply.

Table 2.2.1 Rheological models and their parameters used to characterize fluid food behavior (Ofoli et al., 1987).				
Model	Shear Stress	Apparent viscosity		
Newtonian	$\sigma = \mu$	η = μ		
Power law	$\sigma = K \dot{\gamma}^*$	$\eta = K \dot{\gamma}^{n-1}$		
Bingham Plastic	$\sigma = \sigma_o + \mu_o$	$\eta = \sigma_o \dot{\gamma}^{-1} + \mu_o$		
Herschel- Bulkley	$\sigma = \sigma_o + K \gamma^*$	$\eta = \frac{\sigma_o}{\dot{\gamma}} + K \gamma^{n-1}$		
Casson	$\sigma^{0.5} = \sigma_o^{0.5} + (\mu_{-}\dot{\gamma})^{0.5}$	$\eta = \left[ \left[ \frac{\sigma_o}{\dot{\gamma}} \right]^{0.5} + \mu_{-}^{0.5} \right]^2$		
Mizrahi- Berk	$\sigma^{0.5} = K_o M + K_c \dot{\gamma}^n$	$\eta = \left[K_o M \dot{\gamma}^{-0.5} K_c \dot{\gamma}^{n-0.5}\right]^2$		
Heinz- Casson	$\sigma^{a} = \sigma^{a}_{o} + (\mu_{o}\dot{\gamma})^{a}$	$\eta = \left[ \left[ \frac{\sigma_o}{\dot{\gamma}} \right]^a + \mu_o^a \right]^{\frac{1}{a}}$		
Öfoli	$\sigma^{n_1} = \sigma_o^{n_1} + \mu_{\omega} \dot{\gamma}^{n_2}$	$\eta = \left[ \left[ \frac{\sigma_o}{\dot{\gamma}} \right]^{n_1} + \mu_{\infty} \dot{\gamma}^{n_2 - n_1} \right]^{\frac{1}{n_1}}$		

The Herschel-Bulkley (Herschel and Bulkley, 1926) model is used with a wide range of food products. The model is a generalized power law model, with a yield stress added. The same drawbacks that are observed with the power law model at high shear rates are also seen with the Herschel-Bulkley model.

Measurement of the value of the yield stress generally presents difficulties. The most common method is to extend shear stress versus shear rate curves to zero shear rate. Another method is to estimate the value of the yield stress, utilizing some form of curve fitting computer program. Osorio and Steffe (1985) have proposed a back extrusion method to quantify the yield stress for fluid foods. Given the limitations, the Herschel-Bulkley model is useful in determining rheological properties of the food material.

Another model which has found wide use in the confectionery chocolate industry is the Casson model (Casson, 1959). Casson developed the model for use with pigment suspensions. It is important to note that the drawbacks seen with other models (zero viscosity at infinite shear rates, and infinite viscosity at zero shear rates) do not apply to the Casson model. However, due to the fixed exponent of all the terms, the equation may not accurately describe all sections of the shear stress versus shear rate curve. Another modification of the Casson model is the Mizrahi-Berk model (Mizrahi and Berk, 1972).

Ofoli et al. (1987) have proposed another model which allows for a yield stress, variable shear-thinning and limiting viscosity at high shear rates. Disadvantages are the mathematical complexity of the model and the difficulty in obtaining model parameters without sophisticated computer programs.

#### **2.3. Extrusion**

#### **2.3.1. Introduction**

Ram or piston type extruders were used to stuff sausage casing and other processed meats early in the history of food processing. An early application of the single screw extruder was as a continuous pasta press in the 1930's (Harper, 1981). Single screw extruders were developed in the 1940's for the purpose of making puffed snacks from cereal flours or grits (Harper, 1986). By the late 1950's, extrusion cooked pet food had replaced other methods of production (Harper, 1981). In the 1960's, ready to eat (RTE) breakfast cereals and textured soy protein products were being produced in cooking extruders (Harper, 1981).

Reasons for the increased use of cooking extruders are listed below and discussed in detail by Harper (1981):

1. Versatility: many foods can be produced with the same or similar equipment.

2. High productivity: extruders provide a continuous processing system, having greater production capacity.

3. Low cost: labor and floor space requirements are reduced.

4. Product shapes: a wide variety of shapes are available which are not possible with other production methods.

5. High product quality: cooking extrusion is basically a high temperature short time process.

6. Energy efficient: extruders operate at lower moisture contents, reducing heat requirements for drying.

7. Production of new foods: modification of proteins, starches and other food materials can be achieved in extruders to produce new food products.

8. Low effluents: little or no waste is produced, therefore costly waste treatment is avoided.

Two types of extruders are used by the food industry today. The one that has been

in use the longest is the single screw extruder. In the last few years, twin screw extruders

have been used increasingly in the food industry. While single screw extruders have the ability to manufacture a wide range of food products (eg. breakfast cereals, pet foods, puffed snacks, etc.), use of twin screw machines is increasing because of their expanded range of applications and operational capabilities (Harper, 1986).

Single screw extruders consist of a flighted screw rotating in a closely fitting barrel. The barrel is usually equipped with heating/cooling jackets in order to add or remove heat to the product as it passes through the extruder. The raw material is fed into the screw and as the material is conveyed through the transition section, the screw flights and barrel wall work and mix the material. Through viscous energy dissipation, the food material is heated and cooked. In the metering section of the extruder, pressure is built up before the material exits the die(s).

The screw is a single piece with varying compression ratios and pitches, or a splined shaft which allows screw elements of differing configurations to be used (Harper, 1986). The splined shaft design allows for more flexibility in terms of maintenance and product variation. Single screw extruders often require pre-conditioners or pre-mix equipment to mix the dry and liquid ingredients and allow an equilibrium to be reached before feeding the material into the extruder.

Twin screw extruders, as their name implies, consist of two screws inside a barrel which can be heated or cooled. There are two types: co-rotating or counter rotating. The co-rotating type is the most widely used by the food industry. The screws feature many geometries and can be used in any number of configurations. Unlike single screw extruder elements, the screws and paddles are self-wiping; therefore, there is less build-up of material. The high degree of mixing in twin screw extruders make them well suited for use as heat exchangers for highly viscous food materials (Harper, 1986).

Twin screw extruders have a higher initial cost than single screw extruders. The overall operating costs may be less, however, due to lower floor space requirements, little or no need for premixing equipment, ability to run at lower moisture contents (lower post-process drying requirements), and greater flexibility in types of products made. These factors give twin screw extruders an advantage over single screw extruders.

# **2.3.2.** Viscosity Models Used in Extrusion

Several rheological models for extrusion of flour or protein doughs have been reported in the literature. One of the earliest rheological models was by Harper et al. (1971), who modeled the viscosity as a function of inverse temperature, moisture, and shear rate as described by the power law model.

Bhattacharya and Hanna (1986a) proposed an empirical model derived statistically for corn gluten meal and soy protein concentrates. Dough viscosity was modeled as a function of moisture content and shear rate; temperature, time-temperature history and strain history were not incorporated. Therefore, the model is machine-and ingredientspecific and of limited general use. Effects of moisture content, barrel temperature, shear rate, residence time and shear strain on extrusion cooked waxy and non-waxy corn grits were studied by Bhattacharya and Hanna (1986b), who presented statistical models which indicated that moisture content and temperature are the most significant variables. However, the authors stated that higher moistures reduce the degree of gelatinization, in contrast to research results of several starch chemists studying starch gelatinization (Donovan, 1979; Eliasson, 1980; Biliarderis et al., 1986).

The reduction in degree of gelatinization as moisture content increases is also in conflict with research by Chiang and Johnson (1977a) and Owusu-Ansah et al., (1983) both of which indicate that degree of gelatinization increases with moisture content. This illustrates a problem with relying on statistical models for predicting viscosity changes in extrusion. Bhattacharya and Hanna (1986b) did not include strain or time-temperature history in their model.

Jao et al. (1978) and Cervone and Harper (1978) also developed empirical models incorporating moisture content, temperature and shear rate, but time-temperature and shear history effects were not considered.

Two models which included time-temperature history have been proposed by Remsen and Clark (1978) and Morgan et al. (1988). The model proposed by Remsen and Clark (1978) included parameters for moisture content, shear rate and time-temperature history. Remsen and Clark (1978) did not study time-temperature history at low to intermediate moisture concentrations, but assumed that relative increases in viscosity due to cooking were the same as for suspensions containing 70-75% moisture. Their model also exponentially approaches infinity for large time-temperature histories.

This is in contrast to Morgan et al. (1988) who provided experimental data indicating that protein dough viscosities approach some finite maximum value for timetemperature histories and shear rates encountered in extrusion. The model by Morgan et al. (1988) includes time-temperature history as well as shear rate, moisture content, and temperature. Janssen (1986) incorporates shear rate, temperature and time-temperature history in a model utilizing the power law relationship. However, moisture content and strain history were not incorporated.

#### **CHAPTER 3 MODEL DEVELOPMENT**

#### **3.1. Effect of Shear Rate on Viscosity**

Many of the studies discussed previously use the power law model to characterize shear rate affects on the viscosity (Bhattacharya and Hanna 1986; Janssen 1986; Cervone and Harper 1978; Jao et al. 1978; and Remsen and Clark, 1978). While data shows good fit using the power law equation, the model itself has several drawbacks. The most important one is that it does not accommodate a yield stress. Other serious drawbacks are that it predicts unlimited decreasing apparent viscosity with increasing shear rate, and for a given shear thinning index it predicts zero or infinite viscosities at zero and infinite shear rates, respectively.

Barnes and Walters (1985) contend that there is no such thing as a yield stress. Theoretically this may be true, but relative to the process time of most extrusion operations, dough does not flow unless some minimum force is applied. Therefore, a yield stress may be defined as a material property in terms of the relative time frame of the process system involved. For example, cookie dough does not flatten out when put on a table before other quality parameters such as microbial acceptability are exceeded.

Luxenburg et al. (1985) modeled soy doughs using Bingham plastic and Herschel-Bulkley models with good results. The Bingham plastic model does not allow for variable shear thinning index, and the Herschel-Bulkley model has a variable shear thinning index but approaches zero viscosity for large shear rates. This may present problems since shear rates encountered in extrusion may span 3 to 4 decades. Morgan et al. (1988) used the Casson model to characterize soy protein doughs extruded in a capillary rheometer. The Casson model worked well, but it does not allow for a variable shear thinning index. Ofoli et al. (1987) have proposed a generalized rheological model for the characterization of inelastic fluid foods. The model incorporates a variable shear thinning index, yield stress, and high shear limiting viscosity:

$$\eta = \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right]^{n_1} + \mu_{n_2} \dot{\gamma}^{n_2 - n_1} \right]^{\frac{1}{n_1}}$$
[3.1]

Advantages of this model are that it incorporates a yield stress, variable shear thinning indices and high-shear limiting viscosity. Equation [3.1] is the model used in this study to quantify shear rate effects.

#### **3.2.** Effect of Temperature

Viscosity of Newtonian and non-Newtonian fluids are usually affected by temperature. In general, as temperature increases, viscosity decreases. The relationship between viscosity and temperature can be represented by the equation of Glasstone et al. (1941):

$$\eta_T = \eta_{\gamma} e^{\frac{\Delta E_{\gamma}}{R} \left(T^{-1} - T_{\gamma}^{-1}\right)}$$
[3.2]

where  $\Delta E_{\nu}$  is defined as the molar "free energy of activation" in a stationary fluid (Bird et al. 1960). The free energy of activation ( $\Delta E_{\nu}$ ) is related to the amount of energy required for a molecule to escape its surroundings and move into an adjoining molecular site. Morgan et al. (1988) proposed that a shear rate dependency (such as shown in Eq. 3.1) could be combined with Eq. 3.2, if Metzner's (1959) assumption that the shear thinning index is not affected by temperature is applied. In addition, one must assume that n<sub>2</sub> is not affected by temperature. The combined equation is

$$\eta_{\dot{\gamma},T} = \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right]^{a_1} + \mu_{a_1} \dot{\gamma}^{a_2 - a_1} \right]^{\frac{1}{a_1}} e^{\frac{\Delta s_v}{\pi} \left( T^{-1} - T_r^{-1} \right)}$$
[3.3]

#### **3.3. Effect of Moisture**

The effect of moisture content on viscosity has been described using a logarithmic mixing rule (Cervone and Harper, 1978; Harper et al., 1971; and Morgan et al., 1979). The logarithmic model is given by

$$\eta_{MC} = \eta_{\gamma} e^{b(MC - MC_{\gamma})}$$
[3.4]

Morgan et al. (1988) combined Eqs. 3.3 and 3.4 to give a relationship which combines shear rate, temperature and moisture content effects on apparent viscosity:

$$\eta_{\dot{\gamma},T,MC} = \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right]^{n_1} + \mu_{\infty} \dot{\gamma}^{2-n_1} \right]^{\frac{1}{n_1}} e^{\frac{\Delta K_v}{R} \left( T^{-1} - T_r^{-1} \right) + b(MC - MC_r)}$$
[3.5]

# **3.4. Effect of Time-Temperature History**

When starch and water are heated together, an increase in viscosity can be observed on an amylograph (Shuey and Tipples, 1980). The extent of this increase depends on the temperature and the time of exposure of the starch granule to that temperature. If starch granules are exposed to temperatures below the temperature required for gelatinization to start, no change in viscosity is seen until the threshold temperature is exceeded. Therefore incorporation of time-temperature history requires use of an activation or threshold temperature.

Increases in viscosity of dilute starch solutions is attributed to the starch granule taking up water and a concurrent swelling of the granule (Hoseney, 1986). As the granule swells, starch molecules are leached out causing further increases in viscosity. Gomez and Aguilera (1984) found that this classic gelatinization model of granule swelling and release of starch polymers was inadequate for high-shear extrusion cooking. This was based on a previous work (Gomez and Aguilera, 1983) which found that, as extrusion moisture content decreased, "dextrinization" (i.e. shortening of polymer chains due to mechanical breakdown) appeared to become the predominant mechanism of starch degradation. They proposed a model that assumes the coexistence of three pure states: raw, gelatinized and dextrinized starch. In theory, the actual state of degradation is the sequence:

 $raw \rightarrow gelatinized \rightarrow dextrinized.$ 

A more complex model includes intermediate states of mechanically damaged granules, free polymers, and oligosaccharides and sugars. Different states are due to time-temperature history and shear-strain history in the extruder.

When gelatinization of starch is measured by differential scanning calorimetry (DSC) under low moisture conditions, two endotherms are observed. When excess water is present, the DSC curve shows only one endotherm indicating that water content directly affects gelatinization kinetics.

Various models have been proposed for this phenomenon. Donovan (1979) suggests that, upon hydration and swelling of the amorphous portions of the granule and due to coupling with crystallites, melting of the latter occurs as long as water is present in excess. He postulated that when the amount of water is insufficient for complete melting the remaining crystallites melt at a higher temperature and thus support the second DSC peak.

Another hypothesis for starch gelatinization at low to intermediate moisture contents is given by Evans and Haisman (1982). They proposed that two endothermic peaks reflected two types of melting: granules containing less stable crystallinity melt first, and, upon melting, the polysaccharride chains absorb more water, making less water available for the remaining ungelatinized granules thus causing these granules to melt at higher temperatures.

Biliaderis et al. (1986) have proposed a third explanation for starch gelatinization under low to intermediate moisture conditions. They provided evidence showing that the DSC curve is not representative of the initial crystallite profile, but rather the composite thermal effect of several processes that occur simultaneously during heating: melting, annealing and crystallization. They proposed that the order-disorder phase transitions of starch-water mixes are analogous to those of semicrystalline synthetic polymers. The thermomechanical properties of starch polymers can be altered by the presence of small amounts of water as a plasticizer. In the presence of a plasticizer, the glass transition temperatures of the granule's amorphous portion are decreased which in turn facilitates melting or reorganization of the starch crystallite and the amylose-lipid complexes at lower temperatures.

In this study, it is assumed that starch granules are analogous to semicrystalline synthetic polymers, as proposed by Biliaderis et al. (1986). Completely crystalline polymers follow first order kinetics for melting while purely glassy polymers follow secondorder kinetics. A pseudo-first order kinetic model will be used in this study for time-temperature effects of starch gelatinization on the apparent viscosity. Harper et al. (1978) and Morgan et al. (1979) used this approach with heat setting bovine plasma protein suspensions and soy doughs, respectively.

Pseudo first order polymerization assumes that concentration of one reactive species will remain constant and predicts disappearance of the monomer species. Starch gelatinization is a much more complex reaction than first order; however, this simplification is used to approximate the "average-overall-viscosity" effect caused by gelatinization. Further development of this model is based on Gomez and Aguilera's (1984) proposed

model. They assumed that increases in viscosity are due to the swelling granule and/or leaching of starch polymers outside the granule. This swelling and leaching is assumed to be similar to the viscosity increases caused by an increase in the "effective polymer molecular weight" during a plastic polymerization process (Morgan et al., 1988).

Development of a time-temperature history function based on pseudo first order plastic polymerization processes was done by Morgan et al. (1988) for protein based doughs. Modification of this function for starch based doughs yields an equation for the effects of time-temperature history on viscosity due to gelatinization:

$$\eta_G = \beta_o (Cs)^{\alpha} \left( 1 - e^{k_l} \right)^{\alpha}$$
[3.6]

Morgan et al. (1988) assumed that viscosity of a denaturing protein dough could be described by

$$\eta = \eta_{\eta_{T,MC}} + \eta_{G}$$

$$[3.7]$$

Where  $\eta_{\eta,T,MC}$  represents the undenatured viscosity and  $\eta_G$  represents the increase in viscosity due to gelatinization of the starch granules.

Use of Eq. 3.6 is only valid at constant temperature. In extrusion, the temperature will increase to a maximum with time and may decrease before exiting the die. Therefore, there is a need to incorporate variable time-temperature histories into Eq. 3.6. Morgan et al. (1979) proposed the use of an integrated time-temperature history,  $\psi$ , defined by

$$\Psi = \int_0^t T(t) e^{\frac{\Delta t}{kT}(t)} dt$$
[3.8]

when T(t) is greater than the threshold temperature. Equation 3.8 is then related to Eq. 3.6 by

$$k_t = k_a \psi \tag{3.9}$$

where  $k_s = (k_k k_b/h)$  and represents a reaction transmission coefficient for the material source,  $k_b = Boltzman's$  constant,  $k_t = transmission$  coefficient, and h = Planck's constant. Combining Eqs. 3.6 and 3.9 yields

$$\eta_G = \beta_o (Cs)^{\alpha} \left( 1 - e^{-t_a \psi} \right)^{\alpha}$$
[3.10]

which relates the change in viscosity to time-temperature history.

Morgan et al. (1988) assumed that if the protein dough is held long enough at various temperatures, each treatment will approach the same viscosity. Kubota et al. (1979) studied the gelatinization rate of rice and potato starches and found the maximum viscosity to be a function of time. Similar results were found by Bakshi and Singh (1980) for gelatinization in rice kernels. Using differential scanning calorimetry (DSC) Lund and Wirakartusumah (1984) developed a model for starch gelatinization. Comparison of enthalpy values versus cook time at different temperatures gave results similar to both Bakshi and Singh (1980) and Kubota et al. (1979). Kubota et al. (1979), Bakshi and Singh (1980) and Lund and Wirakartusumah (1984) worked with high moisture systems.

Dolan et al. (1988) found that viscosities collected at different time-temperature histories could be normalized by

$$\eta_n = \frac{\eta - \eta_o}{\eta_n - \eta_o}$$
[3.11]

It is important to note that all viscosities are specific to the cook temperature after either correction or normalization to the same temperature. In other words, the infinite viscosity term is the viscosity after infinite time at one cook temperature; if the cook temperature is changed, then a different infinite viscosity must be used. Dolan et al. (1988) also worked under high moisture (about 90%) conditions. Dolan et al. (1988) stated that the change in viscosity caused by gelatinization is described by

$$\eta_G = A \left( 1 - e^{-k_s \Psi} \right)^{\alpha}$$
[3.12]

Combining Eqs. 3.7 and 3.12 gives:

$$\eta_{\psi} = \eta_{\dot{\gamma}, T, MC} \left[ 1 + A \left( 1 - e^{-k_{x} \psi} \right)^{\alpha} \right]$$
[3.13]

if  $\psi \rightarrow \infty$  then Eq. 3.13 becomes:

$$\eta_{\bullet} = \eta_{\dot{\eta}_{T,MC}}[1+A]$$

$$[3.14]$$

and therefore A becomes:

$$A = \frac{\eta_{m}}{\eta_{\eta, \tau, MC}} - 1$$
[3.15]

By combining Eqs. [3.5], and [3.13] we get a model that incorporates temperature, shear rate, moisture content, and time-temperature history:

$$\eta_{\dot{\gamma},T,MC,\Psi} = \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right]^{a_1} + \mu_{\omega} \dot{\gamma}^{a_2 - a_1} \right]^{\frac{1}{a_1}} e^{\frac{\Delta s}{R} \left( T^{-1} - T_r^{-1} \right) + b(MC - MC_r)} \left[ 1 + A \left( 1 - e^{-t_a \Psi} \right)^{\alpha} \right]$$
[3.16]

#### **3.5. Effect of Strain History**

With increasing time of shear, the viscosity of dispersed starch solutions decreases. As starch granules swell they become more susceptible to mechanical degradation. There is much evidence that there is degradation of the starch granule during extrusion (Mercier, 1977; Colonna et al., 1984; Gomez and Aguilera, 1983; Gomez and Aguilera, 1984; Davidson et al., 1984; Diosady et al., 1985; Doublier et al., 1986). In each case the products of starch breakdown have been measured. Two different models for mechanical degradation of wheat starch have been proposed by Davidson et al. (1984) and Diosady (1985). A serious drawback to both models is that they require the measurement of the extent of starch degradation by gel permeation chromatography (Davidson et al., 1984) or the degree of cook (Diosady, 1985). Another drawback is that both techniques measure degradation and do not allow for predicting what the degradation may be. What is needed is an equation that can be used regardless of system geometries, conditions and raw materials.

