# EFFECTS OF COMPOSITIONAL VARIABLES ON FOULING BEHAVIOR OF THIN STILLAGE

BY

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THESIS

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## ABSTRACT

In the US, ethanol is produced primarily from corn. There are two major commercial processes: corn wet milling (CWM) and dry grind corn (DGC). The DGC industry has grown and made 86% of corn ethanol by the end of 2008. During DGC processing, after distillation, the remaining nonfermentable material known as whole stillage is centrifuged to produce two processing streams; wet cake (30 to 35% solids) and thin stillage (5 to 10% solids). Thin stillage is concentrated to 25 to 30% solids in multi effect evaporators. The presence of fouling in evaporators can increase energy consumption as well as capital and labor costs.

Limited studies have been conducted on fouling of corn ethanol processing. An annular fouling probe was used to evaluate compositional variables on fouling behavior of DGC thin stillage. The objectives of this study were to evaluate effects of starch and sucrose solids in fouling of thin stillage evaporators and to assess effects of wet cake in fouling of thin stillage evaporators.

Four 100 L batches of thin stillage were collected from a dry grind plant and total solids concentrations were measured. Thin stillage was diluted with tap water so thin stillage plus starch or sucrose was 7% total solids. Fisher's least significant difference method was used to detect differences among treatments for maximum fouling resistance and fouling rates after 25, 60, 120, 150 and 300 min ($P < 0.5$). Adding 2% starch to thin stillage increased fouling rates compared with adding 2% sucrose or thin stillage alone. The treatment with additional sucrose showed similar fouling behavior compared to raw thin stillage with 7% total solids. Batches of thin stillage (60 L) were collected to investigate effects of wet cake solids on fouling behavior. Adding 2% wet cake to thin stillage increased the fouling rates compared to thin stillage with 7% total solids. Fouling resistances increased with starch addition, as well as with wet cake addition, at equal total solids contents. Insoluble starch addition had larger effects than soluble sucrose addition. Sucrose alone did not cause increased rapid fouling.

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# CHAPTER 1. INTRODUCTION

## 1.1 Background

The US Clean Air Act dictated that certain areas of the country use reformulated gasoline containing 2% oxygen (Moran et al 2000). Initially, two additives to increase oxygen levels in gasoline were used: ethanol and methyltertiary butyl ether (MTBE), a petroleum derivative. However, MTBE was found in groundwater and due to MTBE's carcinogenic properties, it was phased out. As a result, the demand for fuel ethanol has grown. According to the Renewable Fuels Association, at the end of 2011, the ethanol industry comprised 209 plants in 29 states with total nameplate capacity of 14.7 billion gal (RFA 2012).

Ethanol can be produced from several sources such as cane juice, cane molasses, sorghum, barley and corn. In the US, ethanol is produced primarily from corn. There are two major commercial processes: corn wet milling (CWM) and dry grind corn (DGC) processing. Each method has different equipment, technologies, processing steps, coproducts and volumes of ethanol produced. CWM produces several coproducts but the facilities involve considerable capital investment to build. DGC facilities require lower capital investment and produce one primary coproduct, distillers dried grains with soluble (DDGS). The DGC industry has grown during the last several years as demand for fuel ethanol has increased. By the end of 2008, 86% of corn ethanol was produced commercially using the dry grind process (Mueller 2010).

DDGS is sold as an animal food, primarily for ruminants. During DGC processing, after distillation, the remaining nonfermentable material is known as whole stillage which includes unconverted starch, protein, fiber, oil and minerals. Whole stillage is centrifuged to produce two processing streams; wet cake (30 to 35% solids) and thin stillage (5 to 10% solids). Thin stillage is concentrated from 5 to 10 % solids to 25 to 30% solids in multieffect evaporators (Singh et al 1999). Evaporation and drying operations account for 40 to 45% of thermal energy and 30 to 40% of electrical energy recovered from distillation used in a DGC facility (Meredith 2003). Many approaches have been made to decrease the cost of evaporation. One of them would be to reduce fouling in the evaporators.

Fouling generally is defined as the formation of unwanted materials on the surfaces of processing equipment such as evaporators, which can deteriorate the capacity of the surface to transfer heat under the conditions for which it was designed (Awad 2011; Chen et al 2004).

Fouling has been recognized as a universal problem (Bott 2001; Kuppan 2000; McDonald and Magande 2012) in design and operations. It affects the operation of heat transfer equipment in two ways. First, because the fouling layer has a lower thermal conductivity, resistance to heat transfer is increased. Second, deposits reduce the cross sectional area triggering a greater pressure drop across the apparatus. Although poorly understood, fouling of heat transfer surfaces has been treated as one the most important unresolved problems in heat transfer (Bott 2001).

Fouling of heat transfer surfaces occurs in most chemical and process industries, including oil refineries, desalination, food processing, dairy industries, power generation and energy recovery (Awad 2011). The wide range of process streams and operating environment present in industry make it impossible to classify fouling situations into one single type. In many situations, there is more than one fouling mechanism present; therefore, the fouling problem becomes more complex. The generally favored scheme for classification of heat transfer fouling is based on physical and chemical processes (Awad 2011). It is convenient to classify fouling types into six groups (Table 1.1).

**Table. 1.1 Fouling types (Awad 2011).**

| Types | Definition |
|---|---|
| Particulate | Deposition of suspended particles in the heat exchanger fluids. |
| Crystallization | Deposition of dissolved salts from saturated solutions, onto the heat transfer surface due to solubility changes. |
| Chemical Reaction | Chemical reaction between reactants in the flowing fluid; the surface materials itself is not a reactant. |
| Corrosion | Chemical or electrochemical reaction between the heat transfer surface itself and the fluid steam. |
| Biological | Attachment and growth of microorganisms and their products on the heat transfer surface. |
| Freezing | Formation of ice on a heat transfer surface during chilled water production or cooling of moist air. |

Due to the high cost of fouling, attempts have been made to estimate the overall costs of fouling in different industries and countries. According to Bott (2001) and Awad (2011), fouling related costs can be categorized into four key areas, including higher capital expenditures for

excess surface area (10 to 50%), energy losses due to the decrease in thermal efficiency and increase in the pressure drop, production costs during plant shutdowns for fouling cleaning and costs with use of antifoulants to clean equipment. Total heat exchanger fouling is about 0.25% of the Gross National Product (GNP) costs for highly industrialized countries (Pritchard 1988). The annual costs of fouling in some countries was based on an estimation from 1992 (Awad 2011).

