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MODELING THERMAL AND MECHANICAL EFFECTS OF EXTRUSION ON THIAMIN RETENTION IN EXTRUDED WHEAT FLOUR

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MODELING THERMAL AND MECHANICAL EFFECTS OF EXTRUSION ON THIAMIN RETENTION IN EXTRUDED WHEAT FLOUR

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By

Maria Suparno

A THESIS

Submitted to Michigan State University In partial fulfillment of the requirements For the degree of

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ABSTRACT

MODELING THERMAL AND MECHANICAL EFFECTS OF EXTRUSION ON THIAMIN RETENTION IN EXTRUDED WHEAT FLOUR

By

Maria Suparno

Average shear rate $(\dot{\gamma}_a)$ of a twin-screw co-rotating extruder was investigated to calculate shear history- a factor to model the mechanical effect (R_s) of extrusion. Fluids with different flow behavior indices, which represent different feed materials, were extruded at degrees of fill ranging from 0.4-1.0. Using mixer viscometry assumptions, $\dot{\gamma}_a$ was estimated and then modeled as a function of screw speed and degree of fill.

To calculate extrusion thermal effects on thiamin degradation (R_{β}) , kinetic parameters were obtained by heating flour, mixed with thiamin, at temperatures>100°C in a shearless environment. Two methods (atmospheric and controlled-pressure) to obtain the parameters were compared. The results from the two methods were not statistically different. The parameters obtained from the controlled-pressure method had lower standard error; for 25% moisture content flour, activation energy was 121.0 kJ/g-mol and reaction rate at 80°C was 9.69E-5 min⁻¹.

For extrusion, the same thiamin flour mixture was extruded at screw speeds of 100-300 rpm at two temperatures profiles. R_{β} was calculated using the thiamin kinetic parameters. R_S was calculated by mathematically removing R_{β} from the total thiamin retention. At higher temperature, thermal effects predominated over mechanical effects for thiamin loss, while at lower temperature, mechanical effects slightly prevailed over thermal effects. Mechanical effects caused 28.9% to 64.5% of total thiamin loss.

DEDICATION

To my parents, Suparno and Tjhin Meliana, for their unconditional love, relentless word of encouragement and faith in me. To my brothers, Robert, William and Jeffry, for always looking out for me.

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INTRODUCTION

Extrusion is growing as a processing technology for food products, due to its ability to combine several processes such as mixing, cooking, shaping and texturizing in one energy-efficient process. The list of food products being produced with extruders includes ready-to-eat cereals, beverage powders, pasta and snack products.

When some food materials are processed in an extruder, they are subjected to high temperature in combination with severe shear. These conditions can be beneficial for denaturing anti-nutritional factors, but can also be undesirable, because nutrients are degraded to varying extents (Harper 1973, Björk and Asp 1983). Consequently, for a heat-labile nutrient, fortifying food materials pre-extrusion is necessary. A model to predict the effect of the many variables of the extrusion process on thiamin degradation would be helpful for designing processes.

Few studies have reported the total thiamin degradation in extruded wheat and corn flour (Beetner *et al.* 1974, Guzman-Tello and Cheftel 1987, Ilo and Berghofer 1998, Schmid 2002). Some of these researchers have modeled thiamin retention or thiamin degradation rate as a function of b arrel temperature, s crew speed or moisture c ontent. However, the proportionate effects of shearing and heating on degradation were unknown. By quantifying these two effects (thermal and mechanical), the significance of each could be evaluated and the processing variables could be chosen for an optimum condition.

Mechanical effect of extrusion could be represented by shear rate or shear history. Due to the complexity of mixing in twin-screw extruders, calculating the velocity profile or local shear rates in the extruder is not feasible. Thus, the average shear rate was

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calculated. Mohamed *et al.* (1990) investigated average shear rate in an extruder at fully filled extruder condition (1.0 degree of fill) using the mixer viscometry matching viscosity assumptions. A more extensive study on average shear rate must be conducted, because commercial twin-screw food extruders normally o perated at 0.4-0.8 d egree o f fill. Furthermore, their study only investigated one type of non-Newtonian fluid with flow behavior index = 0.5. Thus, the first objective of the present study was to investigate average shear rate as a function of degree of fill, flow behavior index and screw speed.

To calculate the thermal effects of extrusion on thiamin, thiamin kinetic parameters at high temperature must be available. To date, few studies have investigated thiamin kinetic parameter in flour at high temperature. Hermann and Tunger (1966) reported that moisture content of flour affected thiamin kinetic parameters. Therefore, during high temperature heating, moisture content of flour must be maintained constant to attain the correct kinetic parameter at the corresponding moisture content. Hence, the second objective of this study was to determine thiamin kinetics parameters of thiamin in wheat flour at temperature higher than 100°C.

Subsequent to quantifying the thermal and mechanical effects of extrusion on thiamin retention, a model could be developed to predict thiamin retention in extruded products. The model may save time and cost compared to trial-and-error experiments. In addition, the model would be u seful for scale-up p urposes or for optimizing extrusion processing to achieve minimum thiamin degradation. Thus, the last objective was to model the thermal and mechanical effects of extrusion on thiamin retention.

In summary, the objectives of this research were;

- To model the average shear rate in the extruder as a function of screw speed, flow behavior index and degree of fill (Chapter 2);
- To determine the thermal kinetic parameters of thiamin in wheat flour at high temperature (Chapter 3);
- To model the thermal and mechanical effects of thiamin retention in the extrusion process (Chapter 4).

Figure 1.1 summarizes the goal of this research.



Figure 1.1. Flow chart to describe the goal of this research.

Chapter 1. Literature review

1.1. Food Extrusion

The use of extruders has been increasing over the past several decades in many areas such as the aluminum, plastic and food industries. Several different types of extruders are on the market, e.g., dry extruders, interrupted-flight screw extruders, and single and twin- screw extruders. For over 25 years, single-screw extruders were primarily u sed for products ranging from light density c orn s nacks, t o dense, p artially cooked, and formed pasta. However, as demand for new and high quality products has increased, single screw extruders were no longer adequate. Twin-screw technology thus gained popularity in the food industry because of its ability to produce different shapes, colors, and textures. In food industry, the first application of using a cooking extruder occurred in the mid- 1940s to produce an expanded cornmeal-based snack (Harper 1978). Currently, cooking extruders are used for production of ready-to-eat cereals, snack foods, beverage powders, soft/dry pet foods, pasta products, full or defatted soy flour, soup or gravy bases, and confections.

Food extrusion, by the definition of Rossen and Miller (1973), is a process in which a food material is forced to flow, under different conditions of mixing, heating, and shear, through a die designed to form and/or puff-dry the ingredients. Extrusion has been extensively used in the food industry because it offers several advantages over the processes it replaces. Extruders mix, cook, texturize, and shape food material in one continuous, fully automated, and energy efficient process. A variety of shapes, textures, colors, and appearances can be produced just by changing the die shape, minor ingredients, or processing variables. Examples of processing variables are feed ingredients, the amount of water injected into the extruder barrel, raw material feed rate, screw speed, and barrel temperature. These are the equipment-dependant variables. Equipment-independent variables such as moisture content of extrudate, pressure, shear rate, shear history, residence time, and product characteristics change as a result of modifications made to equipment-dependant variables.

Heat energy during extrusion comes from different sources. One of the energy inputs comes from viscous dissipation, which is the energy dissipated in the form of heat caused by shear or friction between rotating screws and feed materials. This is referred as the shear energy or the mechanical energy (Mohamed et al. 1990). An extruder is usually equipped with electrically heated rods or a steam injection mechanism for adding another energy input, the thermal energy to the process, thus helping to heat feed materials to a temperature of up to 200°C in the barrel. A barrel is divided into three zones: the feeding, kneading and final cooking zone. As materials enter the feeding zone, they are pre-heated and may be injected with water or steam. Water is typically added in this zone to alter the texture or viscosity of the material. The screws compress the lowdensity raw materials and convey them to the kneading zone. In the kneading zone, compression continues to expel entrapped air with decreasing screw pitch. As temperature increases in this barrel section, pressure begins to build. The shear rates, pressure, and temperature are highest in the final cooking zone. In this zone, the screw pitch is the lowest, compressing the material to the greatest degree. At the end of the extruder barrel, the material exits through a die opening, where it expands rapidly as pressure decreases. At this time, moisture in dough flashes off to steam, resulting in product expansion. In these three zones, the combination of twin-lead screw, single-lead screw, and kneading/mixing paddles determine the degree of conveying and compression. Screws can be configured to create high shear or low shear. Assembling different screw configurations varies products characteristics, thus creating potential for product developments. T win-lead s crews a re u sually placed in the feeding z one, and u seful t o convey materials. Single-lead screws are used for compressing material and increasing the d egree of f ill in the extruder. The k neading p addles c an b e s et at 30° , 60° or 90° rotated from one another on the extruder shafts. The paddles are called forward kneading paddles if they are set up in a way that the material will be moved towards the die direction. Reverse kneading paddles will move the material away from the die direction, thus increasing the degree of fill at that point. As raw materials moved towards the final cooking zone, the screws are usually configured such that the degree of fill increases to a maximum of 1.0.

In addition to its ability to manufacture a variety of foods in a continuous process, an extruder is also effective in inactivating spoilage enzymes, trypsin inhibitors and microorganisms (Harper 1981, Cheftel 1989). The intense thermal and mechanical energy inputs during extrusion also trigger many chemical and nutritional changes, such as starch gelatinization, protein denaturation, and degradation of vitamins, flavors, and pigments (Björk and Asp 1983, Harper 1988, Killeit 1994). While starch gelatinization is desirable for digestibility, degradation of vitamins is the undesirable side effect of extrusion. In some food industry, to replenish vitamins degradation, extrudates c an b e sprayed with vitamins after extrusion. Maga (1989) summarized many of the problems associated with this surface coating method. Some disadvantages are heterogeneous distribution, loss due to dripping, additional processing cost and time, and increased possibility of microbial contamination. Thus, the most common method implemented in most food industry is to over-fortify the dry mix prior to extrusion (Ottaway 1993 and L. Morel "pers comm."). A predictive model would be useful to determine the retention of these compounds to calculate the amount of vitamins to be added prior to extrusion. Using the model, the optimum conditions could be determined where minimum degradation is achieved. The resulting generalized model for vitamins degradation would be helpful to minimize experimental time and cost in extrusion process design.

1.2. Thiamin

Since 1943, all bread and grains products in the United States must be enriched with iron and vitamin B complex (niacin, **thiamin**, and riboflavin) because these vitamins are removed during flour milling. Folic acid (vitamin B₉) fortification of grain products was mandated in 1998. The minimum standard for vitamin B content was established by the Food and Drug Administration (Table 1.1) and reported by Fortitech (2001).

 Table 1.1 Federal enrichment standards of vitamin B in mg/kg for cereal-grain products (1998).

Grain products	Thiamin (Vitamin B ₁)	Riboflavin (Vitamin B ₂)	Niacin (Vitamin B ₃)	Folic acid (Vitamin B ₉)
Pasta products	8.83 - 11.0	3.75 - 4.86	59.6 - 75.1	1.99 – 2.65
Bread, rolls, and buns	3.97	2.43	33.1	0.95
Cornmeal	4.42 - 6.62	2.65 - 3.97	35.3 - 52.9	1.55 – 2.21
Flour	6.40	3.97	52.9	1.55
Rice	4.42 - 8.83	2.65 - 5.30	35.3 - 70.6	1.55 - 3.09

Among these four water-soluble vitamins, thiamin is the most susceptible to degradation by thermal processing. Thiamin, a water-soluble B-complex vitamin, is also known as B₁. It is necessary for normal functioning of the cardiovascular, nervous, muscular, and gastrointestinal systems. The coenzyme thiamine pyrophosphate, the active form of thiamin, participates in the breakdown of glucose and in the Kreb's cycle, the central energy-yielding pathway of the b ody. Thiamin also enhances b lood c irculation and blood formation, and assists in hydrochloric acid production, which is necessary for proper digestion. It also optimizes cognitive activity and brain function (Rindi 1996). In addition, thiamin acts as an antioxidant by protecting the body from the degenerative effects of aging, alcohol consumption, and smoking. A deficiency in thiamin results in a disease called beriberi. This deficiency is common in Asia where rice is excessively

milled to create polished rice (Krishna 1999). Thiamin is mostly found in the rice bran, which is removed during milling. Depending on the organ system affected by thiamin deficiency, beriberi has been termed wet, dry or cerebral. Wet (cardiovascular) beriberi symptoms include rapid heart rate, enlargement of the heart, severe swelling, difficulty breathing, and ultimately congestive heart failure. The main features of dry (neural) beriberi are abnormal reflexes, diminished sensation, and weakness in legs and arms. The most severe deficiency in thiamin results in cerebral beriberi, also known as Wenicke-Korsakoff syndrome. Symptoms are profound memory disorder, abnormal eye movements and aphasia. A diet including thiamin is necessary to prevent beriberi. The average dietary thiamin intake for young adult men and women is about 2 mg/day and 1.2 mg/day, respectively. The reference daily intake value recommended by the Food and Drug Administration (1994) is 1.5 mg/day. Sources of thiamin are whole grain cereals, legumes, nuts, lean pork, yeast, enriched bread and flour (Ottaway 1993).

Thiamin consists of pyrimidine and thiazole rings, linked by methylene bridge (Figure 1.2).



Figure 1.2. Chemical structure for thiamin (Ottaway 1993). $X = Cl^{-}$, HCl (Thiamin hydrochloride) $X = NO_3^{-}$ (Thiamin mononitrate) $X = H_3P_2O_6$ (Thiamin pyrophosphate) Thiamin occurs in natural foods either in its free form or in a combined form as a protein complex: a phosphorus-protein complex or the pyrophosphoric acid ester: co-carboxylase (thiamin pyrophosphate). Thiamin is commercially available for addition to food in the form of thiamin hydrochloride and thiamin mononitrate.

1.3. Thiamin analysis in wheat flour

Techniques for analyzing thiamin in food products are well-documented. The thiochrome method is the standard chemical method approved by the Association of Official Analytical Chemists (AOAC, 1995) and the American Association of Cereal Chemists (AACC, 2000). Results obtained by the thiochrome method are equally as precise as those obtained by High Performance Liquid Chromatography (HPLC), which is another accurate, rapid and sensitive method (Toma and Tabekhia 1979, Kamman et al. 1980, Abdel 1992). In this study, the thiochrome method was chosen because of its accuracy within 5% (Labuza and Riboh 1982), and because the necessary equipment was readily available. The thiochrome method involves oxidation of thiamin to thiochrome by adding an oxidizing agent such as potassium ferricyanide under alkaline conditions. In the absence of other fluorescing substances, the thiochrome fluorescence under UV light is linearly proportional to the amount of thiamin present following a standard curve. McFarlane and Chapman (1941) stated that different grain products contain different proportions of organic materials, thus making the optimal amount of oxidizing agent unique to each grain product. An investigation of the thiochrome method for soft wheat flour was recently published by Moore and Dolan (2003). They were the first to optimize the protocol for soft wheat flour analysis. They found that the maximum level of potassium ferricyanide added to aqueous thiamin-HCl extract was ranged from 4.84 to 100 μ g per μ g thiamin solution. A higher or lower amount of agent would decrease the fluorescence reading. Therefore, for our study, a level of 37.28 μ g potassium ferricyanide per μ g thiamin solution was chosen for optimal range. Another finding was that mixing potassium ferricyanide with sodium hydroxide as oxidizing agent yielded a lower experimental error than adding the potassium ferricyanide and sodium hydroxide separately to the thiamin extract. Their improved, accurate, and optimized protocol for soft wheat flour analysis was followed in the present study.

1.4. Thiamin stability

Dwivedi and Arnold (1973) summarized the factors affecting thiamin degradation in food products, which includes pH, temperature, oxidation-reduction potential of systems, sulphites and bisulphites content, presence of aldehydes, amine and radiation. At pH < 5.0, thiamin is quite stable to heat and oxidation; however a bove pH > 5.0, it is easily destroyed by heat. In the presence of heat, thiamin degradation involves the cleavage at the CH 'bridge' between the pyrimidine and thiazole molecules. Thiamin is very sensitive to sulphites and bisulphites especially at high pH. This is the cause of most thiamin degradation in vegetables blanched with sulphites and in meat products where sulphites and bisulphites are usually used as preservatives. Van der Poel (1956) reported that when thiamin was heated in a glucose solution, a brown discoloration and fluorescent compound was produced, which resembled a Maillard reaction of sugars and amino acids. Thiamin's participation in Maillard reaction may be important in the loss of thiamin during heat processing. Its participation is believed to be caused by its nitrogeneousity (Van der Poel 1956, Hermann and Tunger 1966). The breakdown of thiamin, especially during heating, release off-flavors and odors, some which are unpleasant.

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Chapter 2: Average shear rate in a twin-screw extruder as a function of degree of fill, screw speed and flow behavior index

2.1. ABSTRACT

Shear rate is critical in calculating viscous dissipation for cooking extruders. Shear rate profiles in twin-screw extruders a re difficult to measure and predict due to extruder complexity and the changing rheological properties of the product. Alternately, average shear rate ($\dot{\gamma}_a$) can be estimated using mixer viscometry assumptions.

Screw speed was varied at 50, 100, 200, 300, 400 rpm in a twin-screw extruder for fluids with different flow behavior indices, which represent different feed materials. Degree of fill was varied from 0.4-1.0. A modified matching viscosity technique was used to estimate $\dot{\gamma}_a$.

Average shear rate was modeled as a function of extruder constant (k), screw speed and an empirical parameter alpha. Effect of degree of fill was significant on alpha and extruder constant. Thus, both were incorporated in the average shear rate model. The model predicted average shear rate well for average shear rate <200 s⁻¹. The average shear rate estimated with this method may be useful for model mechanical effects during extrusion of cereal products.
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2.2. INTRODUCTION

Shear rate in an extruder can be used to evaluate viscous dissipation, which is the main source of energy to cook the material in the extruder (Mohamed *et al.* 1990). The shear rate term is also needed for calculation of shear history — a potentially useful factor tracking the material process history during extrusion.

Quantifying shear rate in a twin-screw extruder is complex, because the screw configuration usually varies along the barrel. As a result, shear rate also changes along the extruder barrel. Another two factors which further complicate the calculation of local shear rate are that two flows are present in a twin-screw extruder: drag flow, which is proportional to screw speed, and pressure flow, which opposes the drag flow as a result of high pressure at the die (Mohamed *et al.* 1990). The opposing flows and the mixing disrupt the velocity profile. Moreover, the local shear rates in each screw flight are unknown because of the large clearance between the screw root and the barrel. Often, the maximum shear rate is estimated as the screw tip velocity divided by the clearance. However, this maximum shear rate could be much larger than the average shear rate. Therefore, for approximations of shear rate in a twin-screw extruder, an average shear rate term can be used.

Li *et al.* (1996) developed an analytical model for predicting shear rate of a twinscrew extruder. Their approach was to treat the extruder as a mixer and the paddles as non-circular shaped bobs. However, the raw material's flow behavior index data must be known for this model. For some fluids, flow behavior index is easily determined by testing it in a rheometer. In contrast, when material such as flour is processed in an extruder, its flow behavior index changes significantly as flour is transformed to dough.

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Therefore, an average shear rate model relatively independent of flow behavior index (material rheology) would be more convenient.

The mixer viscometry method to determine average shear rate in a mixer has been fully developed by Mackey *et al.* (1987), and has been used by many researchers (Rao and Cooley 1984, Briggs 1995, Lai *et al.* 2000). This technique involves comparing the power consumption curves of a Newtonian fluid and a non-Newtonian fluid during mixing in identical equipment. If both fluids require the same power, the Newtonian viscosity (μ) must be equal to the non-Newtonian average apparent viscosity (η) (Metzner and Otto 1957). Apparent viscosity and average shear rate are related by an appropriate m odel e quation for n on-Newtonian fluids. U sing the e quation, the average shear rate in the mixer can be determined.

This technique has been used in evaluating performance of commercial equipment, such as a scraped-surface heat exchanger (Steffe 1996). However, Mohamed *et al.* (1990) presented the first study using the matching viscosity concept to calculate the average shear rate in an extruder. They determined the average shear rate and extruder constant (k') in the twin-screw extruder using one non-Newtonian fluid for each type of screw (single-lead, twin-lead and paddles) at 100% fill. Cha *et al.* (2003) applied Mohamed's method and conducted another extrusion study at 40% fill using a different non-Newtonian fluid and a combination screw configuration. Both studies predicted average shear rate and modeled it as a function of screw speed and constants.

$$\dot{\gamma}_a = \mathbf{k}' \mathbf{N}^{\alpha} \tag{2.1}$$

where $\dot{\gamma}_a$ is the average shear rate (s⁻¹), k' (rev⁻¹) is a constant unique for the given type of geometry and mixer (extruder) and must be determined from experimental data, α is a constant to a ccount for material conveying in the extruder, and N (rev/s) is the screw speed.

Degree of fill in an extruder is a measure of what proportion of the barrel void volume is filled with raw material. Degree of fill ranges from 0 to 1.0. Mohamed *et al.* (1990) investigated the average shear rate in a 1.0 degree of fill extruder and provided a range of average shear rates in the extruder. Since a commercial food extruder is commonly operated at a range of 0.4-0.8 degree of fill, it is necessary to determine the effect of degree of fill on average shear rate.

Lai *et al.* (2000) showed that k' in a mixer viscometer is virtually independent of the flow behavior index above a certain minimum speed. The same advantage may apply to extruders.

To date, no studies were found relating average shear rate in an extruder to degree of fill and material rheology. Hence, the objectives of this research were

- 1) To develop a method to measure extruder degrees of fill;
- 2) To determine the average shear rate in an extruder at various screw speeds, flow behavior indexes (material rheology) and degree of fill;
- To determine the significance of screw speed, degree of fill and flow behavior index on the extruder constant (k') and alpha (α);
- 4) To model the extruder constant and alpha as a function of the significant variables in 3).
- 5) To determine the accuracy of the model.

2.3. MATERIALS AND METHODS

2.3.1.Rheometer

Fluids with flow behavior indexes (n) ranging from 0.2 to 1.0 were chosen. The Newtonian fluid (n=1) was corn syrup (Sweetose 4300, A.E Staley Mfg. Co. Decatur, IL). The non-Newtonian fluids were two types of methylcellulose food gum (The Dow Chemical Co., Midland, MI); 2.8% (w/w) A40M Methylcellulose® and 8% (w/w) K99 Methylcellulose®.

The fluids were analyzed for their rheological parameters before they were extruded. Plot of shear stress versus shear rate at three different temperatures were obtained using a concentric cylinder Haake VT 550 rheometer (Haake, Paramus, NJ). Using a power-law model,

$$\sigma = K \dot{\gamma}^n \tag{2.2}$$

The effect of temperature on K was determined using the Arrhenius relationship,

$$K = K_o e^{\frac{-E_a}{RT}}$$
(2.3)

For Newtonian fluids (n=1) the consistency coefficient is known as the Newtonian viscosity (μ) . For non-Newtonian fluids, the apparent viscosity (η) is,

$$\eta = \frac{\sigma}{\dot{\gamma}} \tag{2.4}$$

Replacing the shear stress term (σ) with Eq.(2.2), the viscosity becomes a function of shear rate,

$$\eta = K\dot{\gamma}^{n-1} \tag{2.5}$$

2.3.2.Extruder

A laboratory scale twin-screw extruder with co-rotating, intermeshing screws (model MPF-19, APV Baker, Grand Rapids, MI), 19-mm barrels, and 3-mm circular die opening was used for the experiment. The barrel length:diameter ratio was 25:1. The screws were configured to cause high shear by combinations of twin-lead, single-lead and paddles (Table 2.1).

2.3.2.1.Hydraulic diameter and void volume

The hydraulic diameter was calculated as (Komolprasert and Ofoli 1990)

$$D_h = 4\Sigma V_{wi} / \Sigma A_{wi}, \qquad (2.6)$$

Wetted volume (V_w) and wetted area (A_w) for each screw type were calculated using equations in Mohamed *et al.* (1990). The screw configuration used in this study was the same as that in Cha *et al.* (2003). Their calculated hydraulic diameter of 2.25 mm for 0.4 degree of fill extruder was used in the present study. In the present study, calculation of hydraulic diameter at different degree of fill was replaced with a more convenient and straightforward method of plotting individual power consumptions lines for each degree of fill.