Pinto and Tadmor (1970) have proposed the following for quantifying total strainhistory effects on transport properties of polymers:

$$\phi = \int_0^t \dot{\gamma} f(t) dt$$
[3.17]

Morgan et al. (1988) proposed a similar model :

$$\phi = \int_0^t \tilde{\gamma} dt$$
 [3.18]

Viscosity will decrease as the value of  $\phi$  increases until a finite limiting viscosity is obtained. The value of the finite limiting viscosity depends on both the shear rates obtained within the extruder and the length of time at each shear rate.

An equation describing strain history effects on viscosity was proposed by Morgan et al. (1988) and is given by

$$\eta = 1 - \beta (1 - e^{-d\phi}) \tag{3.19}$$

When this equation is incorporated into Eq 3.16, the final equation now incorporates shear rate, temperature, moisture content, time-temperature history, and strain history:

$$\eta_{\dot{\gamma},T,MC,\psi,\phi} = \left[ \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right]_1^n + \mu_{\omega} \dot{\gamma}^{2-n_1} \right]^{\frac{1}{n_1}} e^{\frac{\Delta s}{\pi} \left( T^{-1} - T_r^{-1} \right) + b(MC - MC_r)} \right] \\ \left[ 1 + A \left( 1 - e^{-t_a \psi} \right)^{\alpha} \right] \left[ 1 - \beta (1 - e^{-d\phi}) \right]$$

$$[3.20]$$

There are two important differences between Eq. [3.20] and the one proposed by Morgan et al. (1988): 1) the time-temperature history term has been modified to reflect the differences between protein denaturation and starch gelatinization; and 2) the generalized Casson model was replaced with the model proposed by Ofoli et al. (1987) for describing shear rate effects. Table 3.1 lists the individual terms of the model.

Limitations of the model include:

1. Difficulty in obtaining a yield stress value and the lack of an adequate nonlinear regression computer program to determine the power indices and high shear limiting viscosity for the shear rate term.

2. The order in which one determines the moisture content and temperature effects on viscosity may yield different values for the respective parameters.

3. Determination of the moisture content and temperature effects above gelatinization temperatures may yield different numerical values than if quantified below gelatinization temperatures.

4. Evaluation of time-temperature history parameters is difficult if the heat transfer through the material is rapid; yet, this must be accomplished to allow comparison of data collected at different cook times and cook temperatures.

5. Strain history parameters may be functions of time-temperature history as well as shear rate and time.

Table 3.1. Model parameters and what they describe.				
Shear rate effects	$\eta = \left[ \left[ \frac{\tau_o}{\tau_o} \right]^{a_1} + \mu \dot{\gamma}^{a_2 - a_1} \right]^{\frac{1}{a_1}}$			
	· Щγ]·~··]			
Temperature effects	$e^{\frac{\Delta E_{v}}{R}\left(T^{-1}-T_{r}^{-1}\right)}$			
Moisture content effects	e (MC - MC,)			
Time-temperature history effects	$\left[1+A\left(1-e^{-k_a\psi}\right)^{\alpha}\right]$			
Strain history effects	$[\beta(1-e^{-d\phi})]$			

# 3.6. A procedure for determining the parameters in Eq.[3.20].

Choose a reference temperature (below the gelatinization temperature) and moisture content and then collect shear stress versus shear rate data to obtain a relationship to describe the effects of shear rate on viscosity. Next, vary the temperature (again below gelatinization temperature) and hold the shear rate and moisture content constant to obtain the effects of temperature on viscosity.

Vary moisture content at a temperature below the gelatinization temperature and quantify the effects of moisture on viscosity. Now vary both cook time and cook temperature and measure the effects of time-temperature history on viscosity. Finally, vary the strain history and quantify the effects of strain history on viscosity. A flow chart for determining the model parameters is shown in Table 3.2. Table 3.2. Flow chart for determining model dependencies.

Shear rate dependency				
Hold T=Tr, MC=MC <sub>r</sub> , $\psi$ =0 and $\phi$ =0. Collect viscosity versus shear rate data to determine shear rate effects. Establish $\eta = f(\dot{\gamma})$ See Eq. [3.1]				
Temperature dependency				
Hold at MC=MC; $\psi=0$ ; and $\phi=0$ . Vary temperature and collect viscosity data with $f(\dot{\gamma})$ given by [3.1]; Establish $\eta = f(\dot{\gamma}, T)$ See Eq. [3.3]				
Moisture dependency				
Hold $\psi=0$ and $\phi=0$ . Vary moisture and collect viscosity data with $f(\dot{\gamma}, T)$ given by [3.3] Establish $\eta = f(\dot{\gamma}, T, MC)$ See Eq. [3.5]				
Time-temperature history dependency				
Vary cook time and temperature and collect viscosity data with $f(\dot{\gamma}, T, MC)$ given by [3.5] and $\phi=0$ . Establish $\eta = f(\dot{\gamma}, T, MC, \psi)$ See Eq. [3.16]				
Strain history dependency				
Vary strain history and collect viscosity with $f(\dot{\gamma}, T, MC, \psi)$ given by [3.16] Establish $\eta = f(\dot{\gamma}, T, MC, \psi, \phi)$ See Eq. [3.20]				

# CHAPTER 4 EXTRUSION MODELLING OF PREGELATINIZED POTATO FLOUR

#### 4.1. Abstract

A generalized model is proposed for predicting the effects of shear rate, temperature, moisture content, time-temperature history and strain history on the apparent viscosity of low to intermediate moisture starch-based doughs during cooking extrusion. The model was evaluated for potato flour doughs using an Instron Capillary Rheometer and a 50 mm APV Baker co-rotating twin screw extruder for all effects except strain history. The power law model adequately described shear rate effects in the range 10-10000 sec<sup>-1</sup>. The generalized model fit observed data for temperatures of 25-95°C and moisture contents (wet basis) ranging from 22 to 50%. Time-temperature history variables were not quantified because the potato flour was pregelatinized. Strain history had no significant influence on the viscosity.

### 4.2. Introduction

The predominant ingredient in most extruded snacks and ready to eat (RTE) cereals is starch (Harper, 1986). During cooking extrusion, starch granules undergo many changes leading to increased molecular rearrangement, including loss of crystallinity, degradation and formation of amylose lipid complexes. Changes in the starch granule during gelatinization may significantly affect viscosity. Therefore, the role of temperature, moisture, shear, and feed ingredient composition are important factors involved in changing starch structure during cooking extrusion (Harper, 1986).

Commercialization of extrusion processes is significantly constrained by lack of adequate scale-up information. Two important elements needed for improving food extrusion scale-up and design are effective process engineering analysis methods, and adequate rheological models. Currently, there is no single rheological model which incorporates starch gelatinization, viscoelastic behavior, density and thermal properties as functions of time, temperature, shear rate, and moisture content (Harper, 1986).

Several extrusion models for flour and protein doughs have been reported in the literature (Bhattacharya and Hanna, 1986; Cervone and Harper, 1978; Janssen, 1986; Jao et al., 1978; Remsen and Clark, 1978). However, only the model proposed by Remsen and Clark (1978) incorporates effects of temperature, shear rate, time-temperature history and moisture content.

More recently, Morgan et al. (1988) proposed a generalized viscosity model to describe the rheological changes which occur during the cooking extrusion of protein doughs. This work presents the most comprehensive rheological model yet. The mathematical relationship predicts viscosity as a function of temperature-time history, strain history, temperature, shear rate and moisture content.

Dolan et al. (1988) used the model by Morgan et al. (1988) as the basis for predicting changes in starch viscosity during the gelatinization of high moisture starch solutions. The model was found to predict changes in viscosity due to different time-temperature histories when shear rate, moisture content, temperature and strain history are held constant. While the changes that occur in the starch granule are different for high moisture systems than low moisture systems, it is important to note that time-temperature history is an important factor contributing to viscosity changes in both systems.

The purpose of this study is to extend the work of Morgan et al. (1988) and Dolan et al. (1988) to develop a generalized viscosity model for low to intermediate moisture starch-based foods for use in extrusion. The model will incorporate the effects of timetemperature history, moisture content, temperature, shear-strain history, and shear rate.

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# **4.3. Model Development**

The model presented by Morgan et al. (1988), with some modifications, was used to describe the viscosity of extruded starch based products. The power law model was found to be adequate to describe shear rate effects on the potato flour dough. The effect of time-temperature history on viscosity was modified to account for starch gelatinization kinetics. The resulting expression is

$$\eta = 1 + A \left( 1 - e^{-t_a \Psi} \right)^{\alpha}$$
[4.1]

Incorporating the above changes, the generalized model of Morgan et al. (1988) for extrusion of protein doughs takes the following form for starch-based doughs:

$$\eta_{\dot{\gamma},T,MC,\Psi,\phi} = \left[ e^{\frac{\Delta d_{\Psi}}{a} \left( T^{-1} - T_{r}^{-1} \right) + b(MC - MC_{r})} \right] f(\dot{\gamma}) \left[ 1 + A \left( 1 - e^{-k_{a}\Psi} \right)^{\alpha} \right] \left[ 1 - \beta (1 - e^{-d\phi}) \right]$$

$$[4.2]$$

The first term incorporates the effects of temperature and moisture content on viscosity. It is important to note that  $\Delta E_{\nu}/R$  is not a measure of gelatinization kinetics but rather of how temperature affects the flow of the material. Lubricating effects of water are described by the term b(MC-MC<sub>r</sub>). The f( $\gamma$ ) term represents any apparent shear rate dependent viscosity function (power law, Casson, Herschel-Bulkley, etc.) of the dough at the reference temperature and moisture content and with  $\psi = \phi = 0$ . The next term describes the effects of gelatinization on the final viscosity of the starch dough. Timetemperature history ( $\psi$ ) can range from zero for temperatures below gelatinization temperatures to infinity for either very high temperatures, long exposure time or a combination of the two. Also included are: the energy of activation for gelatinization ( $\Delta E_g$ ) which may be affected by moisture content and  $\alpha$ , an indicator of granule swelling and molecular entanglement. The final term incorporates strain history ( $\phi$ ), which is a measure of the effects of irreversible shear thinning. As strain history increases, the viscosity approaches a finite value  $(\eta_{\omega})$ . If any of the variables is constant, the term that incorporates that variable reduces to unity.

#### 4.4. Materials and Methods

Potato flour (Lamb-Weston, Portland, Oregon) was mixed at room temperature with tap water to 25, 35, and 45% moisture (wb) in a large institutional kitchen mixer. The doughs were allowed to equilibrate at 7°C overnight in Ziploc Bags (Dow Chemical, Indianapolis, Indiana). Final moisture content of the doughs were determined by drying in a vacuum oven overnight at 70°C and 686 mm Hg.

An Instron Capillary Rheometer and a Model 4202 Instron Universal Testing Machine (Instron Corp., Canton, Massachusetts) were used to measure the apparent viscosity of the doughs. Die lengths of 50.8 mm (2 in) and 6.35 mm (1/4 in) and diameters of 0.49 mm (1/8 in) and 1.59 mm (1/16 in) were used, giving L/D values ranging from 2 to 32. Two replicates for each plunger velocity and L/D were performed. Force versus plunger displacement curves were collected and force at the die entrance was calculated by extrapolation of the force versus displacement curves to the die as described by Einhorn and Turetzky (1964). Barrel drag was then subtracted from the corrected force.

A correction for entrance effects was made using the technique described by Bagley (1957). Shear rate and shear stress were then calculated using the Rabinowitsch equation (Whorlow, 1980)

$$\dot{\gamma}_{w} = \frac{3Q}{\pi R_{o}^{3}} + \tau_{w} \left[ \frac{d \frac{Q}{\pi R_{o}^{3}}}{d \tau_{w}} \right]$$
[4.3]

and the standard expression for shear stress at the wall of a capillary:

$$\tau_{w} = \frac{\Delta P R_{o}}{2L}$$
[4.4]

Slip analysis was performed using the method described by Darby (1976).

Temperatures used in this study were 25, 50, 65, and 95°C. At 50 and 65°C, doughs were compressed in the capillary barrel and were held for 10 minutes. Moisture

contents used were 25, 35, and 45%, wet weight basis. Tests were conducted at 50°C for 25% (wb) moisture samples. Cook times of 2, 4, 6 and 12 min at 95°C were performed on 35% (wb) moisture samples after compression. The 45% moisture samples were cooked for 4 and 12 minutes after compression. Effects of temperature ( $\Delta E_v$ ) on viscosity was determined by linear regression of log viscosity versus inverse temperature; the effect of moisture content (b) on viscosity was determined by linear regression of log viscosity was determined by linear regression of log viscosity versus inverse temperature; the effect of moisture content (b) on viscosity was determined by linear regression of log viscosity versus moisture content at constant temperature.

Experimental extrusion tests were conducted using an APV Baker MPF 50D (APV Baker, Inc., Grand Rapids, Michigan) co-rotating twin screw extruder with the screw configuration shown in Table 4.1. Moisture contents were 40 and 50% (wb) and temperatures at the die ranged from 40 to 75°C depending on extruder operating conditions. Feed rates were  $1.26 \times 10^{-1}$ ,  $2.00 \times 10^{-2}$ , and  $8.69 \times 10^{-3}$  kg/s; and screw speeds used were 100, 220, and 350 RPM. Die diameter was  $3.17 \times 10^{-3}$  m and die lengths were  $4.00 \times 10^{-3}$ ,  $1.50 \times 10^{-2}$  and  $2.60 \times 10^{-2}$  m. Pressure drop and extrudate temperature at the die were recorded two minutes after extruder operating conditions had been changed, to allow equilibrium conditions to be attained. Equilibrium conditions were assumed to exist when die pressure and barrel zone temperatures stabilized.

Viscosities of the extrudates were calculated by measuring the pressure drop at the die. Plotting pressure drop versus the three different die L/D's with constant temperature, moisture, and mass flow rate allowed correction for end effects as described by Bagley (1957) for capillary dies. Shear rate was calculated using the Rabinowitsch equation (Whorlow, 1980) and shear stress was calculated using Eq. [4.4] for each die, temperature, moisture and mass flow rate. Temperature and moisture correction on extruder data was performed using  $\Delta E_{\nu}$  and b estimated from the capillary rheometer.

Table 4.1. Screw configurations of MPF-50D/25 APV Baker twin screw extruder.					
Extruder I Screw Conf Length (cm)	L/D:15 iguration ) Screw Type				
17.2 7.6 7.6 5.1 2.5 5.1 6.2 5.1 5.1 12.7 Key to Nota	FS 30F FS 30F 45F FS 30F FS 30F SL ation:	Feed Inlet Extruder die			
FS Fee 30F 30 0 45F 45 0 SL Sing	d Screw legrees Forwarding Paddles legrees Forwarding Paddles gle Lead screw				

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#### 4.5. Results and Discussion

There was apparent slip at some moisture contents, temperatures and shear rates as indicated by the presence of a "shark skin" on the extrudate. Slip analysis was conducted but results were not meaningful. Therefore, no further attempt was made to correct for slip. Inability to correct for slip may be due to a friction coefficient between the wall of the capillary die and the food material which could not be measured. Another cause may be due to a combination of both slip and friction or "slip-stick" where the material sticks until the friction coefficient is exceeded and then slips.

The effect of temperature on viscosity of 0.507 moisture samples is shown in Fig. [4.1]. An Arrhenius relationship was followed over the temperatures covered by these experiments. Over the temperatures encountered during extrusion, a linear relationship between viscosity an inverse temperature is usually observed.

Actual moisture content of the 25, 35, and 45% doughs was determined to be 0.282 (22% wb), 0.507 (33.7% wb), and 0.772 (43.6% wb) g water per g potato flour, respectively. Moisture content effects at 50°C and 100 s<sup>-1</sup> are shown in Fig. 4.2. As illustrated, a simple logarithmic relationship may not be adequate for broad ranges of moisture content. This is similar to the data for defatted soy flour adjusted to 95°C from Morgan et al. (1988).

The power law model was used to describe shear rate effects for this study. Apparent viscosity versus shear rate for potato flour cooked at 95°C for 2, 4, 6, and 12 minutes are plotted in Figure 4.3. Data for 2, 4, and 6 minutes show similar slopes (flow behavior indices) and apparent viscosities. The 12 minute cook data exhibits more shear thinning. This is, in all likelihood, due to degradation of overcooked starch. Therefore, the timetemperature parameter  $\psi$  of Eq. [4.1] was set to infinity. In the process of making potato flour the potato starch is pregelatinized and therefore it would be expected that cooking





Figure 4.2. Corrected viscosity of potato flour dough (adjusted to T=50C and shear rate of  $100 \text{ s}^{-1}$ ) versus moisture content.





of potato flour should show an increase in viscosity. Comparison of the "cooked" data with uncooked viscosities adjusted to the same temperature and moisture verifies that the potato flour is pregelatinized. Therefore, the parameter A in Eq. 4.1, which is an indicator of the relative contribution of gelatinization to viscosity, is zero. Strain history did not significantly affect the viscosity of the potato flour and therefore this parameter was also set to unity and excluded from further analysis.

All Instron Capillary Rheometer and twin-screw extrusion data plotted were then fit into the final model

$$\eta_{pre} = K \dot{\gamma}^{i-1} e^{\frac{\Delta E_{v}}{R} \left(T^{-1} - T_{r}^{-1}\right) + b(MC - MC_{r})}$$
[4.5]

Equation 4.5 gives an  $R^2$  of 0.951. Best fit parameter values are given in Table 4.2 along with the physical description of each term.

As indicated by Table 4.2 the values for  $\Delta E_{\nu}$  free energy of activation, b, and shear thinning index (n) are within the ranges observed by other researchers for other cereal and soy products. Any variation observed in free energy of activation ( $\Delta E_{\nu}$ ) and b is probably due to individual product characteristics. The lower value for the power law index compared to pregelatinized corn flour is to be expected because native potato starch is highly shear thinning. The consistency coefficient is significantly higher than observed for other pregelatinized flours. The greater value of the consistency coefficient is most likely due to the hygroscopic nature of the potato flour which causes potato flour doughs to be extremely sticky at higher moisture contents. The means of the predicted versus observed data are plotted in Fig. [4.4] for the capillary rheometer and twin-screw extruder data. Note that the twin-screw extruder data means fit with the same degree of accuracy as the capillary rheometer data.



Figure 4.4. Observed versus predicted viscosity via Eq. [4.5] for capillary rheometer (CR) and extruder dies (TSE) for potato flour doughs.
Table 4.2. Summary of model parameters and comparison with values from the litera- ture.				
Symbol	Physical Meaning	This Study	Data from literature (various food doughs at similar moisture and temperatures)	
$\Delta E_{v}$	Activation Energy	8729 kcal per g mol	4967; cooked cereal dough 8723; pregelatinized corn flour 7300; soy grits 6900; defatted soy flour dough	
b	Moisture coefficient	8.63	<ul><li>6.7; defatted soy flour</li><li>7.9; corn flour dough</li><li>0.19; soy grits</li></ul>	
n	flow behavior index	0.25	<ul> <li>0.24; defatted soy flour</li> <li>0.34; soy grits</li> <li>0.36; pregelatinized corn flour</li> <li>0.51; cooked cereal dough</li> </ul>	
К	consistency coefficient	34903 (Pa s <sup>n</sup> )	4880; cooked cereal dough 4982; pregelatinized corn flour 16930; soy grits 28800; soy grits	

\* Harper (1981)

### 4.6. Conclusions

A model extending the work of Morgan et al. (1988) and Dolan et al. (1988) for use in extrusion cooking of low moisture starch-based doughs has been presented. This model incorporates shear rate, temperature, moisture content, time-temperature history and strain history. The model was tested with capillary rheometry and twin screw extrusion of low moisture potato flour doughs.

Overall, the results from the capillary rheometer and twin screw extruder are similar over a wide range of shear rates, moisture contents, temperatures, time-temperature and strain histories. The capillary rheometer may, therefore, be used to approximate conditions within an extruder to obtain parameters to describe shear rate, temperature, moisture and time-temperature history.

Specifically:

1. The model was experimentally tested with potato flour doughs over a wide range of experimental conditions: 25-95°C, 0.28-0.77 g water per g potato flour (22-44% wb), shear rate= 10-10000 sec<sup>-1</sup>,  $\psi$ =0 to  $\infty$  and  $\phi$ =0 to  $\psi$ .

2. Due to the pregelatinization of potato flour, time-temperature and strain history effects were absent.

Future research must focus on assessing the kinetic relationship of timetemperature history to starch gelatinization and strain history for ungelatinized starches, measurement of strain history parameters, and addressing slip or friction correction for capillary and extruder dies.

## 4.7. Nomenclature

- A relative amount of viscosity increase due to gelatinization, dimensionless
- b rate constant of effect of moisture content on viscosity, dimensionless
- d rate constant of effect of strain history ( $\phi$ ) on viscosity, s
- D capillary diameter, m
- $\Delta E_{\star}$  free energy of activation, kcal/g mole
- K power law consistency coefficient, Pa s<sup>n</sup>
- L capillary length, m
- MC moisture content, dry weight basis, decimal
- MC reference moisture content, dry weight basis, decimal
- n flow behavior index, dimensionless
- R universal gas constant, 1.987 cal/g mole
- t time, s
- T temperature, 'K
- T<sub>r</sub> reference temperature, <sup>•</sup>K
- $\eta$  apparent viscosity, Pa s
- $\Delta E_s$  Energy of gelatinization, cal/g-mol
- $\eta_{pre}$  predicated viscosity, Pa s
- $\dot{\gamma}$  shear rate, s<sup>-1</sup>
- φ strain history, dimensionless
- $\psi$  time-temperature history, 'Ks
- $\Delta P$  pressure drop, Pa

# CHAPTER 5 EXTRUSION MODELING OF CORN STARCH 5.1. Abstract

A generalized viscosity model for predicting the extrudate viscosity of low to intermediate moisture content starch based products is proposed. The model incorporates the effects of shear rate, temperature, moisture content, time-temperature history and strain history.