**Table 1.2. Annual costs of fouling (Awad 2011).**

| Country | Million (US $) | Fouling Cost (% of GNP) |
|---|---|---|
| US | 14175 | 0.25 |
| UK | 2500 | 0.25 |
| Germany | 4875 | 0.25 |
| France | 2400 | 0.25 |
| Japan | 10000 | 0.25 |
| Australia | 463 | 0.15 |
| New Zealand | 64.5 | 0.15 |

Fouling is widespread in food and bioprocessing (Agbisit et al 2003; Arora et al 2010). Molecules such as proteins, carbohydrates and lipids are heat sensitive and often aggregate and attach to heated surfaces in heat transfer equipment. Bioprocessing fouling studies have been published extensively for dairy processing. However, limited studies have been conducted in the area of corn ethanol processing, particularly with respect to compositional variables on fouling.

## 1.2 Objectives

The purpose of this study was to evaluate DGC thin stillage fouling behavior. Specific objectives were to:

1. Evaluate effects of starch and sucrose solids in fouling of thin stillage evaporators.
2. Assess effects of wet cake in fouling of thin stillage evaporators.
3. Determine effects of aging on fouling in thin stillage and measure fouling variability among batches.

# CHAPTER 2. LITERATURE REVIEW

## 2.1 Dry Grind Process and Wet Milling Process

There are two major commercial processes for converting corn into ethanol: corn wet milling (CWM) and dry grind corn (DGC) processing. Each method has different equipment, technologies, processing steps, coproducts and volume of ethanol produced. Corn wet milling involves isolating and recovering starch from corn. Five processing steps are used to separate starch from germ, fiber and protein in the stream: steeping, germ recovery, fiber recovery, protein recovery and starch washing (Rausch and Belyea 2006). After these steps, a 99.5% pure starch product is achieved (Fig 2.1). To produce ethanol, starch is liquefied and saccharified by enzymes and fermented by yeast.

The corn wet milling process begins with corn that has been cleaned of foreign material. The first step is called steeping, where the kernels are soaked in tanks of sulfurous acid water (2000 ppm S as $SO_2$) at 50 to 55°C for 24 to 48 hr (Rausch and Belyea 2006). The water drawn off from the steeping step contains 5 to 10 % solids (light steepwater) and must be evaporated to 45 to 50% solids (heavy steepwater) to produce corn gluten feed (Fig 2.1). The slurry generated by grinding following steeping is designed to separate germ and fiber from other components. The germ is washed and dried to produce dried germ. Fiber is washed, dried, combined with steepwater to produce corn gluten feed which is used as an ingredient in animal diets. A centrifuge is used to separate gluten from starch. Gluten protein is concentrated using a gluten thickener centrifuge and dewatered using vacuum belt filter and a dryer to produce corn gluten meal (Fig 2.1). Two main products, ethanol and sweeteners, are made from processing starch.

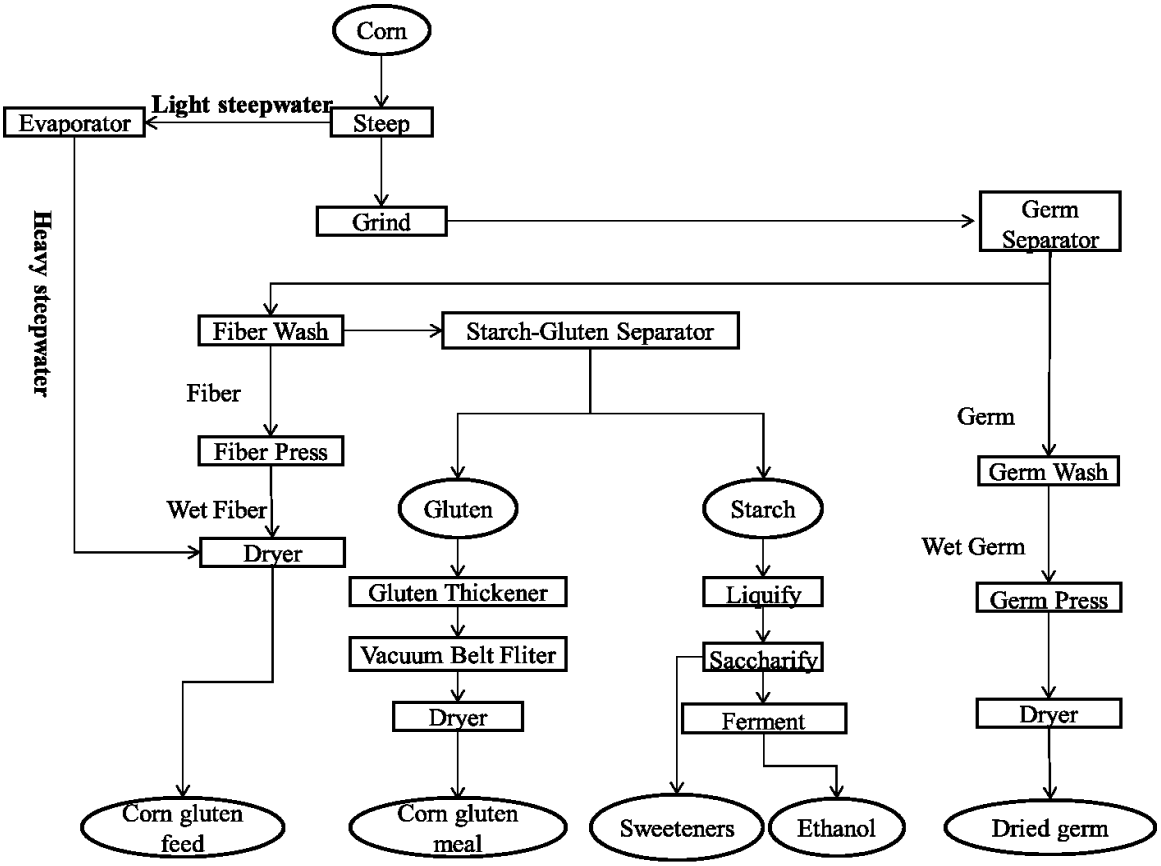


**Figure 2.1. Corn wet milling process diagram.**

Dry grind corn processing involves smaller capital investment. After corn is received at the facility, mills are used to grind kernels into small particles to facilitate water penetration during cooking; hammer mills and roller mills are used (Rausch and Belyea 2006). Those particles are mixed with water to form slurry which will be cooked, liquefied, saccharified and fermented.