Volume of screws (Table 2.2) was measured by water displacement. The void volume (V_0) of the extruder was calculated using equation:

$$V_o = Barrel volume + die volume + die plate volume - (2.7) (total screws volume + end screws volume)$$

Table 2.1.	Screw	configurations	and	volume
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	Screw configuration	Volume (cm ³)
Feed port	8D Twin Lead Screw	40.0
	7x30° Forward Kneading Paddles	11.2
	4D Twin Lead Screws	20.0
	4x60° Forward Kneading Paddles	6.4
	4x30° Reverse Kneading Paddles	6.4
	2D Twin Lead Screws	10.0
	6x60° Forward Kneading Paddles	9.6
	4x30° Reverse Kneading Paddles	6.4
	1D Single Lead Screw	5.9
•	7x90° Kneading Paddles	11.2
Die	2D Single Lead Screws	11.8
	Total screws volume	138.9

Table 2.2. Extruder and screw flight data

Variable	Value
Twin-lead volume (cm ³)	2.5
Single-lead volume (cm ³)	2.95
Paddles volume (cm ³)	0.8
End screw volume (cm ³)	0.574
Barrel length (cm)	1.9
Barrel surface area (cm ²)	5.352
Barrel volume (cm ³)	245.7
Die size (cm)	0.3
Die volume (cm ³)	0.8
Die plate volume (cm ³)	12.0
Void volume (cm ³)	118.4

2.3.2.2.Energy balance in extruder

Total energy input generated by the extruder motor was separated into four energy types (Harper 1981):

$$\Delta E = \Delta E_{\rm H} + \Delta E_{\delta} + \Delta E_{\rm p} + \Delta E_{\rm k} \tag{2.8}$$

where ΔE is the mechanical energy input (J), $\Delta E_{\rm H}$ is the viscous energy dissipation in channel, ΔE_{δ} is the viscous energy dissipation in flight clearance due to drag flow, $\Delta E_{\rm p}$ is the pressure energy and $\Delta E_{\rm k}$ is the change in kinetic energy. Since change in velocity in an extruder is small, $\Delta E_{\rm k}$ is assumed negligible (Harper 1981). Eq. (2.8) become

$$\Delta E = \Delta E_{\rm H} + \Delta E_{\delta} + \Delta E_{\rm p} \tag{2.9}$$

total viscous dissipation

Eq. (2.9) can also be represented in rates by dividing each term by time:

$$\mathbf{P}_{\mathbf{w}} = \mathbf{E}_{\mathbf{v}} + (\mathbf{P}^*\mathbf{Q}) \tag{2.10}$$

where P_w is the power input (J/s) from the motor to the screw shafts, E_v is the rate of viscous dissipation and P*Q is the rate of pressure increase, where P is pressure (Pa) and Q is volumetric flow rate (m³/s). Power input to the screws can also be calculated using the measured torque value during extrusion runs and the manufacturer's correlation.

$$P_{w} = 2.64 * (\% Load - \% Base Torque) * N$$
 (2.11)

Another form to present power consumption for mixers is by a dimensionless power number:

$$N_{P_0} = \frac{E_{\nu}}{\rho N^3 D_h^{5}}$$
(2.12)

2.3.2.3.Extrusion run

Fluid was prepared in batches of approximately 10 kg for each extrusion run. Density was measured. The fluid extrusion was conducted at temperatures ranging from 10-25°C depending on the type of fluid. A water-cooling jacket around the extruder barrel was utilized to cool the barrel when necessary. During extrusion runs for each fluid, the temperature was maintained constant. After fluid flow output was at steadystate, % torque (load and non-load), pressure at die, temperature of fluid at feed inlet and at die outlet, and mass flow rate were measured. Die temperature was measured using a handheld T-Type needle thermocouple (Cole-Parmer, Vernon-Hills, IL) inserted into the die hole. The weight of the extruded fluid was measured for 30 seconds to obtain mass output flow rate. The density of extruded fluid was measured. The fluid density and temperature used for calculation were the averages between inlet and outlet fluid densities and temperatures, respectively.

Data were collected at a set of five screw speeds of 50, 100, 200, 300 and 400 rpm for each fluid. Duplicate experiments were conducted on different days.

2.3.2.4.Degree of fill

To investigate the effect of degree of fill on k', fluid degree of fill was varied. For each fluid, three ranges of degree of fill were chosen: 1.0, 0.7-0.9 and 0.4-0.6. The range was approximated for degree of fill <1.0 because exact degree of fill could not be set beforehand. However, exact degree of fill was measured at the end of each extrusion run.

Degree of fill of 1.0 (fill 1) was ensured visually as the fluid was poured manually into the feed inlet. A funnel with a ball valve attached on top of the extruder feed inlet was utilized to achieve degree of fill less than 1.0. The procedure to measure the exact degree of fill was as follows: After measurements were recorded at one screw speed (N_1) , the ball valve was closed to stop feeding of fluid, and the screw speed was increased to 300 rpm to force the remaining fluid in the barrel out of the die. The fluid exiting the die at this time was collected for 10 minutes and weighed (m_1) . The screw speed was then increased from N_1 to N_2 for the next desired screw speed. At this time, the fluid feed rate was arbitrarily increased to maintain a degree of fill approximately the same as at N_1 . The same procedure was repeated for each screw speed. At the end of the procedure for 400 rpm (N_5) , the barrel was opened, and the tared shafts with screws attached were removed and weighed (m_2) to obtain the fluid remaining on the screws. Fluid remaining on the barrel was scraped and weighed (m_3) .

Measured degree of fill was calculated as follows:

Degree of fill =
$$\frac{\mathbf{m}_1 + \mathbf{m}_2 + \mathbf{m}_3}{\rho V_o}$$
(2.13)

Preliminary measurements taken at 50, 100, 200 and 300 rpm for corn syrup showed that m_2+m_3 differ by only 5% over all screw speeds. Therefore, m_2 and m_3 were only measured at the end of the set of 5 screw speeds (50, 100, 200, 300 and 400 rpm), rather than after each screw speed.

For each screw speed, log N_{Po} (calculated using Eq.(2.12)) was plotted versus measured degree of fill to obtain a regression line. The regression equation was used to interpolate N_{Po} at an exact 0.4 and 0.7 degree of fill. Thus, fill 2 was established at 0.7 and fill 3 at 0.4.

2.3.2.5. Estimation of average shear rate by matching viscosity method (Mohamed *et al.* 1990)

According to Metzner and Otto (1957) and Steffe (1996), when mixing a Newtonian fluid in laminar flow ($N_{Re} < 63$) and assuming that surface tension, elastic and vortexing effects are insignificant, power consumption is inversely proportional to Reynolds number.

$$N_{Po} = \frac{A}{N_{Re}}$$
(2.14)

where

$$N_{\rm Re} = \frac{D_h N \rho}{\mu} \tag{2.15}$$

Mohamed *et al.* (1990) added another parameter to the general mixing model (2.14) for twin screw extruders to account for the conveying and thorough mixing. Thus, the model becomes

$$N_{Po} = \frac{A}{\left(N_{\text{Re}}\right)^{B}}$$
(2.16)

where A and B are constants depending on the screw configuration. A and B were determined using linear regression of $\log N_{Po}$ with $\log N_{Re}$ of the Newtonian fluid (corn syrup).

Once the power number of the non-Newtonian fluid was determined, the correlated Reynolds number was calculated using the established regression equation from Eq.(2.16). The matching viscosity method was applied,

$$\mu = \eta = K \dot{\gamma}_a^{n-1} \tag{2.17}$$

Finally, the average shear rate was calculated by solving for shear rate,

$$\dot{\gamma}_{a} = \left(\begin{array}{c} \frac{\eta}{K_{a}e^{\frac{E_{a}}{RT}}} \end{array}\right)^{\frac{1}{n-1}}$$
 (2.18)

The procedure is summarized in Figure 2.1.



Figure 2.1. Matching viscosity method to determine average shear rate (Steffe 1996).

Once the average shear rate was calculated, the non-linear model (Eq.(2.1)) was transformed to linear regression equation below to determine the extruder constant (k') and α . Regression analysis was done using Excel[®].

$$\log \dot{\gamma}_a = \log k' + \alpha \log N \tag{2.19}$$

Correlations between k' and the fluid's flow behavior index, and k' and degree of fill

were determined. The effects of degree of fill, screw speed and flow behavior index on k' were analyzed using PROC REG in SAS software to determine each significance.

2.4. RESULTS & DISCUSSIONS

2.4.1. Rheometer

2.4.1.1. Newtonian fluid

Plots of shear stress versus shear rate for Corn syrup are presented in Figure 2.2 at temperatures of 24, 35 and 44°C. The graph shows that the viscosity of the fluid, represented by the slope of the line, is constant with increasing shear rate. This verified that corn syrup is a Newtonian fluid, with $n \approx 1$. Table 2.3 summarizes the results obtained from regression analysis.



Figure 2.2 Plot of Shear stress versus Shear rate for Corn syrup.

Temperature (°C)	μ (Pa s)	n	\mathbf{R}^2
24	28.62	1.04	0.99
35	7.20	1.04	0.99
44	2.71	1.05	0.99

Table 2.3. Rheological properties of Corn syrup based on the model $\sigma = \mu \dot{\gamma}$

The temperature dependency of the viscosity was determined from regression from Figure 2.3. The slope was $\frac{E_a}{R}$, and the intercept was the log of reference viscosity.

The temperature dependence equation was

$$\mu = (1.568 * 10^{-15}) e^{\frac{11.17}{T}}$$
(2.20)



Figure 2.3. Consistency coefficient versus reciprocal temperature for corn syrup.

2.4.1.2 Non-Newtonian fluids

Plots of shear stress versus shear rate for one of the non-Newtonian fluids (A40M) at temperatures of 25, 37 and 43°C are presented in Figure 2.4. The curved lines on the graph show that the apparent viscosity changed with shear rate. Table 2.4 summarizes the data obtained by power-law fit.



Figure 2.4. Shear stress versus shear rate for 2.8% A40M Methycellulose.

Table 2.4. Rheological properties of 2.8% A40M Methycellulose based on the model $\sigma = K\dot{\gamma}^n$

Temperature (°C)	K (Pa s ⁿ)	n	\mathbb{R}^2
25	179.48	0.302	0.99
37	139.64	0.321	0.97
43	124.35	0.313	0.95

A plot of the consistency coefficient versus temperature is presented in Figure 2.5 based on the Arrhenius relationship in Eq.(2.3). The slope was $\frac{E_a}{R}$, and the intercept was the reference consistency coefficient. The complete equation was given by

$$\eta = (2.839 * 10^{-1}) e^{\frac{1921.7}{T}} \dot{\gamma}^{n-1}$$
(2.21)



Figure 2.5. Consistency coefficient versus temperature for 2.8% A40M Methycellulose.

Table 2.5 summarizes the rheological parameters, temperature and shear rate dependence of all fluids used for extrusion.

The rheological properties of the non-Newtonian fluids used in the present study, especially those of type A40m were very difficult to reproduce when doing replicate preparations. Slight differences in hydration and mixing procedures altered the consistency coefficient and flow behavior index. Despite using similar gum concentration, the rheological parameters were different, as seen in Table 2.5, and thus the non-Newtonian fluids were not treated as replicates.

Table 2.5. Rheological parameters of fluids used for extrusion and their temperature and shear rate dependence

Fluid	Flow	Consistency	Temperature and shear rate dependance
	behavior	coefficient	
	Index (n)	(K) at 25°C,	
		Pa s ⁿ	
2.8% A40M Methylcellulose®	0.24	137.18	$\eta = 1.075 * e^{\frac{1445}{T}} * \dot{\gamma}^{n-1}$
2.8% A40M Methylcellulose®	0.28	179.48	$\eta = (2.839 * 10^{-1}) * e^{\frac{1921.7}{T}} * \dot{\gamma}^{n-1}$
8% K99 Methylcellulose®	0.60	42.19	$\eta = (1.098 * 10^{-2}) * e^{\frac{2455.2}{T}} * \dot{\gamma}^{n-1}$
8% K99 Methylcellulose®	0.67	47.56	$\eta = (1.785 * 10^{-2}) * e^{\frac{5093.9}{T}} * \dot{\gamma}^{n-1}$
4300 Sweetose® Corn Syrup (Staley)	1.00	24.9	$\mu = (1.006 * 10^{-16}) * e^{\frac{11,980}{T}}$
4300 Sweetose® Corn Syrup (Staley)	1.00	29.04	$\mu = (1.568 * 10^{-15}) * e^{\frac{11,117}{T}}$

2.4.2. Extruder

All extrusion data can be found in Appendix 2.A.

2.4.2.1. Degree of fill

Dimensionless power number for all fluids was calculated using Eq.(2.12). Figure 2.6 shows an example plot of power number versus measured degree of fill. The best fit lines on the power number vs. degree of fill plot were linear for corn syrup with $0.63 \le R^2 \le 0.88$. Therefore, the relationship between log power number and degree of fill was assumed linear in the range of 0.4 and 1.0 degree of fill for all fluids. Using linear regression, trend lines were obtained for all screw speeds (Table 2.6). The trend lines were then used to predict the power number at 1, 0.7 and 0.4 degree of fill.



Figure 2.6. Plot of Power number versus measured degree of fill for corn syrup.

2.4.2.2. Estimation of average shear rate by matching viscosity method (Mohamed et al.

<u>1990)</u>

Figure 2.7 shows the plot of the Power number versus Reynolds number for degree of fill of 1, 0.7 and 0.4 for Corn syrup. Table 2.6 summarizes the slopes (B) and the intercept (A) obtained by linear regression.



Figure 2.7. Plot of Power number versus Reynolds number for corn syrup.

Table 2.6. Equations correlating Power number and Reynolds number for corn syrup at three different degrees of fill

Degree of fill	Equation $N_{Po} = \frac{A}{N_{Re}^{B}}$	R ²
1	$N_{Po} = \frac{10^{5.075}}{N_{Re}^{(-1.278)}}$	0.99
0.7	$N_{Po} = \frac{10^{5.025}}{N_{Re}^{(-1.214)}}$	0.99
0.4	$N_{Po} = \frac{10^{4.761}}{N_{Re}^{(-1.231)}}$	0.95

By assuming that at a constant speed, the power number would be the same for all fluids during mixing if the fluid viscosities are the same, the Reynolds number for non-Newtonian fluids could be calculated using the correlated equations in Table 2.6. Then, the equivalent average shear rate was determined using Eq.(2.18). Figure 2.8 shows a plot of average shear rate versus screw speed for one of the non-Newtonian fluids (A40m, n =0.24).



Figure 2.8. Plot of average shear rate versus screw speed for 2.8% A40M Methycellulose (n=0.24)(Curve equation = $\dot{\gamma}_a = \mathbf{k}' \mathbf{N}^{\alpha}$).

All calculated average shear rates are given in Appendix 2.B. The results of linear regression of Eq. (2.19) are displayed in Table 2.7.

2.4.2.3. Extruder constant

Flow		Overall extruder constant		α		Overall model		
behavior	Fill							
index	degree	Log k'	Std Error	k' (rev ⁻¹)	Value	Std Error	R ²	Std Error
0.24	1.0	1.550	0.0355	35.52	0.747	0.0648	0.98	0.0476
0.24	0.7	1.267	0.0454	18.48	0.914	0.0830	0.98	0.0609
0.24	0.4	0.995	0.0848	9.89	0.936	0.155	0.92	0.0114
0.28	1.0	1.654	0.0587	45.13	1.048	0.107	0.97	0.0788
0.28	0.7	1.462	0.0574	28.98	1.410	0.105	0.98	0.0769
0.28	0.4	1.268	0.117	18.55	1.601	0.214	0.93	0.157
0.60	1.0	1.407	0.0412	25.52	0.671	0.0412	0.96	0.0552
0.60	0.7	1.132	0.0140	13.56	1.263	0.0257	0.99	0.0188
0.60	0.4	0.943	0.0299	8.77	1.736	0.0546	0.99	0.0400
0.67	1.0	1.557	0.0757	36.14	0.987	0.0757	0.94	0.101
0.67	0.7	1.239	0.0668	17.33	1.721	0.122	0.99	0.0896
0.67	0.4	0.753	0.0536	5.66	2.086	0.0979	0.99	0.0719

Table 2.7. Summary of regression analysis (Eq.(2.19)) (extruder constant and alpha)

The value of k' shown in Table 2.7 was an "overall" k' for all screw speeds. An increasing trend was observed with increased degree of fill. The regression results showed an excellent fit for all the data with minimum R^2 of 0.92. Alpha decreased with degree of fill for all fluids. This result suggests that a low degree of fill allowed more mixing of the fluid in the extruder, thus increasing the alpha value.

Research on mixer viscometry showed that speed did not affect the mixer constant above a certain minimum speed (Castell-Perez and Steffe 1990, Mackey *et al.* 1987). Lai *et al.* 2000) added that mixer constant was independent of flow behavior index also. To investigate whether a similar trend would be observed for an extruder, k' was calculated at each screw speed using the known alpha obtained from regression analysis.

$$\mathbf{k}' = \frac{\dot{\gamma}_a}{N^a} \tag{2.22}$$

Figures 2.9, 2.10, 2.11 show the relationship of k' and screw speed (rps) at fill degree of 1.0, 0.7 and 0.4 respectively.



Figure 2.9. Extruder constant (k') vs. screw speed of non-Newtonian fluids with varying flow behavior index (n) at 1.0 degree of fill.

Mohamed's k' values for 1.0 degree of fill were 19.4 rev⁻¹ for single-lead, 28.0 rev⁻¹ for feed-screws and 42.8 rev⁻¹ for 30F paddles (Mohamed *et al.* 1990). In the present study, the screw configuration was a combination of single-lead, twin-lead and paddles. Figure 2.9 shows that most of the k' values fell in the range of 20-40 rev/s (within the range of Mohamed's results) after screw speed of 1.667 rps (100 rpm) for 1.0 degree of fill. A different trend is observed for n=0.28 where k' still increases after 3.33 rps (200 rpm). This inconsistency was caused by decreasingly small torque differences at higher

screw speeds. When the power number was low, the Newtonian viscosity was low. Thus, average shear rate increased (Eq. (2.17)), and so did the extruder constant. A possible reason for the drop in torque reading was that type A40m fluid's texture was slippery and slimy. Its slipperiness might act as a lubricant, yielding a lower torque difference at higher screw speed.



Figure 2.10. Extruder constant vs. screw speed of non-Newtonian fluids with varying flow behavior index (n) at 0.7 fill degree.



Figure 2.11. Extruder constant vs. screw speed of non-Newtonian fluids with varying flow behavior index (n) at 0.4 fill degree.

Very apparent trends are observed in Figures 2.10 and 2.11 where the k' is relatively constant above screw speed of 1.667 rps (100 rpm). A different trend is observed for n =0.28. The same justifications as mentioned above might cause this behavior. For this reason, fluid of n = 0.28 was not included in further calculation and analysis.

These plots suggest that the average k' at screw speed above 1.667 rps (100 rpm) for 1.0, 0.7 and 0.4 degree of fill was 32.23 ± 5.38 , 16.49 ± 2.48 and 8.2 ± 2.15 rev⁻¹, respectively (excluding data of n=0.28).

Effect of screw speed and flow behavior index on k'

Figures 2.9, 2.10 and 2.11 show that k' does not change significantly above screw speed of 1.667 rps (100 rpm) for all fluids but one. This observation was confirmed by statistical analysis (PROC REG in SAS) at 95% confidence level, which proved that screw speed did not significantly affect k' (P = 0.902). Flow behavior index effect on k'

was also not significant (P = 0.426). These results were similar to those found in mixer viscometers, where angular velocity and flow behavior index did not influence the mixer constant.

Effect of degree of fill on k'

On the other hand, degree of fill affected k' significantly (P < 0.0001). Because flow behavior index and screw speed were not significant factors affecting k', all the k' values were fitted as a function of degree of fill only. The best fit was a power law fit (R^2 = 0.86). Figure 2.12 shows that k' increased with degree of fill. The equation of the line was

$$k' = 30.39^*$$
 Degree of fill^{1.508} (2.23)



Figure 2.12. Effect of degree of fill on extruder constant.

2.4.2.4. Evaluation of equation's exponent (alpha)

Table 2.7 shows that alpha ranged from 0.671 to 2.086. Statistical analysis showed that degree of fill and flow behavior index significantly affected alpha (P<0.01). Alpha was fit using multiple linear regression as a function of degree of fill and flow behavior index, yielding R^2 of 0.79. Alpha increased with n and decreased with degree of fill.

It was mentioned earlier that a model that was independent of flow behavior index was preferred due to the difficulty in determining flow behavior index during extruder cooking. Another alpha model was therefore proposed, where alpha was fitted with linear regression as a function of degree of fill only (Figure 2.13, $R^2 = 0.457$).



Figure 2.13. Effect of degree of fill on alpha.

2.4.3. Average shear rate model

Two average shear rate models were developed following Eq.(2.1). For both models, $k' = 30.39^*$ Degree of fill^{1.508} (Figure 2.12).

Model 1 incorporated the flow behavior index in alpha,

$$\dot{\gamma}_a = \mathbf{k} \cdot N^{(-1.308 * \text{degree of fill} + 1.471*n + 1.404)}$$
 (2.24)

Model 2 accounted for degree of fill only,

$$\dot{\gamma}_a = \mathbf{k} \cdot N^{(-1.308 + \text{degree of fill} + 2.144)}$$
 (2.25)

A student t-test, paired with two-tailed distribution, was performed to determine if there was significant difference between the two models. The result showed that inclusion of flow behavior index did not change the predicted average shear rate model significantly (P=0.03). Therefore, using the second model (Eq.((2.25)), average shear rate was predicted at all points and then compared to the experimental average shear rate data (Figure 2.14).

Figure 2.14 shows that the model predicted the average shear rates relatively well for average shear rate <200 s⁻¹. However, at higher average shear rates, the predicted value underestimated the experimental value for fluid n=0.67. For fluid of n=0.67, the alpha values obtained were higher than those of other fluids (Figure 2.13). Because the model 'averaged' the k' and alpha values, the predicted average shear rate would be underestimated.



Figure 2.14. Predicted average shear rate versus the experimental average shear rate data.

2.4.3.1. Fluid suitability

The most challenging task in this study was to find a non-Newtonian fluid suitable for extrusion. This fluid must be thick enough to generate sufficient torque response, and yet had to flow continuously without yield stress. In the present study, the fluid concentration chosen for type A40M and K99 methylcellulose was at its maximum allowable concentration. If the concentration was higher than 2.8% and 8.0% respectively, the fluids would not flow continuously from the feeding funnel.

In addition, the present study determined a more selective criteria when using fluid with higher n value (0.6 and above). Based on two preliminary extrusion run data, it was concluded that fluid with high n, must have a consistency coefficient lower than 50 Pa sⁿ at 25°C, otherwise the calculated average shear rate value would be out of a reasonable range, based on Eq.(2.26).

$$\dot{\gamma}_a = \left(\frac{\eta}{K}\right)^{\frac{1}{n-1}}$$
 (2.26)

2.5. CONCLUSIONS

This study presents an investigation of average shear rate and extruder constant in a twin-screw extruder, following Mohamed *et al.* (1990)'s method. A new procedure to measure the fluid degree of fill in a twin-screw extruder was also developed in this study. Average shear rate was a function of two constants (extruder constant and alpha) which were dependent on degree of fill. Extruder constant increased with degree of fill, while alpha decreased with degree of fill.

A new model independent of flow behavior index was proposed. The model is useful to determine average shear rate at a known degree of fill in an extruder if using the same screw configuration. The model was more accurate at average shear rate $<200 \text{ s}^{-1}$ than at higher average shear rate. The model was used to calculate shear history in extrusion of wheat flour (Chapter 4).

This study answered some questions raised in Mohamed *et al.* (1990). Although the model developed in this study was not highly accurate at the higher screw speeds, the novel methods to determine average shear rate are fundamentally sound and lay a basis for follow-up studies. Results of this study show that choice of fluid and torque response are important factors to ensure high torque response to obtain reasonable average shear rate data.

2.6. FUTURE WORK RECOMMENDATIONS

Follow-up studies should investigate more non-Newtonian fluids with thicker viscosity (following the fluid selectivity mentioned above) for better torque response at higher shear rates.

Since die size affected the machine production capacity, its effect on average shear rate should also be determined.

Lastly, Mohamed *et al.* (1990) investigated the effect of one type of screw flight at 1.0 degree of fill. Changing degree of fill using only one type of screw flight and their effect on average shear rate should be investigated.

2.7. ACKNOWLEDGMENT

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2.8. NOMENCLATURE

- A_w wetted area, *i* is an index for each screw flight, m²
- A constant Eq.(2.16)
- B constant Eq.(2.16)
- D_h hydraulic diameter, m
- E_a activation energy (Joule/g-mole)
- E_{ν} viscous dissipation (J/s)
- ΔE mechanical energy input (J)
- $\Delta E_{\rm H}$ viscous energy dissipation in channel (J)
- ΔE_{δ} viscous energy dissipation in flight clearance due to drag flow (J)
- ΔE_{p} energy to increase the pressure (J)
- ΔE_k change in kinetic energy (J)
- k' extruder constant (rev⁻¹)
- K consistency coefficient (Pa sⁿ)
- K_o reference consistency coefficient (Pa sⁿ)
- m_1 mass of fluid exiting the die (kg)
- m_2 mass of fluid in the screws (kg)
- m_3 mass of fluid in the barrel (kg)
- N screw speed (Revolutions per seconds)
- n flow behavior index, dimensionless
- N_{Po} power number, dimensionless
- N_{Re} Reynolds number, dimensionless
- P pressure (Pa)
- P_w Power input (J/s)
- Q volumetric flow rate (m³/s)
- R gas units (J/g-mole*Kelvin)
- T temperature (Kelvin)
- V_o total void volume of extruder barrel and die (m³)
- V_w wetted volume (m³)

Greek symbols

- α constant in Eq.(2.1)
- σ shear stress (Pa)
- $\dot{\gamma}$ shear rate (1/s)
- $\dot{\gamma}_a$ average shear rate (1/s)
- η non-Newtonian apparent viscosity (Pa s)
- μ Newtonian viscosity (Pa s)
- ρ average density of the fluid before and after it is extruded (kg/m³)

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CHAPTER 3: Thermal kinetic parameters of thiamin in wheat flour at temperature >100°C

3.1. ABSTRACT

Kinetic parameters for thiamin degradation were obtained using two hightemperature heating methods, conducted at: 1) atmospheric pressure (AP) with moisture correction; 2) controlled pressure (CP). At AP conditions, 25% (wb) moisture wheat flour with 0.3% (wb) thiamin was heated in thin steel cells isothermally at 145, 160 and 172°C. To obtain the moisture correction factor, a constant-moisture study was conducted at 80°C using seven moisture contents (5-26.9%).