The model was tested using corn starch dough at various moisture contents. Equipment used included an Instron Capillary Rheometer attached to a Model 4202 Instron Universal Testing Machine and an APV Baker MPF 50 D/25 co-rotating twin screw extruder. Die lengths for the capillary rheometer were  $6.35 \times 10^3$  m and  $2.54 \times 10^{-2}$  m, with a diameter of  $3.18 \times 10^{-3}$  m. Extruder dies of  $6.35 \times 10^{-3}$  m diameter, and  $2.54 \times 10^{-2}$ m and  $3.18 \times 10^{-3}$  m lengths were used.

Dough moisture contents were 0.359 (26.4% wb), 0.476 (32.0% wb), and 0.572 (36.0% wb) g water per g starch for capillary rheometer tests and 0.5 (32% wb) and 0.6 (38% wb) g water per g starch for the extrusion tests. In the capillary rheometer, barrel temperatures were maintained at 50, 55, 60, 75, 85, 95, and 110°C for cook times of 1, 2, 3, 6, 12, and 24 minutes.

Shear rate effects were characterized by the model proposed by Ofoli et al. (1988). Viscosity was found to be a function of cook temperature and moisture content but not cook time. Observed versus predicted viscosity gave an  $R^2$  of 0.95 after accounting for shear rate, temperature, moisture content and time-temperature history in the capillary rheometer. Extrusion tests indicated strain history was important for highly puffed extrudates ( $R^2$ =0.79 before strain correction). Strain history was modelled as a function of mechanical energy input (shaft work). After correcting for strain history effects the fit of the model improved to an  $R^2$  of 0.85.

#### **5.2. Introduction**

The major ingredient in many extruded products is starch (Harper, 1981). Over the last ten years, many research papers have addressed the mechanisms that affect materials during extrusion. Some have measured the effects of screw speed, temperature, moisture content and retention time on the molecular changes seen in the structure of the starch granule (Gomez and Aguilera, 1983; Mercier and Colonna, 1983; Colonna et al., 1984; Doublier et al., 1986).

Others have proposed models to describe the physicochemical changes that occur in the starch granule during extrusion (Owusu-Ansah et al., 1983; Gomez and Aguilera, 1984; Davidson et al. 1984). Owusu-Ansah et al. (1983) measured physicochemical changes in corn starch as a function of temperature (100, 128, 170, 212, 240°C), feed moisture (11, 13.4, 17, 20.6, 23% wb) and screw speed (50, 58, 70, 82, 90 RPM), and reported that temperature, moisture and screw speed could significantly affect gelatinization. Response surface diagrams indicated maximum gelatinization occurred at the lowest temperature (100°C) and highest feed moisture (23%), while the minimum gelatinization occurred at the same temperature but lower feed moisture (11%) and 90 RPM. However, at lower screw speeds a minimum level of gelatinization could not be observed except at points of high moisture and temperature. This was in contrast to expected increases in gelatinization with increasing values of temperature and moisture. They concluded that the anomaly was caused by a high compression screw profile which generated greater mechanical work on the starch and therefore allowed complete gelatinization at lower temperatures. By using a lower compression screw profile at higher temperatures and moisture, greater gelatinization occurred.

Gomez and Aguilera (1984) proposed a physicochemical model for extrusion of corn starch. This model is based on the combination of raw, gelatinized and dextrinized starch. They concluded that the term "gelatinization" should not be used to describe the starch when cooked at moisture contents less than 20% because the starch becomes dex-trinized.

Rheological models can be used by the food technologist and process engineer to predict product quality, and in scale-up of new products and in process control (Harper, 1981). Many rheological models for protein and starch based products have been proposed. One of the earliest proposed models (Harper et al. 1971) suggested that viscosity is a function of inverse temperature, moisture content and shear rate. Cervone and Harper (1978) proposed a model for pregelatinized corn flour which included temperature, moisture and shear rate effects. A model incorporating shear rate, temperature and time-temperature history was used by Remsen and Clark (1978) for defatted soy flours. Bhattacharya and Hanna (1986) presented an empirical model for corn gluten meal and soy protein concentrate as a function of shear rate and moisture content: Morgan et al. (1988) presented a model for protein dough viscosity as a function of shear rate, temperature, moisture content, time-temperature history and strain history. Of these studies, only Morgan et al. (1988) included all of the variables Harper (1986) suggests are necessary for process engineering analyses. While Morgan et al. (1988) have proposed a model for extrusion cooking of protein doughs, there is no similar rheological model for use with starch based products.

The purpose of this paper is to extend the model by Morgan et al. (1988) for protein doughs to starch based products and to test the model with capillary rheometer and twin screw extruder data.

#### **5.3. Model Development**

Morgan et al. (1988) presented the following model for cooking extrusion of protein doughs.

$$\eta_{\dot{\gamma},T,MC,\Psi,\Phi} = \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right] + \mu_r \right]^{\frac{1}{a}} e^{\frac{M}{a} \left( T^{-1} - T_r^{-1} \right) + b(MC - MC_r)} \\ \left[ 1 + \beta_r [A_3(MC)^e Cp]^{\alpha} \left( 1 - e^{-t_a \Psi} \right)^{\alpha} \right] [1 - \beta(1 - e^{-d\Phi})]$$

$$(5.1)$$

Several modifications were made to Eq. [5.1] to make it suitable for use with starch based products. First, the shear rate characterization was changed from the Heinz-Casson model to the generalized model of Ofoli et al. (1987):

$$\eta = \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right]^{n_1} + \mu_{\omega} \dot{\gamma}^{n_2 - n_1} \right]^{\frac{1}{n_1}}$$
[5.2]

This generalized model allows for variable power indices, a yield stress and a high shear limiting viscosity. However, it should be pointed out that this model requires sophisticated regression programs to obtain estimates for the parameters. In its place, any acceptable viscosity model could be used.

The time-temperature history expression also required modification. Morgan et al. (1988) assumed that if the protein dough is held long enough at various temperatures, each sample will approach the same viscosity. Kubota et al. (1979) studied the gelatinization rate of rice and potato starches and found the maximum viscosity to be a function of time and cook temperature. Similar results were found by Bakshi and Singh (1980) for gelatinization in rice kernels. Using differential scanning calorimetry (DSC), Lund and Wirakartusumah (1984) developed a model for starch gelatinization. By comparing enthalpy values versus cook time and temperature, similar results to those of Bakshi and

Singh (1980) and Kubota et al. (1979) were obtained. Kubota et al. (1979), Bakshi and Singh (1980) and Lund and Wirakartusumah (1984) each worked with high moisture systems.

Burros et al. (1987) used DSC to measure gelatinization of corn meal under low moisture (25%) and high temperature (80-140°C) conditions. They found results similar to those of Kubota et al. (1979). The order of the reaction was found to be 0.8 and it was believed to be less than one because of the decreased moisture content. They also indicated that the activation energy for gelatinization depends on moisture content, and increased with decreasing moisture content.

Dolan et al. (1988), working with high moisture systems (about 90%), found that viscosities at different time-temperature histories could be normalized by

$$\eta_n = \frac{\eta - \eta_o}{\eta_n - \eta_o}$$
[5.3]

It is important to note that the infinite and initial viscosities are specific to the cook temperature after either correction or normalization to the same temperature. In other words, the infinite viscosity is the viscosity after infinite time at one cook temperature; if the cook temperature is changed, then a different infinite viscosity is reached.

Morgan et al. (1988) and Dolan et al. (1988) modeled the change in viscosity caused by denaturation and gelatinization by

$$\eta = \eta_{i_l, T, MC} + \eta_G$$
[5.4]

Where  $\eta_G$  is defined by:

$$\eta_G = \eta_{-}^* (1 - e^{-k_e \psi})^\alpha$$
[5.5]

Combining Eq. [5.4] and [5.5] gives:

$$\eta = \eta_{\gamma,T,MC} + \eta \left( 1 - e^{-k_a \Psi} \right)^{\alpha}$$
[5.6]

As  $\psi \rightarrow \infty$  Eq. [5.6] becomes:

$$\eta_{\bullet} = \eta_{\eta,T,MC} + \eta_{\bullet}^{\dagger}$$
[5.7]

Combining Eqs. [5.6], and [5.7],

$$\eta_{\mathbf{y}} = \eta_{\mathbf{y}, \mathbf{T}, \mathbf{MC}} \left[ 1 + A \left( 1 - e^{-t_{\mathbf{x}} \mathbf{y}} \right)^{\alpha} \right]$$

$$[5.8]$$

from which it follows that

$$A = \frac{\eta_{\perp}^*}{\eta_{j_k T, MC}}$$
[5.9]

Finally, the modified Morgan et al. (1988) model becomes

$$\eta_{\gamma,T,MC,\Psi,\Phi} = \left[ \left[ \frac{\tau_o}{\gamma} \right]_1^n + \mu_{\omega} \gamma^{2-n} \right]_1^{\frac{1}{n_1}} e^{\frac{AK_v}{\pi} (T^{-1} - T_r^{-1}) + b(MC - MC_r)} \\ \left[ 1 + A \left( 1 - e^{-k_s \Psi} \right)^{\alpha} \right] \left[ 1 - \beta (1 - e^{-d\Phi}) \right]$$
[5.10]

and can now be used for predicting the viscosity of low moisture starch based products.

#### **5.4. Materials and Methods**

Native corn starch (Melogel, National Starch and Chemical Corp., Bridgewater, NJ) at 8% moisture content (wb) was mixed in an institutional mixer with water to give sufficient quantities for all capillary rheometer tests to be performed.

Moisture contents were 26, 32, and 36% (wb). These moisture contents were chosen because less than 26% moisture caused force readings to exceed the maximum force the capillary rheometer load cell could handle, and moisture contents greater than 36% caused water to be squeezed out of the material giving an uneven moisture distribution in the rheometer barrel. After mixing with distilled water, the samples were allowed to equilibrate overnight at room temperature (24°C) and then smaller samples were placed in polyethylene bags and stored at -10°C until capillary rheometer tests were performed. Twenty four hours before performing the tests, each sample was thawed at 4°C overnight. Prior to testing, each sample was allowed to come to room temperature.

An Instron Capillary Rheometer and a Model 4202 Instron Universal Testing Machine (Instron Corp., Canton, Massachusetts) were used to measure apparent viscosity of the doughs (Figure 5.1). Die lengths of 2.54 cm (1 in) and  $6.35 \times 10^{-1}$  cm (1/4 in), and diameters of 4.90 x  $10^{-2}$  cm (1/8 in) and  $1.59 \times 10^{-1}$  cm (1/16 in) were used, giving L/D ratios ranging from 2 to 16. Three replicates for each plunger velocity, temperature, moisture content, cook time, and L/D were performed. Force versus plunger displacement curves were collected and force at the die entrance was calculated by extrapolation of the force versus displacement curves to the die as described by Einhorn and Turetzky (1964). Barrel drag was then subtracted from the corrected force. A correction for entrance effects was made using the technique described by Bagley (1957).



Figure 5.1. Capillary rheometer assembly.

Shear rate and shear stress were calculated using the Rabinowitsch equation (Whorlow, 1980) (Eq. 5.11),

$$\dot{\gamma}_{w} = \frac{3Q}{\pi R_{o}^{3}} + \tau_{w} \left[ \frac{d \frac{Q}{\pi R_{o}^{3}}}{d \tau_{w}} \right]$$
[5.11]

and the standard expression for shear stress at the wall of a capillary:

$$\tau_{w} = \frac{\Delta P R_{o}}{2L}$$
[5.12]

Slip analysis was performed using the method described by Darby (1976) using dies of same length but different diameter.

Temperatures used in this study were 50, 55, 65,75, 85, 95, and 110°C. At temperatures less than or equal to 60°C, the materials were compressed in the capillary barrel and allowed to equilibrate for 6 minutes. Cook times of 1, 2, 3, 6, 12 and 24 min at 75, 85, 95, and 110°C were performed on each sample after compression.

Shear rate, temperature, moisture and time-temperature history parameters were determined as follows. Holding temperature (50°C), moisture content (32% wb) and time-temperature history ( $\psi = 0$ ) constant, viscosity versus shear rate were fitted to the model of Ofoli et al. (1987), using the Marquardt compromise method in the non-linear regression program of SAS (SAS Institute, Cary, NC). Shear stress and shear rate values from the capillary rheometer were then averaged for each capillary die and Instron cross-head velocity.

Temperature correction was obtained in the following way: holding shear rate, moisture content (32% wb) and time-temperature history constant ( $\psi$ =0), the natural log of the viscosity versus ( $T^{1}-T_{r}^{-1}$ ) was regressed linearly to obtain  $\Delta E_{v}/R$  for temperature correction. The reference temperature, T<sub>r</sub>, was set at 323.15 °K. The moisture correction parameter was determined by holding time-temperature history constant ( $\psi$  =0) and linearly regressing the natural log of the viscosity versus (MC-MC<sub>r</sub>) with MC<sub>r</sub>=0.476 (db). Finally, the time-temperature history correction was performed. Strain history within the capillary rheometer was assumed to be insignificant and set to unity.

Experimental extrusion tests were conducted using an APV Baker MPF 50D (APV Baker, Inc., Grand Rapids, MI) co-rotating twin screw extruder with the screw configuration shown in Table 5.1. Feed rates were  $1.01 \times 10^{-2}$  and  $1.64 \times 10^{-2}$  kg/s, at 200 and 400 RPM. The die diameter was  $3.17 \times 10^{-3}$  m, with lengths of  $6.40 \times 10^{-3}$  and  $2.60 \times 10^{-2}$  m. The pressure drop across the die and extrudate temperature at the die were recorded two minutes after extruder operating conditions had been changed, to allow equilibrium conditions to be attained.

Plotting pressure drop versus the two different die L/D's with constant temperature, moisture, and mass flow rate allowed correction for end effects as described by Bagley (1957) for capillary dies. Shear rate was calculated using the Rabinowitsch equation (Whorlow, 1980) and shear stress was calculated using Eq. [5.4] for each die, temperature, moisture and mass flow rate.

Temperature and moisture correction on the extrusion data were performed using  $\Delta E_{\nu}$  and b estimated from the capillary rheometer. The average residence time within the extruder was determined by adding 1 ml of Red 40 dye to the feed, timing how long it took for the dye to appear at the exit, collecting the colored material at intervals of 20 s (low feed rate) or 15 s (high feed rate) until no dye came out, and recording the total time the dye remained in the extruder. The collected samples were dried, ground and Hunter

Lab color 'a' values were determined for each time interval (a(t)). The mean residence time (t) within the extruder was calculated by

$$t = \int_0^t t \frac{a(t)}{\sum a dt} dt$$
[5.13]

•

Table 5.1. Screw configuration for extrusion test on APV Baker 50 mm twin screw extruder.				
17.8 cm	Feed Screw	Feed Inlet		
7.6 cm	Feed Screw			
6.4 cm	Forwarding paddles 45 offset			
8.9 cm	Forwarding paddles 30 offset			
7.6 cm	Feed Screw			
7.6 cm	Single Lead	Extruder die		

#### 5.5. Results and Discussion

Equilibrium moisture contents of the corn starch samples on a dry weight basis were determined to be 0.359, 0.476, and 0.572 g water per g corn starch. Moisture contents were found to be constant throughout storage.

A non-linear regression analysis of ungelatinized corn starch at 0.476 g water per g corn starch (32% wb) and a temperature of 50°C gave the shear rate correction for all the data:

$$\eta_{\dot{\gamma}} = \left[ \left[ \frac{189434}{\dot{\gamma}} \right]^{0.979} + 69351 \dot{\gamma}^{-0.623} \right]^{\frac{1}{0.979}}$$
[5.14]

A regression coefficient ( $\mathbb{R}^2$ ) of 0.996 indicates a good fit of the data. Shear stress and shear rate values were averaged at each capillary rheometer plunger velocity for each cook time, temperature, and moisture. When the average observed apparent viscosities were plotted against the average predicted values for all moisture contents, temperatures and time-temperature histories using Eq. [5.14], an  $\mathbb{R}^2$  of 0.88 and a slope of 6.02 was obtained. Figure 5.2 is a plot of the observed apparent viscosity versus the predicted apparent viscosity after accounting for shear rate effects. A plot of both predicted (corrected for shear) and observed viscosities versus shear rate can be seen in Figure [5.3]. If the shear rate correction alone were adequate, one would expect the predicted viscosity values to match the observed viscosity values. However, both Fig. [5.2] and Fig. [5.3] indicate that correcting for shear rate alone is not enough.

Corrections for temperature and moisture were, therefore, carried out (Table 5.2). Both values for temperature (free energy of activation) and moisture (b) are within the range seen in the literature for similar materials, temperature and moisture. Figure 5.4 is the plot of the observed versus predicted apparent viscosity, corrected for temperature



Figure 5.2. Predicted versus observed viscosities of corn starch doughs after shear correction for all temperatures, moisture contents and time-temperature histories.



Figure 5.3. Apparent observed and predicted viscosities of corn starch doughs versus shear rate at a moisture content of 0.476 g water/g corn starch.

Table 5.2. Temperature and moisture parameters as determined by linear regression with viscosity measured at a shear rate of 100 s-1.			
Parameter	Estimate	Range from Literature	
$\Delta E_{\star}$	8473.14 <b>°</b> K	3000-8000 °K	
b	-3.99	-150.19	



Figure 5.4. Predicted verses observed viscosities, of corn starch doughs after shear rate and temperature corrections, for all moisture contents and time-temperature histories. and shear rate. Compared to Fig 5.2, the fit has improved ( $R^2=0.91$ , slope=0.482) and all data points appear to fall along a more defined line. However, it is clear from the slope (0.482) of the regression line that further correction is necessary.

Observed apparent viscosity versus predicted apparent viscosity corrected for temperature, moisture and shear rate can be seen in Figure 5.5. There is further improvement in fit as measured by  $R^2$  (0.93), however, the slope of the regression line has decreased significantly (0.347). As can be seen in progressing from Figures 5.2 to 5.5 the data points are becoming more aligned. The decrease in slope of the regression line is an indication that the observed viscosity is greater than the predicted viscosity. This is to be expected since the shear, temperature, and moisture corrections were made on an uncooked material; therefore, applying these corrections to cooked material should result in predicted values less than those of cooked starch. When the observed viscosities corrected to a shear rate of 100 s<sup>-1</sup> are plotted versus cook time at a moisture content of 0.476 g water per g starch (32.0%) (Figure 5.6) an increase in viscosity with time is seen only for the 75°C cook temperature. At the other cook temperatures, no appreciable difference in viscosity is observed at all cook times. By a cook time of 3 minutes, the data for the 75°C cook temperature had reached a constant viscosity. This is consistent with the observations of Kubota et al. (1979), Bakshi and Singh (1980), Lund and Wirakartasumah, (1984), Burros et al. (1987), and Dolan et al. (1988).

When an analysis of the temperature profile within the capillary rheometer barrel was made using the heat conduction equation for infinite cylinders (Ozisik, 1980), the center temperature of the starch material reached and exceeded the gelatinization temperature in one minute or less. Therefore, it was assumed that the product of  $k_a$  and  $\psi$  was very large, indicating very rapid gelatinization. The term,  $\exp(-k_a \psi)$ , therefore is zero for all cook temperatures and cook times.









The correction for time-temperature history then becomes:

$$\eta = \eta_{i_T,MC}[1+A']$$

$$[5.15]$$

where A' is defined as:

$$A' = \frac{\eta_{\omega}}{\eta_{\dot{\gamma}, T, MC}} - 1 = \beta_o (Cs)^{\alpha}$$
[5.16]

The variable A' is, essentially, a ratio of the maximum viscosity due to gelatinization that can be attained (for a specific cook temperature and moisture content) to the ungelatinized viscosity corrected to the cook temperature. It is important to note that A' relates to a particular moisture content and cook temperature. The specificity for moisture content is not due to the lubrication effects of water, but rather to the effect of moisture content on the gelatinization kinetics.

Values of  $\alpha$  and  $\beta_o$  for Eq. 5.15 were determined by holding the temperature constant and regressing ln A' versus ln Cs for all the data. As temperature increased,  $\alpha$ decreased (except at 110°C) while  $\beta_o$  increased (Table 5.3). This was to be expected because the difference between the viscosity of the uncooked starch and the cooked starch also increased as the cook temperature increased. The exact cause of the high  $\alpha$ value at 110°C is not known. However, one possible explanation is that at the high cook temperature, some molecular breakdown may have occurred causing more entanglement between molecules and therefore a greater value of  $\alpha$ .

To find a predictive equation for the constant A', equations for  $\alpha$  and  $\beta_o$  as a function of temperature had to be determined. An Arrhenius relationship for both  $\alpha$  and  $\beta_o$ was assumed and regression of  $\ln \alpha$  or  $\beta_o$  versus 1/T was then performed. Equations [5.15] and [5.16] are the resulting equations for  $\alpha$  and  $\beta_o$ .

$$\alpha = e^{\left(18.9 - \frac{6070.5}{7}\right)}$$
  $R^2 = 0.952$  [5.17]

Table 5.3. Values of constants $\alpha$ and $\beta_o$ as a function of temperature.			
Temperature (°C)	α	βø	
75	2.53	4.90	
85	1.90	5.57	
95	1.70	11.30	
110	2.05	21.96	

$$\beta_o = e^{\left(-6.4 + \frac{2590.5}{T}\right)}$$
  $R^2 = 0.947$  [5.18]

Combining Eqs. [5.16], [5.17], and [5.18] yields an equation for the constant A'.