Corn endosperm starch cannot be utilized directly by yeast, so it must be broken down into simple sugars prior to fermentation. Cooking is used to gelatinize starch for maximum enzyme activity. Systems employed for cooking and liquefaction are batch and continuous. Batch systems consist of a tank that combines cooking and enzyme liquefaction in one tank. Continuous systems separate this process over several unit operations. Continuous cooking is generally more energy efficient and, if designed and operated properly, can yield up to 8% more ethanol per bushel of grain (Butzen 2006). Therefore, most DGC facilities use continuous cooking systems (Lyons 2003). Ground corn mixed with water and backset thin stillage from

post fermentation to produce slurry. Slurry enters a jet cooker where the temperature is raised to 120°C to cause gelatinization. Gelatinization breaks the structure of starch by hydrolyzing α-1,4 glucosidic bonds to produce dextrin. Slurry will be cooled to 80 to 90°C before it enters a liquefaction tank. Enzyme α-amylase is employed to break down the starch molecules and reduce viscosity in the liquefaction tank (Wilkins et al 2006b).

Simultaneous saccharification and fermentation (SSF) has achieved yields over 2.75 gal of ethanol per bu of corn in some facilites (Rendleman and Shapouri 2007). Adding glucoamylase enzymes at a lower temperature produces smaller fermentable sugars such as glucose; this step is called saccharification. After saccharification, slurry will produce ethanol in fermenters where yeast *Saccharomyces cerevisiae* is added. The SSF process takes 50 to 60 hr. The goal is conversion of glucose to ethanol (Rausch and Belyea 2006). The carbon dioxide ($CO_2$) released during fermentation often is captured and used in production carbonated soft drinks, beverages, dry ice and other industrial processes (Bothast and Schlicher 2005).

At fermentation completion, the resulting material (beer) consists of ethanol, water and solids that were not fermented. Beer is released to atmospheric pressure conditions to separate the $CO_2$ and transferred to a holding tank called a beer well. Beer is fed to a recovery system consisting of two distillation columns and a stripping column. The water-ethanol stream is transferred to a molecular sieve, where remaining water is removed using adsorption technology. Purified ethanol is mixed with a small amount of gasoline (2%) to produce fuel grade ethanol.

Distillation is the process of recovering the ethanol from the solids and water in the mash. Alcohol turns to vapor at 78°C and water at 100°C (at sea level). This difference allows water to be separated from the ethanol by heating in a distillation column. Distillation can produce 95% (190 proof) ethanol (Katzen et al 1999).

The remaining water and solids after distillation are referred to as whole stillage which includes fiber, oil, and protein as well as starch. This whole stillage is centrifuged to separate the liquid (thin stillage) from the solid fragments of the kernel (wet cake or distillers grains). Some of the thin stillage (backset) is recycled to the beginning of the dry grind process to conserve the water used by the facility. The remaining thin stillage passes through evaporators to remove a portion of the water to produce syrup or distillers solubles. After evaporation, syrup is mixed with wet cake to create an animal food ingredient known as wet distillers grains with solubles (WDGS) containing 65% moisture. To increase shelf life and lower transportation costs, WDGS

usually is dried to 10 to 12% moisture to produce a coproduct known as distillers dried grains with solubles (DDGS). This coproduct can be used as an ingredient in livestock, poultry and fish diets.

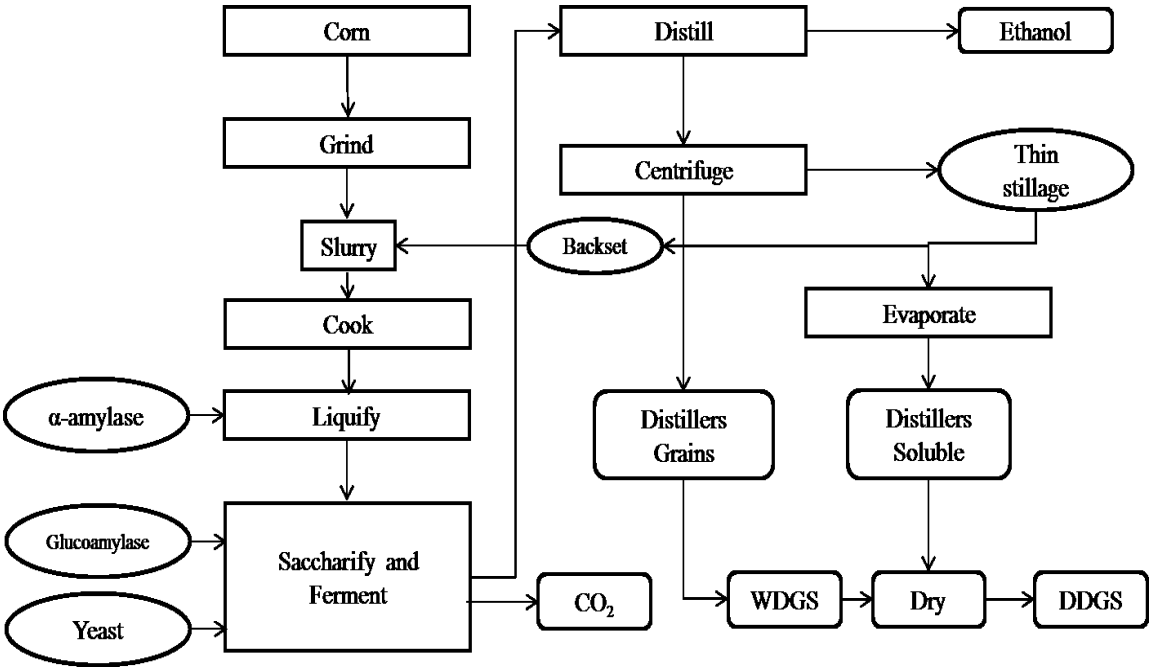


**Figure 2.2. Dry grind corn process diagram.**

## 2.2 Heat Transfer Fouling

### 2.2.1 Fouling Background

In 1959, D. Q. Kern first predicted the growth of fouling deposits on a heat transfer surface (Kern and Seaton 1959). In the early 1950s, the Standards of the Tubular Exchangers Manufacturers Association (TEMA) published the compilation of fouling resistances. The Kern and TEMA models still form the basis for the design of most heat exchangers worldwide (Macchietto et al 2011). Chenoweth (1988) reviewed the TEMA model and made small modifications.

Costs due to fouling can place a burden on industry and economy. Garret (1985) reported more than 90% of industrial heat exchangers suffer from fouling problems. The costs of heat exchanger fouling due to oversizing of equipment, maintenance, fluid treatment, additional hardware, additional energy consumption and loss of production have been estimated to be 0.25%

of the gross domestic product (GDP) of industrialized countries (Garrett-Price et al 1985; Pritchard 1988; Steinhagen et al 1993). In addition, the disposals of cleaning chemicals have contributed to the worldwide concern in heat transfer fouling.