At CP conditions, flour at 16, 22 and 25% (wb) moisture in double-seamed cans was heated in a CP steam retort at 129.4°C. For the AP method, the corrected activation energy for 25% moisture content was 129.5 kJ/g-mol and reaction rate at 80°C was 3.48E-4 min⁻¹. Using the CP method, the activation energy and reaction rate were 121.0 kJ/g-mol and 9.69E-5 min⁻¹, respectively. Results obtained from two methods were not statistically different. These results illustrated that the correction method could be used as an alternative for researchers without access to controlled-pressure equipment and transient heat transfer software

The CP heating method required more complicated setup and computation than the AP method. However, more experimental time was needed to generate data for the AP method. While both methods had their advantages and disadvantages, the CP method was a superior method to obtain high-temperature kinetic parameters, because constantmoisture was achieved even during high-temperature heating, and lower standard error was obtained.

3.2. INTRODUCTION

Thermal processing is commonly used in the food industry, because it is necessary for pathogen inactivation, flavor development, and texture formation. The intensity of heating may degrade the color and nutrients of a product, making it undesirable. If the thermal kinetic parameters (reaction rate constant (k) and activation energy (E_a)) of the quality factors are known, they can be used to predict the degradation during thermal food processing (Thompson, 1982). Thus, the processing method can be improved to minimize the loss of those quality factors.

For many food components, rate of degradation is commonly modeled using Eq.(3.1) for first order degradation kinetics (Stumbo 1973),

$$-\frac{dC}{dt} = kC \tag{3.1}$$

After integrating the left side from initial concentration C_o to C, yielding

$$\ln\left(\frac{C}{C_o}\right) = -\int_0^t k \, dt \tag{3.2}$$

The reaction rate often changes with temperature, following Arrhenius' established equation (Eq. (3.3)).

$$k = k_{ref} \exp\left(\frac{-E_a}{R_g} \left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right)$$
(3.3)

where: k = reaction rate constant (min⁻¹), k_{ref} = reaction rate constant at reference temperature (T_{ref}) (min⁻¹), E_a = activation energy (J/g-mole), R_g = gas constant (J/g-mole K), and 1/T = temperature (1/°K).

Although quality factors (such as vitamin content) are usually degraded by intense heating, many food-processing methods involve other procedures, such as mixing and shearing, which contribute to the degradation. If the vitamin's **thermal** kinetic parameters are known, the degradation due to **thermal** effect can be calculated and quantified as a portion of the total degradation. The significance of all effects contributing to the degradation can then be identified separately, and the processing method can be optimized to obtain the minimum overall degradation.

Thermal kinetic parameters of thiamin have been investigated in a wide variety of high moisture food products, including meat, vegetables and buffer solutions (Mulley *et al.* 1975a, Guzman-Tello and Cheftel 1987, Steet and Tong 1994, Ryan-Stoneham *et al.* 1996). Villota and Hawkes (1986) reviewed and summarized the published kinetic parameters for thiamin. Few researchers have determined the thiamin kinetic parameters in low-moisture system. Guzman-Tello and Cheftel (1987) and Ilo and Berghofer (1998) utilized an extruder to determine thiamin kinetic parameters in flour and corn maize grits, respectively. However, they neglected the changing temperature profile along the extruder barrel and assumed isothermal heating temperature. Neglecting the varying thermal history along the barrel could lead to an underestimation of the kinetic parameters (Dolan 2003). This chapter compares two methods to obtain the thermal kinetic parameters of thiamin in a low moisture system so that the parameters can be used to quantify thermal effect and shear effect on thiamin degradation separately in an extrusion process (Chapter 4).

Typical heating procedures to obtain these parameters are carried out at atmospheric conditions because atmospheric heating involves simpler setup and analysis. However, this type of heating could cause moisture loss from the heated product, if the temperature of the heating medium is above 100°C. Cha *et al.* (2003) investigated

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thiamin kinetics in flour, but high-temperature heating decreased flour moisture content significantly.

The moisture changes could alter the rate of degradation and thus the thermal kinetic parameters obtained might not be the true value at the desired higher moisture content. This statement was supported by Hermann and Tunger (1966), who determined that moisture content (MC) of flour affected thiamin degradation rate. Their study concluded that if flour MC was less than 13% (wet basis)/ 14.9% dry basis (db), the reaction rate was positively correlated with MC. If flour moisture content was higher than 14.9%, the reaction rate was negatively correlated with MC.

Other studies investigated the effect of water activity on the reaction rate rather than the effect of moisture content on reaction rate. For most food products, the relationship between MC and water activity is described in a sigmoidal curve (the adsorption and desorption isotherm). Since the present study did not conduct an isotherm study, an approximate transformation from MC to water activity was based on the plot given by Hermann and Tunger (1966) for 80°C. Studies on the water activity effect also showed that reaction rate reached a maximum at a certain water activity (0.6-0.8, which correlates to ~9-17.6% MC), above which it falls off (Labuza 1980a) both in reducedmoisture systems and frozen systems. Bell and White (2000) also showed these phenomena for thiamin reaction rate.

Since many studies have shown the significance of moisture content, it is important to maintain constant flour MC during heating to obtain accurate thermal kinetic parameters. To minimize moisture loss, the containers must be perfectly sealed. However, heating perfectly-sealed containers in uncontrolled pressure conditions

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(atmospheric) is potentially dangerous because the pressure in the container increases with temperature. As an alternative, I hypothesized that the moisture loss problem could be solved by correcting the high-temperature, changing-moisture kinetic parameters based on a constant-moisture study at a lower temperature. Study at several constantmoisture contents determines the effects of MC on the reaction rate and was conducted at a temperature lower than 100°C to minimize moisture loss.

Another alternative procedure is to obtain the high-temperature kinetic parameters under controlled pressure conditions. Using steam as a heating medium allows rapid heat transfer. However, if the heated sample were a low moisture system (i.e., low thermal conductivity) and placed in a container, a temperature gradient in the container would exist. Since thiamin degradation is affected by temperature, it is necessary to calculate the temperature at various location of the container so that the correct thermal kinetic parameters could be estimated. Two general solutions had been developed and used by many researchers to predict spatially and temporally varying temperatures in canned foods. Numerical solutions, such as finite element, are useful for predicting temperature in irregular-shaped dimensions or varying initial temperature condition (Wang and Sun 2003). For products with regular geometric configurations (such as a cylinder), researchers h ave u sed a nalytical s olutions for p redicting temperature, with c omparable results to using numerical solutions (Lenz and Lund 1977a, Garrote *et al.* 2001, Carroll *et al.* 2003).

To date, no studies have determined the thermal effect on thiamin degradation in low-moisture systems at high-temperature. Therefore, the overall objective of this research was to investigate two different methods to determine kinetic parameters of

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thiamin in flour at high-temperature. The first method was conducted at atmospheric pressure and the second method was conducted at controlled pressure.

3.3. MATERIAL & METHODS

3.3.1. Sample preparations

Soft wheat flour, with moisture content (MC) of approximately 17.6% dry basis (db) (15% wb), was obtained from the Star of the West Milling Co. (Frankenmuth, MI). MC was determined by heating 1 g flour at 130°C for 10 minutes using a Sartorius MA-30 moisture analyzer (Goettingen, Germany). MC in wet basis was converted to dry basis using Eq. (3.4).

$$MC(db) = \frac{MC(wb)}{1 - MC(wb)}$$
(3.4)

Food-grade thiamin hydrochloride (Spectrum Laboratory Products, Gardena, CA) was mixed with flour at a concentration of 0.35% (db) using a V-shaped twin shell dry blender (Patterson-Kelley, East Stroudsburg, PA). To ensure homogeneous distribution of thiamin with a coefficient of variance <10%, the flour and thiamin were mixed for 40 minutes. Thiamin content was analyzed using the fluorometric method (Official Method 953.17, AOAC 1995), following techniques from Moore and Dolan (2003). Method of thiamin analysis is described in Appendix 1.A. Initial concentration of thiamin in flour was analyzed at 9 different locations in the mixed flour to yield $C_0 = 0.36 \pm 0.0189$ % concentration in dry weight basis.

Flour MC was increased to the desired MC by spraying it with water. After addition of water, the mixture was blended in food processor (Cuisinart, Model DLC-2A) for 1 minute to ensure homogeneous distribution of moisture. Flour mixture was stored in refrigerated temperature of ~4°C for at least 24 hr until usage.

3.3.2. Study 1a and 1b: Atmospheric Pressure heating

Custom-made steel cells (Michigan State University Farrall Hall Research and Development Shop, East Lansing, MI) were utilized to contain the flour mixture (Figure 3.1). Each cell was divided into two parts: the lid and the base. The lid was a rectangular piece with 10.6 cm length, 1.2 cm width and 0.9 cm thickness. The base had 0.5 cm inner thickness, 0.1 cm wall thickness and 8.6 cm height. After filling the base with 12 g of the flour mixture, the lid was attached to the base with insertion of two screws on the far right and left of the lid. It was ensured that the top of the flour mixture was always below the oil surface. The lid had a small opening of 0.2 cm in the center, into which a type T 30-gauge Copper-Constantan thermocouple was inserted to measure the temperature at the height and thickness midpoint of the flour.



Figure 3.1. Steel cell for Atmospheric Pressure heating.



Figure 3.2. Setup for Atmospheric Pressure heating.

The sample in the cells was heated in a bath of silicon oil (Fisher Scientific, Pittsburgh, PA) held at different constant temperatures in an Isotemp 10 BP heater bath (Fisher Scientific), as shown in Figure 3.2. The heating time, the center temperature (T_c)

of the sample and the temperature of the oil bath data were recorded every 10 seconds using a Digi-Sense Model 92000-00 Scanning Thermometer data logger (Cole-Parmer Instrument Co., Barrington, IL).

The first sample was taken after the sample temperature had nearly reached a plateau to ensure near-isothermal analysis (within 3°C of desired temperature). The cells were taken out at 3 heating times, such that thiamin retention would be in the 20-85% range. Heating time started as soon as steel cells were placed in the oil bath. At the end of heating time, cells were quickly cooled in an ice bath until sample temperature reached \sim 5°C. All experiments were duplicated. Samples were stored at refrigerated temperature of \sim 4°C until further analysis.

For thiamin analysis, the heated sample was mixed for 1 minute using the Cuisinart processor to ensure homogeneous distribution. Two thiamin readings were obtained from each steel cell.

3.3.2.1 Study 1a: Atmospheric pressure (AP) – Constant-moisture at temperature <100°C Objective: To determine how moisture content affects thiamin reaction rates

Flour mixtures of 6.17, 9.67, 10.7, 17.2, 27.0 and 36.9% (db) MC were used. For flour with <17.2% MC, the flour mixtures were dried in a convection Isotemp oven (Fischer Scientific) at 45°C. The temperature of the oil bath was set at 80°C to minimize flour moisture loss. At each moisture content, three heating times were selected such that thiamin retention would be in the 20-85% range.

3.3.2.1.1. Data analysis

The natural log concentration of the thiamin was plotted against heating time (t) to obtain the reaction rate (Eq.(3.5)) at each moisture content.

$$LnC = LnC_o - kt \tag{3.5}$$

At a constant temperature, the reaction rate changed with moisture content exponentially.

$$k = k_r \exp\left[b(\text{MC} - \text{MC}_r)\right]$$
(3.6)

By linear regression of ln k versus MC, the slope of the line (b) was obtained. A positive b value correlates to faster degradation rate at higher MC. As mentioned before, Hermann and Tunger (1966) found two types of b. In their study, parameter b was a positive value at MC<14.9% (db), and a negative value at MC>14.9%. In the present study, the two slopes were denoted as $b_{(+)}$ for the positive slope, and $b_{(-)}$ for the negative slopes (Figure 3.3). The point where the two slopes intersected was called k_x at MC_x.



Figure 3.3. Example plot of the moisture content effects on reaction rate constant for thiamin.

3.3.2.2. Study 1b: Atmospheric pressure (AP) – High-temperature

Objective: To determine the kinetic parameters of thiamin in flour obtained from hightemperature heating at atmospheric pressure conditions and to correct for moisture loss based on the constant-moisture study in study 1a.

Flour mixtures of 33.3% (db) MC were heated at 145, 160, and 172°C in the oil bath. At each temperature, three heating times were selected such that thiamin retention would be in the 20-85% range.

3.3.2.2.1. Data analysis

The natural log concentration of the thiamin was plotted against heating time (t) to obtain the reaction rate (k) (Eq.(3.5)) at each temperature. Regression statistics were done using Excel[®].

3.3.2.3. Correction method for high-temperature reaction rate constant

Assuming that thiamin activation energy did not change with temperature (as indicated by data from Hermann and Tunger 1966), the constant-moisture study parameters $b_{(+)}$ and $b_{(-)}$ obtained at 80°C were used to correct the moisture loss at higher temperature. When a sample MC dropped from MC_{high} to MC_{low} during a high-temperature heating, the k at MC_{low} was corrected to k at MC_{high} using the proposed correction method. The correction method was divided into two calculation steps, which incorporated the constant $b_{(+)}$ and $b_{(-)}$. First, k at MC_{low} was corrected to k_x using $b_{(+)}$. In the first step, MC_x = MC_r (Refer to Eq.(3.6) for the basic equation).

$$k_{\rm MC_{low}} = k_x \exp\left[b_{(+)}(\rm MC_{low} - \rm MC_x)\right]$$
(3.7)

Secondly, k_x was converted to k at MC_{high} using b₍₋₎. In this step, MC_{high} = MC_r.

$$k_{x} = k_{\text{MC}_{high}} \exp\left[b_{(-)}(\text{MC}_{x} - \text{MC}_{high})\right]$$
(3.8)

Combining both equations,

$$k_{\rm MC_{high}} = \frac{k_{\rm MC_{low}} \exp\left[-b_{(+)} (\rm MC_{low} - \rm MC_{x})\right]}{\exp\left[b_{(-)} (\rm MC_{x} - \rm MC_{high})\right]}$$
(3.9)

Once the corrected k was determined at each temperature, the activation energy (E_a) was calculated from the slope of a regression line of ln k vs average sample temperatures $[1/(T_{avg}+273.15)]$. The average sample temperature was the average of the measured center temperature of the sample and the calculated temperature of the sample at steel wall (°C).

$$T_{avg} = \left(\frac{T_{center} + T_{wall}}{2}\right)$$
(3.10)

 T_{wall} was calculated by assuming that there was no temperature gradient across the steel wall. Then, the heat flux from the oil bath to the cell wall was equal to the flux from the wall to the center of the sample in the steel cells, assuming a straight-line approximation of temperature gradient over the cell half-thickness of 4.5 mm.

$$q = hA_s(T_{oil\ bath} - T_{wall}) = \frac{kA_s(T_{wall} - T_{center})}{\Delta x/2}$$
(3.11)

The heat transfer coefficient of the oil bath (h) was estimated by Lai *et al.* (2003) using the lumped heat-capacity analysis. They determined h as a function of temperature of the heating medium (°C),

$$h = 1.791^* (T_{oilbath}) - 22.28 \tag{3.12}$$

The thermal conductivity of the sample (k) was calculated at the average of the initial and final sample temperature (T in^oC), based on equation provided by Choi and Okos (1986), taking into account carbohydrate and water content only.

$$k = (0.20141 + 1.3874 * 10^{-3} * T - 4.3312 * 10^{-6} * T^{2})x_{carbohydrate} + (0.57109 + 1.7625 * 10^{-3} * T - 6.7036 * 10^{-6} * T^{2})x_{water}$$
(3.13)

3.3.3. Study 2: Controlled Pressure heating

Objective: To determine the thermal kinetic parameters of thiamin in flour at hightemperature heating, at controlled pressure conditions

The heating medium was a continuous steam simulation retort FMC no. 2881 (FMC Corp. Food Processing Systems Division, Madera, CA), provided with a panel for temperature and pressure setup from ABB Automation 1900 (ABB Automation Inc., Warminster, PA). The retort was equipped with six locking male connector thermocouples and one mercury-in-glass thermometer. Cylindical cans (type 201x 211; 5.15 cm inner diameter, and 6.79 cm height) were obtained from Freund Container Co., Chicago, IL. The use of smaller cans was essential to provide a reasonably rapid heating and cooling transfer. A needle type thermocouple Model 1 7/16" with female fitting attached with a C-9 Locking Receptacle and a C-16 heat-resistant gasket (Ecklund-Harrison Technologies, Fort Myers, FL)) was inserted in each can such that the geometric center temperature was recorded (Figure 3.4).



Figure 3.4. Thermocouple was inserted into the center of can (left) so that geometric center temperature was recorded (right).

The cans were packed-filled with approximately 100 g of flour mixture and double-seamed to ensure a hermetic seal. After seaming, the can's thermocouple receptacles were connected to the retort's plug-end thermocouples. Cans were then placed vertically on the bottom of the retort.

All thermocouples were calibrated prior to conducting experiments. During heating, the center temperature of the flour was measured and recorded every 40 seconds using a CALPlex[™] data logger (TechniCal. Inc., New Orleans, LA). Flour mixtures of 19.1, 28.2 and 33.3% MC (db) were heated at retort temperature of 129.4°C. This temperature was near the maximum allowable temperature for this type of retort. The temperature of the retort reached 129.4°C in 2 minutes. Heating time for each flour mixture was chosen appropriately so that thiamin retention ranged from 20-80%. At the end of the designated heating time, cans were cooled with water at 25°C while using overriding air pressure in the retort to prevent can deformation. All experiments were done in triplicate. Samples were stored at ~4°C until further analysis.

For thiamin analysis, the heated sample was mixed for 1 minute using the Cuisinart processor to ensure homogeneous distribution. Two thiamin readings were obtained from each can.

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3.3.3.1 Data analysis

3.3.3.1.1. Temperature calculation

The analytical solution to predict temperatures for a finite cylinder during transient conduction heat transfer, provided by Carslaw and Jaeger (1959) was used to determine the center and off-center temperatures in the can. This solution is valid when there is no spatial variation in initial sample temperature and environmental temperature is suddenly changed to a constant value. In addition, the sample k, ρ and specific heat capacity (c_p) values are constant. The solution for a finite cylinder was a product of the infinite cylinder and the infinite slab solutions. The predicted center temperature was compared with the measured center temperature to determine the accuracy of the solution. The root mean square error (RMSE) of the prediction was calculated as

$$RMSE = \frac{Pr \text{ edicted value} - Measured value}{number of data point s}$$
(3.14)

Temperature was calculated at 25 different points in the can at the r and z points. To d etermine the temperature at location r for an infinite cylinder during heating, the analytical solution was,

$$\frac{T(r) - T_{\infty}}{T_{i} - T_{\infty}} = \sum_{n=1}^{10} \frac{2\left(\frac{hR}{k}\right) J_{0}\left(\lambda_{n} * \frac{r}{R}\right) \exp\left[-\lambda_{n}^{2}\left(\frac{\alpha t}{R^{2}}\right)\right]}{\left[\left(\frac{hR}{k}\right)^{2} + \lambda_{n}^{2}\right] J_{0}\left(\lambda_{n}\right)}$$
(3.15)

To determine the temperature at location z for infinite slab during heating, the analytical solution was,

$$\frac{T(z) - T_{\infty}}{T_{i} - T_{\infty}} = \sum_{m=1}^{10} \frac{2\left(\frac{hl}{k}\right)\cos\left(\lambda_{m} * \frac{z}{l}\right)\sec(\lambda_{m})\exp\left[-\lambda_{m}^{2}\left(\frac{\alpha t}{l^{2}}\right)\right]}{\left[\left(\frac{hl}{k}\right)\left(\frac{hl}{k}+1\right)+\lambda_{m}^{2}\right]}$$
(3.16)

where thermal diffusivity (α) was

$$\alpha = \frac{\mathbf{k}}{c_p * \rho} \tag{3.17}$$

Thermal conductivity (k) was determined based on Eq.(3.13). Density (ρ) was calculated by dividing the mass of the flour in the can by the volume of the can.

Kaletunç (unpublished data) developed an equation to relate temperature and moisture content with specific heat capacity (c_p) for flour.

$$c_p = 1.132 + 0.0058 * (T in °C) + 0.037 * (%MC)$$
 (3.18)

The c_p for this study was evaluated at the average between the highest and lowest temperature. Moisture content in Eq.(3.18) was presented in dry basis.

The heat transfer coefficient of the steam (h) was set at 5500 W/m², giving a Biot number $\left(\frac{hl}{k}\right)or\left(\frac{hR}{k}\right) > 40$, which means that the external resistance is negligible compared to the internal-conduction resistance. Thus, the temperature of the flour at the can wall is virtually the same as the steam temperature.

The temperature at the specific (r, z) location in the finite cylinder was determined as a product of cylinder (Eq.(3.15)) and slab (Eq.(3.16)) solutions. Finite cylinder = infinite cylinder x infinite slab

$$\frac{T(r,z)-T_{\infty}}{T_i-T_{\infty}} = \left(\frac{T_r-T_{\infty}}{T_i-T_{\infty}}\right) \quad x\left(\frac{T_z-T_{\infty}}{T_i-T_{\infty}}\right)$$
(3.19)

Since no analytical solution was suitable for a spatially-varying initial temperature condition, the same analytical solutions (Eq. (3.19)) was used to predict the approximate temperatures during cooling period. A justification for using Eq.(3.19) was that the sample was heated for a sufficiently long time that, at the end of heating time, the temperature gradient within the can was not large (~5°C from center of the can to the edge). Mass-average temperature was calculated at the end of the heating period, and it was set as the initial cooling temperature. Mass-average temperature (Eq.(3.20)) and mass-average thiamin retention (Eq.(3.21)) were calculated by integration over the can volume. For this purpose, Gauss-Legendre quadrature, a powerful numerical integration method, was used to estimate the integral. In this method, the locations of r and z in the can are given at unequally spaced intervals (Figure 3.5) and they are weighted such that a high accuracy is obtained (Stasa 1985). The calculation for the r and z points and the weights of each point are found in Appendix 3.D. The r points were dimensionless,

 $r = \frac{r^*}{R^*}$ where r^* is the axial radius and R^* is the radius of the can. The z points were

also normalized so that $z = \frac{z^*}{l^*}$. Therefore, the integral for mass-average temperature

was,
$$T_{ma} = \int_0^1 \int_0^1 \frac{T_{r,z} dV_{r,z}}{V_{can}}$$
 (3.20)

where V_{can} was the normalized volume of the half-can = $\pi R^2 l = \pi (1)^2 (1)$ (dimensionless).



Figure 3.5. Five-point Gauss-Legendre quadrature for off temperature calculation for half-can.

3.3.3.1.2. Kinetic parameters estimation

The predicted mass-average thiamin retention in the can was evaluated by using the Gauss-Legendre numerical integration. Based on first-order thiamin degradation kinetics, at any time t,

$$\left(\frac{\bar{C}}{C_o}\right)_{predicted} = \int_0^1 \int_0^1 \left(\frac{C}{C_o}\right) \left(\frac{dV_{r,z}}{V_{can}}\right) = \int_0^1 \int_0^1 \frac{\exp\left[-k_r\beta(r,z)\right]2\pi r dr dz}{\pi R^2 l}$$
$$= 2\int_0^1 \int_0^1 \exp\left[-k_r\beta(r,z)\right] r dr dz \qquad (3.21)$$

where $\beta(r,z)$ at time t was

$$\beta(r,z) = \int_{0}^{t} \exp\left[-\frac{E_a}{R_g}\left(\frac{1}{T(t,r,z)} - \frac{1}{T_{ref}}\right)\right] dt$$
(3.22)

The time-temperature history, β (r,z) was calculated using the trapezoidal rule by integrating over each r and z location in the can at each heating time (t). Time intervals varied from 40 seconds to 200 seconds.