By combining Eqs. [5.10] and [5.16], the final predictive equation for viscosity as a function of shear rate, temperature, moisture content, and time-temperature is

$$\eta_{\dot{\gamma},T,MC,\Psi} = \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right]^{a_1} + \mu_{\omega} \dot{\gamma}^{a_2 - a_1} \right]^{\frac{1}{a_1}} e^{\frac{\Delta E_v}{R} \left( T^{-1} - T_r^{-1} \right) + b(MC - MC_r)} \left[ 1 + A \left( 1 - e^{-t_o \Psi} \right)^{\alpha} \right]$$
[5.19]

A plot of observed versus predicted viscosity after shear rate, temperature, moisture content and time-temperature history corrections using Eq. [5.19] is shown in Figure [5.7]. Clearly the goodness of fit has been improved ( $R^2$ =0.95, slope=0.72). Further regression analysis using forward stepwise regression (Table 5.3) indicates that the shear rate is the most important variable. This is to be expected, since viscosity is very dependent on shear rate. Moisture content is the next contributor to the model in order of importance. Again, this is not surprising; it implies that at the moisture contents used in this study, the lubrication effects of moisture contribute more to the viscosity than the effects of temperature or time-temperature history. Time-temperature history was next in importance, followed by temperature effects.

The temperature correction might have been expected to be more important because of the large value of  $\Delta E_{\star}/R$  which indicates a high degree of temperature thinning. At low moisture contents, moisture and time-temperature history should be of greater importance compared to temperature in contributing to viscosity. This is because moisture can have a greater effect on the friction between the material and the capillary wall and therefore contribute to lubrication effects. While time-temperature history effects are a function of time, temperature and moisture content are not a function of



temperature, moisture, and time-temperature history for corn starch doughs.

Table 5.4 moisture	Table 5.4. Stepwise regression of observed viscosity versus temperature, shear rate, moisture content and time-temperature history corrections for native corn starch.					
SUMMARY OF STEPWISE REGRESSION PROCEDURE FOR DEPENDENT VARIABLE η <sub>pre</sub>						
STEP	VARIABLE PARTIAL MODEL ENTERED R <sup>2</sup> R <sup>2</sup> C(P) F PROB>F					
1	Ϋ́	0.9379	0.9379	216.1	8304.9	0.0001
2	MOIST	0.0142	0.9521	43.2	162.7	0.0001
3	Α'	0.0034	0.9555	3.1	42.13	0.0001
4	TEMP	0.0001	0.9556	4.0	1.07	0.3022

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time. It is also important to note that while the model was developed assuming no interaction between terms but in actuality the order in which each term is determined may affect the value of its parameters.

Results of extrusion tests can be seen in Table 5.5. The moisture content and temperature ranges are similar to the conditions used in the capillary rheometer tests. Shear rate ranges are higher than those observed for capillary rheometer tests. Average residence times within the extruder ranged from 45 to 85 seconds. While it should be recognized that residence time within a section is highly dependent upon the screw configuration, at the present time there is no accurate method to quantify actual residence time within an extruder zone on the basis of screw geometry. Extrudates varied in appearance from opaque and slightly swelled to translucent and very highly puffed depending on the die length, screw RPM and mass flow rate.

Figure [5.8] gives a plot of data from twin screw extrusion runs with all data corrected for shear, temperature, moisture and time-temperature history using Eq. [5.19]. Some of the predicted viscosities for the extrusion data are greater than the observed viscosities, indicating that a correction for strain history may be appropriate. Predicted viscosities which were greater than the observed viscosities were from extrusion tests that gave a product that was very highly puffed and translucent in appearance (compared with an opaque, marshmellow-like, non-puffed appearance).

Vergnes and Villemaire (1987) found a semi-logarithmic relationship between the power law consistency coefficient and work input for low moisture molten corn starch. Therefore, the relationship between shaft work and viscosity of the extrudate may be useful in attempting to quantify the effects of strain history. Use of the mechanical energy input for characterizing the effect of strain history may also be more practical because quantification of shear rate within each zone of the extruder is not possible

Table 5.5. Data from twin screw extrusion tests on corn starch.							
Die Temp.	Shear Stress (Pa)	Shear Rate (s <sup>-1</sup> )	Residence time (s)	Moisture Content (db)	η <sub>ψ</sub> (Pa s)	η (Pa s)	N <sub>obe</sub> (Pas)
83.9 84.4 87.8 95.6 96.1 96.1 96.1 97.2 98.3 100.6 101.7 104.0 105.6	245691 82542 264421 68523 55327 118835 35364 299127 31395 104229 215059 336694 80833	245 145 220 215 158 140 150 231 239 145 139 225 144	56.1 75.1 59.6 53.1 71.6 84.5 69.8 58.8 51.0 80.4 75.4 64.9 71.2	0.60 0.61 0.67 0.65 0.65 0.61 0.45 0.58 0.50 0.49 0.49 0.49	460 518 247 360 263 387 428 903 374 917 967 672 878	460 518 247 360 263 387 332 903 290 712 967 672 682	1004 569 1201 317 350 849 236 1293 132 719 1549 1498 561
106.7 112.8 112.8	119117 113813 170817	244 143 226	59.0 66.8 45.7	0.50 0.49 0.48	716 867 698	556 673 <sup>.</sup> 698	488 794 757



Figure 5.8. Observed versus predicted viscosities corrected for shear rate, temperature, moisture, and time-temperature history in extruder dies for corn starch.

from currently available knowledge, except in some highly specific situations (Mohamed, 1988). Total shaft power for the APV Baker MPF 50D/25 twin screw extruder was determined using the equation

 $E_{s=4.75 \times 10^{-4} (\% Torque) (RPM)/Q$  [5.20]

When the corrected viscosity versus mechanical energy supplied by the extruder shaft was plotted, a definite relationship is observed (Figure 5.9). Non-linear regression analysis of observed viscosities corrected to 150 s<sup>-1</sup>, 50°C, and 0.476 g/g moisture versus mechanical energy gave

$$\eta_{\bullet} = 282019 \, e^{(-5.9 \times 10^{-7} E_{\rm F})} + 4300$$
[5.21]

with an  $R^2$  of 0.88. Using the value of the viscosity at infinite strain history (as determined from regression), and correcting for shear rate, temperature and moisture, a correction for strain history can be obtained.

The final equation for predicting the viscosity of starch-based doughs in the twin screw extruder is

$$\eta_{\dot{\gamma},T,MC,\psi,\phi} = \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right]_1^n + \mu_{\omega} \dot{\gamma}^{2-n_1} \right]^{\frac{1}{n_1}} e^{\frac{\Delta K_v}{R} \left( T^{-1} - T_r^{-1} \right) + b(MC - MC_r)} \\ \left[ 1 + A \left( 1 - e^{-t_a \psi} \right)^{\alpha} \right] \left[ 1 - \beta (1 - e^{-d\phi}) \right]$$
[5.22]

A plot of the observed versus predicted extrudate viscosities corrected for shear rate, temperature, moisture, time-temperature history and strain history using Eq. [5.22] is seen in Fig. [5.10]. The data appears scattered but regression analysis indicates a good fit ( $R^2$ =0.85). The observed versus predicted viscosities do appear to fall along one line

indicating that shear, temperature, moisture, time-temperature and strain history corrections may adequately be used to predict the viscosity of corn starch extrudates over the temperatures and moisture contents used. Table 5.6. gives the value or relationship for each parameter in Eq. 5.22.

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Figure 5.10. Observed versus predicted viscosities corrected for shear rate, temperature, moisture, time-temperature, and strain history in extruder dies for corn starch.

Table 5.6. List of model parameters for Eq. 5.22.		
Parameter	Value or relationship	
$   \begin{array}{c}     \tau_{o} \\     \mu_{-} \\     n_{1} \\     n_{2} \\     \Delta E_{v} \\     b \\     A'   \end{array} $	189434 Pa 69351 Pa s 0.979 0.356 8473.14 *K -3.99 $e^{\left(-6.371+\frac{2530.5}{T}\right)}(Cs)^{e^{\left(18.39-\frac{6070.7}{T}\right)}}$	
k₄Ψ	∞	
β	Dependent on T, MC, and $\eta_{\bullet}$	
d	and η <sub>o</sub> -5.87 x 10 <sup>8</sup>	
#### **5.6.** Conclusions

A model to predict the viscosity of extruded starch-based products was developed using the model proposed by Morgan et al. (1988). This model incorporates shear rate, temperature, moisture content, time-temperature history and strain history. The model is flexible enough to allow its use under a wide range of operating conditions and extrusion equipment and yet simple enough that the parameters can be determined via capillary rheometry and standard non-linear and linear regression techniques.

Viscosities of cooked and uncooked corn starch measured via capillary rheometry at moisture contents of 0.359, 0.476, and 0.572 g water per g starch (26.4%, 32.0% and 36% mc wb respectively), cook times of one to 24 minutes, temperatures of 50, 75, 85, 95 and 110°C and shear rates of one to 300 s<sup>-1</sup> were found to fit the model with reasonable accuracy. When capillary rheometer data was corrected for shear rate a fit of the observed versus predicted viscosity gave an  $R^2$  of 0.88 and a slope of 0.15. Subsequent correction for temperature, moisture content, and time-temperature history improved the fit and the slope to a final  $R^2$  of 0.95 and a slope of 0.72.

Data for capillary rheometer and twin screw extrusion tests fell along the same line under low strain history conditions. Extrusion tests indicated that when strain history is large, correction for strain history is necessary. Modification of the model proposed by Morgan et al. (1988) for strain history to include shaft work input as proposed by Vergnes and Villemaire (1987) yielded a final equation that gave a reasonable fit  $(R^2=0.85)$  for extrusion data.

Further research is necessary to quantify strain history effects. One problem encountered in this research was the lack of rheological equipment to enable the independent measurement of the effects of strain history on low moisture and, hence, high viscos-

ity starch doughs outside the extruder. A combination shearing and capillary rheometer as described by Vergnes and Villemaire (1987) may be what is needed to perform this necessary work.

Also, a redesign of the capillary rheometer so that it has a wider barrel so heat transfer to the center of the starch dough is slower, may be necessary to quantify the time-temperature effects at values less than infinity. Further investigation into the phenomena of slip and friction within the capillary die also needs to be done.

# 5.7. Nomenclature

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A, A', A <sub>3</sub>	relative amount of viscosity increase due to gelatinization, dimensionless
b	rate constant of effect of moisture content on viscosity, dimensionless
Cs	starch concentration, wet basis decimal
Ср	protein concentration, dry basis decimal
d	rate constant of effect of strain history ( $\phi$ ) on viscosity, s
D	capillary diameter, m
$\Delta E_{v}$	free energy of activation, kcal/g mole
Es	mechanical energy supplied by the extruder, Jm <sup>-3</sup>
L	capillary length, m
MC	moisture content, dry basis decimal
MC,	reference moisture content, dry basis, decimal
n <sub>i</sub> ,	power indices, dimensionless
R <sub>o</sub>	capillary radius, m
R	universal gas constant, 1.987 cal/g mole
t	time, s
Т	temperature, 'K
T,	reference temperature, *K
Q	volumetric flow rate, m <sup>3</sup> s <sup>-1</sup>
α	index of molecular weight effects on viscosity, dimensionless
β,,β,	material constant describing effects of temperature and moisture on
	gelatinization, dimensionless
β	material constant describing effect of strain history on viscosity at
	$\phi = \infty$ , dimensionless
η	apparent viscosity, Pa s

η <sub>G</sub>	contribution to viscosity by gelatinization, Pa s		
η,	normalized apparent viscosity ratio, dimensionless		
η_	viscosity at $\psi = \infty$ , Pa s		
η <sub>ή,T,MC, γ.</sub> φ	apparent viscosity corrected for shear rate, temperature, moisture		
	content, time-temperature history and strain history, Pa s		
η <sub>Ψ</sub>	apparent viscosity at time-temperature history $\psi$ , Pa s		
η_	viscosity at $\psi = \infty$ , Pa s		
η	change in apparent viscosity due to gelatinization at $\psi = \infty$ , Pa s		
η <sub>,,<i>τ</i>,<i>м</i>с</sub>	apparent viscosity before gelatinization, Pa s		
η,	apparent viscosity at $\phi = \infty$ , Pa s		

3	material exponent for describing effect of moisture content on protein de		
	turation, dimensionless		
Ϋ	shear rate, s <sub>-1</sub>		
φ	strain history, dimensionless		
Ψ	time-temperature history, 'K-s		
τ	yield stress, Pa		
T.,	shear stress at wall, Pa		
μ,	high shear limiting viscosity (Casson), Pa s <sup>0.5</sup>		
η_	high shear limiting viscosity (Ofoli), Pa s <sup>n2-n1</sup>		
ΔΡ	pressure drop, Pa		

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# CHAPTER 6 A RHEOLOGICAL MODEL FOR NATIVE WHOLE WHEAT FLOUR DOUGH EXTRUDATES

# 6.1. Abstract

A generalized viscosity model for predicting the extrudate viscosity of low to intermediate moisture content starch based products is proposed. The model incorporates the effects of shear rate, temperature, moisture content, time-temperature history and strain history.

The model was tested using whole wheat flour doughs at varying moisture contents. Equipment used included an Instron Capillary Rheometer attached to a Model 4202 Instron Universal Testing Machine and an APV Baker MPF 50 D/25 co-rotating twin screw extruder. Die lengths of the capillary rheometer were  $6.35 \times 10^3$  m and  $2.54 \times 10^2$  m, with diameter of  $3.18 \times 10^{-3}$  m and  $1.59 \times 10^{-3}$  m. Extruder dies of  $6.35 \times 10^{-3}$  m diameter, and  $2.54 \times 10^{-2}$  m and  $3.18 \times 10^{-3}$  m lengths were used.

Whole wheat flour dough moisture contents were 0.333, 0.337, 0.385 and 0.436 g water per g starch (25.0%, 25.2%, 27.8%, and 30.4%, wb respectively) for capillary rheometer tests. In the capillary rheometer, barrel temperatures were maintained at 50, 55, 60, 75, 85, 95, and 110°C at cook times of 1, 2, 3, 6, 12, and 24 minutes.

Shear rate was modelled by the generalized model proposed by Ofoli et al. (1987). Overall fit of the model improved as temperature, moisture content and time-temperature history were accounted for. The fit was not as good for whole wheat flour as was observed for corn starch and potato flour ( $R^2$ = 0.56). The apparent lack of fit may be due to the presence of flour components such as bran, protein, and lipids which the model does not account for and which may have altered the gelatinization kinetics of the starch.

#### **6.2.** Introduction

The food industry is constrained from effective use of extruders because of lack of an adequate model which describes the effects of extrusion process variables on the extrudate viscosity. Many researchers have proposed rheological models for extrusion cooking of cereal products (Harper et al. 1971; Remsen and Clark, 1978; Cervone and Harper, 1978; Bhattacharya and Hanna, 1986; Morgan et al., 1988). While all these models account for shear rate, moisture, and temperature, only Remsen and Clark (1978) and Morgan et al. (1988) included time-temperature history effects.

In Chapters 4 and 5, the equation below was used to model the viscosity of potato flour and corn starch:

$$\eta_{pre} = \left[ \left[ \frac{\tau_o}{\dot{\gamma}} \right]_1^n + \mu_u \dot{\gamma}_2^{n_2 - n_1} \right]^{\frac{1}{n_1}} e^{\frac{\Delta d_v}{R} \left( T^{-1} - T_r^{-1} \right) + b \left( \Delta C - \Delta C_r \right)} \\ \left[ 1 + A' \left( 1 - e^{-t_e} \psi \right)^{\alpha} \right] \left[ 1 - \beta \left( 1 - e^{-d\psi} \right) \right]$$
[6.1]

However, it is commonly accepted that various components of cereal doughs (protein, lipids, and pentosans) or ingredients added to the product (sugar, salt, etc.) can greatly affect the extent of gelatinization (Eliasson, 1983; Lund, 1984; Olkku, 1978; Ghiasi et al. 1982). The proposed model does not account for the effects of non-starch components on the gelatinization kinetics of starch. Since it was observed in Chapter 5 that starch gelatinization significantly affects viscosity, it is reasonable to expect that the presence of dough components such as protein, salts, or lipids may affect the changes in viscosity during cooking extrusion. The effects of these dough constituents can, therefore, be evaluated by applying the model to a product containing significant levels of one or more non-starch components. Native whole wheat flour provides an ideal material for this exercise.

ing the viscosity of native whole wheat flour extrudates.

#### **6.3.** Materials and Methods

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Whole wheat flour (International Multifoods, Minneapolis, MN) containing 14-14.5% protein (wb) provided the feed material for the extrusion runs. Moisture contents used were 0.333, 0.337, 0.385, and 0.436 g water per g flour (25.0%, 25.2%, 27.8%, and 30.4%, wb respectively). The indicated moisture contents were used because at higher moisture contents, rapid loading of the capillary rheometer was difficult due to the stickiness of the material, and at lower moisture contents damage to the Instron load cell or capillary rheometer plunger might occur.

Flour and water were mixed in an institutional mixer and allowed to equilibrate at room temperature (24°C) overnight before being placed in plastic freezer bags and stored at 0°C. Prior to capillary rheometer tests, the sample was allowed to thaw for a minimum of 12 hours. Moisture content was determined by drying overnight at 100°C. No change in moisture content was observed during frozen storage.

An Instron Capillary Rheometer and a Model 4202 Instron Universal Testing Machine (Instron Corp., Canton, Massachusetts) (Figure 6.1.) were used to measure apparent viscosity of the doughs. Dies of 2.54 cm (1 in) and 0.635 cm (1/4 in) length, and 4.90 x  $10^{-2}$  cm (1/8 in) and 1.59 x  $10^{-1}$  cm (1/16 in) diameter were used, giving L/D ratios ranging from 2 to 16. Three replicates for each plunger velocity, temperature, moisture content, cook time and L/D ratio were performed.

Force versus plunger displacement data were collected and force at the die entrance was calculated by extrapolation of the force versus displacement curves to the die as described by Einhorn and Turetzky (1964). Barrel drag was then subtracted from the corrected force. A correction for entrance effects was made using the technique described by Bagley (1957). Pressure drop through the capillary die was assumed to be the force at the die entrance over the barrel diameter.



Figure 6.1. Capillary rheometer assembly.

Shear rate and shear stress were then calculated using the Rabinowitsch equation,

$$\dot{\gamma}_{w} = \frac{3Q}{\pi R_{o}^{3}} + \tau_{w} \left[ \frac{d \frac{Q}{\pi R_{o}^{3}}}{d \tau_{w}} \right]$$
[6.2]

and the standard expression for shear stress at the wall of a capillary:

$$\tau_{w} = \frac{\Delta P R_{o}}{2L}$$
[6.3]

Slip analysis was performed using the method described by Darby (1976).

Temperatures used in this study were 50, 75, 85, 95, and 110°C. At 50°C the materials were compressed in the capillary barrel and allowed to equilibrate for 6 minutes. Cook times of 1, 2, 3, 6, 12 and 24 min at 75, 85, 95, and 110°C were performed at each moisture content after compression.

Shear rate, temperature, moisture and time-temperature history parameters were determined as follows. Holding temperature (50°C), moisture (0.333% db) and time-temperature history constant ( $\psi$ =0), viscosity versus shear rate were fitted to the model of Ofoli et al. (1987), using the Marquardt compromise method in the non-linear regression program of SAS (SAS Institute, Cary, NC). Then holding moisture content (0.333% db) and time-temperature history ( $\psi$ =0) constant, ln  $\eta$  versus ( $T^{-1}-T_r^{-1}$ ) with  $T_r$ =323.15 °K were regressed linearly to obtain  $\Delta E_r/R$  for the temperature correction. The moisture correction parameter was determined by holding time-temperature history constant ( $\psi$ =0) and linearly regressing ln  $\eta$  versus (MC-MC<sub>r</sub>), with MC<sub>r</sub>=0.333 db. Finally, correction for time-temperature was performed.

Experimental extrusion tests were conducted using a APV-Baker MPF 50 D (APV Baker, Inc., Grand Rapids, MI) co-rotating twin screw extruder with the screw configuration shown in Table 6.1. Feed rates of  $1.01 \times 10^{-2}$  and  $1.64 \times 10^{-2}$  kg/s, were used at 200 and 400 RPM. Two dies  $3.17 \times 10^{-3}$  m in diameter and  $6.40 \times 10^{-3}$  and  $2.54 \times 10^{-2}$  m in length were used. Pressure drop and extrudate temperature at the die were recorded two minutes after extruder operating conditions had been changed to allow equilibrium conditions to be attained.

Table 6.1. extruder.	Screw configuration for extrusio	n tests on APV Baker 50 mm twin screw
17.8 cm	Feed Screw	Feed Inlet
8.9 cm	Forwarding paddles 30 offset	
7.6 cm	Feed Screw	
6.4 cm	Forwarding paddles 45 offset	
10.2 cm	Single Lead	
8.9 cm	Forwarding paddles 30 offset	
7.6 cm	Feed Screw	
7.6 cm	Single Lead	Extruder die

# **6.4. Results and Discussion**

Final equilibrium moisture content of the wheat flour samples were determined to be 0.333, 0.335, 0.385, and 0.436 g water per g wheat flour (25.0%, 25.2%, 27.8%, and 30.4%, wb respectively). No loss in water was observed during storage.

The extrudates exhibited the appearance of slip, with a "shark skin" texture on the surface. However, analysis for slip was found to be inconclusive at all moisture contents and temperatures. The inability to correct for slip may be due to a "slip-stick" phenomenon where there is a combination of friction and slip occurring at the capillary wall. Because "slip-stick" rather than pure slip occurred, Darby's (1976) method for slip correction did not yield meaningful results. It was either impossible to obtain a slip coefficient because of wide variations in the data, or a negative apparent shear rate was obtained. Another reason for the difficulties encountered in slip correction may be a varying friction coefficient within the die, depending on the plunger velocity, die geometry or a combination of the two. Due to the non-cohesiveness of the raw material, it was impossible to correct for this friction.