However, fouling of heat exchangers is one of the least understood problems in processing industries. There was no conference focused specifically on heat exchanger fouling until 1979 (Müller-Steinhagen 2011). There have been fouling studies such as Butterworth (2002) and Macchietto (2011) for crude oil, Enrique (2010) and Pugh (2005) for seawater, Jenner et all (1998) for freshwater, Bansal and Chen (2006) for milk and Blanpain and Lalande (1997) for beer.

In the food industry, reduced product quality, safety and plant efficiency can be caused by fouling. Monitoring fouling and cleaning requires high demands for the measuring and analyzing system. Therefore, methods were developed to detect and monitor fouling in heat exchangers (Wallhäußer et al 2012). In most cases, methods to monitor fouling can be divided into three categories: experimental, numerical and computational. Experimental methods include measuring pressure drop, temperature, electrical parameters and acoustic parameters.

Pressure drop uses pressure difference between inlet and outlet (Riverol and Napolitano 2005). Fouling resistance is based on temperature change, mass flow rate and thermal conductivity of the heating medium, and the fouling layer. Therefore, knowing the temperature changes of inlet and outlet, the parameters of flow, medium and fouling layer, fouling resistance can be calculated (Nema and Datta 2005). For electrical parameters method, electrical and thermal resistance were measured to determine fouling (Chen et al 2004). Acoustic parameters change when fouling occurs and can be measured when one transducer is used as a transmitter, and one is used as receiver (Withers 1994). Even though a variety of methods have used to determine fouling, many fouling related problems still remain unsolved.

### 2.2.2 Fouling in the Dairy Industry

Fouling and cleaning of dairy process equipment has been attributed to about 80% of total production costs in the dairy industry (Van Asselt et al 2005). Due to this, many researchers have investigated mechanisms of fouling in dairy processing. Bansal and Chen (2006) reviewed publications in dairy processing fouling and concluded that milk fouling depends on five

categories: milk composition, operating conditions in heat exchangers, type and characteristics of heat exchangers, presence of microorganisms and location of fouling (Bansal and Chen 2006).

Milk composition is the most important factor in dairy fouling. Fouling can be classified into two types, known as Type A and Type B. Type A happens at temperatures between 75 to110°C and the deposited milk film consisted of 50 to 70% protein, 30 to 40% minerals and 4 to 8% fat. Type B takes place at temperatures above 110°C and deposits consist of 70 to 80% minerals (mainly calcium phosphate), 15 to 20% protein and 4 to 8% fat. According to Bylund (2003), even though whey proteins constitute only 5% of the total milk solids, they cause 50% of the fouling deposits in type A fouling. Moreover, there are only two major whey proteins, β-Lactoglobulin (β-Lg) and α-lactalbumin (α-La) in milk to cause fouling; the first one is dominant with high heat sensitivity (Bylund 1995). As pH decreased, the heat stability of milk proteins decreased (Xiong 1992) (Skudder et al 1986), but the concentration of ionic calcium increased (Lewis and Heppell 2000).

Operating conditions, such as air content, turbulence and temperature, can influence milk fouling. Air bubbles formed on the heat transfer surface in milk can enhance fouling (Burton 1968). With increasing velocity or turbulence, fouling has been shown to decrease (Bansal and Chen 2006; Belmar-Beiny and Fryer 1993; Changani et al 1997; Paterson and Fryer 1988; Santos et al 2004).

Compared to air content and turbulence, temperature of milk in heat exchanger is the single most important operating factor influencing fouling. If surface reactions control fouling rate, fouling will depend on bulk fluid temperature (Belmar-Beiny and Fryer 1993). Increasing the temperature cause increased fouling. At temperatures greater than 110°C, the nature of fouling changed from type A to type B (Burton 1968)In initiating fouling, surface temperature was found to be more important than bulk temperature due to the fact that no fouling was observed when the surface temperature was less than 68°C, even though the bulk temperature was up to 84°C (Chen and Bala 1998).

The variation in Reynolds number and average boundary layer thickness had no effect on the milk fouling rate. However, it was not the same case in corn processes (Delplace et al 1997). Belmar-Beiny et al (1993) found the amount of whey protein fouling deposited in a tubular fouling apparatus decreased with increasing Re (Reynolds number). (Karabelas et al 1997) found that deposition decreased more when Re increased from 1,800 to 4,000 than when

Re increased from 4,000 to 9,000. They observed an asymptotic effect of increased flow velocity on heat transfer resistance.

Even though there are various types of heat exchangers on the market, plate heat exchangers are used in dairy most commonly because they offer higher turbulence and lower surface temperature. Microwave heating also resulted in less fouling; however, microwave system's short lifespan can raise the product cost (Metaxas and Meredith 1983). Ohmic heating exchanger, which was used widely in the early 21$^{th}$ century, let an electrical current go through milk to heat. Information about this kind of heat exchangers is limited (Bansal and Chen 2006).

According to Bott (2001), biofouling happens with two mechanisms: deposition of microorganisms directly on the heat transfer surfaces and attachment of microorganisms on the deposit layer. Either way affects the product quality and influences the fouling process (Flint et al 1997).

Even though the mechanism of fouling in the dairy industry is not fully understood, it is believed that fouling is decided by the reaction of proteins in general; the mass transfer of proteins between the fluid and heat transfer surface also plays an important role (Bansal and Chen 2006). Fouling, however, can be reduced by choosing proper thermal and hydraulic conditions such as increasing flow rate and decreasing temperature. Microwave and ohmic heating also result in less fouling.

Although there are many differences between the composition of milk and thin stillage, it is helpful to understand the factors which contribute to milk fouling. In corn process fouling, no study has been published to show how much fouling protein can cause and which kind of protein is sensitive to heat.

### 2.2.3 Fouling in the Dry Grind Industry

Heat transfer fouling is a phenomenon of deposition of materials on heated surfaces. As a common problem in bioprocess industries, fouling in evaporators or tubes can create problems such as heat transfer losses, deposition corrosion, pressure losses and environmental impact. Fouling brings higher maintenance costs from removing the fouling deposits with chemicals and replacing equipment damaged or corroded by fouling. (Visser and Jeurnink 1997) estimated total fouling cost in the dairy industry in the Netherlands exceeding $40 million/year. In the US, fouling costs exceeded $104 million/year in the dairy industry (Singh 1991). Keeping heat

transfer surfaces clean is important for reliable and efficient energy recovery (Agbisit et al 2003; Arora et al 2010; Changani et al 1997; Singh et al 1999; Wilkins et al 2006a; Wilkins et al 2006b).

There has been work on the fouling of heat transfer in fluid dairy processing (Burton 1968; Georgiadis et al 1998). There are limited studies regarding heat transfer fouling of thin stillage evaporator corn processing. Singh et al (1999) found that thin stillage from corn wet milling fouled at a rate 67% less than DG thin stillage. They suggested this was due to higher oil content in DGC thin stillage than CWM thin stillage.