The activation energy (E_a) and k_r of flour with MC=19.05, 28.20 and 33.33% were estimated by non-linear regression using Solver in Excel® while minimizing the sum of squares of the residuals between the measured and the predicted mass-average thiamin retention.

$$SSQ = \sum_{i=1}^{n} \left[\left(\frac{\overline{C}}{C_o} \right)_{\text{predicted},i} - \left(\frac{\overline{C}}{C_o} \right)_{\text{measured},i} \right]^2$$
(3.23)

Written in Visual Basic application in Excel®, the Bootstrap data-based simulation program was used to generate 1,000 new values of E_a and k_r (Efron and Tibshirani 1993) as follows. The bootstrap assigns measures of accuracy to statistical estimates. Given there were n paired values of measured and predicted thiamin retention (in our study, n=18),

$$\left[\left(\frac{\bar{C}}{C_o}\right)_{\text{predicted}}, \left(\frac{\bar{C}}{C_o}\right)_{\text{measured}}\right]_1, \left[\left(\frac{\bar{C}}{C_o}\right)_{\text{predicted}}, \left(\frac{\bar{C}}{C_o}\right)_{\text{measured}}\right]_2, \dots, \left[\left(\frac{\bar{C}}{C_o}\right)_{\text{predicted}}, \left(\frac{\bar{C}}{C_o}\right)_{\text{measured}}\right]_n$$

The Bootstrap program randomly chose the paired retention values from the original data points to generate a new set of n paired values. Some pairs might be chosen more than once. Using the new set of n paired values, new values of E_a and k_r were estimated by non-linear regression using Solver. This process was repeated 1,000 times to obtain the real probability distribution of E_a and k_r , instead of just assuming a normal probability distribution. A probability distribution is a function that expresses the relative frequency at which measurement values can occur. The probability distribution was plotted using MATLAB software. The distribution was also reported for its 90% joint confidence region. The 90% c.r was used because of the 95% confidence limit of the two

parameters (i.e., $(0.95)^2 = 0.90$). The elliptical confidence region was plotted using MATLAB.

T-test for results from study 1a, study 1b and 2 were conducted to determine whether the values were statistically different from each other. Since the number of observations was not similar between each study, a pooled t-test was conducted, where

t - test =
$$\frac{\mu_a - \mu_b}{\sqrt{se(\mu_a)^2 + se(\mu_b)^2}}$$
 (3.24)

 μ_a = value (activation energy, reaction rate constant or moisture content parameter) from study a and $se(\mu_a)$ = standard error of μ_a ,

 μ_b = values (activation energy, reaction rate constant or moisture content parameter) from study b and $se(\mu_a)$ = standard error of μ_b .

To be significantly different, the t-test values had to be more than the $t_{critical}$ at 95% confidence (0.05, degrees of freedom). Degree of freedom is the total number of data in both studies minus 2.

The complete experimental design is summarized in Table 3.1.

		Heating medium set temp	Sample Moisture content, %		Heating
Study #	Description	(°C)	(wb)/(db)	Heating time (min)	medium
la	Constant Moisture	80	5.8 / 6.15	300, 960, 1440	Oil bath
la	Constant Moisture	80	8.8 / 9.67	162, 360, 600	Oil bath
1a	Constant Moisture	80	9.7 / 10.7	180, 480, 725	Oil bath
la	Constant Moisture	80	14.7 / 17.2	60, 120, 240	Oil bath
la	Constant Moisture	80	21.3 / 27.0	61, 180,270	Oil bath
la	Constant Moisture	80	26.9 / 36.9	60, 210, 300	Oil bath
1b	High Temperature, Atmospheric Pressure	145	25.0 / 33.3	25, 60, 70	Oil bath
1b	High Temperature, Atmospheric Pressure	160	25.0 / 33.3	20, 40, 60	Oil bath
1b	High Temperature, Atmospheric Pressure	172	25.0 / 33.3	10, 15, 20	Oil bath
2	High Temperature, Controlled Pressure	129.4	16.0 / 19.1	20, 40, 60	Steam retort
2	High Temperature, Controlled Pressure	129.4	22.0 / 28.2	40, 60, 80	Steam retort
2	High Temperature, Controlled Pressure	129.4	25.0 / 33.3	40, 60, 80	Steam retort

Table 3.1. Summary of the experiments conducted to obtain thermal kinetic parameters of thiamin

3.4. RESULTS AND DISCUSSIONS

Study 1a and 1b. Atmospheric heating



Figure 3.6 shows plots of flour center temperature versus heating time.

Figure 3.6. Plots of flour center temperature versus time for study 1a and 1b.

^a Samples were taken out at 10, 15 and 20 minutes of heating time

^b Samples were taken out at 20, 40 and 60 minutes of heating time

^c Samples were taken out at 25, 60 and 80 minutes of heating time

3.4.1. Study 1a. Atmospheric Pressure heating- Constant-moisture

The average oil bath temperature was 80.8°C. Moisture content of flour mixture stayed relatively constant with a maximum c.v at 10.4% during heating (Appendix 3.A.). Thiamin concentration value was reproducible within each experiment with maximum c.v at 10.9%. Concentration of thiamin was plotted against heating time on a semi-log plot for MC \leq 17.2 (Figure 3.7) and MC \geq 17.2 (Figure 3.8). Moisture contents reported in the plots were the mean values of 16 moisture content readings (4 initial flour MCs and 4 MCs at each heating time). In Figure 3.7, the reaction rate (slope) increased with moisture content, but the opposite was true in Figure 3.8.



Figure 3.7. Semi-log plot of thiamin concentration versus heating time for 6.15, 9.67, 10.7% moisture content (db) flour heated isothermally at 80°C in an oil bath. The thinner trend lines represent the 2^{nd} replication.



Figure 3.8. Semi-log plot of thiamin concentration versus heating time for 17.2, 27.0, 36.9% moisture content (db) flour heated isothermally at 80°C in an oil bath. The thinner trend lines represent the 2^{nd} replication.

The effect of sample moisture contents on k is summarized in Figure 3.9. Parameter $b_{(+)}$ and $b_{(-)}$ were 0.439 and -0.128 respectively.



Figure 3.9. Effect of flour mixture moisture content (db) on reaction rate constant at 80°C heating. k is in min⁻¹.

According to Hermann and Tunger (1966), thiamin was more thermostable in a dry medium than in moist product until MC reached 14.9% (db). In the present study, the same trend was observed but different values of k_x , $b_{(+)}$ and $b_{(-)}$ were obtained. Figure 3.10 compares the graphs obtained from Hermann and Tunger with results from the present study.



Figure 3.10. Plot of Ln k versus MC % (db) of Hermann and Tunger (1966) (HT) at 90 and 110°C and the present study. k is in (min⁻¹).

Figure 3.10 shows that the slopes obtained from the present study were steeper compared to Hermann and Tunger's (especially at MC>14.9%). A possible reason of this occurrence was that their published study did not specify the container used for heating the flour or whether moisture content was kept constant throughout. If MC decreased during heating time, the true reaction rate value would be lower than the reported value because reaction rate was slower at higher MC (A in Figure 3.11). Thus, in the Ln C vs time plot, the true k value would be smaller than the reported value. Especially at high

MC where unbound water could evaporate rapidly, the reported k could be much higher than the true k. Consequently, the true $b_{(-)}$ value (B in Figure 3.11) could be a steeper slope. However, at the lower MC, moisture was bound tightly to flour particles, thus even if the container was not tightly sealed, the moisture loss during heating was minimum, Thus, the slope from their study was similar to the present study at the lower MC.



Figure 3.11. Possible reason for the difference between the result in Hermann and Tunger (HT) (1966) and the present study.

3.4.2. Study 1b. Atmospheric Pressure heating- High-temperature heating

Average oil bath temperature was calculated to be 144.8, 159.2 and 170.6°C. The average sample temperature was calculated at each heating temperature using Eq. (3.10). The T_{avg} were 141.9, 156.8 and 166.4°C. Thiamin concentration value was reproducible within each experiment with c.v ranging from 0.67-13.4%. Thiamin concentration versus heating time was plotted in Figure 3.12. Reaction rate constants (k) were the negative slopes obtained from the graph.



Figure 3.12. Semi-log plot of thiamin concentration versus heating time for flour mixture heated isothermally at 144.8, 159.2 and 170.6°C average oil bath temperature. T_{avg} is the average sample temperature. The thinner trend lines represent the 2nd replication.

Figure 3.12 shows that higher temperature caused higher degradation rates of thiamin. The retention of thiamin in the flour mixture at oil bath temperatures of 144.8, 159.2 and 170.6°C indicated a first-order reaction, as shown by the linear fit on a semi-log plot (Figure 3.12).

3.4.2.1. Corrected high-temperature reaction rate constant

During high-temperature heating, the flour mixture MC dropped from 33.3% to

~6.0% (Figure 3.13).



Figure 3.13 Plot of flour moisture content versus heating time during high temperature heating in study 1b.

Reaction rate constants were corrected to 33.3% MC using the constant $b_{(+)}$ and $b_{(-)}$ based on Eq.(3.9) to account for the moisture loss. The corrected and uncorrected k were plotted against reciprocal of T_{avg} to obtain the respective activation energy.



Figure 3.14. Arrhenius plot for the corrected and uncorrected reaction rate constants. k is in min⁻¹. T_{avg} is the average sample temperature.

The reaction rate constant increased after it was corrected from the MC_{low} to the MC_{high}, as expected. The reaction rate calculated at 80°C ($k_{80°C}$) increased from 1.85x10⁻⁵ min⁻¹ to 3.48x10⁻⁴ min⁻¹. However, the increase in k values only yields a 3.7% increase of activation energy from 124.9 to 129.6 kJ/g-mole.

3.4.3. Study 2: Controlled Pressure heating

Predicted center temperature versus measured center temperature of the flour in the heated cans was plotted for 33.3% MC. The plots for the other two MCs can found in Appendix 3.E. The RSME for predicted versus measured temperature for flour 19.1%, 28.2% and 33.3 % flour MC were 12.3, 10.1 and 8.06°C, respectively.



Figure 3.15. Plot of measured versus predicted center temperature for 33.3% (db) MC flour in 201x211 cans heated at 129.4°C retort temperature.

The plot above shows that there was good agreement between the predicted temperature and the measured temperature, suggesting a good accuracy of the analytical solutions.

Temperatures at each r and z location determined by Gauss-Legendre quadrature were calculated. The mass-average thiamin retentions in the cans were calculated based on Eq.(3.21). Activation energy and reference reaction rate at 80°C were changed by iteration to obtain minimum sum of squares (Eq.(3.23)) of thiamin retention. The reference temperature chosen was 80°C as it was the average of the initial and final sample temperature. Figure 3.16 shows good agreement between measured retention and predicted retention for 33.3% MC. Appendix 3.F shows those of 19.1% and 28.2% MC.



Figure 3.16. Plot of measured thiamin retention vs predicted thiamin retention for 33.3%MC (db) flour in 201x211 cans heated at 129.4°C retort temperature.

For 19.1% MC, Solver was unable to converge to a reasonable value of E_a and k_r regardless of any initial values and reference temperature. The coefficient of variance for this MC's measured retention was the highest (14%). Thus, a higher RMSE was expected.

Table 3.2 shows that estimated E_a from 28.2% and 33.3% MC was not significantly different. It was deduced from Hermann and Tunger (1966)'s data that MC had no significant effect on activation energy. Therefore, for data of 19.05% MC, the value of E_a was fixed at the average of the two E_a values of 28.2 and 33.3% MC, and Solver iterated on k_r only. Table 3.2 listed the E_a and k_r values for all MCs.

MC % (db)	$k_{80^{\circ}C} (\min^{-1})$	$k_o (\min^{-1})$	E_a (kJ/g-mole)	RMSE	^b R ²
19.1	2.91E-04	1.20E+14	^a 119.31	0.126	0.75
28.2	1.45E-04	3.66E+13	117.59	0.0239	0.97
33.3	9.69E-05	7.67E+13	121.03	0.0360	0.92

Table 3.2. Activation energy, reference rate constant and pre-exponential constant generated from study 2

^a = average of 117.59 and 121.03 kJ/g-mole ^b = R^2 obtained from the plot of measured thiamin retention vs predicted thiamin retention

The bootstrap program estimated 1,000 values of E_a and $k_{80^{\circ}C}$ based on random generation of the 18 retention data for flour with 28.2% and 33.3% MC.

In the case of 19.05% MC, bootstrap predicted 1,000 values of $k_{80^{\circ}C}$ only. A 95% confidence interval was defined as the 25th and 975th sample of the 1000 values, sorted in ascending order. The confidence interval was (2.49x10⁻⁴, 3.79x10⁻⁴) min⁻¹.

Results from the bootstrap program for 28.2% and 33.3% MC are shown in Table

3.3.

	Mean $k_{80^{\circ}C} \pm$ Std deviation	Mean $E_a \pm$ Std deviation	Correlation
MC % (db)	(min ⁻¹)	(kJ/g-mole)	coefficient, $ ho$
28.2	$1.46E-4 \pm 3.22E-6$	117.5 ± 0.27	-0.62
33.3	9.67E-5 ± 6.62E-6	121.1 ± 1.48	-0.94

Table 3.3. Statistic analysis from bootstrap results of 1.000 E_a and k_r values.

For both data, the correlation coefficient fell below the critical value of 0.99, which meant that there was not high correlation between the E_a and k_r values. An example of the bivariate three-dimensional normal probability distribution of the two parameters is shown in Figure 3.17 for flour with 33.3% MC. The volume under the curve is equal to one.



Figure 3.17. 3-D bivariate normal probability distribution [90 & 95% confidence region] for estimated activation energy (kJ/g-mol) and reaction rate constant k_{80} (min⁻¹) for MC=33.3% flour obtained from bootstrap data.

The two contour lines represent the confidence regions, and the highest frequency of the appearance is at the peak. Confidence region was plotted instead of confidence interval because each pair of E_a and k_r value was correlated to one another; thus the region would show the appearance frequency of each pair. A 95% confidence region means that 95% of the bootstrap data lay within this region. The contour lines of the confidence regions are plotted in a two-dimensional plot in Figure 3.18. The 95 and 90% contour joint confidence region for MC = 33.3% flour are shown in Figure 3.18. Figure 3.18 also shows that the parameters in Table 3.2 (k_r = 9.69E-05 min⁻¹, E_a = 121.0 kJ/g-mole) and Table 3.3 (k_r = 9.67E-05, E_a = 121.1 kJ/g-mole) fell within the joint confidence region. Appendix 3.G. shows the confidence region for MC = 28.2% flour.



Figure 3.18. 90% and 95% joint confidence region for estimated E, activation energy (kJ/g-mol) and reaction rate constant k_{80} (min⁻¹) for MC=33.3% flour obtained from bootstrap data.

3.4.4. Comparison of the kinetic parameters obtained by the two methods

Two methods were proposed in this study to obtain the high-temperature kinetic parameters. In the first method (study 1b), since moisture content decreased during heating, reaction rate constant was corrected using the parameters obtained in the constant-moisture study (study 1a). In the second method (study 2), moisture content was maintained constant at high temperature, and a smaller standard error (more accuracy) was obtained.

3.4.4.1. Activation energy

Table 3.4 shows that the activation energy obtained from study 1 b and 2 were comparable. A student t-test on the two values shows that t= 0.310, thus they were not significantly different at 95% confidence level (using t (0.05,22) = 1.717 as the test of significance). Despite the changing moisture content during heating, the activation energy in Study 1b:Uncorrected was similar to that of study 2. Furthermore, the two studies were conducted at different temperatures. Hence, it could be concluded that activation energy of thiamin was independent of moisture content and temperature. The values obtained in this study were also within the range of activation energy in most food products (Table 3.7).

Study #	Heating medium	Activation energy	Regression Statistics	Number of data points	
	temperature (°C)	(kJ/g-mole)	Std error of E_a		
Study 1b: Uncorrected	144.8, 159.6, 170.6	124.9	^a 1.07	6	
Study 1b: Corrected Atmospheric pressure heating	144.8, 159.6, 170.6	129.6	^a 7.27	6	
Study 2 Controlled pressure heating	129.4	121.0	^b 1.48	18	

Table 3.4. Comparison of activation energies for MC= 33.3% flour

^aBased on linear regression analysis

^bStandard deviation based on 1,000 bootstrap data

3.4.4.2. Reaction rate constant

Table 3.5 shows that the corrected reaction rate in study 1b was higher than the reaction rate in study 2. However, a student t-test on the two values shows that t = 1.311, meaning that they were not significantly different at 95% confidence level (using t(0.05,22) = 1.717 as the test of significance).

Study #	Temperature (°C)	k_{80°C} (min ⁻¹)	Regression Statistics Std error of k _r	Number of data points
Study 1b: Uncorrected	144.8 159.6 170.6	1.85*10 ⁻⁵	^a 1.297*10 ⁻⁵	6
Study 1b: Corrected	144.8 159.6 170.6	3.48*10 ⁻⁴	² 1.914*10 ⁻⁴	6
Study 2	129.4	9.69*10 ⁻⁵	^b 6.67*10 ⁻⁶	18

Table 3.5. Comparison of reaction rate constant for MC= 33.33% flour

^aBased on linear regression analysis ^bStandard deviation based on 1,000 bootstrap data

Effect of moisture content on reaction rate

It was concluded from this study, that for MC $\leq 17.23\%$, reaction rate increased with MC and for MC $\geq 17.23\%$, reaction rate decreased with MC. The latter statement was justified by results from study 1a and study 2 (Table 3.6) where a similar trend was observed. A student t-test on the two $b_{(-)}$ values shows that t=1.871, thus the $b_{(-)}$ value obtained from study 1 a and study 2 were not significantly different (using t (0.05,7) = 1.895 as the test of significance). This shows that temperature did not affect $b_{(-)}$ which validate the assertion that thiamin activation energy did not change with temperature.

		Regression Statistics		
Study #	$b_{(-)}$ value	R ²	Std error	Number of data points
Study 1a conducted at 80°C	-0.128	0.85	0.0273	6
Study 2 Conducted at 129.4°C	-0.0769	0.99	0.00088	3

Table 3.6. Moisture content parameter $b_{(-)}$ based on two studies

Thiamin reaction rate reached a maximum at 17.27% MC for several reasons. Firstly, thiamin reacts readily in Maillard reaction, and Maillard reaction proceeds optimally at MC ranging from 11.1% to 25% MC (Hermann and Tunger 1966). Therefore, it was expected that the maximum thiamin loss (i.e maximum reaction rate) would occur at the specified range of MC. Secondly, at the low MC, water molecules bind tightly to ionic groups, such as carboxyl and amino groups. There is no aqueous phase available for dissolution and diffusion for taking part in the Maillard reaction; thus thiamin loss is minimum. Reaction rate passed a maximum and then started to decrease at higher MC. At this time, water is unbound and exists as free water found in capillary pores, and the reactant becomes too 'diluted'.

In this study, two methods were utilized to obtain the rate of thiamin degradation in wheat flour (min⁻¹).

<u>From Atmospheric Pressure methods</u>, a wider range of moisture content was studied: at flour MC < 17.2% (dry basis) or 14.7 %(wet basis),

$$k(T, MC) = 3.48 * 10^{-4} \exp\left[\frac{-129596}{R_g}\left(\frac{1}{T(^{\circ}K)} - \frac{1}{353}\right) + 0.439(MC - 33.3)\right]$$

at flour MC >17.2%,

$$k(T, MC) = 3.48 * 10^{-4} \exp\left[\frac{-129596}{R_g}\left(\frac{1}{T} - \frac{1}{353}\right) - 0.128(MC - 33.3)\right]$$

From Controlled Pressure methods,

At flour MC > 19.1% (dry basis) or 16% (wet basis)

$$k(T, MC) = 9.69 * 10^{-5} \exp\left[\frac{-121030}{R_g}\left(\frac{1}{T} - \frac{1}{353}\right) - 0.0769(MC - 33.3)\right]$$
	-		_		-	_		-	_	_					
References	Feliciotti and Esselen (1957)	Feliciotti and Esselen (1957)	Ryan-Stoneham et al. (1996)	Mulley et al.(1975a)	Steet and Tong (1994)	Lenz and Lund (1977b)	Ramaswamy et al. (1990)	Ramaswamy et al.(1990)	Herrmann and Tunger (1966)	Cha et al. (2003)	Present study using atmospheric heating (Study 1b)	Duccout study wine control lod	rresent study using courroned pressure heating (Study 2)		
${}^{a}R^{2}$	0.99	0.99	0.99	0.99	0.99	0.99	0.96	0.99	N/A	0.99	0.99				
k ₁₂₁ (min ⁻¹)	0.0147	0.0150	0.0114	0.00897	0.0188	0.0227	0.0060	0.0066	0.0587	0.00338	°0.00127	0.0200	0.00943	0.000708	
Activation energy (kJ/g-mol)	118.4	119.7	105.4	115.1	110.9	107.1	118.0	71.1	132	67.3	°129.6	119.0	117.6	121.0	
Heating Temperatures (°C)	109, 119, 129, 139, 149	109, 119, 129, 139, 149	110,120,130	121.1, 126.7, 132.2, 137.8	110, 120, 130	115.6, 126.7, 137.8	110, 120, 130, 140, 150	110, 120, 130, 140, 150	90, 110	140, 151, 161	144.8, 159.6, 170.6	129.4	129.4	129.4	
Moisture content, 1 % (wb/db)			80/400	85/566	70/233				20/25	^b 20/25	^b 25/33.3	16/19.1	22/28.2	25/33.3	E
Product	Carrots (puree)	Green beans (puree)	Peas (puree)	Beef (puree)	Beef (puree)	Pork (puree)	Thiamin in water	Thiamin in mixture	Wheat flour	Wheat flour	Wheat flour	Wheat flour	Wheat flour	Wheat flour	1 1 1 1 2 4

Table 3.7. Activation energy and rate constants for thiamin loss in food products

*R⁴ from plot ln k versus 1/T b changing moisture during heating ^c corrected based on constant-moisture study

3.5. CONCLUSIONS

The atmospheric pressure heating study involved a much simpler setup and mathematical analysis m ethod to o btain k inetic parameters. But at h igher t emperature, flour mixture moisture content is difficult to hold constant. Based on this study, it was concluded that a changing-moisture high-temperature parameter could be corrected based on a lower temperature constant-moisture study. A limitation of this method is that more experiments are needed to generate data. However, this method could be used by researchers without access to controlled-pressure equipment or to an interactive program code of the analytical conduction heat solution.

Another method was proposed where experiments were conducted at controlledpressure heating. Although it involved a more complex calculation and experimental setup, the reaction rate constant obtained was more accurate, as moisture content was kept constant throughout the heating period, and lower standard error was obtained.

Results of this study showed that the activation energy of thiamin was independent of sample moisture content and temperature. On the other hand, thiamin reaction rate was affected significantly by sample moisture content. Thus, a product developer should be aware of the maximum degradation range when formulating a product with moisture content near the range, if thiamin retention is a concern.

The thiamin kinetic parameters obtained from this study could be used to quantify the thermal effects on thiamin degradation separately from other significant effects of a food process (Chapter 4).

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3.6. FUTURE WORK RECOMMENDATIONS

Thiamin kinetic parameters should be investigated in the lower moisture range (<15%) using the controlled-pressure heating.

Using a smaller can size is recommended as it will reduce sample come-up time.

3.7. ACKNOWLEDGMENT

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3.8. NOMENCLATURE

- 1/T 1/temperature in °Kelvin
- A_s surface area, m²
- $b_{(+)}$ moisture content parameter (positive slope)
- $b_{(\cdot)}$ moisture content parameter (negative slope)
- C dry basis thiamin concentration in flour, concentration
- \overline{C} mean average thiamin retention, concentration
- C_o initial dry basis thiamin concentration in flour, concentration
- c_p specific heat capacity, J/(kg °C)
- E_a activation energy, J/(g-mol)
- *h* heat transfer coefficient, $W/(m^2 \circ C)$
- k thermal heat conductivity, W/(m °C)
- k reaction rate constant, \min^{-1}
- k_r reference reaction rate constant, min⁻¹
- k_x maximum reaction rate constant, min⁻¹
- *l** half length of can, 0.03395 m
- *l* normalized half length of can (dimensionless) = 1
- MC moisture content of flour, db
- MC_r reference moisture content, db
- MC_x moisture content at maximum reaction rate, db
- q conducted heat, J/s
- R_g Ideal-Gas Constant, 8.3144 J/(g mol °K)
- R^* radius of can, 0.0258 m
- R normalized radius of can (dimensionless) = 1
- r radial location relative to radius R (dimensionless) $r = \frac{r}{D^*}$
- r* radial location, m
- T temperature, °C
- T_{avg} average sample temperature for study 1a and 1b, °C
- T_{center} measured sample temperature for study 1a and 1b, °C
- T_i initial sample temperature, °C
- T_{ma} mass-average temperature for study 2, °C
- T_{wall} wall temperature for study 1a and 1b, °C
- Toilbath oil bath temperature for study 1a and 1b, °C
- T_r temperature at r location for study 2, °C
- T_{ref} reference temperature, °K
- T_z temperature at z location for study 2, °C
- T_{∞} environment temperature for study 3, °C
- t heating time, min
- Δx wall thickness, m

- x_{water} water content, in wet basis, fraction
- x_{carbo} carbohydrate content, fraction

hydrate

- $V_{\rm can}$ $\frac{1}{2}$ volume of the can (dimensionless)
- z axial location relative to length *l* (dimensionless) $z = \frac{z^*}{l^*}$
- z* axial location, m

Greek symbol

- α thermal diffusivity, m²/s
- β time temperature history, s
- λ_n eigen value, dimensionless

for slab, λ_n satisfies $\lambda_n \tan \lambda_n = \left(\frac{hl}{k}\right)$

for cylinder, λ_m satisfies $\lambda_m J_1(\lambda_m) - \left(\frac{hR}{k}\right) J_o(\lambda_m)$

 J_o bessel function of type zero, dimensionless

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Chapter 4. Modeling thermal and mechanical effect of extrusion processing of wheat flour on thiamin retention in extruded products

4.1. ABSTRACT

Some researchers have reported the total thiamin degradation in extruded wheat and corn flour, but the mechanical effects could not be uncoupled from thermal effects. Using the proposed model, thermal effect and mechanical effect were quantified separately.