The reference moisture content was set at 0.333 g water per g (25.0% wb) flour. A yield stress of 93.8 kPa was estimated by extrapolating shear stress versus shear rate curves to zero shear rate. After determining the yield stress, the other parameters in the shear rate model were determined via non-linear regression.

The fit of the non-linear regression parameters as measured by  $R^2$  (0.88) was not as good as that observed in Chapters 4 and 5 for potato flour and corn starch. This poor fit may be due to the presence of bran, protein and other components in the whole wheat flour which are not accounted for by the model. Temperature and moisture correction terms are listed in Table 6.2. Values for both are within the ranges seen by other researchers for similar materials.

Table 6.2. Temperature and moisture correction parameters for whole wheat flour at $100 \text{ s}^{-1}$			
Parameter	Estimate	Range of previous values	
Temperature ( $\Delta E_{\nu}$ )	5354.38	2000-5000 <b>*</b> K	
Moisture (b)	-7.91	-15.00.19	

Note: All estimates are significant at the 95% level.

Comparison of average observed versus predicted viscosities at all shear rates, temperatures, moisture contents, and time-temperature histories corrected for shear rate only can be seen in Figure 6.2. Regression analysis ( $R^2=0.56$ , slope=1.86) of observed versus predicted values indicate that shear rate correction alone is inadequate to describe the viscosity of whole wheat flour.

Figure 6.3 shows observed versus predicted viscosities corrected for shear rate and temperature at all moisture contents and time-temperature histories. Temperature correction improves the fit of the line ( $\mathbb{R}^{2=}0.635$ ) and the slope approaches unity (slope=0.83). While the correction for temperature improves the fit, the data still appears to be somewhat scattered as seen in Figure 6.3.

Correcting the predicted viscosities for moisture content gives further improvement in the fit ( $R^2=0.638$ ) of the average observed versus predicted viscosities. A plot of observed versus predicted viscosity can be seen in Figure 6.4. The slope of the line has decreased to 0.76 indicating that predicted viscosities corrected for moisture, temperature and shear rate are less than observed viscosities. These predicted viscosities are lower because most of the observed viscosities were either fully or partially cooked and therefore the starch and protein molecules had undergone gelatinization or denaturation, respectively. It is commonly accepted that viscosity increases as starch gelatinizes and protein denatures, therefore the predictive model must incorporate a term to quantify the effects of gelatinization on viscosity.

Comparison of the observed and predicted viscosities of wheat flour cooked at 75°C and 85°C at a moisture content of 0.337 g water per gram solids (25.2% wb) and 75°C with a moisture content of 0.385 g water per gram solids (27.8% wb) indicated that no increase in viscosity occurred at varying cook times and therefore the



Figure 6.2. Predicted versus observed viscosities corrected for shear rate at all temperatures, moisture contents and time- temperature history for whole wheat flour doughs.



Figure 6.3. Predicted versus observed viscosities corrected for shear rate and temperature at all moisture contents and time-temperature histories for whole wheat flour doughs.



Figure 6.4. Predicted versus observed viscosities corrected for shear rate, temperature, and moisture content at all time-temperature histories for whole wheat flour doughs. time-temperature history variable was set to zero ( $\psi$ =0). The lack of differences between the predicted and observed viscosities may be caused by the low moisture contents and lower cook temperatures.

Lund (1984) observed that the transition temperature on a differential scanning thermogram increased slightly as the moisture content decreased. This transition temperature is indicative of the onset of gelatinization. Presence of gluten, lipids and solutes can also compete with the starch for water and thus affect the onset of gelatinization. The combination of low moisture contents and the presence of gluten in the whole wheat flour most likely caused the gelatinization temperature to shift higher, leading to the lack of noticeable differences between the observed and predicted viscosities corrected for shear, temperature, and moisture content.

Using observed and predicted viscosities at a 24 minute cook time and at each temperature where a noticeable difference between the observed and predicted viscosity occurred, ln A' versus ln(Cs) were regressed for each cook temperature. A relationship between  $\alpha$  and  $\beta_o$  and the inverse temperature was then determined. An Arrhenius relationship between inverse temperature and  $\beta_o$  was observed. This is similar to what was observed for corn starch (Chapter 5.). However, unlike cornstarch, an Arrhenius relationship was not observed between  $\alpha$  and the inverse temperature. The equations for  $\alpha$  and  $\beta_o$  are

$$\alpha = -143.5 + \frac{50688.3}{T}$$

$$\beta_o = e^{\left(-60.0 + \frac{204.9}{T}\right)}$$
[6.4]
[6.5]

Viscosity was observed to be a function of cook time and therefore timetemperature history parameters were calculated according to the procedure described by Morgan et al. (1988) and Dolan et al. (1988). The parameter  $\Delta E_g$  was found to be unaffected by moisture content. This is in agreement with Dolan's (1988) findings that there is little difference between  $\Delta E_g$  values for high moisture corn starch solutions of varying starch concentrations. Burros et al. (1987) estimated activation energies for corn starch. Over the moisture content ranges used in their study, no significant difference between activation energies was observed. The moisture content range for this study is within the range studied by Burros et al. (1987).

In this study, the activation energy  $(\Delta E_g)$  was found to be 25100 cal/g-mole. The constant  $k_a$  was found to be slightly affected by moisture content, however, this may be due to normal sample variations and not because of any moisture content dependency. Values for  $k_a$  were 2.5 for 0.436 g water per g solids (30.4% wb) and 1.1 for 0.385 and 0.337 g water per g (27.8% and 25.2% wb, respectively) solids.

Figure 6.5 is a plot of observed viscosity versus predicted viscosity corrected for shear rate, temperature, moisture content and time-temperature history. The fit of the data improved ( $R^2$ =0.687) when compared to the fit after correcting for shear rate, temperature, and moisture content alone; the slope was also slightly improved (0.815). This improvement is not as dramatic as that observed for native corn starch (Chapter 5). Reasons for this may include a) "slip-stick" phenomena or friction effects may have had a greater effect on the viscosity of whole wheat flour than observed for native corn starch, b) the presence of protein, bran and other flour components that were not accounted for in the model may have had an effect on the time-temperature parameters, and c) the low moisture content used in this study may have amplified either of these effects or made it very difficult for the capillary rheometer to measure the effects.



Figure 6.5. Predicted versus observed viscosities corrected for shear rate, temperature, moisture, and time-temperature history for whole wheat flour doughs.

Another possibility is the likely presence of an elastic component due to gluten in the whole wheat flour. Gluten is developed by mixing flour and water together and then kneading (mixing) the dough. The shear rate term in the model does not account for energy losses due to elasticity of the dough and therefore this may be why the overall fit of the model is less for whole wheat flour than for corn starch.

It should be recognized that gluten development is probably the major contributor to viscosity below starch gelatinization temperatures. In the capillary rheometer it may be assumed that gluten development was negligible because very little mixing occurs in the instrument. Therefore, gluten development occurred during sample preparation and not during capillary rheometer tests.

Stepwise regression after log-log transformation gave results similar to those for native cornstarch where the order of importance for each model parameter was shear rate, temperature, time-temperature history and moisture content. Table 6.4 lists the stepwise results for whole wheat flour.

Extrusion test results after correction for shear rate, temperature, moisture content and time temperature history are plotted in Fig. [6.6]. Extrudate properties varied from unpuffed and unswelled material to a highly puffed bread-like material which did not hold its puffed appearance upon cooling. Unlike the case for corn starch, strain history does not appear to affect wheat flour during extrusion. A relationship between observed viscosity and shaft work input, as was seen for native corn starch, could not be determined and therefore the strain history correction term was set to unity. Regression through the origin for observed versus predicted viscosity corrected for shear rate, temperature, moisture content and time-temperature history indicates a better fit ( $R^2$ =0.788) than the data from the capillary rheometer when one compares  $R^2$  values (0.788 versus 0.687).

Table 6.3. Results of stepwise regression for whole wheat flour doughs.					
SUMMARY OF STEPWISE REGRESSION PROCEDURE FOR DEPENDENT VARIABLE $\eta_{pre}$					
VARIABLE ENTERED	PARTIAL R <sup>2</sup>	MODEL R <sup>2</sup>	C(P)	F	PROB>F
Ϋ́	0.4953	0.4953	669.14	1026.39	0.0001
TEMP	0.1391	0.6344	198.65	397.65	0.0001
Α'	0.0538	0.6882	17.79	180.31	0.0001
MOIST	0.0046	0.6929	4.00	15.79	0.0001



Figure 6.6. Observed versus predicted viscosities corrected for shear rate, temperature, moisture, and time-temperature history in extruder dies for whole wheat flour doughs.

Inability to correct for strain history for whole wheat flour compared to corn starch may be attributed to the differences in the general make-up of the two materials. Corn starch is nearly 100% starch, whereas the whole wheat flour consists of starch, bran, wheat protein and some lipids. The inclusion of water and the mixing in the extruder most likely caused development of the gluten which may have contributed to increase in viscosity that was not counteracted by a lowering of the viscosity by mechanical breakdown of starch.

A list of the parameter values or the relationship used in Eq. 6.1 are given in Table 6.5. It is important to note that the order in which values were determined may affect the final results. Also, some of the values depend on either temperature or moisture content or both.

Table 6.5. List of parameter values for Eq. 6.1.			
Parameter	Value or relationship		
το	93.8 kPa		
μ_	105000 Pa s		
$n_1$ $n_2$ $\Delta E_{v}$	1.0 0.40 5354.4 °K		
b A'	$e^{\left(-59.99+\frac{20648.6}{7}\right)}(Cs)^{\left(-143.6+\frac{50688.3}{7}\right)}$		
$\Delta E_{g}$ $\mathbf{k}_{a}$ $[1 - \beta(1 - e^{-d\phi})]$	25100 cal/g-mole. 2.5 s <sup>-1</sup> - <sup>•</sup> K at 0.436 g/g db 1.1 s <sup>-1</sup> - <sup>•</sup> K at 0.337 & 0.385 g/g db 1.0		

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#### **6.5.** Conclusions

Capillary rheometer tests were performed on whole wheat flour at moisture contents of 0.333 to 0.436 g water per g solids (25.0% to 30.4% wb), cook times of one to 24 minutes, temperatures of 50, 55, 60, 75, 85, and 110°C and shear rates of one to 1000 s<sup>-1</sup> to obtain the variables needed use Eq. 6.1. Overall fit ( $R^2$ =0.687) of the observed versus predicted viscosities for whole wheat flour was less than was observed for native corn starch ( $R^2$ =0.950). This may be due to the effects of flour components (bran, protein, fat) which were not present in the corn starch and are not accounted for by the general model.

No differences due to time-temperature history were observed for samples containing 0.337 g water per g solids (25.2% wb) and cooked at 75°C and 85°C, but at the other moisture contents and cook temperatures, viscosity did change with cook time. The presence of flour components competing for water probably affected the gelatinization kinetics at the low moisture content and lower cook temperatures, causing no measurable change in viscosity at different time-temperature histories.

Use of the parameters obtained from the capillary rheometer in Eq. 6.1 gave good agreement between observed and predicted viscosity ( $R^2=0.788$ ) for whole wheat extrudates. Different strain histories did not appear to affect the twin screw extrusion data and therefore the strain history term was set to unity for all extrusion tests. Again the presence of the different flour components may have had an effect on the ability to correct for strain history.

Future research should include the effects of flour constituents (e.g. bran, protein, fat) or other additives (salt or sugar for example) on the model. Specifically, the effects of flour constituents on the time-temperature history and strain history correction should be determined. Further research into quantification of strain history within the extruder is

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also necessary. The question of whether an accurate measurement of shear rate in each extruder zone is necessary to quantify strain history or if measurement of work input alone is adequate must be answered.

# 6.6. Nomenclature

- A' relative amount of viscosity increase due to gelatinization, dimensionless
- d rate constant of effect of strain history ( $\Phi$ ) on viscosity, s
- b rate constant of effect of moisture content on viscosity, dimensionless
- Cs starch concentration, wet basis decimal
- D capillary diameter, m
- $\Delta E_{\star}$  free energy of activation, kcal/g mole
- $\Delta E_s$  energy of gelatinization, cal mole<sup>-1</sup>
- k, reaction transmission coefficient, \*K<sup>-1</sup> s<sup>-1</sup>
- L capillary length, m
- MC moisture content, dry basis, decimal
- MC<sub>r</sub> reference moisture content, dry basis, decimal
- n<sub>i</sub> power indices, dimensionless
- $\Delta P$  pressure drop, Pa
- Q volumetric flow rate, m<sup>3</sup> s<sup>-1</sup>
- R<sub>o</sub> capillary radius, m
- R universal gas constant, 1.987 cal/g mole
- t time, s
- T temperature, <sup>°</sup>K
- T, reference temperature, 'K
- $\alpha$  index of molecular weight effects on viscosity, dimensionless
- $\beta$  material constant describing effect of strain history on viscosity at  $\phi = \infty$ , dimensionless
- $\beta_{a}$  material constant describing effects of temperature on gelatinization, dimensionless

- $\eta$  apparent viscosity, Pa s
- $\eta_{\text{pre}}$  predicted apparent viscosity, Pa s
- $\dot{\gamma}$  shear rate, s<sup>-1</sup>
- $\mu_{-}$  high shear limiting viscosity, Pa s<sup>n2-n1</sup>
- φ strain history, dimensionless
- $\psi$  time-temperature history, s <sup>•</sup>K

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## **CHAPTER 7 SUMMARY AND CONCLUSIONS**

# 7.1. Overall Summary

A generalized viscosity model based on the work of Morgan et al. (1988) for the cooking extrusion of low to intermediate moisture content starch based products was developed. The model describes the effects of shear rate, temperature, moisture content, time-temperature history, and strain history on the viscosity of the extrudate, assuming no interaction among the various effects.

The model is flexible enough to allow its use under a wide range of operating conditions and extrusion equipment. This is demonstrated by its ability to accurately fit data from both a capillary rheometer and an extruder. As a result, model parameters for shear rate, temperature, moisture content and time-temperature history can be determined by using capillary rheometry, thus saving time and material by not having to perform all tests on an extruder. The simplicity and flexibility of the model when compared to other proposed models is also evident when data analysis is performed. This is because a standard statistical package with the ability to perform both non-linear and linear regression is all that is required to determine the model parameters.

Overall, results from the capillary rheometer and twin screw extruder were similar over a wide range of shear rates, moisture contents, temperatures, time-temperature and strain histories.

Tests were conducted using potato flour at temperatures of 25-95°C, moisture contents of 0.28 to 0.77 g water per g potato flour (22 to 44% wb), and shear rates from 10-10000 s<sup>-1</sup>. Shear rate effects were found to be best described by the power law model. Correction for moisture content and temperature improved the fit of the observed versus predicted viscosities to give an  $R^2$  of 0.951. Since the starch in potato flour is gelatinized in the process of making the flour, no differences were observed between samples cooked at different temperatures and cook times. Therefore, the time-temperature history portion of the model was set to unity. Extrusion tests over different strain histories did not affect the viscosity of the potato flour doughs, either, and so the strain history term was set to unity. Lack of measurable strain history effects may also have been due to the pregelatinization of the starch.

Cooking extrusion of native corn starch were simulated in a capillary rheometer at moisture contents of 0.359 to 0.572 g water per g starch (26.4% to 36.4% wb). Temperatures of 50, 55, 60, 75, 85, 95, and 110°C at cook times of one to 24 minutes after compression within the capillary rheometer were used to determine the effects of temperature and time-temperature history. Shear rates within the capillary rheometer dies ranged from one to 300 s<sup>-1</sup>.

Shear rate effects were best described by the model proposed by Ofoli et al. (1987). A fit of the observed versus predicted viscosity yielded an  $R^2$  of 0.877 when all the data were modelled as a function of shear rate only. Subsequent correction for temperature, moisture content, and time-temperature history improved the fit, with a final  $R^2$  of 0.950.

Cook temperature and moisture content were found to be important for predicting the viscosity of cooked corn starch. Due to the small barrel diameter of the capillary rheometer, cook time was not a factor when effects of time-temperature history were modelled. This is because the center temperature of the starch material within the rheometer barrel reached the barrel wall temperature in three minutes or less. However, moisture content and cook temperature were found to be very important factors when modelling the effects of gelatinization on the viscosity of cooked starch.

Data from capillary rheometry and twin screw extrusion tests were identical under low strain history conditions. Extrusion tests indicated that when strain history is large, correction for strain history is necessary. Estimation of shear rate, within each zone of the extruder is extremely difficult and therefore was not done. However, modification of the strain history term to include shaft work input (mechanical energy) as proposed by Vergnes and Villemaire (1987) yielded a final equation that gave a reasonable fit ( $R^2$ =0.846) for the extrusion data. With the present knowledge on estimating the shear rate within each extruder zone, the use of shaft work input (mechanical work input) may be a viable alternative to describing strain history.

Capillary rheometer tests for whole wheat flour doughs with moisture contents of 0.333 to 0.436 g water per g solids (25% to 30.4% wb) were cooked from one to 24 minutes at the same temperatures as those for corn starch. Shear rates ranged from one to  $1000 \text{ s}^{-1}$ . Shear rate effects were modelled using the generalized model proposed by Ofoli et al. (1987); the generalized model reduced to the Herschel-Bulkley model. Variables determined for moisture content and temperature effects were similar to those found in the literature for similar materials. Viscosity was found to be a function of moisture content and cook temperature of the whole wheat flour dough. Low moisture content (0.337 g water/g solids) and lower cook temperatures (75 and 85°C) were observed to produce no differences in viscosity with changing cook times. At other moisture contents and cook temperatures, viscosity changed with cook time.

Presence of flour components competing for water probably affected the gelatinization kinetics at the low moisture content and lower cook temperatures, causing no measurable change in viscosity at different time-temperature histories. The overall fit  $(R^2=0.687)$  of the observed versus predicted viscosities for the capillary rheometer tests was not as good as was seen for corn starch  $(R^2=0.950)$  and potato flour  $(R^2=0.951)$ . This apparent lack of fit may be due to the presence of whole wheat flour components such as bran, protein and some lipids whose presence were not accounted for in the model. Different strain histories did not appear to affect the twin screw extrusion viscosities and therefore the strain history term was set to unity for all extrusion tests. The presence of the different flour components may also have had an effect on the ability to correct for strain history. This may be especially true if development of the gluten was occurring within the extruder. Gluten development may have counteracted any degradation of the starch molecule due to the strain history, therefore giving the inconclusive results.

#### 7.2. Conclusions

A generalized model has been developed to describe the effects of shear rate, temperature, moisture content, time-temperature history and strain history on the viscosity of low moisture starch based products.

The model was evaluated for corn starch, potato flour and whole wheat flour extrudates. It was found to be less accurate in modeling the viscosity of whole wheat flour, in comparison to the other two materials. The presence of bran, protein and some lipids in the whole wheat flour accounted for the lack of accuracy. In particular, gluten development may have contributed elastic effects which contributed to the drop in accuracy.

Capillary rheometer and twin screw extrusion data overlapped each other at small strain histories. Therefore, capillary rheometer can be used to determine shear rate, temperature, time-temperature and moisture content parameters for use in twin screw extrusion. However, use of the capillary rheometer to quantify strain history parameters is not practical because of the very small strain histories that occur in the rheometer.

Starch gelatinization affects the final viscosity of the extrudate. The extent of the effect depends on moisture content, cook temperature and, for some materials, cook time. Non-starch components such as bran, protein, and lipids affect starch gelatinization kinetics and therefore influence the final viscosity.

# **CHAPTER 8 SUGGESTIONS FOR FUTURE RESEARCH**

The four primary activities for future research are to:

1). determine the effects of ingredients such as protein, bran, lipids, salt and sugar on the viscosity of the extrudates;

2). develop or modify a technique which will enable one to determine the effect of cook time at varying cook temperatures on time-temperature history and, therefore, viscosity;

3). develop equipment to measure strain history parameters outside the extruder; and

4). investigate the phenomena of slip or "slip-stick" and sliding friction in the extruder and capillary dies.

#### 8.1. Effects of non-starch ingredients.

In determining the effects of non-starch ingredients on the viscosity, it is important that these effects are examined before and after gelatinization. This is because the presence of bran, proteins, fats, simple sugars and salts are known to have an effect on the gelatinization kinetics, even though the mechanism is not known. It is important that every attempt be made to keep the modified model as simple as possible.

Some possible methods for evaluating these effects include:

1. Starting with starch-water mixtures, adding different quantities of protein to the mixture and measuring the effects on the viscosity of both cooked and uncooked mixtures. Repeat these experiments, replacing the protein with bran, lipids, sugar and salt.

2. To measure the effects of these non-starch constituents on the gelatinization kinetics, gelatinization could be characterized by means other than viscosity such as differential scanning calorimetry and thermomechanical analysis, or by measuring starch gelatinization via enzymatic methods.
3. Finally, once the effects of each individual ingredient are known some attempt should be made to quantify their effects on gelatinization.

# **8.2.** Development of methods to quantify time-temperature history effects.

Measuring the effects of time-temperature history in the Instron Capillary Rheometer is difficult because the center temperature of the starch dough reaches the gelatinization temperature in a very short time (three minutes or less). This can be further compounded by loading difficulties due to the small diameter of the rheometer barrel. If sample loading is impeded, the time before compression of the sample may not be consistent across all tests. Therefore, some alternative method is needed to determine timetemperature history parameters.

Modification of the capillary rheometer barrel is necessary to achieve both improvement of sample loading and better quantification of time-temperature history parameters. The easiest way to achieve this would be to increase the diameter of the barrel. By increasing the barrel diameter, the heat transfer to the center of the starch dough cylinder may be slowed enough to have a mixture of gelatinized, partially gelatinized and ungelatinized starch across the radius. It is also important to have strict temperature control of the barrel wall.