Agbisit et al (2003) concluded that fouling rates for raw light steepwater (LSW) was 5.3 times higher than membrane filtered light steepwater (FSW); maximum fouling resistances of LSW were 10 times larger than FSW. They found that microfiltration (0.1 micron nominal pore size) of CWM steep water reduced fouling rate by 80%.

Influence of thin stillage pH on deposit concentration, fouling rate and induction period was studied by Wilkins et al (2006). The pH that resulted in the lowest fouling rate and longest induction period was between pH 4.0 and 4.5. At pH 3.5, it had a shorter induction period and a greater initial fouling rate than did thin stillage adjusted to pH 4.0 and 4.5. Also, as pH increased, protein contents of fouling deposits decreased and ash contents of fouling deposits increased. Adjusting thin stillage pH to 4.0 or 4.5 resulted in reduced fouling as opposed to thin stillage pH 3.5.

Arora et al (2010) investigated fouling characteristics of thin stillage (7.0% total solids) from a dry grind facility, filtered thin stillage (FTS, 3.5% total solids) and diluted thin stillage (DTS, 3.5% total solids). At 10 hr of fouling, a 50% reduction in fouling resistance was observed when solids level decreased from 7.2 to 3.5%, with no change in composition. Microfiltration of thin stillage resulted in a 90% reduction of the fouling resistance value for the same reduction in total solids content and at the same time interval.

Wilkins et al (2006) found that as dry solids concentration of thin stillage increased, the fouling rate increased. Compared with Re = 880, Re = 400 had smaller fouling rates and shorter induction periods. Only two Re levels were studied in this research. The optimal Re on fouling measurements observed with thin stillage was not reported.

There are limited published data studying the causes of increased evaporator fouling in corn processing. The effects of total solids content, flow rate and Re have not been quantified fully.

### 2.2.4 Theory of the Annular Fouling Probe

The annular fouling probe for measuring fouling resistance was used in previous work (Agbisit et al 2003; Arora et al 2010; Singh et al 1999; Wilkins et al 2006a; Wilkins et al 2006b). Annular fouling probes have been operated to measure fouling in other applications as well as corn ethanol processing, including autoxidation reactions (Panchal and Watkinson 1993; Wilson and Watkinson 1996), olefin-kerosene (Asomaning and Watkinson 1992) and styrene polymerization (Fetissoff et al 1982). Also, there are other common types of equipment employed to measure heat transfer fouling in addition to annular probes, such as cylindrical test sections and pilot scale heat exchangers (Chenoweth 1988).

The probe consists of a metal rod heated by electrical current or a heating medium such as water or oil. Outside the rod is a cylindrical housing (Fig 3.1). Test fluid flowing through the space between the stainless steel rod and cylindrical housing will foul on the surface of the rod. Fouling resistance can be calculated by monitoring outer wall temperature.

The fouling on heat transfer equipment depends many factors which include, but are not limited to, the shape and material of the equipment, flow rate, surface temperature, and flow composition (Knudsen 1981). In most cases, fouling resistance ($R_f$) is used to express the fouling behavior and represent the fouling effect (Bohnet 1987).

$R_f$ is calculated by measuring the difference of overall heat transfer coefficients between unfouled and fouled probe conditions (Agbisit et al 2003; Arora et al 2010; Singh et al 1999; Wilkins et al 2006a).

$$R_f = \frac{1}{U_{fouled}} - \frac{1}{U_{unfouled}} \qquad (2.1)$$

Where $U_{unfouled}$ is the initial overall heat transfer coefficient for time t = 0 (clean surface). $U_{fouled}$ is the overall heat transfer coefficient of a fouled probe at time t.

$$U = \frac{Q}{A(T_s - T_b)} \quad (2.2)$$

Where Q is the power supplied to the system, $T_S$ is the rod surface temperature and $T_b$ is the bulk fluid temperature. Rod surface temperature ($T_S$) is determined by:

$$T_S = T_C - \frac{(X/R)Q}{A} \quad (2.3)$$

Where $T_C$ is the inner wall temperature measured by the obtaining the mean value of thermocouples, X/R is the distance of thermocouples from the surface divided by thermal conductivity of the probe metal. It is determined using a calibration procedure described by Fischer et al (1975) and A is the total heated surface area of the probe.

The limitation of annular fouling probes include relatively small amounts of deposit that can be collected for further analysis; the probe can be kept at constant power but not constant temperature; the probe cannot be used to measure pressure drops or mass deposition rates. However, annular fouling probes are small, transportable, easy to operate, require small batches of fluid to operate, and generate precise data (Chenoweth 1988; Wilkins et al 2006a). Therefore, they have been used widely in dairy and other food processing industries (Wilkins et al 2006a).

**Table 2.1. Parameters used in other fouling studies.**

| | (Singh et al 1999) | (Agbisit et al 2003) | (Wilkins et al 2006a) | (Wilkins et al 2006b) | (Arora et al 2010) |
|---|---|---|---|---|---|
| **Source of Material** | Corn wet-milling plant and a DG processing facility. | Corn wet-milling facility | DG processing facility | DG processing facility | DG processing facility |
| **Storage Temp** | 4°C | 2°C | 4°C | 4°C | 4°C |
| **Number of batches** | One 227 L batch | One 200L batch<br>One 120L batch | Four 120 L batches | Three 90 L batches | Two 160L batches |
| **Measure Total solids Content** | Commercial analytical laboratory (Silliker Laboratories Group, Cedar Rapids, IA). | Two stage oven method (Approved Methods 44-18 and 33-19, AACC 2000) | Two stage oven method (Approved Methods 44-18 and 33-19, AACC 2000) | Two stage oven method (Approved Methods 44-18 and 33-19, AACC 2000) | Two stage oven method (Approved Methods 44-18 and 33-19, AACC 2000) |
| **Equipment** | Annular fouling probe (Heat Transfer Research, Dallas, TX) | Annular fouling probe (Heat Transfer Research, Dallas, TX) | Annular fouling probe (Heat Transfer Research, Dallas, TX) | Annular fouling probe (Heat Transfer Research, Dallas, TX) | Annular fouling probe (Heat Transfer Research, Dallas, TX) |