Soft wheat flour at 25% moisture content (wb), mixed with 0.3% thiamin (wb) was extruded at screw speed of 100-300 rpm with barrel temperature profile from feed port to die of $50/85/115/130/155^{\circ}$ C at constant degree of fill [0.65 (± 0.08)], $50/80/110/140/165^{\circ}$ C at 0.58 (± 0.04) degree of fill, and at varying fill. Effect of moisture content was also investigated by varying the dough moisture content from 23 to 32% (wb). Thiamin content of all extruded samples was analyzed using a fluorometric analysis method. The thermal effect of extrusion on thiamin was calculated using the kinetic parameters o btained in C hapter 3, a ccounting for the v arying t ime-temperature h istory along the extruder barrel. The mechanical effect was calculated by mathematically removing the thermal retention from the total thiamin retention.

Total thiamin degradation was affected by barrel temperature and moisture content. Higher temperature resulted in lower retention while, higher moisture contents increased thiamin retention. Thiamin loss decreased with screw speed at constant degree of fill. At 155°C die temperature, mechanical effects caused 47.3% to 64.5% of total thiamin loss. At 165°C die temperature, mechanical effects caused 42.2% to 53.3% of total thiamin loss, indicating that as temperatures increase, thermal effects predominate over mechanical effects with respect to thiamin loss. A different trend was observed at when degree of fill was varied as screw speed increased; thiamin loss increased with screw speed. However, at 165°C die temperature, mechanical effects c aused 28.9% to 48.3% of total thiamin loss; thus also indicating that thermal effect predominates over mechanical effects. A final thiamin retention model was developed as a function of thermal and mechanical effects of extrusion.

4.2. INTRODUCTION

The intensity of extrusion cooking has many positive and negative impacts on extruded products. One of the negative impacts is the degradation of vitamins. In a commercial extrusion process, thiamin is among the many vitamins, which is usually fortified in the raw material pre-mix, to meet the minimum standard regulated by United States Food and Drug Administrations. A model to predict thiamin retention in an extrusion process would be helpful so that the process could be optimized to achieve minimum thiamin degradation.

Many studies have observed the trend of thiamin retention in extruded food products. Some of the similar trends were that increasing extrusion temperature reduced thiamin retention, while increasing moisture content increased thiamin retention (Beetner et al. 1974, Maga and Sizer 1978, Cheftel 1986, Guzman-Tello and Cheftel 1987, Ilo and Berghofer 1998). Among these studies, several modeled thiamin retention. Beetner et al. (1974, 1976) modeled thiamin retention in extruded corn grits and triticale, respectively as a function of barrel temperature, screw speeds and moisture content. Guzman-Tello and Cheftel (1987) and Ilo and Berghofer (1998) modeled thiamin reaction rate and activation energy (thiamin kinetic parameters) as a function of temperature, dough moisture content, and screw speed. However, for their model development, they assumed near-isothermal temperatures in the extruder, which was not the case, because barrel temperatures varied from feed port to die. Their near-isothermal assumptions in developing the kinetic parameters caused ~30% underestimation of activation energy and 80% underestimation of reaction rate constant (Dolan 2003). These models were developed as functions of equipment-dependant variables (e.g. barrel temperature, screw

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speed). These types of models are limited in their applicability to predict thiamin retention in different sized extruders. Although two extruders are running at the same screw speed, a larger extruder may have a different residence time compared to the smaller extruder, yielding a different thiamin retention. Extruder size also affects other equipment-independent variables such as overall degree of fill, shear history or specific mechanical energy input (SME). Therefore, a model that is developed as a function of equipment-independent variables would be more valuable for scale-up purposes.

An equipment-independent model was proposed by Cha *et al.* (2003) for thiamin retention in extruded wheat flour. They proposed a model where total thiamin retention (R_7) was a product of the thermal effect (R_β) and mechanical effect (R_S) of extrusion. As mentioned earlier, temperature affected thiamin retention. A shorter heating time should result in higher thiamin retention. However, extrusion at higher screw speed (shorter residence time) decreased thiamin retention (Guzman-Tello and Cheftel 1987, Schmid *et al.* 2002). These facts suggest that mechanical or shear effect also plays a role in thiamin degradation. Cha *et al.* (2003) isolated thermal effects by heating flour mixed with thiamin isothermally in an oil bath to estimate kinetic parameters. Using the kinetic parameters, R_β was calculated, taking account of the changing product temperature profile along the extruder barrel and the product residence time. The mechanical effect (R_S) was calculated by mathematically removing thermal effect from the total thiamin retention. The quantified R_S was then modeled as a function of SME and shear history.

Results of their study showed that R_s decreased with increasing SME and shear history. However, as the shear effect terms increased, product temperature also increased because of their equipment limitations on cooling the extruder. Since extrusion was only conducted at one barrel temperature profile, they were not able to determine whether there was interaction between mechanical effects and temperature. In addition, their extrusion study was only conducted at one constant degree of fill and at one dough moisture content, thus the applicability of the developed model for different degrees of fill and moisture contents was unknown.

Therefore, the objectives of this present study were 1) to investigate the effect of temperature, degree of fill and moisture content on thiamin retention and 2) to develop a model to predict thiamin retention as a function of thermal effects and mechanical effects of extrusion. The average shear rate model from Chapter 2 was used to calculate shear history to describe mechanical effects and the thermal kinetic parameters from Chapter 3 was used to calculate thermal effects of extrusion on thiamin retention.

4.3. MATERIALS AND METHODS

4.3.1. EXTRUSION

4.3.1.1. Equipment specification

The extruder used for this study was a co-rotating and intermeshing twin-screw extruder (APV, Grand Rapids, MI MP19TC-25). The length: diameter ratio of the extruder was 25:1, the barrel diameter was 19 mm, and the die diameter was 3 mm. Screw configuration was set up for high shear effect (Table 4.1). A control panel was connected to the extruder to monitor the percent torque required to turn the screws, the screw speed (rpm), die pressure (psi), product temperature (°C), and barrel temperature (°C). Product temperature was measured using five thermocouples, flush-mounted on the bottom of the barrel and die plate, adjacent to the electrical heating rods and watercooling jackets. The distances of thermocouples from the feed port were 12.55, 27.16, 34.14, 41.92, and 47.48 cm. Pressure at the die was measured using a pressure transducer (Dynisco, Model #EPR3-3M-6, Hickory, NC), located at 7 mm before the die entrance. Desired barrel temperature was achieved and maintained using electrical heating rods to add heat, and a water-cooling jacket to remove heat when necessary. The rate of flour entering the feed port was controlled using a K-Tron K2M twin-screw volumetric feeder (K-Tron Corp., Pitman, NJ). Water added to attain desired moisture content of dough was pumped into the extruder by an E2 Metripump positive displacement metering pump (Bran & Luebbe, Northhampton, UK). The water injection port was located at 5.5 cm from the feed opening.

	Length (cm)	Screw Type		
Feed port	15.2	8D* Twin Lead Screw (TL)		
	3.32	7x30° Forward Kneading Paddles (FKP)		
	7.60	4DTwin Lead Screws		
	1.90	4x60° Forward Kneading Paddles		
	1.90	4x30° Reverse Kneading Paddles		
	3.80	2D Twin Lead Screws		
	2.85	6x60° Forward Kneading Paddles		
	1.90	4x30° Reverse Kneading Paddles		
↓	1.90	1D Single Lead Screw (SL)		
	3.32	7x90° Kneading Paddles		
Die	3.80	2D Single Lead Screws		

Table 4.1 Screw configuration for high shear extrusion

*D = 19 mm

4.3.1.2. Pre- extrusion preparation

Soft wheat flour, with moisture content of approximately 15% wet basis (wb) /17.6% dry basis (db) was obtained from the Star of the West Milling Co. (Frankenmuth, MI). Moisture content was determined by heating 1 g flour at 130°C for 10 minutes using a Sartorius MA-30 moisture analyzer (Goettingen, Germany). Food-grade thiamin hydrochloride (Spectrum Laboratory Products, Gardena, CA) was mixed with flour at a concentration of 0.35% (db) using a V-shaped twin shell dry blender (Patterson-Kelley, East Stroudsburg, PA). To ensure homogeneous distribution of thiamin with a coefficient of variance <10%, the flour and thiamin were mixed for 40 minutes. Thiamin content was analyzed using the fluorometric method (Official Method 953.17, AOAC 1995). Method of thiamin analysis is described in Appendix 1.A. An initial concentration of thiamin in flour was analyzed at 9 different locations in the mixed flour to yield $C_0 = 0.36 \pm 0.0189$ % concentration (dry basis).

The flour feeder and water pump feeder were calibrated prior to extrusion runs to determine the a mount of water n eeded to a chieve d esired m oisture c ontent. F lour was

dyed blue at 40% concentration (w/w), using water-based blue (#1070-0500, draftstore.com, Cordova, TN, USA) for mean residence time measurement.

4.3.1.3. Extrusion processing

Approximately 60 g of extrudate samples for thiamin analysis were collected after the process reached constant readings of die pressure, die temperature, and torque (steady-state condition). At the time of extrudate collection for thiamin analysis, die pressure (psi), barrel and product temperature (°C) and percent torque (load torque) were measured. Base (non-load) torque was measured before each extrusion run. In addition to temperature at five zones, product temperature at the die was measured by inserting a handheld T-Type needle thermocouple (Cole-Parmer, Vernon-Hills, IL) into the die hole during the extrusion run. Following data collection, 0.5 g of blue-dyed flour was dropped into the feed port for mean residence time measurement. Time taken for dye to appear in the extrudate was recorded, followed by extrudate collection at the die outlet, at 5- second intervals until dye disappeared from extrudate. Table 4.2 shows the extrusion conditions tested. All samples were dried overnight at 22°C, 40% RH until they reached constant moisture content of 13.63% (db). Samples were first ground in a Krups coffee grinder (Peoria, IL, USA) and then in a Udy Cyclone Mill (Udy Corp., Fort Collins, CO) with a 0.5 mm screen. Powdered extrudates were stored at 4°C until analysis for thiamin and moisture content.

After an extrusion run at 200 rpm, dough mass was measured by first deadstopping the extruder, then taking the dough in the die plate, wrapping it tightly using a plastic wrap, and weighing it. The volume of the dough was measured by water displacement. The density of the dough was measured as the mass divided by the volume,

based on two readings.

Extrusion condition	Barrel Temperature (Zone 1/2/3/4/Die) (°C)	Screw Speed (rpm)	Flour Feed rate (g/min)	Dough Moisture content wb/db (%)
la	50/85/115/130/155	100	28.0	25.0 / 33.3
1b	50/85/115/130/155	150	32.0	25.0 / 33.3
1c	50/85/115/130/155	200	33.5	25.0 / 33.3
1d	50/85/115/130/155	250	36.0	25.0 / 33.3
le	50/85/115/130/155	300	39.0	25.0 / 33.3
2a	50/80/110/140/165	100	28.0	25.0 / 33.3
2b	50/80/110/140/165	150	32.0	25.0 / 33.3
2c	50/80/110/140/165	200	33.5	25.0 / 33.3
2d	50/80/110/140/165	250	36.0	25.0 / 33.3
2e	50/80/110/140/165	300	39.0	25.0 / 33.3
2f	50/80/110/140/165	200	33.5	23.0 / 29.8
2g	50/80/110/140/165	200	33.5	28.0 / 38.8
2h	50/80/110/140/165	200	33.5	32.0 / 47.1
3a	50/80/110/140/165	100	35.9	25.0 / 33.3
3b	50/80/110/140/165	150	35.9	25.0 / 33.3
3c	50/80/110/140/165	200	35.9	25.0 / 33.3
3d	50/80/110/140/165	250	35.9	25.0 / 33.3
3e	50/80/110/140/165	300	35.9	25.0 / 33.3

Table 4.2. Extrusion conditions (all experiments were duplicated on different days)

In extrusion conditions 1 and 2, approximate constant fill was maintained by increasing the feed rate as screw speed was increased. Effect of temperature on thiamin retention was studied by using two different temperature profiles (conditions 1 and 2). Dough moisture content was varied in conditions 2f, 2g and 2h at a constant screw speed and temperature. Degree of fill was varied at condition 3 by maintaining constant feed rate as screw speed was increased. Data from condition 3 was used to determine whether the model developed from a constant degree of fill (conditions 1 and 2) extrusion

condition could accurately predict data in a varying degree of fill extrusion condition (condition 3).

4.3.2. ANALYSIS

4.3.2.1. Residence Time

Residence time (RT) is the time spent by each flour particle in the extruder. Due to the axial mixing in the extruder, each flour particle exits at different times. Residence time can be measured using the dye-tracer technique (Peng *et al.* 1994). A 0.5 g of bluedyed flour was fed into the feed port. Time taken for the dye to appear in the extrudate was recorded, followed by colored-extrudate collection at the die outlet, at 5- second intervals until dye disappeared from extrudate. These colored-extrudates were air-dried at room temperature (37°C) for at least 2 days and then ground using Krups coffee grinder for 5 seconds. A 1.5 g o f ground colored-extrudate was analyzed for intensity of blue color (*b**) using a HunterLab D25 colorimeter (Hunter Associates Laboratories, Inc., Reston, VA, USA). An extrudate strand with no dye added was used as a color control. Real color value was reported as blue color minus control sample color. Before usage, the colorimeter was calibrated using a black tile and white tile (Standard No. C2-30954).

$$\overline{t} = \sum_{i} t_{i} E(t_{i}) \Delta t_{i}$$
(4.1)

where t is the exit time and E(t) is the normalized color units

$$E(t) = \frac{b^{*_i}}{\sum_i b^{*_i} \Delta t_i}$$
(4.2)

E(t) was plotted against exit time (t) to obtain the residence time distribution curve.

4.3.2.2. Color-concentration calibration curve

Due to the effect of saturation, color value does not increase linearly with concentration at higher concentration. Therefore, a calibration curve of dye concentrations versus b^* value was made to ensure that b^* value from the colored-extrudates were within the linear range. Five batches of blue-dyed flour with different concentrations (0.4, 1, 2, 6% (w/w)) were prepared and then extruded at 200 rpm, 33.3% MC (db), 32.7 g/min flour feed at 160°C. The concentrated extrudate samples were collected after steady-state condition was reached. They were analyzed using the same method mentioned in section 'Residence Time'. Color values from these concentrated extrudate samples (b') were then plotted against the dyed-flour concentrations. If b^* from the colored-extrudates was within the linear range of the plot, conversion of b^* values to dyed-flour concentrations was unnecessary and b^* color units was used for the calculation in Eq.(4.2).

4.3.2.3. Degree of fill

The degree of fill during extrusion run varied in each barrel section due to the varying screw configuration. As flour particles moved towards the die, the screws were configured such that the degree of fill would increase to a maximum of 1.0. The degree of fill at section i (f_i) could be estimated by visual observation during dead-stopping of extruder where screw speed and flour feed rate were stopped instantly at the end of an extrusion run and the extruder was opened rapidly.

If an approximate f_i v alue w as k nown, the time spent b y e ach flour p article in section *i* c ould b e c alculated. B y approximation, the r esidence time of the p article in section *i* at exit time *t* was

$$\Delta t_i \approx \frac{f_i * V_i}{Q} \left(\frac{t}{\overline{t}}\right) \tag{4.3}$$

The void volume of the extruder in each section i was calculated using the equation below (V_i) ,

 $V_i = \text{Barrel volume in section}_i - \text{screw volume in section}_i$ = (Length of barrel in section_i * barrel surface area) - screw volume in section_i (4.4)

The length of barrel and screw volume in each section and barrel surface area are specified in Chapter 2.

The overall extruder degree of fill could be calculated without the labor-intensive method of dead-stopping the extruder at each run. Using the mean residence time (\overline{t}) and extruder void volume (V),

Degree of fill =
$$\frac{\dot{m}\bar{t}}{V\rho}$$
 (4.5)

4.3.2.4. Thiamin

Method of thiamin analysis is described in Appendix 1.A. For each experimental condition, thiamin analysis of the extrudate was performed in duplicate.

4.3.3. MODELING

The model developed by Cha *et al.* (2003) was based on the assumption that an extruder is a continuous chemical reactor (Levenspiel 1999), by which the nutrient particle travels at different speed to the exit stream due to the axial mixing in the extruder, following the residence times distribution of E(t). The mean concentration of a nutrient at the exit stream can be calculated as the sum of the nutrient concentration exiting from time = 0 to $t = \infty$ multiplied by E(t),

$$\left(\frac{\bar{C}}{C_o}\right)_{exit} = \int_0^\infty \left(\frac{C}{C_o}\right)_{nutrient} E(t)dt$$
(4.6)

In an extruder, two main variables affected nutrient degradation, thermal and mechanical effects. The thermal component is included in Eq. (4.6), as $\left(\frac{C}{C_o}\right)_{nutrient}$ can be modeled

as a function of temperature. Since mechanical effects are also responsible for nutrient degradation, C ha *et a l.* (2003) incorporated mechanical effects into Levenspiel's basic model as an empirical function (f(S)). Thus, the model for thiamin retention in an extrusion process is

$$\left(\frac{\bar{C}}{C_o}\right)_{exit} = \left\{\int_0^\infty \left(\frac{C}{C_o}\right)_{thiamin} E(t)dt\right\} f(S)$$

$$R_T = R_\beta \times R_S$$
(4.7)

Where R_T = total thiamin retention in the extruded flour, R_{β} = thiamin retention due to thermal effect of extrusion, R_S = thiamin retention due to mechanical effect of extrusion.

4.3.3.1. Thermal effect of extrusion on thiamin retention = R_{β}

To calculate the thermal effect of extrusion on thiamin retention, first we defined that thiamin retention followed a first-order kinetic reaction,

$$\left(\frac{C}{C_o}\right)_{thiamin} = \exp(-kt) \tag{4.8}$$

where the reaction rate constant (k) can be modeled as a function of temperature and moisture content (Guzman-Tello and Cheftel 1987, Ilo and Berghofer 1990).

$$k = k_r \exp\left[\frac{-E_a}{R}\left(\frac{1}{T} - \frac{1}{T_r}\right) + b(MC - MC_r)\right]$$
(4.9)

The thermal kinetic parameters k_r and E_a and the moisture content parameter, b were estimated by isolating the thermal effect on thiamin by heating thiamin in flour in a shearless environment (Chapter 3, study 2). The extruder barrel was set at progressively higher temperature from feed inlet to die; thus the product temperature became a timedependent variable (T = T(t)). Temperature as a function of time T(t) is determined using the measured temperature at five locations of extruder barrel. Moisture content of dough is usually maintained constant throughout extrusion process and it is therefore not timedependent.

Since the residence **time** that the thiamin particle spent in each barrel section was known (Eq.(4.3)), and the **temperature** at each barrel section was also known (T(t)=T(x)), then we could calculate the time-temperature history (β) of each thiamin particle traveling along the barrel with an exit time *t*.

$$\beta(t) = \int_{0}^{t} \exp\left[\frac{-E_{a}}{R}\left(\frac{1}{T(t)} - \frac{1}{T_{r}}\right)\right] dt \approx \sum_{i} \exp\left[\frac{-E_{a}}{R}\left(\frac{1}{T(x_{i})} - \frac{1}{T_{r}}\right)\right] \left[f_{i}\frac{V_{i}}{Q}\left(\frac{t_{i}}{\overline{t}}\right)\right] (4.10)$$

Thus, Eq. (4.8) became

$$\left(\frac{C}{C_o}\right)_{thia\,\min} = \exp\left\{-k_r \exp[b(MC - MC_r)]\right\}\beta$$
(4.11)

Eq. (4.11) represented the thiamin retention for only one exit time. By adding up each thiamin particle with various exit times (from the initial until the end of the residence time distribution curve), the final equation for R_{β} was

$$R_{\beta} = \int_{0}^{\infty} \left\{ \exp\left(-k_{r} \left(\exp\left[b(MC - MC_{r})\right]\right) \int_{0}^{t} \beta(t) dt\right) \right\} E(t) dt$$
(4.12)

4.3.3.2. Mechanical effect of extrusion on thiamin retention $=R_S$

The mechanical or shearing effects (S) of an extruder can be represented using specific mechanical energy, shear rate or shear history (Komolprasert and Ofoli 1990).

Specific mechanical energy (SME) is defined as the net mechanical energy input per unit mass (Levine, 1989).

$$SME (J/kg) = \frac{E_v}{\dot{m}} = \frac{P_w - \Delta PQ}{\dot{m}}$$
(4.13)

where $P_w = 2.64 * (\%Load - \%Base Torque) * N$ (given by extruder manufacturer).

On the other hand, shear history may be a more accurate indicator of a process history than SME, because shear history accounts for the duration of shearing (Cha *et al.* 2003). Shear history (Φ) can be approximated as the product of the average shear rate of the extruder and the mean residence time of product in the extruder.

$$\Phi = \dot{\gamma}_a \, \overline{t} \tag{4.14}$$

The average-shear-rate model $(\dot{\gamma}_a)$ for the extruder used in this study was developed in Chapter 2 and it was a function of extruder constant (k'), degree of fill, screw speed (N) and constant alpha (α).

$$\dot{\gamma}_a = \mathbf{k}' N^{\alpha} \tag{4.15}$$

where k' = 30.39* Degree of fill^{1.508} and α = -1.308 * Degree of fill + 2.144

In summary, R_T = total measured thiamin retention in extrudate,

$$R_{\beta} = \exp\left(-k_{r} \exp\left[b(MC - MC_{r})\right]\right) \int_{0}^{\infty} \exp\left\{\left(\int_{0}^{t} \exp\left[\frac{-E_{a}}{R}\left(\frac{1}{T(t)} - \frac{1}{T_{r}}\right)\right]\right) dt\right\} E(t) dt,$$
$$R_{S} = R_{T} / R_{\beta} = f(SME) \text{ or } f(\Phi)$$
(4.16)

4.3.3.3. Model validation

Once the model for R_{β} and R_S was developed, the accuracy of the models was determined. Data from a varying degree of fill extrusion conditions (condition 3 and Schmid 2002) was utilized. Schmid (2002) conducted their extrusion studies at barrel temperature profile of 40/60/90/130/150°C at 200, 250 and 300 rpm at 22% wb / 28.2% db dough moisture content. R_S values were calculated using their shear terms (screw speed, shear history and specific mechanical energy) profile and R_{β} values were also calculated using their mean residence time and product temperature data. The product of R_S and R_{β} was termed as predicted R_T . Predicted R_T was plotted versus experimental (or measured) R_T . The root mean square error (RMSE) of the prediction was calculated as

$$RMSE = \frac{Pr \text{ edicted value} - Measured value}{number of data point s}$$
(4.17)

4.3.4. THIAMIN LOSS

The significance of mechanical effect and thermal effect on thiamin retention could be calculated by first transforming the retention equation to loss equation. Total thiamin loss was

$$X_T = 1 - R_T = 1 - R_\beta R_S \tag{4.18}$$

If there were no mechanical effect during extrusion, R_S would be = 1, thus the total loss would be solely due to thermal effects $(X_T) = X_\beta = 1 - R_\beta$.

The thiamin loss due to mechanical effects was defined as the difference,

$$X_S = X_T - X_\beta \tag{4.19}$$

Then, the significance of mechanical effect was calculated as the percentage of the effect on total loss.

4.4. RESULTS AND DISCUSSIONS

4.4.1. Mean residence time

Minimum b^* color units of the dyed extrudates read from Hunter colorimeter was -5.0 color units, which is within the linear range of the concentration calibration curves (Appendix 4.A). Thus, color b^* values were used in the calculation of E(t). An example plot of residence time distribution curve is shown in Figure 4.1. The mean residence times for extrusion conditions 1 and 2 extruded at barrel temperature 50/85/115/130/155°C and 50/80/110/140/165°C are summarized in Table 4.3.



Figure 4.1. Residence time distribution curves of flour extruded at 50/80/110/140/165°C barrel temperature at 100, 200 and 300 rpm. MRT = mean residence time.