Use of thermal analysis methods such as differential scanning calorimetry (DSC) or thermomechanical analysis (TMA) may also be useful to determine the timetemperature constants. Burros et al. (1987) and Lund and Wirakartusumah (1984) describe methods to determine starch gelatinization kinetics and the effects of moisture content on the kinetics. Care must be taken, however, that the parameters obtained by DSC or TMA actually describe the same effects of time-temperature history on viscosity as observed in either test. Use of DSC or TMA would be easier than redesigning the capillary rheometer and would also reduce the size of the starch-water sample needed.

## 8.3. Development of equipment for measuring strain history.

Measurement of strain history outside the extruder is difficult for low to intermediate moisture products, because most rheological equipment cannot handle the high torque requirements of these products. Therefore, it is necessary to design new equipment for the measurement of strain history parameters as an alternative to the extruder. Strain history within the capillary rheometer is negligible in comparison to an extruder and therefore unacceptable for strain history measurement.

Elements of the new equipment should include the ability to:

1) measure shear rate accurately,

2) vary shear rate,

3) measure torque and subsequently shear stress,

4) control temperature and moisture, and

5) quantify mechanical energy input.

## 8.4. Investigation of slip or friction within the capillary die.

Examination of slip phenomena in the capillary die is also necessary. Attempts to quantify slip using the techniques described by Darby (1976) did not produce useful results. In addition, due to the non-cohesive nature of the product, a friction coefficient could not be determined using uniaxial compression. At the present time possible solutions to this problem are not obvious to this author.

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#### **CHAPTER 9 LITERATURE CITED**

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APPENDICES

Appendix 1. Temperature, moisture content, cook time, shear stress, shear rate, and observed viscosity of potato flour doughs.

Temperature (°C)	Moisture Content (g solids	Cook Time (min)	Shear Stress (Pa)	Shear Rate (s <sup>-1</sup> )	Observed Viscosity (Pa s)
50005555555555555555555555555555555555	0.22 0.22 0.337	555500000005555555555555555552222222244444444	$\begin{array}{c} 492865\\ 545802\\ 498704\\ 388596\\ 38799\\ 384689\\ 3879973\\ 547062\\ 38799773\\ 582062\\ 505999773\\ 582062\\ 505999773\\ 582062\\ 505999773\\ 582062\\ 505999773\\ 582062\\ 505999773\\ 582062\\ 505999773\\ 582062\\ 505999773\\ 582062\\ 505999773\\ 582062\\ 58206$	$\begin{array}{c} 43.9\\ 178.6\\ 178.6\\ 9\\ 122.2\\ 22.2\\ 61.1\\ 367.0\\ 602.5\\ 60$	$\begin{array}{c} 11227\\ 3056\\ 3056\\ 11360\\ 3148\\ 62782\\ 61452\\ 8953\\ 1586\\ 95279\\ 32614\\ 1517\\ 4822\\ 82593\\ 1586\\ 1553\\ 1586\\ 1553\\ 1233\\ 1201\\ 469\\ 266\\ 231\\ 391\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 469\\ 266\\ 231\\ 232\\ 232\\ 462\\ 391\\ 232\\ 232\\ 462\\ 391\\ 232\\ 391\\ 232\\ 266\\ 232\\ 266\\ 232\\ 232\\ 232\\ 232$

Temperature (°C)	Moisture Content (db)	Cook Time (min)	Shear Stress (Pa)	Shear Rate (s <sup>-1</sup> )	Observed Viscosity (Pa-s)
95 95 95 95 95 95 95 95 95 95 95 95 95 9	$\begin{array}{c} 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.337\\ 0.436\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5\\ 0.5$	66666622222555555555555555555555555555	$\begin{array}{r} 43866\\ 18026\\ 47680\\ 32945\\ 62882\\ 37520\\ 40290\\ 44085\\ 37540\\ 44085\\ 37540\\ 44389\\ 25216\\ 35508\\ 77371\\ 76295\\ 59964\\ 32083\\ 7614\\ 32083\\ 76214\\ 35575\\ 83009\\ 131029\\ 43124\\ 127521\\ 51008\\ 47614\\ 27468\\ 21364\\ 44601\\ 43289\\ 193320\\ 43440\\ 102996\\ 103559\\ 18628\\ 63550\\ 80997\\ 160901\\ \end{array}$	$\begin{array}{r} 476.8\\ 155.4\\ 476.8\\ 155.4\\ 1654.8\\ 53.6\\ 3099.2\\ 186.8\\ 987.9\\ 987.9\\ 3099.2\\ 197.0\\ 66.0\\ 1579.0\\ 1579.0\\ 1579.0\\ 1579.0\\ 1579.0\\ 526.0\\ 46.7\\ 219.6\\ 829.3\\ 829.3\\ 4250.7\\ 4250.7\\ 125.3\\ 381.5\\ 381.5\\ 381.5\\ 1311.8\\ 358.0\\ 519.0\\ 2861.0\\ 4159.0\\ 258.0\\ 410.0\\ 2061.0\\ 3277.0\\ \end{array}$	$\begin{array}{c} 92\\ 116\\ 100\\ 212\\ 38\\ 700\\ 13\\ 236\\ 38\\ 45\\ 14\\ 128\\ 538\\ 49\\ 235\\ 114\\ 104\\ 687\\ 1632\\ 1632\\ 1632\\ 1632\\ 1632\\ 378\\ 520\\ 123\\ 380\\ 726\\ 343\\ 540\\ 836\\ 25\\ 72\\ 155\\ 39\\ 49\end{array}$

Appendix 1 (cont 14)

Moisture Content	Temperature	Cook Time	L/D	Shear Stress	Shear Rate	Observed Viscosity
(g starch g water)	(°C)	(min)		(Pa)	(s-1)	(Pas)
$0.359 \\ 0.359 \\ 0.3599 \\ 0.3599 \\ 0.3559 \\ 0.3559 \\ 0.3559 \\ 0.3559 \\ 0.3559 \\ 0.355$	50 50 50 50 50 50 50 50 50 50 50 50 50 5	000000000000000000000000000000000000000	<b>~~~~</b>	907224 1153052 850644 1166709 1293525 1100370 1293525 11009154 1257431 1205730 390204 629789 594670 283288 437028 495559 249730 565795 946244 753093 823330 1597613 377912 4955556 413986 378498 5189715 460440 1075011 476049 655542 1974435 653981 294116 794455 425712	$\begin{array}{c} 55.0\\ 41.7\\ 70.7\\ 101.1$	$\begin{array}{c} 16495.0\\ 27519.1\\ 12031.7\\ 21174.4\\ 12870.9\\ 9461.5\\ 10906.1\\ 63829.0\\ 9558.9\\ 10708.1\\ 30015.7\\ 10444.3\\ 11032.8\\ 16664.0\\ 9711.7\\ 4546.4\\ 2907.8\\ 3572.3\\ 3573.5\\ 611336.6\\ 158658.9\\ 10213.8\\ 158658.9\\ 10213.8\\ 158658.9\\ 10213.8\\ 4335.6\\ 4043.6\\ 2980.6\\ 45773.9\\ 50041.4\\ 2988.6\\ 45773.8\\ 9369.4\\ 13937.8\\ 9369.4\\ 13937.8\\ 9369.4\\ 14285.6\\ 7804.7\\ 122698.6\\ 14285.$

Appendix 2. Moisture content, temperature, cook time, die L/D, shear stress, and shear rate of corn starch.

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$\begin{array}{c} 7680.0\\ 5271.2\\ 2673.7\\ 40551.7\\ 3604.3\\ 715279.0\\ 3604.3\\ 7152790.0\\ 111599.8\\ 32755669976\\ 739831.0\\ 2776522.0\\ 83276562.0\\ 811232497.0\\ 256558511.0\\ 101323297.0\\ 932535.5\\ 739831.0\\ 101323297.0\\ 932535.5\\ 7393255.5\\ 101323297.0\\ 932536.0\\ 1013232751.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\ 22215.2\\$

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).35985 <th>იიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიი</th> <th>~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~</th> <th><math display="block">\begin{array}{c} 6852\\ 8652\\ 27322450920\\ 455985120\\ 27353245098512\\ 450985120\\ 455985120\\ 456849742\\ 456849742\\ 451765216\\ 5111222339150253\\ 4517455998\\ 19778458833\\ 4517455998\\ 199778458833\\ 444951257593\\ 4449512582\\ 4517455998\\ 199778458\\ 4517455998\\ 199778458\\ 425457593\\ 3038552\\ 44495355\\ 44495355\\ 44495355\\ 445579333\\ 45174558\\ 45174558\\ 4517455\\ 4517455\\ 4517455\\ 4517455\\ 4517455\\ 4517455\\ 4517455\\ 451745</math></th> <th><math display="block">\begin{array}{c} 5.76477855584466196396679555567942644999048377988874129723556679426449990483798887412972355567942644999048379888741297235556679426449990483798887412972355566794264499904837988874129723555667942651121212123300706337988741297235566794264499904837988741244148445666725556794266379555567942663798874124414844566672555679426637988741297235566794266379887412441484456667255567942663798874112464499904837988741124644999048379887411246449990483798874112464499904837988741124644999048379887411246449990483798874112464499904837988741124644999048379887411246449990483798874112464499904837988741124644999048379887411246449990483798874112464499904837988741124644999048379887499048379887411424499904837988799887411424499904837988799887411424499904837988799887499904837988799887499904837988799887998879988799887998879988799</math></th> <th><math display="block">\begin{array}{c} 1128999988399998085040749993194718866337223736469122222222222222222222222222222373843899237237384389923732597237304925555111189923732597237306455733843380695573113899234417384388069557311389923441738438806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731857866637786457378438095573843809557311389923441738438069557738438009557738438009557738438009557738438009557738438009557738438009557738438009557788438009557788438009557788438009557788438009557788438009557788438009557788438009557788438009557788438000000000000000000000000000000000</math></th>	იიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიიი	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	$\begin{array}{c} 6852\\ 8652\\ 27322450920\\ 455985120\\ 27353245098512\\ 450985120\\ 455985120\\ 456849742\\ 456849742\\ 451765216\\ 5111222339150253\\ 4517455998\\ 19778458833\\ 4517455998\\ 199778458833\\ 444951257593\\ 4449512582\\ 4517455998\\ 199778458\\ 4517455998\\ 199778458\\ 425457593\\ 3038552\\ 44495355\\ 44495355\\ 44495355\\ 445579333\\ 45174558\\ 45174558\\ 4517455\\ 4517455\\ 4517455\\ 4517455\\ 4517455\\ 4517455\\ 4517455\\ 451745$	$\begin{array}{c} 5.76477855584466196396679555567942644999048377988874129723556679426449990483798887412972355567942644999048379888741297235556679426449990483798887412972355566794264499904837988874129723555667942651121212123300706337988741297235566794264499904837988741244148445666725556794266379555567942663798874124414844566672555679426637988741297235566794266379887412441484456667255567942663798874112464499904837988741124644999048379887411246449990483798874112464499904837988741124644999048379887411246449990483798874112464499904837988741124644999048379887411246449990483798874112464499904837988741124644999048379887411246449990483798874112464499904837988741124644999048379887499048379887411424499904837988799887411424499904837988799887411424499904837988799887499904837988799887499904837988799887998879988799887998879988799$	$\begin{array}{c} 1128999988399998085040749993194718866337223736469122222222222222222222222222222373843899237237384389923732597237304925555111189923732597237306455733843380695573113899234417384388069557311389923441738438806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731138992344173843806955731857866637786457378438095573843809557311389923441738438069557738438009557738438009557738438009557738438009557738438009557738438009557738438009557788438009557788438009557788438009557788438009557788438009557788438009557788438009557788438009557788438000000000000000000000000000000000$
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Appendix 2. (Cont'd).

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$\begin{array}{c} 832.7\\ 6238.1\\ 2930.6\\ 1566.7\\ 1077.5\\ 529.1\\ 1277.2\\ 1521.1\\ 1175.4\\ 1276.1\\ 936.3\\ 2896.0\\ 191.2\\ 1647.9\\ 1096.6\\ 1091.4\\ 1056.6\\ 521.8\\ 995389.0\\ 1058.4\\ 1058.4\\ 1058.4\\ 1169.7\\ 1148.2\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 1791.9\\ 1093.8\\ 10$

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Appendix 3. Temperature, moisture content, cook time, shear stress, shear rate, observed viscosity of whole wheat flour doughs.

Temperature	Moisture	Cook Shear	Shear Observed
- (°C)	Content (db)	Time Stress	Rate Viscosity
	(00)		
50000000000000000000000005555555555555	$\begin{array}{c} 0.333\\ 0.333\\ 0.3333\\ 0.3333\\ 0.3333\\ 0.3333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.3333333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.333333\\ 0.3333333\\ 0.3333333\\ 0.3333333\\ 0.3333333\\ 0.33333333\\ 0.3333333\\ 0.3333333\\ 0.3333333\\ 0.33333333\\ 0.3333333\\ 0.3333333\\ 0.3333333\\ 0.33333333\\ 0.33333333\\ 0.3333333333$		10.0 $27309.2$ 2.6 $19701.0$ 38.7 $16461.7$ 56.4 $12389.0$ $147.9$ $8031.7$ $114.6$ $6373.8$ $116.8$ $6556.8$ $191.8$ $5396.1$ $174.6$ $4520.7$ $3.4$ $61165.8$ $4.0$ $56227.7$ $7.6$ $39970.6$ $50.5$ $12538.6$ $38.2$ $13821.4$ $35.5$ $14125.9$ $61.2$ $9897.4$ $83.3$ $9163.9$ $67.9$ $9688.4$ $138.1$ $5459.0$ $192.7$ $5417.8$ $160.6$ $5516.1$ $228.1$ $4139.8$ $235.2$ $4164.0$ $203.9$ $3984.6$ $19.2$ $10089.5$ $22.3$ $12592.1$ $31.2$ $15206.8$ $40.7$ $9315.9$ $53.0$ $11460.6$ $33.7$ $6032.5$ $97.0$ $3907.3$ $112.7$ $5859.5$ $107.2$ $5340.0$ $32.6$ $8225.1$ $44.4$ $8218.6$ $38.1$ $8294.4$ $60.7$ $6264.1$ $68.5$ $6319.5$ $60.1$ $6255.0$ $154.9$ $3874.1$ $134.2$ $3652.8$ $139.7$ $3730.8$ $53.0$ $4714.6$ $11.1$ $36929.4$ $54.5$ $4264.4$

Appendix 3. (Cont'd).

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60	0 333	6	301211	100 0	3013 3
00	0.333	U U	204214	T00.0	2042.2
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60	0.333	6	352556	132.8	2653.9
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25	0 337	6	1511021	12 0	100225 2
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25	0 337	6	1850707	19.4	95295 8
25	0.557	U U	1050707	13.1	95295.0
25	0.337	6	1757001	35.3	49788.4
	0.007	č	107707		
25	0.337	6	10//62/	94.0	11462.2
25	0 227	č	1450454	2000	-7022 1
23	0.337	Ö	1402404	200.0	1023.1
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50	0 337	6	1054201	174 2	6051 1
50	0.337	ý.	1034201	113.4	0051.1
50	0.337	6	609094	114.9	5302.2
Ē		ž	1110000		0000.0
50	0.337	6	1112767	379.9	2928.8
ĔŇ	0 227	č	1101054	107 0	2215 4
<b>30</b> -	0.337	σ	1101034	49/.0	2213.4
50	0 337	6	1119621	051 N	1172 6
50	0.337	U	1110024	374.0	11/2.0
50	0 337	6	1534447	1595 1	962 0
30	0.337		1001111	1000.1	502.0
75	0.337	1	29285	21.6	1357.9
	0.007				
15	0.337	1	26355	92.0	286.6
76	Å 337	ĩ	60330	151 0	160 7
15	0.337	1	00330	121.0	430./
75	0 337	1	117130	16 0	7200 6
15	0.557	<u>+</u>	11/133	10.0	1300.0
75	0 337	2	15620	21 0	742 2
ίč	0.007	2	15020		
/5	0.33/	2	15620	11.5	201.6
76	0 227	õ	221575	2021	722.4
13	0.33/	2	2213/3	· JUZ.4	132.1
75	0 337	2	110560	10 2	7712 7
22	0.221	4	110000	10.2	1113.1
75	0.337	2	171800	332.3	517.0
÷č	0.007	2	1 2 2 2 2 2 2		
15	0.337	2	138010	222.0	624.4
75	0 227	้ว	00505	FOF 1	165 7
15	0.33/	Z	70303	<b>JYJ.</b> I	102./
75	0 227	2	152275	22 0	6681 1
12	0.221	2	TICCII	22.0	0004.1
75	0.337	2	82970	52 9	1569 2
<u></u>	ו > > 1	2	100000		1100.1
/5	0.337	2	136005	120.5	1128.4
'nč	ñ 559	5	101070	1001	1117.7
10	U.33/	2	1049/3	100.1	1113./
75	0 227	Ō	102270	2252 6	50 /
15	0.221	2	122710	3232.0	53.4
75	0 227	2	210840	1 Q Q	10664 5
12	0.331	2	210010	T3+0	T0001.0
75	0.337	3	115189	4.8	23805.1
<u></u>	ו•••	ž			
/5	0.337	3	20/906	105.1	1977.7
	0.224	ว้	017075	202.0	1070
15	0.33/	3	ZT 1012	202.9	10/2.9
75	0 227	2	110560	12 0	1000/ 0
15	0.331	Ş	THUJON	T3.0	TOODA . O
75	0 227	২	22797	20 1	1422 2
12	V. J. J.	2	20131	2 <u>0</u> .1	1100.0
75	0.337	3	130473	40.5	3219.8
		ž	100310	10.5	
15	0.337	3	155200	96.3	1612.0

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Appendix 3. (Cont'd).

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75	0.337	3	197175	145.9	1351.8	
75	0 227	č	125021	15 0	7006 7	
15	0.337	ç	123924	13.3	1900.1	
75	0.337	6	125924	27.1	4640.3	
75	0.337	6	187419	45.8	4089.6	
75	0.337	č	120610	100.0	1202 5	
15	0.337	0	130010	100.2	1303.5	
75	0.337	6	265500	165.7	1602.1	
75	0 337	6	94357	111 7	844 5	
12	0.337	č	175700	101 0	1 / / 0 2	
15	0.337	D	1/5/00	121.3	1440.5	
75	0.337	6	58564	419.3	139.7	
75	0 337	6	244027	985 7	247 6	
75	0.227	č	220170	1150 4	506 7	
15	0.337	D	230170	1152.4	200.1	
75	0.337	6	137633	11.6	11862.2	
75	0 337	6	183022	34 7	5276 9	
75	0.337	č	06712	51.7	1650 7	
15	0.337	Ď	00/12	52.3	1020.1	
75	0.337	6	209213	119.0	1758.3	
75	0 337	6	131013	164 4	796 8	
75	0.337	č	102400		720.1	
/5	0.337	Ď	103468	140.0	/39.1	
75	0.337	6	65888	219.5	300.2	
75	0 337	Ġ	131774	446 1	295 4	
75	0.337	č	101111		233.4	
/ 5	0.337	b	207424	803.4	240.2	
75	0.337	6	215476	1144.7	188.2	
75	0 337	12	275269	37 0	7445 1	
75	0.337	10	272071		$(1 \land C )$	
15	0.337	12	3/28/1	60.7	0140.3	
75	0.337	12	111271	78.1	1425.0	
75	0 337	12	560290	251 0	2222	
75	0.337	10	145117		7720.0	
15	0.337	12	145117	10.0	1120.9	
75	0.337	12	133403	116.2	1148.5	
75	0 337	12	86550	312 2	277 2	
75	0.337	10	246101	1460 6	226.7	
15	0.337	μZ	340191	1402.0	230.1	
75	0.337	12	137630	851.6	161.6	
75	0 337	12	55640	7.5	7463 5	
75	0.227	12	110016	15 6	2627 0	
15	0.337	12	119010	43.0	2027.0	
75	0.337	12	164799	83.4	1975.2	
75	0.337	12	113717	153.8	739.4	
75	0 227	12	112162	220 6	626 1	
12	0.337	12	143103	220.0	020.4	
15	0.337	12	140238	449./	311.9	
75	0.337	12	124129	713.7	173.9	
75	0 337	12	231120	1502 6	117 2	
15	0.337	12	234423	1392.0		
/5	0.337	12	210514	1345.1	156.5	
75	0.337	24	133725	59.7	2240.2	
75	0 337	21	100071	100 6	503 2	
15	0.337	24		100.0	J0J.Z	
15	0.337	24	341640	1299.0	263.0	
75	0.337	24	248908	1186.6	209.8	
75	0 337	21	66966	12.2	5100 0	
12	0.337	24	100000	12.2	J433.3	
15	0.337	24	136414	32.3	4225.1	
75	0.337	24	153899	67.6	2275.2	
75	0.334	21	240285	1 Å 7 Å	1635 0	
15	0.001	27	210200	1040		
15	0.331	24	293011	194.9	1504.1	
75	0.337	24	124942	261.1	478.5	
7 <b>5</b>	0 227	21	75011	215 0	240 0	
	0.001	27	100001		270.0	
15	0.337	24	183834	481.6	381.1	

Appendix 3. (Cont'd).