**Table 2.2. Operating conditions used in other fouling studies.**

| | (Agbisit et al 2003) | (Wilkins et al 2006a) | (Wilkins et al 2006b) | (Arora et al 2010) |
|---|---|---|---|---|
| **$T_b$** | 40 ± 1°C | 40 ± 2°C | 40 ± 2°C | 60 ± 1°C |
| **Power** | 947 ± 16 W | constant | constant | 970 ± 15 W |
| **A** | 0.0034 $m^2$ | 0.0034 $m^2$ | 0.0034 $m^2$ | 0.0034 $m^2$ |
| **x/k** | Calibration procedure described by Fischer et al. (1975). | Calibration procedure described by Fischer et al. (1975). | Calibration procedure described by Fischer et al. (1975). | Calibration procedure described by Fischer et al. (1975). |
| **$T_c$ initial** | 99 ± 1°C | 100°C | 100°C | 100°C |
| **$T_c$ max** | 200°C | 200°C | 200°C | 200°C |
| **Flow Rate** | 13 ± 0.5 l/min | 5.2 m/sec | 5.2 m/sec | |

# CHAPTER 3. EFFECTS OF THIN STILLAGE COMPOSITION ON FOULING BEHAVIOR

## 3.1 Introduction

In the US, fuel ethanol is produced primarily from corn. During DGC processing, after distillation, the remaining nonfermentable material is known as whole stillage which includes starch, protein, fiber, oil, minerals and yeast. Whole stillage is centrifuged to produce two processing streams; wet cake (30 to 35% solids) and thin stillage (5 to 10% solids) (Wilkins et al 2006a). Even though the thin stillage contains 90% water, it cannot be discharged into lakes and rivers because of the organic content (Arora et al 2010). Thin stillage consists of soluble proteins, fat, fiber and minerals, which will deposit on heat transfer surface to increase heat transfer resistance (Arora et al 2009). The presence of fouling in evaporators will require increased energy consumption as well as capital and labor costs. Therefore, it is important to understand which factor caused fouling and develop new technology or methods to reduce the fouling in corn processing.

Thin stillage is concentrated from 5 to 10% solids to 25 to 30% solids in multieffect evaporators (Singh et al 1999). Evaporation and drying operations account for 40 to 45% of thermal energy and 30 to 40% of electrical energy used in a DGC facility (Meredith 2003). Fouling of heat transfer surfaces presents challenges to technology providers and plant operators in the dry grind industry such as energy lost, extra capital investment and more maintenance. Growth of deposits reduces evaporator capacity and performance of equipment to the point where it must be shut down and cleaned (Arora et al 2010). Cost of cleaning evaporators has led to investigation of the fouling phenomenon (Chenoweth 1988; Steinhagen et al 1993).

Fouling is a complex phenomenon and depends on several parameters. In 2006, Bansal and Chen found that evaporator fouling largely depended on the composition of input stream, which means in corn processing components of thin stillage can affect fouling. During ethanol production, processing steps are designed to convert granular starch to glucose, but a proportion of the starch is not converted, and causes nonfermented starch to pass into stillage. This affects DDGS composition and nutritional characteristics as well as evaporator performance. Therefore, in the dry grind process, changes in thin stillage composition such as starch and sugar may change fouling tendencies. Thin stillage and wet cake share some compounds such as proteins, fat, ash, cellulose and xylan (Kim et al 2008). During whole stillage centrifugation, wet grains

are separated from thin stillage. Therefore, it is important to study how wet grains can affect fouling behavior. The objectives were to: 1) evaluate effects of starch and sucrose solids in fouling of thin stillage evaporators and 2) assess effects of wet cake in fouling of thin stillage evaporators.

## 3.2 Materials and Methods

### 3.2.1 Experimental Equipment

The annular fouling probe for measuring fouling resistance used in other studies (Agbisit et al 2003; Arora et al 2010; Wilkins et al 2006a; Wilkins et al 2006b) had a stainless steel rod which contained a resistance heater and four thermocouples located near the heated surface to monitor surface temperatures. Among those four thermocouples, three of them were used to measure the probe wall interior temperature. The fourth one was connected to an electrical relay that cut off power to the probe above 170°C and was not used to gather data. Temperatures were recorded at 1 min intervals by a datalogger (OM-3000, Omega Engineering, Stamford, CT). Data were downloaded to computer though a card reader.

Surrounding the rod was a cylindrical housing. Fluid flowed through the annular space between the stainless steel rod and cylindrical housing (Fig 3.1). Fouling deposits from the probe surface resulted in increased heat transfer resistance, which resulted in increased temperature inside the probe. The change in heat transfer coefficient was calculated from the change in temperatures.