As seen from Figure 4.1, the residence time of flour particles decreased as screw speed was increased. In contrast, residence time was only slightly decreased as barrel temperature was increased, which was the reverse trend found by Altomare and Ghossi (1986)'s (Table 4.3). However, both in the present study and theirs, the effect was nominal. Increasing dough moisture content slightly decreased the residence time (Table

4.4)

Extrusion condition	Screw speed (rpm)	Product temperature at die (°C)	Mean residence time (s)	Dough feed rate (g/min)	Degree of fill
1a	100	154.1 (± 0.46)	175.6 (± 7.49)	34.5	0.71 (± 0.04)
1b	150	156.7 (± 1.15)	152.2 (± 15.7)	39.0	0.70 (± 0.09)
1c	200	157.0 (± 1.15)	144.1 (± 0.82)	40.6	0.69 (± 0.00)
1d	250	156.3 (± 1.50)	119.3 (± 0.12)	43.3	0.61 (± 0.00)
1e	300	154.5 (± 1.73)	96.2 (± 4.39)	47.0	0.53 (± 0.03)
2a	100	162.3 (± 0.29)	160.5 (± 10.2)	34.5	0.65 (± 0.05)
2b	150	163.1 (± 0.52)	135.1 (± 0.14)	39.0	0.62 (± 0.00)
2c	200	164.2 (± 1.85)	124.3 (± 1.52)	40.6	0.59 (± 0.01)
2d	250	163.4 (± 1.33)	113.9 (± 5.80)	43.3	0.58 (± 0.04)
2e	300	163.4 (± 0.75)	95.1 (± 0.36)	47.0	0.52 (± 0.00)
3a	100	161.8 (± 0.69)	158.9 (± 11.0)	42.9	0.80 (± 0.07)
3b	150	161.5 (± 0.58)	135.4 (± 10.9)	42.9	0.68 (± 0.07)
3c	200	159.9 (± 0.52)	120.5 (± 2.28)	42.9	0.61 (± 0.01)
3d	250	161.5 (± 1.10)	109.7 (± 6.98)	42.9	0.55 (± 0.04)
3e	300	163.4 (± 0.75)	101.6 (± 2.18)	42.9	0.48 (± 0.06)

Table 4.3. Data for extrusion at barrel temperature 50/85/115/130/155°C and 50/80/110/140/165°C for 33.3% MC (db) dough (based on two extrusion days)

Table 4.4. Data for extrusion at barrel temperature 50/80/110/140/165°C at 200 rpm for various moisture contents (based on two extrusion days)

Extrusion condition	Moisture content % (wb)/(db)	Product temperature at die (°C)	Mean residence time (s)	Dough feed rate (g/min)	Degree of fill
2f	23 / 29.8	165.9 (± 0.14)	121.5 (± 0.77)	39.7	0.58 (± 0.00)
2c	25 / 33.3	164.2 (± 1.85)	124.3 (± 1.52)	40.6	0.59 (± 0.01)
2g	28 / 38.8	161.7 (± 0.42)	117.2 (± 2.53)	42.2	0.56 (± 0.01)
2h	32 / 47.1	162.6 (± 0.64)	112.7 (± 0.29)	44.5	0.54 (± 0.00)

4.4.2. Degree of fill

Figure 4.2 shows that the flour changed to a viscoelastic melt at the cooking zone. The degree of fill was increased to 1.0 at this point, due to compressing nature of the single-lead screws and the kneading paddles. Most single-lead and paddles had the highest degree of fill (Table 4.5). Due to the difficulty in weighing shafts after deadstopping, degree of fill at each location was approximately visually.



Figure 4.2. Pictorial view of an opened extruder barrel, showing the extruder degree of fill at specific barrel sections opened after dead- stopping at 200 rpm.

Section	Screw configuration	Approximate degree of fill			
1	8D TL	0.4			
2	7x30° FKP	0.8			
3	4D TL	0.1			
4	4x60° FKP	1.0			
4	4x30° RKP	1.0			
5	2D TL	0.2			
	6x60° FKP	1.0			
	4x30° RKP	1.0			
6	1D SL	1.0			
	7x90° KP	1.0			
	2D SL	1.0			
	Die plate	1.0			

Table 4.5. Visual observation of sectional degree of fill after dead-stop at 200 rpm

TL = Twin-lead screws, FKP = Forward kneading paddles, RKP = Reverse kneading paddles, SL = single-lead screws. D = 19 mm.

The overall degree of fill of all extrusion run was calculated using Eq.(4.5), with known values of the dough flow rate, mean residence time, void volume and dough density. The overall degree of fill is shown in Table 4.3 for extrusion condition 1 and 2. At these conditions, constant overall degree of fill was expected, as feed rate was increased simultaneously as screw speed was increased. Exactly constant degree of fill was only achieved at the lower screw speed (100, 150 and 200 rpm) for condition 1. However, for condition 2, a smaller variation of degree of fill was attained. For condition 3, flour feed rate was maintained constant as screw speed was increased from 100 to 300 rpm

4.4.3. Effect of screw speed on thiamin retention (Measured, Thermal and Mechanical retention)

At each extrusion conditions 1 and 2, we attempted to maintain constant degree of fill and die temperature. The cooling system was able to remove excess heat at the higher screw speed, so the standard deviation of the die temperatures was low (Table 4.3). For conditions 1 and 2, the average die temperatures were 155.7 (\pm 1.66)°C and 163.2 (\pm 1.85)°C, respectively. Over the screw speed range, average degree of fill was maintained at 0.65 (\pm 0.08) for condition 1 and at 0.58 (\pm 0.04) for condition 2. The standard deviations were nominal such that die temperature and degree of fill would be referred as constant die temperature and degree of fill in the further discussions.

4.4.3.1. Condition 1, barrel temperature = 50/85/115/130/155°C, constant degree of fill

For condition 1, the observed overall trend was <u>measured</u> thiamin retention (R_T) increased with screw speed (Figure 4.3). Nevertheless, screw speed of 100-250 rpm seemed to have little influence on thiamin retention. The measured thiamin retention increasing from 0.81-0.88.

Since temperature was maintained constant, the only factor contributing to <u>thermal</u> effect on retention (R_{β}) was the residence time. The residence time that thiamin particles were exposed to thermal heat was shorter at higher screw speed. Thus, an increasing thermal retention trend was observed as screw speed was varied from 100-300 rpm (Figure 4.3).

On the other hand, no apparent trend was observed for <u>mechanical</u> retention (R_S) at those screw speed range as retention values stayed approximately at 0.90.



Figure 4.3. Thermal and mechanical effects on thiamin retention versus screw speed for samples extruded at barrel temperature 50/85/115/130/155°C (condition 1). Data shown are the averages from two replications, on different days.

4.4.3.2.Condition 2a-e, barrel temperature = 50/80/110/140/165°C, constant degree of fill

For condition 2a-3, the same trend was also observed where R_T increased with screw speed. Figure 4.4 shows that, at screw speed of 150-250 rpm, R_T was also not affected. R_T was lower than that of condition 1, because temperature profile was higher at condition 2. R_T values ranged from 0.67-0.77. R_β also increased with higher screw speed, due to the shorter residence time. No evident trend was observed for R_S at that screw speed range.



Figure 4.4. Thermal and mechanical effects on thiamin retention versus screw speed for samples extruded at 50/80/110/140/165°C (condition 2a-e). Data shown are the averages from two replications, on different days.

4.4.3.3. Condition 3, barrel temperature = 50/80/110/140/165°C, varying degree of fill

Degree of fill dropped from 0.80 to 0.48 as screw speed increased from 100 to 300 rpm. The trend observed in Figure 4.5 where thiamin retention decreased with screw speed was also observed in many published literature (Beetner *et al.* 1974, Guzman-Tello and Cheftel (1987), Schmid (2002)).



Figure 4.5. Thermal and mechanical effects on thiamin retention versus screw speed for samples extruded at 50/80/110/140/165°C (condition 3). Data shown are the averages from two replications, on different days.

Data from conditions 2 and 3 were combined to compare the measured thiamin retention. Figure 4.6 shows that at screw speed of 150 and 200 rpm, measured thiamin retention at condition 2 overlapped with that at condition 3. However, at screw speed of 250 and 300 rpm, condition 2 had a higher degree of fill than condition 3, thus higher thiamin retention was observed. At screw speed of 100 rpm, condition 3 had a higher degree of fill, thus higher thiamin retention was observed at this condition. A possible reason why higher degree of fill caused higher retention were that higher degree of fill

allowed less mixing in the extruder, therefore less thermal effect (shorter residence time) for the thiamin particle.

Therefore, the trend of lower thiamin retention at higher screw speed which are observed in condition 3 and in other published literature was due to the decreasing degree of fill. Since many researchers extruded products at a varying degree of fill condition, data from this condition type [condition 3 and Schmid (2003)] were used to determine the accuracy of the model which were developed from data at constant degree of fill.



Figure 4.6. Plot of measured thiamin retention for condition 2 at constant degree of fill and condition 2 at varying degree of fill. Data shown are the averages from two replications, on different days.

4.4.4. Effect of moisture content on thiamin retention

To study the effect of moisture content on thiamin retention, moisture content was varied at 4 levels, at screw speed of 200 rpm and at condition 2's barrel temperature profile (condition 2c, 2f-h).

 R_T increased markedly with moisture content. This finding was in agreement with Guzman-Tello and Cheftel (1987). The reaction rate constant was lower at higher moisture content (Chapter 3) and mean residence time slightly decreased at higher moisture content, yielding a higher R_β with increasing moisture content. Figure 4.7 shows that R_S was not a strong function of moisture content.



Figure 4.7. Thermal and mechanical effects on thiamin retention versus moisture content for samples extruded at 200 rpm and 50/80/110/140/165°C barrel temperature. Data shown are the averages from two replications, on different days.

4.4.5. Modeling thiamin mechanical retention, R_S at constant fill condition

Figure 4.3, 4.4 and 4.7 represented R_s as a function of screw speed at constant fill condition. The calculated R_s was also fitted as a function of shear history and specific mechanical energy. Shear history and SME values for each extrusion condition can be found in Appendix 4. Since no apparent trend was also observed for the other shear terms at the two conditions, a linear regression analysis was performed to determine statistically whether R_s was influenced as the shear term increased, for each condition (Table 4.6).

Table 4.6 shows that R_S did not change significantly (zero slope) at the specified range of screw speed, shear history and SME. Since none of the shear terms significantly affected R_S , the R_S data of the two temperature profile were paired for t-test in Excel® to determine whether there was significant difference between the R_S of condition 1 and condition 2a-e at 95% confidence level. The two-tailed student t-test analysis of the mean R_S indicated that R_S at condition 2a-e was significantly higher (P < 0.001) than R_S at condition 1. It could be concluded from this t-test that, there was interaction between R_S and temperature. Due to equipment limitations, the extruder barrel temperature could not be set higher than 165°C; therefore, we were unable to conduct more temperature studies. Extrusion at lower temperatures could be done, but thiamin retention and calculated R_S would be too close to 1.0, which could result in inaccurate modeling.

Table 4.6.	The sign	nificance	of the	shear	term	on the	thiamin	mechanical	retention.	R_{s}	
										/	

Shear term	Shear range	Condition 1	Condition 2a-e
Screw speed (Rpm)	100-400	p = 0.795	p = 0.129
Shear history (dimensionless)	4000-12000	p = 0.381	p = 0.119
SME (kJ/kg)	100-600	p = 0.208	p = 0.116

p<0.05 means that the slope of the regression line was not equal to 0 at 95% confidence level

Despite the difference between the R_s of the two temperatures profile, they behaved in a similar trend (dropping from retention of 1.0 to a certain minimum) (Figure 4.3 and 4.4). Therefore, we n eglected the interaction between R_s and temperature and combined the two temperatures data for model development.

 R_S data points in Figure 4.7 did not show an apparent trend with moisture content. The effect of moisture content on R_S was then determined using linear regression analysis. The calculated p values was 0.40, indicating that moisture content did not influence R_S . This result showed that there was no interaction between R_S and moisture content.

4.4.5.1. Combining data for model development

Another extrusion study which was conducted at a constant degree of fill and the present study's temperature range was Cha *et al.* (2003). Their extrusion run was conducted at die temperature varying from 155°C to 167°C, dough moisture at 20% (wb) /25% (db) and at approximately 0.44 degree of fill. Since we neglected the temperature effect on R_S and there was no interaction between R_S and moisture content, data from Cha *et al.* (2003)'s extrusion run was combined with the present study. Thus, for full model development of R_S , all data from constant degree-of-fill extrusion were included, which consisted of conditions 1, 2 and Cha *et al.* (2003). The combined R_S was fitted as a function of screw speed, shear history and specific mechanical energy (SME). Among the three shear terms, R_S versus specific mechanical energy (SME) had the better fit with $R^2 = 0.64$ (Figure 4.10). The R^2 values indicated that there was considerable variability with the widely different extrusion conditions.
<u>4.4.5.2. Model development, $R_{\rm S} = f(\text{screw speed})$ </u>

Figure 4.8 shows that R_S data of Cha et al. (2003) decreased significantly as screw speed was increased from 100 to 150 rpm and then stayed relatively constant at 0.85 from screw speed 150 to 300 rpm. The justification for this was, during their extrusion run, cooling water was insufficient to remove the increasing heat as screw speed was increased. As a result, product temperature increased significantly (DT increased from 155.5 at 100 rpm and to an average of 163.2°C as screw speed was increased from 150-300 rpm). Since the present study determined that there was an interaction between R_S and temperature, a significant decrease in R_S from 100 to 150 rpm was expected.

Model: $R_s = 0.864 + 0.136[\exp(-0.0166 * SS)]$.



Figure 4.8. Plot of thiamin mechanical retention versus screw speed for all data. DT = Die Temperature in °C, and MC = dough moisture content in db. DT in Cha*et al.*(2003) ranged from 155.5-167°C and <math>MC = 25% (db).

<u>4.4.5.3. Model development, $R_{\rm S} = f(\text{shear history})$ </u>

Although the R^2 of R_s versus shear history (Figure 4.9) plot was similar to that of R_s versus screw speed (Figure 4.8) at 0.60, inclusion of mean residence time, degree of fill and screw speed in shear history represented the extrusion shearing history better. Comparing data based on screw speed alone was not sufficient because degrees of fill and mean residence time of the two data could be different. An apparent example was, when data from Cha *et al.* (2003) at 100 rpm (Figure 4.8) was translated to shear history, the data separated from the present study's as their degree of fill and mean residence time was lower. Then, it was apparent that at shear history < 4,000 (Figure 4.9), R_s dropped from 1.0 to 0.9 and decreased slowly to a minimum within shear history range of 4,000-13,000 to an approximate R_s value of 0.87.

Model: $R_s = 0.869 + 0.131[\exp(-0.000571*\Phi)]$.



Figure 4.9. Plot of thiamin mechanical retention versus shear history for all data. DT = Die Temperature in °C, and MC = dough moisture content in db. DT in Cha*et al.*(2003) ranged from 155.5-167°C and <math>MC = 25% (db).

<u>4.4.5.4. Model development, $R_{\rm S} = f(\rm SME)$ </u>

SME represents the net mechanical energy input per unit mass, which was calculated using parameters such as extruder torque and pressure reading. The model of R_S as a function of SME has the best fit among the three shear terms ($R^2 = 0.64$). It is shown in Figure 4.10 that for Cha *et al.* (2003) data, there was an overall decrease of R_S . The reason was explained earlier where there was temperature difference for Cha *et al.* (2003) data as SME was increased. The figure also shows that R_S was higher for DT = 155°C. SME should account for the temperature effects (barrel temperature affects dough viscosity, thus affecting torque reading), but since there was interaction between shear effect and temperature, the same trend was observed in Figure 4.10.





Figure 4.10. Plot of thiamin mechanical retention versus specific mechanical energy for all data. DT = Die Temperature in °C, and MC = dough moisture content in db. DT in Cha *et al.* (2003) ranged from 155.5-167°C and MC = 25% (db).

4.4.5.5. Model validation

To determine the accuracy of the three R_S models, data from a varying degree of fill extrusion conditions (condition 3 and Schmid (2002)) were utilized. R_S values were calculated using their shear term profiles and R_β values were also calculated using their mean residence times and product temperature data. The product of R_S and R_β equaled predicted R_T . Then, R_T was plotted against measured (experimental) R_T (Figure 4.9). The line was a 45 degree line intersected at (0,0).



Figure 4.11. Plot of predicted measured retention versus experimental retention for data from condition 3 and Schmid *et al.* (2002) using $R_s = 0.869 + 0.131[\exp(-0.000571*\Phi)]$ model.

Figure 4.11 shows the predicted R_T versus the experimental R_T , using the shear history model to predict R_S . There was a good agreement between the predicted and the experimental R_T , especially for condition 3. Some of the data from Schmid (2002) were under-predicted and some were over-predicted. The under-predicted data was due to the following reasoning: Their mean residence time values were much shorter, which increased their calculated R_{β} values and thus most of their calculated R_S was higher than the present study's. Therefore, when using our R_S model to predict R_T , the predicted values became lower than the observed R_T . Predicting R_T using the SME and screw speed models yielded a RMSE of 0.00394 and 0.00396, respectively. Low RMSE means that the model can still be used to predict mechanical effect of extrusion on thiamin retention for extrusion temperature from 150- 165°C, using known value of screw speed, shear history and specific mechanical energy.

Since there was interaction between temperature and mechanical effects, its relationship should be investigated by doing extrusion at multiple temperature profiles. In doing so, the R_T prediction could be used for extrusion at various temperatures.

Therefore, the final model for thiamin retention in terms of shear history was

$$R_T = \left\{ \exp\left[-1.62 \times 10^{-6} \left[-0.0773 (MC - MC_r)\right]\right] \int_0^\infty \exp\beta \times E(t) dt \right\} + \left\{ 0.869 + 0.131 \left[\exp\left(-0.000571 \times \Phi\right)\right] \right\}$$

(4.20)

and in terms of <u>SME in (kJ/kg)</u> was

$$R_{T} = \left\{ \exp\left[-1.62 \times 10^{-6} \left[-0.0773 (MC - MC_{r}) \right] \right] \int_{0}^{\infty} \exp\beta \times E(t) dt \right\} + \left\{ 0.834 + 0.166 \left[\exp\left(-0.00485 * SME \right) \right] \right\}$$

$$(4.21)$$

where
$$\beta(T,t) = \int_0^t \exp\left[\frac{-120,942}{R}\left(\frac{1}{T(t)} - \frac{1}{T_r}\right)\right] dt$$

and T is in °K, t is time in seconds, MC_r is percent moisture content in dry basis (33.3%).

4.4.6. Thiamin loss (thermal and mechanical)

Table 4.7 shows that overall, percentage loss caused by thermal effects decreased as screw speed increased. At condition 1, thermal loss dropped from 9.8% to 4.0% as screw speed was increased. This was due to the shorter residence time at higher screw speed. Thermal loss was higher at condition 2 (higher temperature). Thermal loss was also higher at lower moisture content, as shown in Chapter 3. Percentage loss caused by mechanical effects did not show an apparent trend. However mechanical loss was higher at condition 2, suggesting there was interaction between mechanical effect and temperature. Mechanical loss was not affected by moisture content, suggesting there was no interaction between mechanical effect and temperature.

Mechanical effects also predominated over thermal effects as moisture content increased (Table 4.7-2f, 2g, 2h). This was because at higher moisture content, thiamin reaction rate decreased (Chapter 3), causing less thiamin to be degraded thermally; hence, more of the loss was caused by mechanical effects.

At higher screw speeds, mechanical effects slightly predominated over thermal effects for thiamin loss. At condition 1, mechanical effects caused 47.3% to 64.5% of the total thiamin loss. At higher temperature (conditions 2 and 3), mechanical effects caused 42.2% to 53.3% and 28.9% to 48.3%, respectively of the total thiamin loss. Thus, thermal effects slightly prevailed over mechanical effects for thiamin loss at higher temperature.

days
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processing for
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Thiamin
e 4.7.
Table

o il Xs/Xr (%)	 47.3 (± 3.82) 46.7 (± 8.57) 46.7 (± 8.57) 45.9 (± 13.6) 59.4 (± 4.08) 64.5 (± 15.4) 	11) 42.2 (± 2.62) 44) 40.2 (± 9.60) 23.5.6 (± 3.51) 23.3.9 (± 4.06) 23.3 (± 12.3) 33.3 (± 12.3)	(4) 38.4 (± 6.63) (7) 60.4 (± 14.9) (0) 65.6 (± 4.68)	(4) 28.9 (± 11.7) 3) 35.2 (± 6.72) 3) 39.8 (± 8.04) 3) 45.1 (± 9.38) 45.3 (± 3.63) 43.6 (± 3.63)
Loss due to mechanica effects, X ₆	$\begin{array}{l} 0.088 (\pm 0.0 \\ 0.077 (\pm 0.0 \\ 0.077 (\pm 0.0 \\ 0.099 (\pm 0.0 \\ 0.080 (\pm 0.0 \end{array} \end{array}$	0.138 (± 0.0 0.112 (± 0.0 0.097 (± 0.0 0.103 (± 0.0 0.122 (± 0.0	$\begin{array}{c} 0.139\ (\pm\ 0.0\\ 0.151\ (\pm\ 0.0\\ 0.117\ (\pm\ 0.0\end{array} \end{array}$	$\begin{array}{l} 0.084 (\pm 0.0 \\ 0.099 (\pm 0.0) \\ 0.116 (\pm 0.0) \\ 0.138 (\pm 0.0) \\ 0.156 (\pm 0.0) \end{array}$
Loss due to thermal effects, X_{β}	$\begin{array}{l} 0.098 (\pm 0.00) \\ 0.088 (\pm 0.01) \\ 0.086 (\pm 0.01) \\ 0.067 (\pm 0.00) \\ 0.040 (\pm 0.00) \end{array}$	$\begin{array}{c} 0.190 (\pm 0.03) \\ 0.162 (\pm 0.01) \\ 0.173 (\pm 0.01) \\ 0.169 (\pm 0.00) \\ 0.106 (\pm 0.03) \end{array}$	$\begin{array}{c} 0.218 (\pm 0.00) \\ 0.088 (\pm 0.01) \\ 0.058 (\pm 0.01) \end{array}$	$\begin{array}{c} 0.198 (\pm 0.01) \\ 0.179 (\pm 0.00) \\ 0.173 (\pm 0.01) \\ 0.167 (\pm 0.03) \\ 0.166 (\pm 0.00) \end{array}$
Observed thiamin loss, X_{T}	$\begin{array}{c} 0.187 (\pm 0.01) \\ 0.165 (\pm 0.05) \\ 0.163 (\pm 0.02) \\ 0.166 (\pm 0.00) \\ 0.119 (\pm 0.02) \end{array}$	0.328 (± 0.04) 0.275 (± 0.02) 0.270 (± 0.04) 0.273 (± 0.02) 0.229 (± 0.08)	0.357 (± 0.03) 0.239 (± 0.06) 0.175 (± 0.05)	0.282 (± 0.03) 0.278(± 0.02) 0.289(± 0.02) 0.304(± 0.00) 0 372 (+ 0 03)
Degree of fill	$\begin{array}{c} 0.71 (\pm 0.04) \\ 0.70 (\pm 0.09) \\ 0.69 (\pm 0.00) \\ 0.61 (\pm 0.00) \\ 0.53 (\pm 0.03) \end{array}$	0.65 (± 0.05) 0.62 (± 0.00) 0.59 (± 0.01) 0.58 (± 0.04) 0.52 (± 0.00)	0.58 (± 0.00) 0.56 (± 0.01) 0.54 (± 0.00)	$\begin{array}{c} 0.80(\pm\ 0.07)\\ 0.68\ (\pm\ 0.07)\\ 0.61\ (\pm\ 0.01)\\ 0.55\ (\pm\ 0.04)\\ 0.48\ (\pm\ 0.06)\end{array}$
Mean residence time (s)	$\begin{array}{c} 175.6 (\pm 7.49) \\ 152.2 (\pm 15.7) \\ 144.1 (\pm 0.82) \\ 119.3 (\pm 0.12) \\ 96.2 (\pm 4.39) \end{array}$	160.5 (± 10.2) 135.1 (± 0.14) 124.3 (± 1.52) 113.9 (± 5.80) 95.1 (± 0.36)	$121.5 (\pm 0.77) \\ 117.2 (\pm 2.53) \\ 112.7 (\pm 0.29)$	158.9 (± 10.8) 135.4 (± 10.9) 120.5 (± 2.28) 109.7 (± 6.98) 101 6 (+ 2.18)
Die Temperature (°C)	$154.1 (\pm 0.46) \\ 156.7 (\pm 1.15) \\ 157.0 (\pm 1.15) \\ 157.0 (\pm 1.15) \\ 156.3 (\pm 1.50) \\ 154.5 (\pm 1.73) \\ 154.$	$162.3 (\pm 0.29) 163.1 (\pm 0.52) 164.2 (\pm 1.85) 163.4 (\pm 1.33) 163.4 (\pm 0.75) $	165.9 (± 0.14) 161.7 (± 0.42) 162.6 (± 0.64)	$161.8 (\pm 0.69)$ $161.5 (\pm 0.58)$ $159.9 (\pm 0.52)$ $161.5 (\pm 1.10)$ $161.5 (\pm 1.10)$ $163.4 (\pm 0.75)$
Screw Speed (rpm)	100 150 200 250 300	100 150 200 250 300	200 200 200	100 150 250 300
MC % (wb/db)	25/33.3 25/33.3 25/33.3 25/33.3 25/33.3	25/33.3 25/33.3 25/33.3 25/33.3 25/33.3	23/29.8 28/38.9 32/47.1	25/33.3 25/33.3 25/33.3 25/33.3
Extrusion condition	la 1b 1c 1c 1d 1d	2a 2b 2c 2d 2d	2f 2g 2h	3a 3b 3d 3d

4.4.7. Obtaining the moisture content parameter (b) in extrusion

The moisture content parameter, *b*, described how reaction rate was affected by moisture content. Two moisture content parameters for thiamin were obtained in a shearless environment using different methods in Chapter 3. The first method was conducted at atmospheric heating condition, at 80°C and the second method was at controlled-pressure heating condition, at 129.4°C. A student t-test showed that the parameters obtained from the two studies were not significantly different at 95% confidence level. The moisture content parameter could also be obtained using the extrusion data. For this purpose, another R_S model as a function of shear history was developed using all data at constant fill at the reference moisture content of 33.3% (db) (condition 1a-e, 2a-e). Using the model, R_S was calculated at its respective shear history. R_S was modeled as a function of shear history had the best \mathbb{R}^2 . $R_S = 0.886 + 0.114[\exp(-0.0899 * \Phi)]$).