75	0.337	24	287628	810.9	354.7
75	0.337	24	161385	872.4	185.0
85	0.337	1	91106	12.0	7612.7
85	0.337	1	170494	34.6	4928.1
85	0.337	1	150317	60.5	2484.8
ÅŠ	0 337	ī	121034	113.2	1069 7
85	0.337	1	300318	216 4	1307 0
85	0.337	1	1227/7	210.7	152 0
05	0.337	1	12/615	272.5	400.9
	0.337	1	124015	500.1	JZZ.J 254 1
05	0.337	1	204000	5/0.L	354.1
00	0.337	1	238495		214.5
80	0.337	1	299993	808.3	3/1.1
85	0.337	Ţ	119312	20.1	5942.3
85	0.337	1	109975	30.5	3603.7
85	0.337	1	159105	68.7	2314.6
85	0.337	1	191317	141.0	1356.4
85	0.337	1	297715	205.2	1451.1
85	0.337	1	128358	115.3	1113.2
85	0.337	1	131449	247.2	531.8
85	0.337	Ĩ	193758	684.8	282.9
85	0.337	ī	293159	1415.9	207.0
85	0 337	ī	328950	1881 4	174 8
85	0 337	う	68330		6823 5
85	0.337	2	124940	17 0	2610 1
85 ·	0.337	2	102512	112 0	1622 6
05	0.337	22	126000	164 2	
05	0.337	42	130300	104.2	034.5
05	0.337	2	144461	277.1	50/.0
00	0.337	2	144401		520.3
85	0.337	2	295434	1160.6	254.6
82	0.337	2	228084	994.3	229.4
85	0.337	2	82970	17.0	4873.3
85	0.337	2	97610	33.5	2915.5
85	0.337	2	107072	69.2	1547.8
85	0.337	2	170332	146.1	1165.9
85	0.337	2	114044	147.0	775.7
85	0.337	2	116808	158.5	737.2
85	0.337	2	138607	302.3	458.6
85	0.337	2	203681	685.5	297.1
85	0.337	Ž	297876	1397.6	213.1
85	0.337	2	262739	1207.6	217.6
85	0.337	3	126902	17 4	7291 8
ÅŠ	0 337	ž	167899	20.7	8112 0
85	0.337	3	104770	59.2	1771 2
0.5 Q.5	0.337	2	222211	106 2	2105 1
g c	0.337	2	272711	150.3	1200 6
05	0.331	2	203020 71005	127.3	1230.0
0J 0F	0.337	2	11903	120.0	4//.0
80 05	0.33/	2	221120	596./	421.0
82	0.331	2	284535	888.9	320.1
85	0.337	3	191807	46.5	4126.4
85	0.337	3	210678	84.5	2492.1
85	0.337	3	210351	141.6	1485.3

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Appendix 3. (Cont'd).

85	0.337	3	172933	153.4	1127.5
85	0.337	2	88988	69.9	1273.3
80	0.337	3	132322	2/8.2	480.5
80	0.337	2	21/999		200.0
00	0.337	5	290000	1920.2	140.J 22124 4
05	0.337	6	56611	15 7	22134.4
85	0.337	6	101520	15 6	6517 0
85	0 337	6	127246	76.9	1655 7
85	0.337	ě	76456	102.9	743.2
85	0.337	Ğ	149342	136.0	1098.2
85	0.337	6	187411	327.1	573.0
85	0.337	6	239470	778.0	307.8
85	0.337	6	234267	1204.0	194.6
85	0.337	6	327487	1841.6	177.8
85	0.337	6	143813	<u>5.8</u>	25007.4
85	0.337	6	98913	93./	1056.2
80	0.337	Ø	84209	139.0	600.1
00	0.337	0	165450	220.1	033.0
85	0.337	6	220926	807 6	273 6
85	0 337	Ğ	275264	1498 8	183 7
85	0.337	ĕ	324558	2061.0	157.5
85	0.337	Ğ	189385	91.5	2069.6
85	0.337	12	147395	29.4	5016.5
85	0.337	12	175700	175.1	1003.4
85	0.337	12	132422	136.7	968.7
85	0.337	12	150320	198.4	757.7
85	0.337	12		295.8	487.3
80	0.337	12	240700	002.0	303.4
05 85	0.337	12	207045	1163 5	221.4
85	0.337	12	93708	19 1	4906 9
85	0.337	12	114532	34.5	3319.5
85	0.337	12	144465	56.4	2562.2
85	0.337	12	99563	121.5	819.6
85	0.337	12	174398	128.6	1356.0
85	0.337	12	129823	169.7	764.8
85	0.337	12	168543	326.8	515.8
85	0.337	12	208238	631.2	329.9
85	0.337	12	311/05	1348.7	231.1
80 05	0.331	1Z 24	202090 125502	1233.0	220.1
00 Q.K	0.331	24	207006	20.0	029J.J 10540 1
85	0.337	24	169843	59 A	2838 2
85	0.337	24	250865	88.0	2851.3
85	0.337	24	169841	35.4	4800.4
85	0.337	$\overline{24}$	227107	261.0	870.1
85	0.337	24	94213	424.2	222.1
85	0.337	24	389794	1700.8	229.2
85	0.337	24	137960	502.0	274.8

Appendix 3. (Cont'd).

	A 337			10.0		
80 95	0.337	24	212442	10.8	1110.4	
85 85	0.337	24	213442	83 1	3275 7	
85	0.337	24	228085	133.4	1709.7	
85	0.337	24	207260	282.6	733.5	
85	0.337	$\overline{2}\overline{4}$	170493	501.1	340.2	
85	0.337	24	184159	597.9	308.0	
85	0.337	24	239798	638.1	375.8	
85	0.337	24	254114	1036.7	245.1	
85 110	0.337	24	203520	1535.2	132.0	
110	0.337	1	351400	8.6	41030 0	
110	0.337	1	309425	17.3	17911 1	
110	0.337	ī	277220	75.8	3659.5	
110	0.337	ī	162031	135.8	1193.1	
110	0.337	1	125916	335.4	375.4	
110	0.337	1	234270	185.7	1261.5	
110	0.337	1	140560	530.2	265.1	
	0.337	1	219625	1/2.3	284.4	
	0.337	1	230232	466 7	250.2	
110	0.337	1	102492	602.9	170.0	
110	0.337	ī	140560	692.6	202.9	
110	0.337	ī	219625	729.6	301.0	
110	0.337	1	256230	837.4	306.0	
110	0.337	1	169849	17.9	9505.9	
	0.337	2	1/5/00	49.5	354/.3	
110.	0.337	2	165031	215 8	1070.0	
110	0.337	2	234270	202.8	1155.1	
īīŏ	0.337	ī	187411	214.8	872.6	
110	0.337	2	70280	219.1	320.7	
110	0.337	2	184985	776.3	238.3	
110	0.337	2	241588	1366.6	176.8	
	0.337	2	51247	43.2	1186.1	
110	0.337	2	117135	102 6	$\frac{41}{11}$	
110	0.337	2	165937	114.8	1445.4	
110	0.337	2	234268	177.6	1319.1	
110	0.337	2	187413	252.2	743.0	
110	0.337	2	70280	289.2	243.1	
110	0.337	2	169985	818.1	207.8	
	0.337	2	241588	129/.8		
	0.331	2	29209 7001	12./	2311.0	
110	0.337	2	48809	95 1	513 4	
110	0.337	ž	83949	155.8	538.7	
ĪĪŎ	0.337	ž	216700	3.7	57805.3	
110	0.337	3	354326	1937.2	182.9	
110	0.337	3	234270	1316.4	178.0	
110	0.337	3	16985	310.8	54.6	

Appendix 3. (Cont'd).

110	0.337	3	133240	521.3	255.6	
110	0 337	2	105420	652 6	161 5	
	0.337	2	240000	414 6	600.3	
110	0.337	2	240900	414.0	000.3	
110	0.337	3	234268	991.0	236.4	
50	0.385	6	109257	8.3	13097.9	
50	0.385	6	280946	29.7	9458.8	
50	0 385	ĥ	374595	<b>4</b> 5 <b>4</b>	8246 9	
50	0.305	č	507265	107 1	1727 0	
50	0.305	0	507265		4/3/.3	
50	0.385	6	212063	161.4	3192.1	
50	0.385	6	296555	58.4	5074.4	
50	0.385	6	593110	263.8	2248.1	
50	0.385	6	639934	409.0	1564.5	
50	0 385	Å	671150	880 7	762 1	
50	0.305	č	075500	1542 0	632.2	
50	0.305	0	975509	1043.0	52522	
50	0.385	6	109257	2.1	52522.2	
50	0.385	6	280947	34.8	8066.0	
50	0.385	6	374596	69.1	5420.9	
50	0.385	6	507264	165.8	3059.2	
50	0 385	š	515069	225 6	2283 3	
50	0.305	ĉ	206555	22J.0	5633 0	
20	0.305	D D	290000	52.0	5555.9	
50	0.385	6	593110	392.2	1512.3	
50	0.385	6	639934	544.6	1175.0	
50	0.385	6	671150	1047.5	640.7	
50	0.385	Ĝ	975509	1970.5	495.1	
75	0 385	ĭ	50726	8 5	5944 8	
75	0.305	1	152170	27.2	1715 6	
75	0.305	1	175500	32.3	4/13.0	
/5	0.385	Ţ	1/5592	4/.0	3088.8	
75	0.385	1	253632	108.6	2336.0	
75	0.385	1	401910	167.8	2394.8	
75	0.385	1	105355	53.1	1984.8	
75	0 385	1	226318	208 4	1086 2	
75	0.305	1	271101	215 3	785 7	
75	0.305	1	271191	543.3	272 4	
/5	0.305	Ţ	200210	820.2	3/3.4	
75	0.385	Ţ	411665	1326.6	310.3	
75	0.385	1	50726	5.8	8707.4	
75	0.385	1	152179	31.8	4787.4	
75	0.385	ĩ	175592	49.9	3522.1	
75	0 385	1	253632	122 1	2077 5	
75	0.305	1	401010		1052 2	
75	0.305	1	401910			
/5	0.385	Ţ	220310	302.4	024.4	
75	0.385	1	2/1191	616.9	439.6	
75	0.385	1	291677	1166.2	250.1	
75	0.385	1	398495	2226.7	179.0	
7Š	0 385	5	70227		6234 5	
75	0.205	5	132660	22.1	1002 5	
10	0.305	2	132003	52.4	4072.J 2011 E	
/5	0.385	2	202906	<u> </u>	3044.5	
75	0.385	2	238024	116.7	2039.8	
75	0.385	2	351183	186.7	1880.9	
75	0.385	2	105355	150.5	700.1	
<i>ή</i> š	0 285	2	226319	267.0	615 1	
75	0.305	22	206000	150 1	150 2	
13	0.303	2	200000	439.4	430.2	

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Appendix 3. (Cont'd).

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75	0.385	2	255583	954.0	267.9
75	0.385	2	355085	1441.2	246.4
75	0 385	2	70237	11 7	5985 6
75	0.205	2	122660	24.2	
15	0.385	2	132009	34.3	3862.6
75	0.385	2	202906	60.6	3350.9
75	0.385	2	238024	123.4	1929 4
75	0.305	້າ	251102	201 0	17/0 2
15	0.305	2	201102	201.0	1/40.5
/5	0.385	2	105355	1/.2	6110./
75	0.385	2	226318	415.4	544.8
75	0 385	2	206808	508 9	406 4
75	0.305	2	255502	1101 0	200.3
15	0.305	2	200000		232.1
/5	0.385	2	355085	2092.9	169.7
75	0.385	3	105355	14.1	7497.5
75	0 385	Â.	152179	31 7	4794 8
75	0.205	2	257521	100 4	2722.U 2254 1
75	0.305	2	257554	109.4	2354.1
75	V.385	3	12608	140.3	111.2
75	0.385	3	115110	109.4	1052.6
75	0 385	Ž	195102	257 7	757 2
75	0.305	3	102151	227.1	500 7
15	0.305	2	193131	322.1	599.7
75	0.385	3	316065	856.8	368.9
75	0.385	3	353134	1287.0	274.4
75	0 385	ž	50726	11 8	4201 3
75	0.305	2	105255	22.2	2070 7
15	0.305	2	105355	32.2	3270.7
. /5	0.385	3	1521/9	50.7	2999.3
75 、	0.385	3	257534	106.6	2416.0
75	0 385	3	179494	164 8	1089 0
75	0.205	2	115110	104.0	1100 5
15	0.305	2	115110	97.5	1100.3
/5	0.385	3	195102	338.1	577.0
75	0.385	3	193151	452.4	426.9
75	0 385	à	316065	1234 3	256 1
75	0.305	22	252124	1021 0	102 0
	0.305	2	222124	1021.0	193.0
/5	0.385	6	66335	6.3	10499.8
75	0.385	6	187298	41.8	4485.1
75	0.385	6	214612	65.8	3260 0
75	0 385	Ğ	272112	146 1	1960 6
	0.305	ĉ	273133		1400
/5	0.385	Ø	304359	214.0	1422.4
75	0.385	6	113159	55.3	2046.1
75	0.385	6	199004	274.6	724.6
75	0 385	Å	288751	597 8	101 2
75	0.305	ç	200731	1057.0	
10	0.303	Ó	290102	100/./	214.9
75	0.385	6	417518	1922.3	217.2
75	0.385	6	66335	2.8	23966.7
75	0 385	Ř	193151	<u>4</u> 0 k	-4758 3
75	0.305	ĉ	214612	20.0 67 1	2100.0
12	0.303	õ		0/.1	7727.2
75	0.385	6	2/3143	142.3	1918.8
75	0.385	6	304359	217.3	1400.7
75	0 385	Ř	112159	92 2	1226 7
75	0.305	ž	100001	202.1	250 7
10	0.303	õ		202.1	000.1
15	0.385	6	288751	568.1	508.Z
75	0.385	6	290702	1027.3	283.0
75	0.385	ĥ	417518	1772 1	235 6
	0.000	v			200.0

Appendix 3. (Cont'd).

75	0.385	12	70237	10.7	6581.2
10	0.385	12	10//8/	34.1	4923.5
75	0.305	12	222410	52.9	4203.1
75	0.305	12	230220	175 0	2099.0
75	0.305	12	159740	88.8	1708 3
75	0.305	12	261436	404 0	647 0
75	0.385	12	335575	756.0	443.9
75	0.385	12	300457	1091.4	275.3
75	0.385	12	351183	1736.5	202.2
75	0.385	12	81943	11.5	7131.0
75	0.385	12	167788	36.6	4580.2
75	0.385	12	222416	59.7	3723.6
75	0.385	12	230220	117.6	1957.2
/5	0.385	12	409/14	209.3	1957.8
75 75	0.305	$\frac{12}{12}$	133779		520.0
75	0.305	12	201430	404.J QQ5 1	337.1
75	0.305	12	300457	1242 5	241 8
75	0.385	12	351183	1993.3	176.2
75	0.385	24	62433	9.5	6545.0
75	0.385	$\overline{2}\overline{4}$	183396	33.7	5437.6
75	0.385	24	218514	50.5	4331.0
75	0.385	24	292653	110.8	2642.2
75	0.385	24	386301	161.4	2393.8
75	0.385	24	115110	73.7	1562.6
15	0.385	24	2/1191	390.0	695.3
75	0.305	24	JZJ009 251691	$\begin{array}{c} 0 \perp 0 \cdot 0 \\ 0 2 2 & 7 \end{array}$	525.2 272 5
75	0.305	24	364840	1611 1	272.5
75	0.385	24	62433	3.7	16970.3
75	0.385	24	183396	35.3	5200.4
75	0.385	24	218514	58.9	3708.8
75	0.385	24	292653	141.2	2072.8
75	0.385	24	386302	241.1	1602.3
75	0.385	24	115110	62.0	1857.4
75	0.385	24	271191	399.0	679.8
75	0.385	24	323869	633.3	511.4
15	0.385	24	221081	923.8	2/1.8
75 85	0.305	24	J04040 115110	24 0	ZZU.9 1627 9
85	0.305	1	136571	29.0	4027.9
85	0.385	1	212661	54.9	3872.6
85	0.385	ī	230220	70.0	3289.5
85	0.385	ī	187298	159.6	1173.7
85	0.385	Ī	105355	100.3	1049.9
85	0.385	1	222416	248.9	893.6
85	0.385	1	226318	356.5	634.9
85	0.385	1	300457	817.4	367.6
85	0.385	1	261436	1257.8	207.9
80	0.385	T	112110	4/.5	2421 <b>.</b> 9

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55555555555555555555555555555555555555	0 385 0 385 0 385 0 3855 0 0 3855 0 0 3855 0 0 3855 0 0 3855 0 0 3855 0	๚๚๚๚๚๚๚๚๚๚๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛๛	136571 136571 136571 230220 187298 105355 231196 226318 300457 261436 148277 212661 228269 218514 304359 148277 304359 148277 304359 148277 304359 148277 304359 148261 228269 122914 1263269 122924 2126514 228269 128514 300457 304359 89747 156081 187298 282898 282898 270237 1638657 273146	$\begin{array}{c} 59.0\\ 76.0\\ 1179.5\\ 519.4\\ 400.5\\ 519.4\\ 100.9\\ 1160.9\\$	$\begin{array}{c} 2315.5\\ 1796.3\\ 2269.6\\ 1043.6\\ 0\\ 445.2\\ 370.7\\ 208.9\\ 10701.6\\ 5017.5\\ 2069.5\\ 869.8\\ 934.1\\ 155.6\\ 193.1\\ 437.5\\ 2069.5\\ 8934.1\\ 193.1\\ 437.5\\ 2069.5\\ 8934.1\\ 193.1\\ 437.5\\ 2069.5\\ 8934.1\\ 193.1\\ 193.1\\ 437.5\\ 2069.5\\ 8934.1\\ 193.1\\ 193.1\\ 193.1\\ 193.1\\ 435.2\\ 352.3\\ 170.4\\ 135.1\\ 10223.9\\ 6224.8\\ 352.3\\ 170.4\\ 135.1\\ 2860.7\\ 446.8\\ 355.0\\ 255.0\\ 255.0\\ 255.0\\ 216.6\\ 169.2\\ 216.6\\ 169.2\\ 216.6\\ 169.2\\ 216.6\\ 169.2\\ 216.6\\ 255.2\\ 2030.3\\ 776.0\\ 255.2\\ 216.6\\ 169.2\\ 216.6\\ 355.0\\ 255.2\\ 216.6\\ 169.2\\ 216.6\\ 169.2\\ 216.6\\ 169.2\\ 216.6\\ 25243.8\\ 352$	

Appendix 3. (Cont'd).

Appendix 3. (Cont'd).

85	0.385	6	124865	257.3	485.3
85	0.385	ő	159983	402.4	397.5
85	0.385	6	185347	534.1	347.0
85	0.385	6	284849	1010.5	281.9
85	0.385	6	325820	1418.5	229.7
85	0.385	6	73163	9.5	7733.6
85	0.385	6	187298	30.4	6169.7
85	0.385	6	228269	46.1	4947.3
85	0.385	6	273143	103.7	2633.6
85	0.385	6	179494	156.3	1148.0
85	0.385	6	124865	109.7	1137.9
85	0.385	6	123383	291.9	548.0
85	0.385	6	185347	475.3	390.0
85	0.385	6	284849	1322.7	215.4
85	0.385	6	325820	1991.2	163.6
85	0.385	12	48775	10.0	4880.1
85	0.385	12	146326	34.8	4209.1
85	0.385	12	187298	49.9	3754.4
85	0.385	12	228269	110.0	20/4.8
85	0.385	12	239975	164.9	1454.9
85	0.385	12	11/061	83.3	1405.4
85	0.385	12	214612	366.0	586.5
85	0.385	12	208/59	451.5	462.3
80	U.305	12	300437	1101.0	200.9
85	0.305	12	338981	1/03.2	
0J 0E	0.305	12	40//5	0.5	03030.3
05	0.305	12	10720		2220 A
0J Q5	0.305	12	228260	172 3	1321 7
0J Q5	0.305	12	220209	240 0	
85	0.305	12	125841	45 4	2770 2
85	0.305	12	214612	386 0	556 1
85	0.385	12	208759	477 3	437 3
85	0 385	12	300457	1367 0	219 8
85	0 385	12	358987	2199 8	163 2
85	0.385	24	52677	6.8	7784.2
85	0.385	24	167788	36.4	4605.3
85	0.385	$\overline{2}\overline{4}$	197053	54.4	3624.7
85	0.385	$\overline{2}\overline{4}$	214612	115.0	1865.6
85	0.385	$\overline{2}\overline{4}$	228269	173.3	1317.2
85	0.385	$\overline{2}\overline{4}$	105355	37.9	2776.2
85	0.385	$\overline{24}$	199004	347.5	572.6
85	0.385	24	163885	415.5	394.4
85	0.385	$\overline{2}\overline{4}$	247779	1056.2	234.6
85	0.385	$\overline{2}\overline{4}$	339477	1939.1	175.1
85	0.385	$\overline{2}\overline{4}$	52677	4.1	12763.7
85	0.385	$\overline{2}\overline{4}$	167788	47.5	3534.2
85	0.385	24	197053	75.9	2596.3
85	0.385	24	214612	141.7	1514.3
85	0.385	24	228269	205.5	1110.7
85	0.385	24	105355	118.7	887.8

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85 85 85 85 110 110 110 110 110 110 110 110 110 11	0.00000000000000000000000000000000000	44444111111111111111111111112222222222	$\begin{array}{r} 199004\\ 163886\\ 247779\\ 339445\\ 216563\\ 1773641\\ 382400\\ 395081\\ 28688\\ 84971\\ 28688\\ 84971\\ 286880\\ 395081\\ 28688\\ 84971\\ 286880\\ 321918\\ 28688\\ 84971\\ 28688\\ 84971\\ 128688\\ 84971\\ 128688\\ 24002\\ 49152\\ 20208\\ 111208\\ 28528\\ 20088\\ 21918\\ 250228\\ 111208\\ 20088\\ 21918\\ 20088\\ 21918\\ 20088\\ 21918\\ 20088\\ 20088\\ 21918\\ 20088\\ 20088\\ 21918\\ 20088$	$\begin{array}{c} 393.5\\ 393.5\\ 1080.3\\ 29.6\\ 0\\ 123.6\\ 0\\ 123.6\\ 0\\ 123.6\\ 0\\ 123.6\\ 0\\ 123.6\\ 0\\ 123.6\\ 0\\ 123.6\\ 0\\ 123.6\\ 0\\ 123.6\\ 0\\ 123.6\\ 0\\ 133.6\\ 0\\ 134.0\\ 1\\ 123.6\\ 0\\ 134.0\\ 1\\ 123.6\\ 0\\ 134.6\\ 0\\ 0\\ 134.6\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\ 0\\$	$\begin{array}{c} 505.7\\ 377.4\\ 187.0\\ 187.0\\ 187.4\\ 3103.6\\ 43100.6\\ 43100.6\\ 43100.6\\ 43100.6\\ 43100.6\\ 43100.6\\ 43100.6\\ 43100.6\\ 43100.6\\ 43100.6\\ 43100.6\\ 43100.6$	

Appendix 3. (Cont'd).