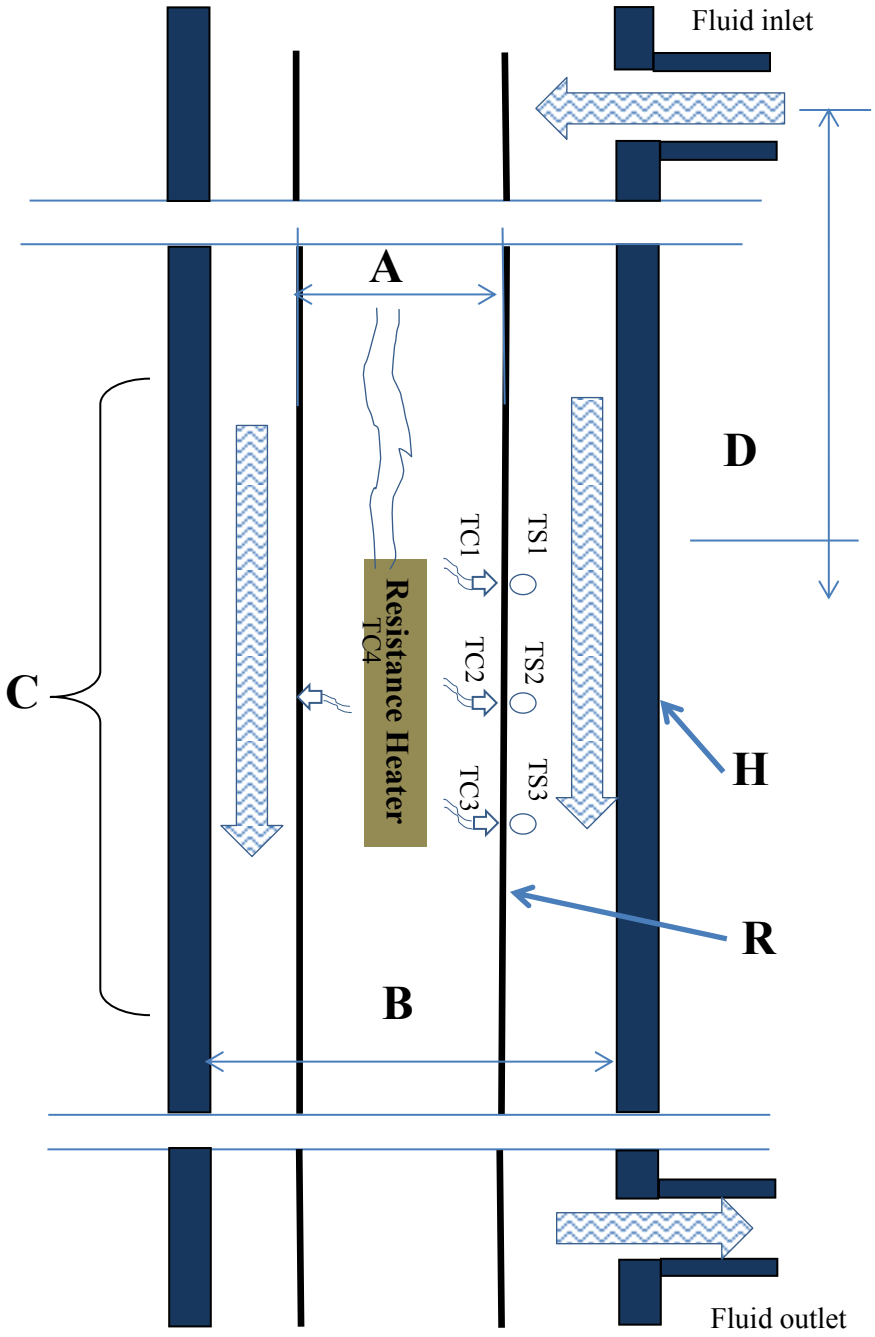


**Figure 3.1. Annular fouling probe. TC1-3: Temperature measured by thermocouples, TC4: Heater shut off control thermocouples, TS1-3: Heated probe surface temperature, H: Wall of housing, R: Rod.**

$R_f$ was calculated by measuring the difference of overall heat transfer coefficients between unfouled and fouled probe condition (Agbisit et al 2003; Arora et al 2010; Singh et al 1999; Wilkins et al 2006a).

$$R_f = \frac{1}{U_{fouled}} - \frac{1}{U_{unfouled}} \quad (3.1)$$

Where $U_{unfouled}$ was the initial overall heat transfer coefficient at time t = 0 (clean surface). Time t = 0 was defined as when the mean probe surface temperature reached 100°C. $U_{fouled}$ was the overall heat transfer coefficient of a fouled probe at time t. The heat transfer coefficient was calculated as the amount of heat passing through one unit area per unit time when the temperature changed one degree:

$$U = \frac{Q}{A(T_S - T_b)} \quad (3.2)$$

Where Q was the power supplied to the heater; $T_S$ was the rod surface temperature recorded with a datalogger and computer; $T_b$ was the bulk fluid temperature. Rod surface temperature ($T_s$) was determined by:

$$T_S = T_C - \frac{(X/K)Q}{A} \quad (3.3)$$

Where $T_C$ was the inner wall temperature measured by obtaining the mean value of four thermocouples and three were used to record temperature change and the fourth one was used to make sure the power shut down when $T_C$ reached 170°C. The fouling resistance obtained at 170°C was considered the maximum fouling resistance. Where X/K was the distance of thermocouples from the surface divided by thermal conductivity of the probe metal; where A was is the total surface area (0.0034 $m^2$) of the probe. Heated probe area (A) was 0.0034 $m^2$ and X/K values were, 0.091 and 0.10 $m^2$•K/ kW for the three thermocouples. Previous work (Agbisit et al 2003; Arora et al 2010; Wilkins et al 2006a; Wilkins et al 2006b) used the power input of 420 ± 20 W. The power was measured using a multimeter (Tenma model 72605, Newark

Electronics, Springfield, IL) and a clamp-on power meter (model 382060, Extech Instruments, Waltham, MA); Power supplied to the probe was measured by a wattmeter (PC5-110D, Ohio Semitronics, Hilliard, OH) and recorded by the same data logger every 1 min.

**Table 3.1. Fouling probe specifications (Wilkins et al 2006a).**

| Parameter | Label in Fig.3.1 | Value |
|---|---|---|
| Material SS 316 | - | SS316 |
| Probe diameter (mm) | A | 10.7 |
| Housing outer diameter (mm) | B | 25.4 |
| Length of heated probe section (mm) | C | 102 |
| Length from fluid entrance to start of heated section (mm) | D | 294 |
| Temperature measured by thermocouples | TC1,2,3 | - |
| Shut off control thermocouples | TC4 | - |
| Adjusted Heated probe surface temperature | TS1,2,3 | - |

### 3.2.2 Experimental Procedure

For each experiment, a 25 L sample was placed in a stainless steel tank. A top mounted impeller stirred the liquid continuously and a pump (Waukesha Foundry Company, Waukesha, WI) recirculated the test fluid through a shell and tube heat exchanger (1.5 m, Graver Technologies, Glasgow, DE). The flow rate was measured using a rotameter (Dwyer Instruments Inc, Michigan City, IN). Another pump (Waukesha Foundry Company, Waukesha, WI) pumped the hot water to heat the experiment liquid to 55 ± 5°C (Fig 3.2). Thin stillage temperature was maintained at 55 ± 5°C throughout each test. During the experiment, a 400 mL thin stillage sample was collected and a digital lab scale was used to measure the density and Brookfield viscometer (spindle No. 2) was used to measure viscosity. For each 400 ml thin stillage sample, viscosity was measured at 55°C and rpm at 100. For each density and viscosity test, sample size was 400 ml; each test had three replications.

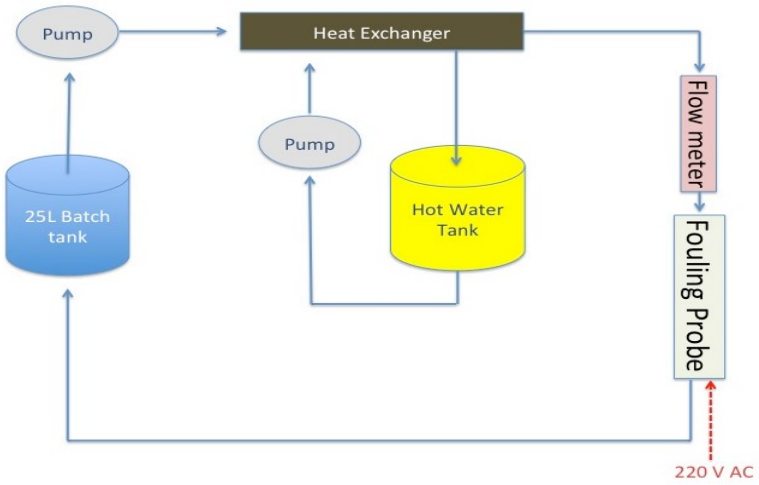


**Figure 3.2. Experiment equipment.**

After thin stillage temperature reached 46°C, the 220 V AC power was supplied to the fouling probe and the temperature increased until the probe reached an average initial probe temperature of 100°C. Subsequently, constant power was maintained at 420 ± 20 W. Each test was terminated when probe temperature reached 170°C or after 300 min.