 R_{β} was calculated using the established thiamin kinetic parameters, accounting for the time-temperature history along the extruder barrel. Predicted R_T was then computed using the calculated value of R_{β} and R_S . Parameter b was estimated by non-linear regression using Solver in Excel®, while minimizing the sum of squares of the residuals between the measured R_T and predicted R_T .

Using bootstrap program, 1,000 *b* values were generated. Table 4.8 shows the moisture content parameters obtained from study 1, study 2 in Chapter 3 and extrusion. A student t-test on the *b* values between study 2 (chapter 3) and extrusion shows that t = 0.071, thus the two values were not significantly different [using t(0.05, 17) = 1.740 as test of significance]. Bootstrap and t-test method can be found in Chapter 3. Since the

result obtained in a shearless environment was similar to the result obtained in an intense shear environment (extrusion), it could be deduced that there was no interaction between shear and moisture content, which confirmed our previous findings.

				Number of data
	b value	^a R ²	Std error	points
Chapter 3, Study 1a, Atmospheric				
pressure heating	-0.128	0.85	^a 0.0273	6
Chapter 3, Study 2, Controlled				
pressure heating	-0.0769	0.99	^a 0.00088	3
Chapter 4, Extrusion study	-0.0647	0.99	^b 0.0294	16

Table 4.8. Moisture content parameter b based on three studies

^aValues obtained from linear regression of Ln reaction rate constant versus MC (db) ^bStandard deviation based on 1,000 bootstrap data.

4.5. CONCLUSION

Thiamin r etention in extruded flour was investigated at different s crew speeds, moisture contents, temperatures and degrees of fill. Increasing screw speed at a constant degree of fill increased thiamin retention slightly, however, had no effect on mechanical retention. Increasing moisture content resulted in higher thiamin retention but moisture content did not influence mechanical retention. A higher barrel temperature also yielded in lower total thiamin retention and mechanical retention. The latter result indicated that there was interaction between temperature and mechanical retention. Increasing screw speed at varying degree of fill extrusion condition decreased thiamin retention. Comparing data from extrusion at constant fill and varying fill condition at constant temperature, higher retention was obtained at higher degree of fill.

Constant degree-of-fill extrusion models for mechanical retention as a function of screw speed, shear history and specific mechanical energy were developed, using two temperatures d ata from the p resent s tudy and d ata from C ha *et a l*. (2003). T he t hree models were then assessed for accuracy for a varying degree of fill extrusion condition.

The model with shear history was the best predictor, yielding reasonably accurate experimental thiamin retention ($\mathbb{R}^2 = 0.76$). This suggests that the model could be used to predict thiamin retention at t emperatures ranging from 1 50-165°C. S ince s hear h istory and specific mechanical energy are equipment-independent variables, modeling R_S as a function of these two shear terms is more applicable for scale-up purposes. R_β could be calculated using the known thiamin reaction rate, activation energy, product temperature profile and mean residence time from extrusion run. Then, experimental time for thiamin analysis could be reduced, as total thiamin retention could be calculated. Since the model was equipment-independent, this model could be used to predict thiamin retention in any extruder. The optimum extrusion condition could also be determined so that maximum thiamin retention was achieved.

4.6. FUTURE WORK RECOMMENDATIONS

Since the present study determined that there was interaction between temperature and mechanical retention, 2 or 3 more temperature profiles should be conducted to determine how mechanical retention behaved with temperature.

Extrusion should be conducted at lower dough moisture content than 23.0% (wb)/ 29.8% (db) to obtain lower thiamin retention, reasonably in the range of 0.2-0.4 so that mechanical retention could be modeled optimally.

4.7. NOMENCLATURE

- *b* moisture content parameter
- b^* blue color intensity, Hunter color units
- C dry basis, thiamin concentration in flour, %
- C_{o} dry basis, initial thiamin concentration in flour, %
- DT die temperature, °C
- E(t) normalized residence time distribution curve, 1/s
- E_a activation energy, J/gmol (chapter 3)
- E_{v} viscous dissipation of mechanical energy, W
- f_i visual degree of fill in barrel section, fraction
- *i* index for barrel sections or time, dimensionless
- k reaction rate constant, 1/s
- k_r reaction rate constant at reference temperature, 1/s (chapter 3)
- k' extruder constant, 1/rev (chapter 2)
- MC moisture content (db), wt/wt
- MC_r reference moisture content (db), wt/wt
- \dot{m} dough mass flow rate = mass flow rate of flour + mass flow rate of injected water, kg/s
- N screw speed, rps
- ΔP die pressure, Pa
- P_w total mechanical energy input to the extruder from the motor, W
- Q volumetric flow rate, m³/s
- *R* ideal gas constant, 8.3144 J/gmol-K
- R_T measured thiamin retention, fraction
- R_{β} thermal effect on thiamin retention, fraction
- R_S mechanical effect on thiamin retention, fraction
- T temperature, °K
- T_r reference temperature, °K
- \overline{t} mean residence time, s
- t exit time, s
- Δt_i residence time in barrel section *i*, s
- V void volume = $1.18E-4 m^3$
- V_i void volume in each barrel section *i*, m³
- X_T measured thiamin loss, fraction
- X_b thiamin thermal loss, fraction
- X_S mechanical thiamin loss, fraction

Greek symbols

- β time-temperature history, s
- ρ dough density = 1200 kg/m³
- ϕ shear history, dimensionless
- $\dot{\gamma}_a$ average shear rate, 1/s

4.8. REFERENCES

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Chapter 5: Conclusions and novelty of model development

In Chapter 2, matching viscosity a ssumptions b ased on mixer viscometry were applied to estimate the average shear rate in an extruder. The average shear rate was modeled as a function of degree of fill and screw speed. The extruder constant increased as degree of fill was increased. In general, at constant screw speed, average shear rate increased at higher extruder degree of fill. In this study, a novel method was developed to measure extruder degree of fill and extruder constant was modeled as a function of degree of fill.

In Chapter 3, thiamin kinetic parameters were obtained using two methods: atmospheric-pressure heating condition and controlled-pressure heating condition. Moisture content parameter were determined to correct the changing-moisture hightemperature kinetic parameters. After the correction, the kinetic parameters were comparable to the results from controlled-pressure heating; thus, the correction methods could be applied for researchers without access to controlled-pressure equipment. In this study, a novel method was developed to correct the kinetic parameters where loss of moisture was unavoidable for heating at atmospheric-pressure condition.

In Chapter 4, thermal effects and mechanical effects of extrusion on thiamin retention were quantified separately. Results indicated that there was interaction between thermal and mechanical in thiamin degradation. Thermal effects on thiamin retention were calculated, accounting for the time-temperature history in each barrel section. The mechanical effects were calculated by mathematically removing the thermal retention from the total thiamin retention. The best thiamin retention prediction was when using shear history to model the mechanical effects. The moisture content parameter was also

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obtained from an extrusion study, and was similar to results from Chapter 3, indicating that there is no interaction between mechanical effect and moisture content. In this chapter, results from chapters 2 and 3 were utilized to obtain a model for predicting thiamin retention in extruded products as a function of degree of fill, mean residence time, product temperature, moisture content, screw speed. **APPENDIX**

Appendix 1

Thiamin analysis and standard curve

Appendix 1.A. Thiamin analysis

Thiamin c ontent was analyzed u sing the fluorometric m ethod (Official Method 953.17, AOAC 1995). Procedure was adapted from Schmid (2002) and Moore and Dolan (2003). Thiamin fluorescence was measured using spectrofluorometer SF-330 Varian (Palo Alto, CA) at excitation wavelength of 373 nm and emission wavelength of 410 nm. A xenon lamp was used as the light source for UV light.

Reagents and Materials

- A. Sodium hydroxide solutions 15%
- B. Hydrochloric solution 0.1 N
- C. HPLC grade Isobutyl alcohol (2-methyl-1propanol)
- D. Quinine sulfate stock solution Dissolve 10 mg quinine sulfate in $0.1N H_2SO_4$ to make 1L. Store in light-resistant containers.
- E. Quinine sulfate standard solution Dilute 1 volume quinine sulfate stock solution with 39 volumes $0.1N H_2SO_4$. Store in light-resistant container.
- F. Thiamin Hydrochloride standard solutions Primary stock standard solution (1000 μ g/ml = 1g/1000 ml)
 - Weigh <u>1 g</u> USP Thiamin Hydrochloride Reference Standard (Spectrum Laboratory Products, Gardena, CA) which has been dried to constant weight over CaSO₄ in desiccators.
 - 2. Dilute to <u>1000 ml</u> with 20% ethanol which has been adjusted to pH 3.5- 4.3 with 0.1N HCl.
 - 3. Store at approximately 10°C in glass stoppered, light resistant bottle.

Secondary Stock Standard Solution (100 µg/ml)

- 1. Dilute <u>100 ml</u> aliquot of primary stock standard solution to <u>1000 ml</u> with 20% ethanol which has been adjusted to pH 3.5-4.3 with HCl.
- 2. Store at ca 10°C in glass-stoppered, light resistant bottle.

Working standard solution (15.6 µg/ml)

- 1. Dilute <u>15.6 ml</u> thiamin-HCl stock solution and 5.0 gram of salt (NaCl) to <u>100 ml</u> with ca 0.1 N HCl. (1 ml = $0.2 \mu g$ thiamin-HCl).
- 2. Prepare solution on day used.
- G. Oxidizing Stock Solution (0.2796%)
 - 1. Dissolve <u>0.2796 g</u> of Potassium Ferrocynide in 15% NaOH solution to make <u>100</u> <u>ml.</u>
 - 2. Prepare solution on day used.
- H. Oxidizing Working Solution (0.01398%)
 - 1. Take <u>10 ml</u> of aliquot of the oxidizing stock solution and dilute it to <u>200 ml</u> with 15% NaOH.
 - 2. Prepare solution on day used.

Extraction procedures

Thiamin extraction

- 1. Weigh ≈ 10 g of salt, and record mass.
- 2. Weigh ≈ 1 g of flour sample and record mass.
- 3. Place the salt and the flour sample in a 250 ml centrifuge tube.
- 4. In a 200 ml volumetric flask, add 200 ml of 0.1 N HCl.
- 5. Add HCl into the centrifuge tube.
- 6. Hand-shake tube for 15 seconds.
- 7. Put in shaking water bath (Precision Scientific, Chicago, IL) for 1/2 hour
- 8. Cool tubes to room temperature with ice cubes for 45 minutes.
- 9. Centrifuge tubes at 5000 rpm (4,066 x g) for 15 minutes using a RC-5B centrifuge (Sorval Instruments, Newton, CT).

Thiamin oxidation

For oxidized tubes

- 1. Add 2.5 ml aliquots of thiamin extract of the centrifuged flour mixture solution.
- 2. Add 10 ml of oxidizing working solution.
- 3. Add 13 ml of anhydrous isobutyl alcohol (Sigma).
- 4. Hand-shake tube for 15 seconds.

For blank tubes (unoxidized)

- 1. Add 2.5 ml of the centrifuged flour mixture solution.
- 2. Add 10 ml of NaOH.
- 3. Add 13 ml of isobutyl alcohol.

- 4. Hand-shake tube for 15 seconds.
- 5. Shake all oxidized and blank tubes together in a mechanical shaker (Mexi-Mix III, Termolyne, Dubuque, IA) for 2 minutes and centrifuge for 3 minutes at 10,000 rpm (11,950 x g).
- 6. Pipet 3.3 mL of isobutanol thiochrome extract (upper layer) to plastic cuvette for thiochrome measurement.

Fluorometer setup for thiochrome measurement

- 1. Set excitation slit at 5 nm, emission slit at 10 nm, sensitivity at x1/10 for oxidized samples and at x10 for blanks.
- 2. Calibrate fluorometer with 0.25 mg/L of quinine sulfate solution at excitation wavelength of 343 nm and emission wavelength of 459 nm.
- 3. For isobutanol thiochrome extract, dial excitation wavelength at 373 nm and emission wavelength at 410 nm.

Appendix 1.B. Standard Curve and Thiamin Calculation

Standard curve

When new reagents of sodium hydroxide and hydrochloric solution were prepared, a new standard curve was created. Standard curve is done at four concentrations in duplicate. The setup for each tube is shown in Table 1.B.1.

Tube #		Working standard solution (ml)	Oxidizing solution (ml)	15% NaOH solution (ml)	Final Thiamin Concentration (µg/ml)
1	Oxidized	3.00	12.00		3.60
2	Oxidized	2.25	9.00		2.70
3	Oxidized	1.55	6.20		1.86
4	Oxidized	0.75	3.00		0.90
5	Un-Oxidized	3.00		12.00	3.60
6	Un-Oxidized	2.25		9.00	2.70
7	Un-Oxidized	1.55		6.20	1.86
8	Un-Oxidized	0.75		3.00	0.90

Table 1.B.1. Amounts of reagents used to determine standard curve

Methods

For oxidized samples

To 40 ml tubes, add the amount indicated above:

- Working solution
- Oxidizing agent
- Immediately, add 13 ml isobutanol, and hand-shake for 15 secs

Un-oxidized tubes

To 40 ml tubes, add the amount indicated above:

- Working solution
- 15% NaOH
- Immediately, add 13 ml isobutanol, and hand-shake for 15 secs

Shake all oxidized and blank tubes together in a mechanical shaker (Mexi-Mix III, Termolyne, Dubuque, IA) for 2 minutes and centrifuge for 3 minutes at 10,000 rpm $(11,950 \times g)$.

Pipet 3.3 ml of isobutanol thiochrome extract (upper layer) to plastic cuvette for thiochrome measurement.



Figure 1.B.1. Standard curve for fluorescence reading vs thiamin concentration constructed in duplicate on two different days.

To construct a standard curve, plot final thiamin concentration versus fluorometric reading (oxidized-blank). Determine the slope and the intercept.

Fluorometric reading (oxidized-blank) = thiamin concentration (µg/ml) * slope + intercept

Thiochrome Fluorescence Calculation

% thiamin calculation (w/w) =

Thiamin concentration * $\left(\frac{SM}{SD} + \frac{FM}{FD} + ml_{HCL}\right)$ * $\frac{1}{ml_{sample}}$ * $ml_{isobutanol}$ * $\frac{10^{-6}g}{\mu g}$ * $\frac{1}{mass_{sample}}$ * 100% SM = salt mass (g) = SD = salt density (g/ml) = 2.170 g/ml FM = flour mass (g) FD = flour density (g/ml) = 0.475 g/ml ml_{samplc} = volume of thiamin extract solution added into the 50 ml centrifuge tube (ml) $ml_{isobutanol}$ = volume of isobutanol solution added to sample (ml) mass_{sample} = mass of sample (g)

% thiamin in dry basis = % thiamin (w/w) / (1 - MC (w/w))

Appendix 2

Extrusion data collection for Chapter 2

Appendix 2.A Data collection during extrusion run

Avg density 1.0 Degree of fill	(g/ml) =	1.375	$\eta = 1.006*10^{-16} \exp(11980/T) \gamma^{n-1}$			
Screw Speed (rpm)	Temp (°C)	Viscosity (Pa.s)	Non-load Torque (%)	Load Torque (%)	Die Pressure (psi)	Mass flow rate (g/min)
50	23.6	35.01	11.6	15.6	30	92.2
100	24.6	30.57	13.0	20.0	40	177.8
200	23.3	36.72	14.1	26.8	100	312.2
300	24.2	32.27	14.9	29.6	100	354.0
400	24.4	31.41	15.3	31.0	90	457.0
50	24.4	31.41	10.8	14.6	40	128.4
100	23.1	37.74	11.9	18.4	60	177.6
200	22.6	40.14	13.2	26.6	90	324.0
300	23.5	35.74	14.1	30.0	110	355.2
400	24.4	31.41	15.0	31.0	90	457.0
	·····					
Average		1 2/7		c.co+10-15	(111177	n n-1
density	(g/mI) =	1.307	η = 1.	568+10 ***	exp (1111//	Ι) γ
0.7-0.9 Degr	ee of fill					
Screw	Temp	Viscosity	Non-load Torque	Load Torque	Die Pressure	Mass flow rate
Speed (rpm)	(°C)	(Pa.s)	(%)	(%)	(psi)	(g/min)
50	22.8	39.05	11.30	14.6	10	40.4
100	23.3	36.47	12.25	18.2	20	86.6
200	23.2	37.23	13.30	20.9	50	108.2
300	23.0	38.00	14.50	25.6	30	126.8
400	24.2	32.49	14.80	27.7	40	170.8
50	22.1	35.98	11.75	14.95	10	46.2
100	22.9	32.50	12.80	16.6	20	78.0
200	22.9	32.70	13.75	20.95	30	85.0
300	23.8	29.18	14.65	21.8	30	139.6
400	23.7	29.37	15.20	26.5	40	150.6

Table 2.A.1. Data collection during extrusion run for corn syrup, n = 1.00

Avg density $(g/ml) = 1.367$ $\eta = 1.568*10^{-15} \exp(11117/T) \gamma^{n-1}$						
0.4-0.6 Degre	e of fill					
Screw		Viscosity	Non-load Torque	Load Torque	Die Pressure	Mass flow rate
Speed (rpm)	Temp (°C)	(Pa.s)	(%)	(%)	(psi)	(g/min)
50	22.2	42.70	11.30	13.8	0	22.0
100	22.5	40.97	12.25	17.2	10	26.2
200	23.0	38.00	13.30	19.0	0	18.6
300	23.3	36.47	14.50	21.4	0	19.0
400	22.7	39.59	14.80	21.5	0	16.8
50	22.8	32.91	11.75	13.6	10	23.6
100	22.2	35.53	12.80	16.8	10	26.6
200	22.8	32.91	13.75	17.4	10	31.6
300	23.8	29.00	14.65	21.7	20	26.6
400	24.6	26.39	15.20	23.2	10	29.2

Table 2.A.1. (continued). Data collection during extrusion run for corn syrup, n = 1.00

Average density $(g/ml) = 0.825$					
1.0 Degree of fill					
Screw Speed (rpm)	Temp (°C)	Non-load Torque (%)	Load Torque (%)	Die Pressure (psi)	Mass flow rate (g/min)
50	9.4	10.95	11.65	10	55.0
100	9.3	11.95	12.65	10	54.0
200	9.6	13.25	13.95	10	49.6
300	9.2	13.95	14.75	10	56.8
400	9.8	14.70	15.30	10	51.0
0.7-0.9 Degree of fill	l				
	Temp	Non-load	Load	Die Pressure	Mass flow rate
Screw Speed (rpm)	(°C)	Torque (%)	Torque (%)	(psi)	(g/min)
50	12 2	11.00	11 45	0	AC
JU 100	13.2	11.00	11.00	U	4.0 0 <
100	12.1	11./3	12.05	U	У.О 1 <i>4 с</i>
200	12.5	13.23	13.93	U	14.0
300	12.9	14.00	14.05	U	22.2
400	13.0	14.65	15.3	0	18.2
0.4-0.6 Degree of fil	<u>l</u>				
	T	NT 7 -	. .	D' 7	N/ 7
 Sorow Grand (mar)	1 emp	Non-load	Load	Die Pressure	Mass flow rate
Screw Speed (rpm)	(1)	1 orque (%)	Torque (%)	(psi)	(g/min)
50	13.8	11.00	11.65	0	1.2
100	14.5	11.75	12.55	0	7.8
200	14.4	13.25	13.9	0	15.8
300	14.0	14.00	14.7	0	9.6
400	14.2	14.65	15.25	0	12.6
300 400	14.0 14.2	14.00 14.65	14.7 15.25	0 0	9.6 12.6

Table 2.A.2. Data collection during extrusion run for A40m, n = 0.24

Average density $(g/ml) = 0.843$ 1 0 Degree of fill							
Screw Speed (rpm)	Temp (°C)	Non-load Torque (%)	Load Torque (%)	Die Pressure (psi)	Mass flow rate (g/min)		
50	18.1	11.15	11.95	10	55.0		
100	17.8	12.20	12.90	10	54.0		
200	17.7	13.50	14.25	10	49.6		
300	17.7	14.50	14.95	10	56.8		
400	17.7	15.30	15.65	10	51.0		
0.7-0.9 Degree of fil	<u> </u>	······································	W M				
Screw Speed (rpm)	Temp (°C)	Non-load Torque (%)	Load Torque (%)	Die Pressure (psi)	Mass flow rate (g/min)		
50	17.8	11.15	11.95	0	4.6		
100	18.55	11.95	12.75	0	12.8		
200	17.8	13.35	13.85	0	14.6		
300	17.8	14.25	14.75	0	22.2		
400	17.9	14.85	15.40	0	18.2		
0.4-0.6 Degree of fil	0.4-0.6 Degree of fill						
				_			
Screw Speed (rpm)	Temp (°C)	Non-load Torque (%)	Load Torque (%)	Die Pressure (psi)	Mass flow rate (g/min)		
50	17 85	11 15	11 85	0	1 2		
100	17.00	12.13	12 80	0	78		
200	17.90	12.20	12.00	0	7.0 15 Q		
200	17.00	13.30	13.73	0	13.0		
500	17.80	14.30	14.00	U	9.0		
400	17.95	15.30	15.50	U	12.0		

Table 2.A.3. Data collection during extrusion run for A40m, n = 0.28

Average densi 1.0 Degree of fill	ty (g/ml) = 1	1.038			
Screw Speed (rpm)	Temp (°C)	Non-load Torque (%)	Load Torque (%)	Die Pressure (psi)	Mass flow rate
			(/0)		
50	9.35	11.05	12.3	20	79.6
100	9.50	11.85	13.65	20	128.4
200	9.60	13.25	15.25	20	173.6
300	9.50	14.15	16.15	20	233.0
400	9.70	14.75	16.75	20	199.4
0.7-0.9 Degree of fill					
Screw Speed (rpm)	Temp (°C)	Non-load Torque (%)	Load Torque (%)	Die Pressure (psi)	Mass flow rate (g/min)
50	10.80	10.95	12.25	10	41.6
100	11.00	12.05	13.25	10	48.8
200	11.10	13.45	14.65	10	71.6
300	11.20	14.25	15.55	10	80.0
400	11.30	14.95	16.40	10	114.0
0.4-0.6 Degree of fill	L				
Screw Speed	m (100)	Non-load	Load Torque		Mass flow rate
(rpm)	Temp (°C)	Torque (%)	(%)	Die Pressure (psi)	(g/min)
50	13.3	11.05	11.95	0	15.6
100	13.35	11.85	12.85	0	19.0
200	13.35	13.25	14.15	0	28.2
300	13.35	14.15	15.25	0	35.0
400	13.50	14.75	15.90	0	37.0

Avg density	(g/ml) =	0.995			
1.0 Degree of fil	1	<u></u>			
				Die	
Screw Speed	Temp	Non-load		Pressure	Mass flow
(rpm)	(°C)	Torque (%)	Load Torque (%)	(psi)	rate (g/min)
50	23.55	11.40	12.80	30	62.40
100	23.95	12.50	13.90	30	108.20
200	24.35	13.60	15.60	30	192.60
300	24.80	14.50	16.60	30	284.40
400	24.65	15.10	17.50	40	372.00
0700 Dograd a	f fill				
0.7-0.9 Degree 0			-,	Dia	<u></u>
Screw Speed	Temn	Non-load			Mass flow
(mm)	(°C)	Torque (%)	Load Torque (%)	(psi)	rate (g/min)
(1)	()	101940 (70)	2000 101900 (70)		
50	21.75	11.00	12.15	10	41.40
100	22.20	12.15	12.90	0	33.20
200	22.15	13.50	14.40	0	56.60
300	22.15	14.35	15.30	0	71.40
400	22.15	15.00	16.00	0	62.80
0.4-0.6 Degree o		<u> </u>		. <u>In 112</u>	
	_			Die	
Screw Speed	Temp	Non-load		Pressure	Mass flow
(rpm)	(°C)	Torque (%)	Load Torque (%)	(ps1)	rate (g/min)
50	10.05	11.00	10.05	10	10.90
50	19.05	11.20	12.25	10	10.80
100	20.25	12.35	13.20	10	12.20
200	20.35	13.55	14.45	10	27.60
300	20.25	14.35	15.20	10	30.80
400	20.30	15.05	15.90	10	35.20