Appendix 3. (Cont'd).

110	0.385	3	113159	1075.8	105.2
110	0 205	Š	70011	15020	
110	0.305	2	/0041	1202.0	52.0
110	0.385	3	307285	23.1	13275.3
110	0 205	ž	166012	53°E	7110 0
110	0.305	2	100012	23.5	/110.0
110	0.385	3	280947	49.5	5670.1
110	0 395	2	115567	1200	3337 7
110	0.305	2	410007	120.0	5221.1
110	0.385	3	553114	223.4	2476.0
110	0 385	2	91698	324 9	282 3
	0.305	2	101450	527.9	202.5
110	0.385	3	101453	6/9.8	149.2
110	0 385	ર	113159	1525 5	74 2
110	0.005	ž		1 4 1 0 7	
TIŬ	0.385	3	/8041	1419.1	55.0
110	0.385	6	224367	15.0	14962.5
110	0 205	č	201010	10.2	7002 0
110	0.305	O	204049	40.2	7093.9
110	0.385	6	119012	30.4	3911.7
110	0 395	Ğ	303100	1100	2732 1
110	0.305	0 0	302400	140.0	2132.4
110	0.385	6	398008	204.2	1948.8
110	0 385	6	95600	96 0	995 K
	0.305	č	70000	1 ( 1 )	
110	0.385	6	/6090	101.3	4/1./
110	0 385	6	74139	328 3	225 8
110	0.205	č	02001		111 7
110	0.305	Ö	03094	121.0	111./
110	0.385	6	136571	1354.4	100.8
110	0 295	č	221267	10 6	12061 5
110	0.305	0	224301	10.0	12001.5
110	0.385	6	284849	41.7	6836.4
110	0 385	ĥ	110012	22.2	3569 2
	0.305	č	117012	120.1	
110	0.385	6	382400	- 138.1	2/08.4
110	0.385	6	398008	201.1	1979.2
110	0.205	č	05600		217 2
110	0.385	D	92000	440.L	211.2
110	0.385	6	76090	110.1	691.2
110	0 295	č	7/120	265 7	270 0
110	0.305	0	14133	205.1	279.0
110	0.385	6	83894	764.4	109.8
110	0 385	6	126571	2516 2	54 3
110	0.505	10	100011	2010.2	
110	0.385	12	40824	10.9	4315.4
110	0.385	12	13657	17.3	790.2
110	0 295	12	115110	10 5	2272 1
110	0.305	12	TIDIIO	40.5	2373.1
110	0.385	12	93649	101.9	919.0
110	0 385	12	191200	163 1	1172 3
	0.505	10	100014		
TIŬ	0.385	Τζ	122914	100.2	1157.5
110	0.385	12	113159	205.8	549.8
110	0 205	12	117061	211 6	2721
110	0.305	12	11/001	514.0	572.1
110	0.385	12	148277	952.1	155.7
110	0 385	12	200955	1806 1	111 3
110	0.305	14	200955	1000.1	
110	0.385	12	46824	14.4	3245.1
110	0.385	12	12194	18 0	677 9
	0.305	10	57777		1000 4
TTV	0.303	Τζ	20120	41.5	1222.4
110	0.385	12	93649	103.8	902.3
110	0.305	12	101200	167 1	1217 6
TTO	0.305	12	171200	17/.4	1414.0
110	0.385	12	130231	278.3	467.9
110	0 385	12	112150	321 0	352 5
	0.202	14			222.2
TTO	V.385	12	TT/00T	414./	282.3
110	0.385	12	148277	1024.0	144.8
110	0.305	10	200055		100 6
TIO	0.303	12	200322	<b>TQDN'A</b>	0.0UL

Appendix 3. (Cont'd).

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110	0.385	24	74139	1.5	50447.7	
	0.385	24	/6090	14.5	5238.4	
110	0.305	24	10510	20.1	139.1	
110	0.305	24	218514	1911	1206 9	
110	0.305	24	114135	176.9	645 1	
110	0.385	24	114135	278.5	409.8	
īī0	0.385	24	150228	494.6	303.7	
110	0.385	$\overline{24}$	158032	992.3	159.3	
110	0.385	24	161934	1440.1	112.4	
110	0.385	24	976	1.9	517.5	
110	0.385	24	23412	24.6	950.0	
	0.385	24	31216	98.1	316.2	
	0.305	24	09/4/ 1250/1	$\frac{1}{22}$	500.0 5572 C	
110	0.305	24	114135	<u>22.0</u> <u>41</u> 7	2736 8	
110	0.385	24	150228	345.9	434.3	
<b>ī</b> ī0	0.385	24	158033	871.9	181.3	
<u>1</u> 10	0.385	$\overline{24}$	161934	1704.8	95.0	
50	0.436	6	52677	5.3	10000.6	
50	0.436	6	204857	30.0	6827.3	
50	0.436	6	300457	52.3	5742.2	
50	0.436	Ó	446783	122.4	3650.2	
50	0.430	Ø	402391 210016	180.7	2008.3	
50	0.436	6	376546	246 3	1528 9	
· 50	0.436	6	515069	784.5	656.6	
50	0.436	Ğ	713097	1566.9	455.1	
50	0.436	Ğ	137547	13.8	9935.8	
50	0.436	6	236724	38.5	6143.4	
50	0.436	6	353134	101.2	3488.4	
50	0.436	6	464668	200.8	2313.7	
50	0.436	6	334925	1/4./	1910.9	
50	0.430	06	1934/0			
50	0.436	6	412478	746 9	552 2	
50	0.436	Ğ	515231	1368.0	376.6	
50	0.436	Ğ	295254	1010.7	292.1	
75	0.436	1	42272	15.2	2788.0	
75	0.436	1	68936	34.4	2005.7	
75	0.436	1	128117	76.1	1684.6	
75	0.436	1	186973	145.9	1281.3	
/5	0.436	1	1/0/14	1/9./	949.9	
15 75	0.430	⊥ 1	177969	230.1	555.9 155 Q	
75	0.436	1	246479	645 R	381 6	
75	0.436	1	322894	1130.8	285.5	
75	0.436	ī	221278	965.1	229.3	
75	0.436	ī	41297	12.1	3425.4	
75	0.436	1	73570	35.1	2097.4	
75	0.436	1	119093	79.5	1498.2	

Appendix 3. (Cont'd).

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75	0.436	1	158683	155.4	1020.9
75	0 436	1	165268	227 0	725 2
	0.400	4	103200		723.2
15	0.436	1	90235	128.3	703.2
75	0.436	1	182745	326 3	560 0
75	0.120	1	221250	757.0	
15	0.430	1	231338	121.8	305.3
75	0.436	1	321430	1622.1	198.2
75	0 426	1	252222	1260 5	104 2
15	0.430	Ţ	252552	T202.2	104.3
75	0.436	2	37395	16.8	2222.0
75	0 136	ō	85101	<b>1</b> 1 0	2075 7
	0.430	2	100070	2֥4	2013.1
15	0.436	2	186313	55./	3354.5
75	0.436	2	135921	129.0	1053.8
75	0 136	5	112725	122 0	1002 5
	0.430	2	143723	102.0	1002.3
75	0.436	2	92348	129.7	712.0
75	0 436	2	171039	354 6	482 3
75	0 426	5	221046		224.2
15	0.430	2	231840	/15.0	324.3
75	0.436	2	295904	1310.3	225.8
75	0 436	- 2	106565	10117	199 7
	0.430	2	190303	1041.7	100.7
/5	0.436	2	45199	12.1	3726.9
75	0.436	2	85682	36 4	2355 6
75	0 436	วี	151266		1500.0
15	0.430	2	121200	95.2	1590.8
75	0.436	2	174454	164.0	1063.6
75	0 436	Ž	1/1286	2070	682 1
	0.430	2	171200	207.0	
15	0.436	2	97713	82.5	1184.8
75	0.436	2	164211	338.7	484.8
75	0 426	5	225505	· 000 5	270 6
15	0.430	2	225505	009.5	270.0
75	0.436	2	304440	1676.7	181.6
75	0 436	2	205263	1251 3	164 0
	0.430	2	205205		202.0
15	0.430	3	41947	14.0	2998.4
75	0.436	3	84544	37.3	2269.0
75	0 136	ž	12/965	76.7	1620 3
	0.450	2	124005	10.1	1020.3
15	0.436	3	145676	140.0	1040.7
75	0.436	3	164211	160.7	1021.6
75	0 426	ž	02210	1121	
15	0.450	2	92340	142.1	0.00.0
/5	0.436	3	157057	324.1	484.5
75	0 436	3	214612	626 1	342 8
75	0.426	ž	211107	1067 1	201 6
15	0.430	Ş	511107	100/.1	291.0
75	0.436	- 3	305334	1512.5	201.9
75	0 436	3	22924	85	2683 5
75	0.400	2	110000	12.1	
15	0.430	3	110980	43.1	20/4.4
75	0.436	3	121207	74.1	1636.5
75	0 136	ž	135021	121 5	1010 0
12	0.400	Š	100221	104.0	
/5	U.436	3	1/0552	141.7	1203.3
75	0.436	२	103567	104 5	991 0
75	0 426	Š	1 5 6 3 9 5	212.2	
12	V.430	2	120372	212.2	500.5
75	0.436	3	228513	843.3	271.0
75	0 436	ž	279971	1521 2	184 0
	0.100	2	213311	1000 0	
15	<b>U.436</b>	3	220628	T228.0	164.8
75	0.436	6	53003	19.4	2737.9
<b>י</b> ב	0 126	č	07551	21.7	2010 4
10	0.430	Q	31221	. 34 . /	2010.4
75	0.436	6	220465	101.0	2182.2
75	0.436	ĥ	134945	120.8	1117.0
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Appendix 3. (Cont'd).

75	0.436	6	193151	134.4	1437.3
75	0.436	6	85845	157.8	544.0
75	0.436	Ğ	145351	325 5	446 6
75	0 436	č	252007	627 0	401 2
	0.430	Ő	252007	1077.7	401.5
/5	0.436	6	26/615	10/3./	249.2
75	0.436	6	222579	889.1	250.3
75	0.436	6	63733	22.6	2822.8
75	0.436	6	88446	43.0	2055.7
75	0 436	Å	97226	71 9	1208 6
75	0.436	c c	1 1 1 2 1 2		
15	0.430	0	144213		954.5
/ 2	0.436	6	153480	143.4	10/0.0
75	0.436	6	87145	48.3	1804.3
75	0.436	6	159496	268.6	593.8
75	0.436	6	249568	778.1	320.7
75	0 436	Š	325170	1583 4	205 4
75	0.436	č	225260	1060 2	120 0
	0.430	10	235200	1300.3	
/5	0.436	12	60807	24.1	2457.5
75	0.436	12	94624	23.4	4040.3
75	0.436	12	151529	82.5	1837.6
75	0.436	īž	86820	115.4	752.4
75	0 436	12	118687	171 3	680 8
75	0.436	12	11/705	1/4.5	417 1
15	0.430	12	114/05	2/3.2	41/.1
/5	0.436	12	199979	377.4	529.9
75	0.436	12	252007	819.7	307.4
75	0.436	12	339152	1689.0	200.8
75	0.436	12	230464	1902.6	121.1
75	0 436	12	64221	72 8	881 7
75	0.430	12	00011	12.0	1007 1
75	0.430	12	33014	47.0	
/5	0.436	12	116899	114.8	1018.1
75	0.436	12	149741	261.5	572.7
75	0.436	12	81618	145.6	560.5
75	0.436	12	117224	105.3	1113.2
75	0 436	12	198516	367 3	540 5
75	0.430	12	262727	026.2	21/ 2
15	0.430	12	202/3/	030.2	314.2
/5	0.436	12	323495	1522.9	213.7
75	0.436	12	333624	1867.3	178.7
75	0.436	24	64384	11.1	5825.4
75	0.436	24	100152	29.0	3459.3
75	0.436	24	104380	37.9	2755.3
75	0.436	$\overline{2}\overline{4}$	316065	146 8	2153 7
75	0 136	21	212120	202 0	15/0 0
75	0.430	24	122014	202.0	1000 0
15	0.430	24	122914	99.4	1230.0
/5	0.436	24	184046	346.9	530.5
75	0.436	24	263062	743.8	353.7
75	0.436	24	358012	1480.2	241.9
75	0.436	24	313138	1634.7	191.6
75	0 436	24	36582		5829 1
75	0 120	21	03610	22.2	2006 0
10	0.430	24	33043	22.3	2030.U 2150 5
12	0.436	24	TTPUSP	23.8	2128.5
75	0.436	24	201930	147.4	1369.6
75	0.436	24	164129	207.9	789.6

55555555555555555555555555555555555555	0.43366666666666666666666666666666666666	44444411111111111111111111112222222222	$\begin{array}{c} 10883\\ 10883\\ 229846\\ 229846\\ 59766\\ 127467\\ 17980\\ 127467\\ 179850\\ 127467\\ 1797950\\ 127467\\ 1797950\\ 127467\\ 172340\\ 50792\\ 276487\\ 110200\\ 864951\\ 22648951\\ 110200\\ 144538\\ 172340\\ 172340\\ 172340\\ 111200\\ 144538\\ 111200\\ 144538\\ 110200\\ 144538\\ 110200\\ 144538\\ 110200\\ 144538\\ 110200\\ 144538\\ 110200\\ 144538\\ 110200\\ 144538\\ 110200\\ 144558\\ 110200\\ 144558\\ 110200\\ 144558\\ 110200\\ 144558\\ 110200\\ 125677\\ 127696\\ 156732\\ 99339\\ 146382\\ 2238187\\ 127792\\ 127696\\ 156732\\ 99339\\ 1466382\\ 2238187\\ 1277926\\ 156732\\ 99339\\ 1466382\\ 2238187\\ 190062\\ 1664709\\ 91399\\ 1663822\\ 2238187\\ 190062\\ 1664709\\ 106005\\ 17543\\ 162585\\ 92993\\ 1662585\\ 92993\\ 1662585\\ 92993\\ 1662585\\ 92993\\ 1662585\\ 100062\\ 1662585\\ 100062\\ 10$	$\begin{array}{c} 69.6\\ 62.8\\ 91.0\\ 80.3\\ 170.3\\ 13.3\\ 14.9\\ 90.7\\ 8.6, 7.3\\ 14.9\\ 91.3\\ 14.9\\ 91.3\\ 14.9\\ 91.3\\ 14.9\\ 91.3\\ 14.9\\ 91.3\\ 14.9\\ 177.5\\ 15.5\\ 23.8\\ 14.4\\ 8.9, 12.3\\ 12.2\\ 65.5\\ 23.8\\ 14.4\\ 11.4\\ 23.8\\ 8.14.4\\ 12.2\\ 65.5\\ 12.4\\ 12.2\\ 65.5\\ 12.4\\ 12.2\\ 65.5\\ 12.4\\ 12.2\\ 65.5\\ 12.4\\ 12.2\\ 65.5\\ 12.4\\ 12.2\\ 65.5\\ 12.4\\ 12.2\\ 65.5\\ 12.4\\ 12.2\\ 65.5\\ 12.4\\ 12.2\\ 12.5\\ 12.4\\ 12.2\\ 12.5\\ 12.4\\ 12.2\\ 12.5\\ 12.4\\ 12.2\\ 12.5\\ 12.4\\ 12.2\\ 12.5\\ 12.4\\ 12.2\\ 12.5\\ 12.4\\ 12.2\\ 12.5$	$\begin{array}{c} 653 \\ 653 \\ 753 \\ 753 \\ 753 \\ 751 \\$

Appendix 3. (Cont'd).

Appendix 3. (Cont'd).

	والمتحديد والمتحديد والمتحد				
85	0.436	3	202906	376.9	538.3
85	0.436	3	244528	707.3	345.7
85	0.436	3	307936	1383.0	222.7
85	0.436	3	235423	1777.5	132.4
85	0.436	3	59343	23.8	2498.6
85	0.436	3	111371	42.0	2654.8
85	0.436		152505	103.5	1473.7
85	0.436	3	195102	208.2	937.3
ÅŠ	0 436	3	173803	204 0	851 8
ŘŠ	0 436	ž	134458	174 4	771 1
85	0 436	ž	185347	367 8	504 0
85	0.436	2	257200	783.3	328 4
85	0.436	2	308011	1424 6	216 9
05	0.430	2	226210	1100 /	
05	0.430	5	220310	10 6	100.1
00	0.430	Ö	57555		4301.4
00	0.430	<b>D</b>		39.0	29/0.1
85	0.436	Ø	103079	104.5	1598.4
85	0.436	b b	200630	155.0	1294./
85	0.436	6	106656	148.5	718.4
85	0.436	6	91048	174.7	521.2
85	0.436	6	137547	337.2	407.9
85	0.436	6	201605	633.1	318.4
85	0.436	6.	296555	1166.6	254.2
85	0.436	6	254283	1008.6	252.1
85	0.436	6	56092	15.5	3609.2
85	0.436	6	99664	47.0	2122.1
85	0.436	6	128930	96.8	1331.3
85	0.436	6	150391	173.2	868.2
85	0.436	6	146652	211.6	693.1
85	0.436	6	98852	208.6	473.9
85	0.436	6	153643	373.8	411.0
85	0.436	6	205507	635.7	323.3
85	0.436	6	289238	1132.1	255.5
85	0.436	6	230220	936.1	245.9
85	0.436	12	44873	12.7	3543.0
85	0.436	12	114135	36.4	3136.0
85	0.436	12	111208	64.3	1730.4
85	0.436	$\overline{1}\overline{2}$	227944	137.7	1655.0
85	0.436	īī	168275	158.6	1060.9
85	0.436	$\overline{12}$	99502	195.2	509.8
85	0.436	12	141774	352.2	402.6
85	0.436	12	190875	622.5	306.6
85	0.436	12	306147	1131.1	270.7
85	0.436	12	239000	958.5	249.3
85	0.436	12	44873	9.6	4674 7
85	0.436	12	100965	36.5	2765 7
85	0.436	15	144863	88.0	1646 0
85	0.436	12	204044	183.7	1110 7
85	0 436	15	175592	183.5	-956 7
8Š	0 436	12	87796	120 6	728 2
85	0.436	12	134945	285 0	473.4
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85555555555555555555555555555555555555
222444444444444444444444444444444444444
$\begin{array}{c} 22255\\ 786\\ 786\\ 786\\ 786\\ 786\\ 786\\ 786\\ 786$

1	11	1	1	1	1
11263	134415	123483	1113493	112425	627
23938278	12396546821	2496547051	352953737	34160382	988
106384766	04294737061	92579769696	96362460430	8160160710	1750
					•
08366617	1092559447	18114272792	3372364561	6260766363	1850

Appendix 3. (Cont'd).

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Appendix 3. (Cont'd).

110        1	0.436 0.43	1111 1200000000000000000000000000000000	$\begin{array}{c} 163869\\ 46776\\ 49783\\ 39053\\ 76773\\ 91942\\ 1117054\\ 127057\\ 94862\\ 11175657\\ 312160\\ 37129\\ 108359364\\ 15752939\\ 1083568253\\ 498262\\ 11373738\\ 686257\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 552676\\ 197182\\ 55777\\ 197275\\ 192754\\ 1912754$	$\begin{array}{c} 1938.7\\ 19.0\\ 35.9\\ 46.6\\ 109.4\\ 176.2\\ 318.0\\ 5917.3\\ 1712.7\\ 47.1\\ 105.7\\ 216.5\\ 802.3\\ 1172.3\\ 1072.3\\ 25.3\\ 24.3\\ 25.3\\ 1072.3\\ 25.3\\ 24.3\\ 1072.3\\ 25.3\\ 1072.3\\ 25.3\\ 1072.3\\ 25.3\\ 1072.3\\ 25.3\\ 1072.3\\ 25.3\\ 1072.3\\ 25.3\\ 1072.3\\ 25.3\\ 1072.3\\ 25.3\\ 1072.3\\ 1072.3\\ 25.3\\ 1072.3\\ 1$	$\begin{array}{c} 84.5\\ 2456.3\\ 1388.3\\ 401.0\\ 3838.1\\ 401.0\\ 3838.1\\ 401.0\\ 3838.3\\ 167.6\\ 102.8\\ 823.8\\ 351.4\\ 102.8\\ 355.4\\ 298.5\\ 167.6\\ 11332.8\\ 355.4\\ 298.5\\ 167.6\\ 11332.8\\ 355.4\\ 298.5\\ 102.8\\ 355.2\\ 298.3\\ 15590.2\\ 247.1\\ 189.3\\ 599.3\\ 15590.2\\ 314.1\\ 20590.3\\ 15590.2\\ 314.1\\ 313.2\\ 2052.6\\ 2157.7\\ 405.8\\ 163.8$	
$\begin{array}{c} 110\\110\\110\end{array}$	0.436	12 12	25949 76285 76415	97.5 166.9	266.1 457.1	
110	0.436	12	/6415 113484	202.4	3/1.5	
110	0.436	12	142424	754.8	188.7	

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Appendix 3. (Cont'd).