Table 2.A.5. Data collection during extrusion run for K99, n = 0.67

Appendix 2.B. Average shear rates data

Flow behavior index, n	Fill degree	Screw speed (Rpm)	Measured average shear rate (1/s)
0.24	1.0	50	32.3
0.24	1.0	100	50.9
0.24	1.0	200	85.1
0.24	1.0	300	104.3
0.24	1.0	400	167.3
0.24	0.7	50	17.7
0.24	0.7	100	24.5
0.24	0.7	200	56.4
0.24	0.7	300	77.4
0.24	0.7	400	114.1
0.24	0.4	50	10.5
0.24	0.4	100	10.9
0.24	0.4	200	31.8
0.24	0.4	300	48.0
0.24	0.4	400	60.7
0.28	1.0	50	40.9
0.28	1.0	100	75.6
0.28	1.0	200	128.2
0.28	1.0	300	230.6
0.28	1.0	400	401.9
0.28	0.7	50	24.8
0.28	0.7	100	52.2
0.28	0.7	200	139.8
0.28	0.7	300	348.8
0.28	0.7	400	395.7
0.28	0.4	50	15.0
0.28	0.4	100	34.2
0.28	0.4	200	124.4
0.28	0.4	300	395.1
0.28	0.4	400	277.7

Table 2.B.1 Average shear rates data for non-Newtonian fluid

Flow behaviour		Screw speed	Observed average shear
index, n	Fill degree	(Rpm)	rate $(1/s)$
0.60	1.0	50	22.7
0.60	1.0	100	32.7
0.60	1.0	200	68.6
0.60	1.0	300	74.8
0.60	1.0	400	83.8
0.60	0.7	50	10.6
0.60	0.7	100	25.8
0.60	0.7	200	65.1
0.60	0.7	300	105.8
0.60	0.7	400	141.6
0.60	0.4	50	6.1
0.60	0.4	100	23.5
0.60	0.4	200	64.1
0.60	0.4	300	152.5
0.60	0.4	400	231.9
0.67	1.0	50	24.5
0.67	1.0	100	83.1
0.67	1.0	200	113.1
0.67	1.0	300	181.8
0.67	1.0	400	212.2
0.67	0.7	50	10.4
0.67	0.7	100	54.9
0.67	0.7	200	143.2
0.67	0.7	300	275.3
0.67	0.7	400	404.3
0.67	0.4	50	3.3
0.67	0.4	100	19.9
0.67	0.4	200	77.5
0.67	0.4	300	153.6
0.67	0.4	400	271.8

Table 2.B.1 (Continued). Average shear rates data for non-Newtonian fluid

Appendix 3

Data and Figures for Chapter 3

Appendix 3.A. Data for constant-moisture study (study 1a)

Reported moisture	^a average initial	^a average final	Coefficient
content, % (db)	moisture content,	moisture content at the	of variance
	%(db)	end of heating %(db)	%
6.15	6.41	5.71	7.70
9.67	10.7	8.50	9.47
10.7	12.6	9.7	10.4
17.2	19.8	15.4	8.82
27.0	30.4	23.5	8.70
36.9	41.6	33.0	6.89

Table 3.A.1. Moisture content of flour mixture

^aBased on four readings

Table 3.A.2. Thiamin concentration value of 80°C heating for MC= 6.15, 9.67 and 10.7%

MC (wb)) = 5.8	MC	(wb) = 8.8	MC	(wb) = 9.7
MC (db)	= 6.15	MC (db) = 9.67	MC	(db) = 10.7
	% Thiamin		% Thiamin		% Thiamin
Time (min)	Basis	Time (min)	Basis	Time (min)	Basis
0	0.403	0	0.403	0	0.403
0	0.357	0	0.357	0	0.357
0	0.349	0	0.349	0	0.349
0	0.352	0	0.352	0	0.352
0	0.376	0	0.376	0	0.376
0	0.351	0	0.351	0	0.351
0	0.350	0	0.350	0	0.350
0	0.353	0	0.353	0	0.353
300	0.324	162	0.349	180	0.290
300	0.341	162	0.356	180	0.288
300	0.311	162	0.344	180	0.286
300	0.302	162	0.342	180	0.283
960	0.308	360	0.324	480	0.271
960	0.309	360	0.322	480	0.268
960	0.300	360	0.324	480	0.272
960	0.318	360	0.326	480	0.273
1440	0.303	600	0.327	725	0.246
1440	0.303	600	0.325	725	0.242
1440	0.298	600	0.319	725	0.264
1440	0.294	600	0.311	725	0.265

MC (wb) = 14.7	MC (w	(b) = 21.3	MC (w	b) = 26.9
MC (db) = 17.2	MC (d	(b) = 27.0	MC (d	b) = 36.9
Time (min)	% Thiamin Dry Weight Basis	Time (min)	% Thiamin Dry Weight Basis	Time (min)	% Thiamin Dry Weight Basis
0	0.403	0	0.403	0	0.403
0	0.357	0	0.357	0	0.357
0	0.349	0	0.349	0	0.349
0	0.352	0	0.352	0	0.352
0	0.376	0	0.376	0	0.376
0	0.351	0	0.351	0	0.351
0	0.350	0	0.350	0	0.350
0	0.353	0	0.353	0	0.353
60	0.326	61	0.343	60	0.351
60	0.313	61	0.339	60	0.351
60	0.286	61	0.362	60	0.381
60	0.280	61	0.353	60	0.379
120	0.170	180	0.326	210	0.340
120	0.194	180	0.346	210	0.350
120	0.202	180	0.317	210	0.348
120	0.222	180	0.315	210	0.355
240	0.113	270	0.292	300	0.325
240	0.110	270	0.294	300	0.327
240	0.103	270	0.287	300	0.312
240	0.089	270	0.282	300	0.315

Table 3.A.3. Thiamin concentration value of 80°C heating for MC=17.2, 27.0 and 36.9%

Table 3.A.4. Regression analysis for constant-moisture study

Moisture content %	Average k (1/min) (± SD)	Regression Statistics				
(db)		R ²	Std error			
6.15	0.000055(± 3.84E-5)	0.43	1.985*10-5			
9.67	0.000184(± 1.37E-5)	0.70	3.795*10 ⁻⁵			
10.7	0.000222(± 2.22E-4)	0.80	3.502*10 ⁻⁵			
17.2	0.005860(± 3.72E-4)	0.96	3.860*10-4			
27.0	0.000893(± 2.74E-4)	0.84	1.215*10-4			
36.9	0.000532(± 3.43E-4)	0.73	1.020*10 ⁻⁴			

Appendix 3.B. Data for high-temperature heating at atmospheric pressure (study 1b)

T _{avg} =	141.9	Tav	s = 156.8	$T_{avg} = 166.4$			
Time (min)	% Thiamin Dry Weight Basis	Time (min)	% Thiamin Dry Weight Basis	Time (min)	% Thiamin Dry Weight Basis		
0	0.403	0	0.403	0	0.403		
0	0.357	0	0.357	0	0.357		
0	0.349	0	0.349	0	0.349		
0	0.352	0	0.352	0	0.352		
0	0.376	0	0.376	0	0.376		
0	0.351	0	0.351	0	0.351		
0	0.350	0	0.350	0	0.350		
0	0.353	0	0.353	0	0.353		
25	0.275	20	0.212	10	0.261		
25	0.274	20	0.209	10	0.256		
25	0.266	20	0.222	10	0.279		
25	0.269	20	0.221	10	0.287		
60	0.174	40	0.088	15	0.162		
60	0.174	40	0.085	15	0.165		
60	0.186	40	0.103	15	0.204		
60	0.188	40	0.101	15	0.209		
70	0.163	60	0.061	20	0.104		
70	0.163	60	0.060	20	0.105		
70	0.165	60	0.058	20	0.121		
70	0.165	60	0.063	20	0.118		

Table 3.B.1. Thiamin concentration of 25% MC (wb)/ 33.3% MC (db) at high-temperatures (Study 1b)

Table 3.B.2 Regression analy	sis of high-temperature atmosp	heric heating data (Study 1b))
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		Average reaction rate	Regression analysis Reaction rate constant				
	T _{avg} (°C)	constant (1/min)					
		(± SD)	R ²	Std error			
Uncorrected	141.95	0.0113(± 9.57E-4)	0.988	0.000384			
Uncorrected	156.82	0.032(± 8.38E-4)	0.960	0.00206			
Uncorrected	166.45	0.088(± 3.13E-3)	0.960	0.00206			
Corrected	141.95	0.269(± 2.22E-2)					
Corrected	156.82	0.926(± 8.77E-2)					
Corrected	166.45	2.222(± 1.46E-2)					

Table 3.C. Thiamin retention data from study 2

Appendix 3.C. Thiamin retention data from controlled-pressure heating (study 2)

5.0% 3.3%	-	Predicted C/Co	0.684	0.684	0.684	0.684	0.684	0.684	0.498	0.498	0.498	0.498	0.498	0.498	0.359	0.359	0.359	0.359	0.359	0.359
MC (wb) = 2, MC (db) = 33		Measured C/Co	0.739	0.726	0.708	0.669	0.638	0.633	0.517	0.503	0.489	0.497	0.529	0.520	0.333	0.324	0.332	0.303	0.385	0.402
	Heating	time (min)	40	40	40	40	40	40	60	60	60	60	60	60	80	80	80	80	80	80
2.0% .2%		Predicted C/Co	0.607	0.607	0.607	0.607	0.607	0.607	0.402	0.402	0.402	0.402	0.402	0.402	0.263	0.263	0.263	0.263	0.263	0.263
MC (wb) = 22 MC (db) = 28		Measured C/Co	0.593	0.612	0.605	0.610	0.606	0.609	0.377	0.377	0.378	0.373	0.353	0.376	0.288	0.282	0.287	0.313	0.291	0.299
	Heating	time (min)	40	40	40	40	40	40	09	60	60	60	60	60	80	80	80	80	80	80
6.0% .1%		Predicted C/Co	0.723	0.723	0.723	0.723	0.723	0.723	0.328	0.328	0.328	0.328	0.328	0.328	0.127	0.127	0.127	0.127	0.127	0.127
MC (wb) = 16 MC (db) = 19		Measured C/Co	0.525	0.540	0.664	0.591	0.490	0.440	0.370	0.322	0.373	0.360	0.325	0.343	0.263	0.265	0.223	0.244	0.260	0.262
	Heating	time (min)	20	20	20	20	20	20	40	40	40	40	40	40	60	60	60	60	60	60

Appendix 3.D. Gauss-Legendre quadrature (Stasa 1985)

Gauss-Legendre started with the integral of

$$I = m \sum_{i=1}^{n} w_i f(x_i)$$

where *n* is the number of Gauss-Legendre points and w_i is the weights and x_i is the sampling point and m is $\frac{b-a}{2}$.

For study 2

b was defined as the normalized radius of the can (b=1) and a was the normalized center of the can (a=0).

For n = 5 Gauss-Legendre, r and z points were calculated as

$$r = \frac{1}{2}(b+a) + \frac{1}{2}(b-a)t$$
$$z = \frac{1}{2}(b+a) + \frac{1}{2}(b-a)t$$

n	t	r and z	z*	l*	i and j	W
		points				
	0	0.5	0.0170	0.0340	3	0.56888889
	0.53846931	0.76923	0.0262	0.0340	4	0.47862867
5	-0.53846931	0.23077	0.00783	0.0340	2	0.47862867
	0.90617985	0.95309	0.0324	0.0340	5	0.23692689
	-0.90617985	0.04691	0.00159	0.0340	1	0.23692689

Gauss-Legendre integral was transformed into a double-integral for r and z points,

$$I = m_r m_z \sum_{i=1}^{5} \sum_{j=1}^{5} w_i w_j f(r_i, z_j) = \frac{1}{4} \sum_{i=1}^{5} \sum_{j=1}^{5} w_i w_j f(r_i, z_j)$$
Evaluating the integral for mass-average temperature by using the Gauss-Legendre integration, Eq. (3.19) became

$$T_{mass average} = \frac{1}{4} \sum_{i=1}^{5} \sum_{j=1}^{5} w_{i} w_{j} 2r_{i}T_{r,z}$$

Implementing the Gauss-Lagendre integral into Eq. (3.20) for improved accuracy, the final equation for mean average thiamin retention was

$$\left(\frac{\overline{C}}{C_o}\right) = \frac{1}{4} \sum_{i=1}^{5} \sum_{j=1}^{5} w_i w_j 2r_i \exp\left[-k_r \beta\right]_{r,z}$$



Appendix 3.E. Plot of measured vs predicted center temperature for study 2

Figure 3.E.1. Plot of measured vs predicted center temperature for 19.1% MC (db) flour in 201x211 cans heated at 129.4°C retort temperature.



Figure 3.E.2. Plot of measured vs predicted center temperature for 28.2% MC (db) flour in 201x211 cans heated at 129.4°C retort temperature.



Appendix 3.F. Plot of measured vs predicted thiamin retention in study 2

Figure 3.F.1. Plot of measured vs predicted thiamin retention for 19.1% MC flour in 201x211 cans heated at 129.4°C retort temperature.



Figure 3.F.2. Plot of measured vs predicted thiamin retention for 28.2% MC flour in 201x211 cans heated at 129.4°C retort temperature.



Appendix 3.G. Confidence region for 28.2% MC flour

Figure 3.G. 90% joint confidence region for estimated activation energy (kJ/g-mol) and reaction rate constant k_{80} (min⁻¹) for MC=28.8% flour obtained from bootstrap data.

Appendix 4

Data for Chapter 4

Appendix 4.A. Color concentration curve



Figure 4.A. Plot of Hunter b' color units versus blue-dye concentration (%wb) of flour extruded at 200 rpm at 160°C (Based on two color readings).

Minimum b^* values from mean residence time ground extrudate is -4.0.

Appendix 4.B. Condition 1 extrusion data

Table 4.B.1. Processing data for extrusion at condition 1 at constant degree of fill

Temperature profile (°C) at zone 1/2/3/4/5	Temperature profile (°C) at zone 1/2/3/4/5	Temperature profile (°C) at zone 1/2/3/4/5	erature profile (°C) at zone 1/2/3/4/5	profile (°C) at zone /2/3/4/5	e (°C) at zone	at zone					
50 85 115 130 155	50 85 115 130 155	50 85 115 130 155	85 115 130 155	115 130 155	130 155	155					
Screw Sneed Product Temperature (°C) at zone	Screw Speed Product Temperature (°C) at zone	Product Temperature (°C) at zone	ct Temperature (°C) at zone	erature (°C) at zone	e (°C) at zone	at zone		Non-load	Load Torque	Die Pressure	Total dough
Reps (rpm) 1 3 4 Die	(rpm) 1 3 4 Die	1 3 4 Die	3 4 Die	3 4 Die	4 Die	Die		Torque (%)	(%)	(psi)	mass flow rate (kg/s)
1 100 51 34.00 125 125 153.7	100 51 34.00 125 125 153.7	51 34.00 125 125 153.7	34.00 125 125 153.7	125 125 153.7	125 153.7	153.7		12.65	34.00	250	0.000575
2 100 51 105 125 144 154.5	100 51 105 125 144 154.5	51 105 125 144 154.5	105 125 144 154.5	125 144 154.5	144 154.5	154.5		12.80	30.50	190	0.000575
1 150 51 106 126 126 157.7	150 51 106 126 126 157.7	51 106 126 126 157.7	106 126 126 157.7	126 126 157.7	126 157.7	157.7		13.35	36.20	260	0.000650
2 150 51 103 124 142 155.7	150 51 103 124 142 155.7	51 103 124 142 155.7	103 124 142 155.7	124 142 155.7	142 155.7	155.7		13.35	31.50	210	0.000650
1 200 49 106 121 121 158.0	200 49 106 121 121 158.0	49 106 121 121 158.0	106 121 121 158.0	121 121 158.0	121 158.0	158.0	_	13.85	35.00	260	0.000677
2 200 52 108 126 143 156.0	200 52 108 126 143 156.0	52 108 126 143 156.0	108 126 143 156.0	126 143 156.0	143 156.0	156.0		13.90	32.00	240	0.000677
1 250 49 103 122 122 157.6	250 49 103 122 122 157.6	49 103 122 122 157.6	103 122 122 157.6	122 122 157.6	122 157.6	157.6	_	14.20	33.00	170	0.000721
2 250 50 107 125 142 155.0	250 50 107 125 142 155.0	50 107 125 142 155.0	107 125 142 155.0	125 142 155.0	142 155.0	155.0		14.30	33.00	280	0.000721
1 300 49 102 118 118 153.0	300 49 102 118 118 153.0	49 102 118 118 153.0	102 118 118 153.0	118 118 153.0	118 153.0	153.0		14.50	33.80	390	0.000784
2 300 52 108 120 137 156.0	300 52 108 120 137 156.0	52 108 120 137 156.0	108 120 137 156.0	120 137 156.0	137 156.0	156.0		14.60	41.50	210	0.000784

SME (kJ/kg)	161.9	134.3	230.4	183.0	273.2	233.7	285.7	283.5	322.6	451.6
Shear history (dimensionless)	6385.5	5495.2	9551.3	7074.1	11059.0	11216.1	11704.0	11732.2	10967.1	12243.2
Average shear rate (1/s)	35.1	32.5	57.6	51.0	77.1	77.5	98.2	98.3	118.7	122.4
Degree of fill	0.74	0.68	0.76	0.63	0.68	0.69	0.60	0.61	0.51	0.55
Mean residence time (s)	182.1	169.1	165.8	138.6	143.4	144.8	119.2	119.4	92.4	100.0
Screw Speed	100	100	150	150	200	200	250	250	300	300
Reps	1	2	1	2	1	2	1	2	1	2
Condition	la		1b		lc		1d		le	

Table 4.B.2. Calculated data for extrusion at condition 1 at constant degree of fill

Appendix 4.C. Condition 2 extrusion data

Table 4.C.1. Processing data for extrusion at condition 2a-e die temperature at constant degree of fill (varying feed rate)

)						•)	
			Tem	peratu	re prof.	ile (°C)	at zone				
					1/2/3/	4/5					
			50	80	110	145	165				
		Scrain Sneed	Prod	uct Tei	nperati	ure (°C)	at zone	Non-load	I ond Tornia	Dia Dracenna	Total dough
Condition	Reps	(udu)	4	2	ŝ	4	Die	Torque (%)	(%)	(psi)	mass flow rate (kg/s)
2a	1	100	53	98	123	150	162.0	13.00	47.60	220	0.000575
	2	100	54	97	114	150	162.5	12.75	39.90	270	0.000575
2b	1	150	53	66	124	147	163.5	13.40	46.90	240	0.000650
	2	150	53	96	118	149	162.6	13.15	42.30	250	0.000650
2c	1	200	53	100	127	148	165.8	14.00	46.00	200	0.000677
	2	200	53	106	121	148	162.6	13.70	37.80	230	0.000677
2d	1	250	53	100	129	146	164.5	14.50	40.80	170	0.000721
	2	250	53	103	122	150	162.2	13.95	34.90	230	0.000721
2e	1	300	54	103	129	143	164.0	14.80	48.10	210	0.000784
	2	300	55	104	124	148	162.7	14.35	36.20	150	0.000784

SME (kJ/kg)	263.4	206.1	338.6	294.4	414.5	311.7	400.1	318.1	559.3	366.9
Shear history (dimensionless)	5509.4	4381.7	6750.8	6771.9	8771.4	9069.2	11670.0	10287.0	11462.6	11358.2
Average shear rate (1/s)	32.5	28.9	50.0	50.1	71.3	72.2	98.1	94.5	120.2	119.9
Degree of fill	0.69	0.61	0.62	0.62	0.59	0.60	0.60	0.55	0.53	0.52
Mean residence time (s)	169.4	151.7	135.0	135.2	123.0	125.6	118.9	108.9	95.4	94.7
Screw Speed (rpm)	100	100	150	150	200	200	250	250	300	300
Reps	1	2	1	2	1	2	1	2	1	2
Cond	2a		2b		2c		2d		2e	

Table 4.C.2. Calculated data for extrusion at condition 2a-e at constant degree of fill

		Total dough	mass flow rate (kg/s)	0.000661	0.000661	0.000677	0.000677	0.000703	0.000703	0.000741	0.000741
		Die	Pressure (psi)	320	280	200	230	150	160	120	120
			Load Torque (%)	55.50	44.30	46.00	37.80	37.50	31.80	35.00	28.00
			Non-load Torque (%)	14.00	13.70	14.00	13.70	14.00	13.70	14.00	13.70
) at zone	165) at zone	Die	166.0	165.8	165.8	162.6	162.0	161.4	163.0	162.1
ile (°C) '4/5	145	ure (°C	4	149	150	148	148	149	149	149	147
re prof 1/2/3/	110	nperat	3	127	123	127	121	127	121	127	113
peratu	80	uct Tei	2	101	103	100	106	110	105	99	66
Tem	50	Prod	1	54	53	53	53	54	53	53	53
		Moisture	content, wb/db (%)	23 / 29.8	23 / 29.8	25 / 33.3	25 / 33.3	28 / 38.8	28 / 38.8	32 /47.1	32 /47.1
			Screw speed (rpm)	200	200	200	200	200	200	200	200
			Condition	2f		2c		2g		2h	

Table 4.C.3 Processing data for extrusion at varying moisture content (constant fill)

Condition	Screw Speed (rpm)	Moisture content, wb/db (%)	Mean residence time (s)	Degree of fill	Average shear rate (1/s)	Shear history (dimensionless)	SME (kJ/kg)
2f	200	23 / 29.8	120.9	0.58	70.6	8543.0	550.2
	200	23 / 29.8	122.0	0.58	71.0	8666.1	405.4
2c	200	25 / 33.3	123.0	0.59	71.3	8771.4	414.5
	200	25 / 33.3	125.6	0.60	72.2	9069.2	311.7
2g	200	28 / 38.8	115.4	0.55	68.6	7916.5	293.2
	200	28 / 38.8	119.0	0.57	6.69	8319.6	225.5
2h	200	32 / 47.1	112.7	0.54	67.5	7608.6	248.6
	200	32 / 47.1	112.7	0.54	67.5	7608.2	169.1

Table 4.C.4. Calculated data for extrusion at varying moisture content (constant degree of fill)

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Appendix

		Ba	rrel set a	tempers t zone 1,	ature prc /2/3/4/5	ofile (°C)				
		50	80	110	145	165				
		Pr	oduct T	emperat	ture (°C) at zone				
Condition	Screw Speed (rpm)	1	7	ю	4	Die	Non-load Torque (%)	Load Torque (%)	Die Pressure (psi)	Total dough ma flow rate (kg/s
3a	100	52	97	122	149	162.4	13.25	46.50	240	0.000715
	100	52	100	122	150	161.2	12.90	30.80	190	0.000715
3b	150	52	98	123	150	161.0	13.85	43.00	220	0.000715
	150	52	97	121	149	162.0	13.50	34.00	150	0.000715
3c	200	53	66	125	150	159.4	14.35	37.50	150	0.000715
	200	52	66	125	149	160.3	14.00	37.00	170	0.000715
3d	250	53	66	126	149	160.5	14.55	37.20	130	0.000715
	250	53	98	127	150	162.4	14.30	37.40	160	0.000715
3e	300	52	66	129	153	162.7	14.85	34.80	120	0.000715
	300	54	66	129	152	164.0	14.50	36.60	140	0.000715

Table 4.D.1. Processing data for extrusion at condition 3 at varying degree of fill (constant feed rate)

the second s	_	_	_	_	-	_	_	_	_	_
SME (kJ/kg)	203.1	109.0	267.7	188.3	283.9	281.9	347.5	354.3	367.4	407.0
Shear history (dimensionless)	5352.5	6778.2	6429.5	8138.6	8991.1	8545.7	9512.9	11198.9	12385.8	10862.0
Average shear rate (1/s)	35.8	40.2	51.0	56.2	73.4	72.1	91.8	96.8	119.7	109.0
Degree of fill	0.75	0.85	0.63	0.73	0.62	0.60	0.52	0.58	0.52	0.43
Mean residence time (s)	149.5	168.5	126.0	144.8	122.5	118.6	103.7	115.7	103.5	7.66
Screw Speed (rpm)	100	100	150	150	200	200	250	250	300	300
Condition		3a		3b		3c		3d		3e

Table 4.D.2. Calculated data for extrusion at condition 3 at varying degree of fill

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