After each test, the fouling probe was taken out of the housing and a wet sponge was used to remove most of the fouling deposit without scratching the probe surface. The probe was soaked in 5% (w/v) NaOH solution for more than 10 hr. After soaking, any remaining deposits were removed using a wet sponge and paper towels. To clean the fouling apparatus, 40 L of 1% (w/v) detergent solution (Alconox, Inc., New York, NY) was recirculated for 15 min. Clean hot water, 50 L, was used to rinse the system for 10 min followed by another two 50 L clean hot water rinses using 10 min recirculation periods.

Fouling rate was calculated as the slope of the linear regression line for each test plotted with fouling resistance vs time. Analysis of variance (ANOVA) was calculated (SAS Release 8.0, Cary, NC). Dependent variables were fouling rate, maximum fouling resistance and time to reach 170°C; independent variables were different treatments. Fisher's least significant difference method was used to determine if treatments were different ($p<0.05$) from one another. To study the effect of variability of different components (starch and sucrose), dependent variables were fouling rate and maximum fouling resistance, and the independent variable was the extra 2% total solids component added to thin stillage. To study the effect of wet cake addition, dependent

variables were fouling rate and maximum fouling resistance, and the independent variable was the added 2% wet cake.

### 3.2.3 Experimental Material for Experiment One

Thin stillage was collected from a dry grind plant and total solids concentrations were measured. Commercial thin stillage total solids concentrations ranged from 5 to 10% (Arora et al 2009). Therefore, thin stillage was diluted with tap water to 5% total solids, so thin stillage plus additional starch or sucrose was 7% total solids. The tests were stopped when probe temperature reached 170°C or after 300 min. Three batches (100 L) of thin stillage were collected and stored at room temperature until tested. Each batch was divided into 4 samples (25 L).

Treatments were prepared by adding starch or sucrose to 25 L batches. Power input to the probe was (410 ± 10 W) and batch temperature was 55 ± 5°C.

**Table 3.2. Experimental design (% total solids).**

| Treatment | Raw Thin Stillage | Added Starch | Added Sucrose |
|---|---|---|---|
| 1 | 7 | - | - |
| 2 | 5 | 2 | - |
| 3 | 5 | - | 2 |

Density of thin stillage was measured by weighing 400 ml of thin stillage at 50 ± 5°C. Viscosity of thin stillage was measure using Brookfield RVT viscometer with spindle no. 2 (Brookfield Engineering, Brookfield, MA) at 50 ± 5°C. When the Reynolds number is less than about 2,000, pipe flow is laminar; at values greater than 2,000, flow is turbulent (Belmar-Beiny et al 1993).

Reynolds number (Re) for each flow rate was determined by:

$$\mathrm{Re} = \frac{\rho \upsilon D}{\mu} \quad (3.4)$$

Where $\rho$ = density [kg/m$^3$], $\upsilon$ = fluid velocity [m/s], D =inner diameter annulus housing - diameter of probe [m] (0.147 m) and $\mu$ = absolute viscosity [cP].

**Table 3.3. Parameters of treatments for experiment one.**

| Label | Treatment (Added compounds) | Flow Rate (gal/min) | Fluid Velocity (m/s) | Temperature (°C) | Viscosity (cP) | Density (Kg/m$^3$) | Reynolds Number |
|---|---|---|---|---|---|---|---|
| Block 1 test 1 | Starch | 4 | 0.006058 | 48.5 | 0.000608 | 1039.5 | 1522 |
| Block 1 test 2 | Thin stillage | 4 | 0.006058 | 55.2 | 0.000512 | 1035 | 1800 |
| Block 1 test 3 | Sucrose | 4 | 0.006058 | 54.1 | 0.000512 | 1029 | 1789 |
| Block 2 test 1 | Starch | 4 | 0.006058 | 52.1 | 0.000704 | 1030 | 1302 |
| Block 2 test 2 | Sucrose | 4 | 0.006058 | 50.5 | 0.000512 | 1008 | 1753 |
| Block 2 test 3 | Thin stillage | 4 | 0.006058 | 48.7 | 0.000512 | 1025 | 1782 |
| Block 3 test 1 | Thin stillage | 4 | 0.006058 | 53.4 | 0.000512 | 1029 | 1789 |
| Block 3 test 2 | Starch | 4 | 0.006058 | 53.6 | 0.000704 | 1037 | 1311 |
| Block 3 test 3 | Sucrose | 4 | 0.006058 | 50.9 | 0.000512 | 1025 | 1782 |
| Block 4 test 1 | Sucrose | 4 | 0.006058 | 53.5 | 0.000512 | 1007 | 1751 |
| Block 4 test 2 | Starch | 4 | 0.006058 | 50.2 | 0.000704 | 1037 | 1311 |
| Block 4 test 3 | Thin stillage | 4 | 0.006058 | 54.6 | 0.000512 | 1021 | 1775 |

**Table 3.4. Reynolds numbers of thin stillage.**

| Treatment | Average Reynolds Number |
|---|---|
| Starch | 1362[a] |
| Sucrose | 1769[b] |
| Thin stillage | 1787[b] |

[1] Mean of four tests.

[2] Values with the same letter are not different from one another (P<0.05).

Fisher's least significant difference method ($p < 0.05$) was used to detect differences among for Reynolds Numbers (Table 3.4). Thin stillage with added starch had a lower Reynolds number than the other treatments.

**Table 3.5. Initial dry matter of thin stillage from a commercial DGC facility.**

| Sample | Dry Matter (%) | Mean ± SD |
|---|---|---|
| Batch 1 test 1 | 7.99 | |
| Batch 1 test 2 | 8.15 | |
| Batch 1 test 3 | 7.78 | 7.97±0.034[a] |
| Batch 2 test 1 | 8.08 | |
| Batch 2 test 2 | 8.11 | |
| Batch 2 test 3 | 7.23 | 7.81±0.250[a] |
| Batch 3 test 1 | 8.90 | |
| Batch 3 test 2 | 8.78 | |
| Batch 3 test 3 | 8.93 | 8.87±0.006[b] |
| Batch 4 test 1 | 8.31 | |
| Batch 4 test 2 | 8.16 | |
| Batch 4 test 3 | 8.22 | 8.23±0.006[a] |

[1] Mean of nine tests.

[2] Values with the same letter are not different from one another ($P<0.05$).

Each test had three replications; the dry matter value was the mean value of three samples. A total of 12 samples were collected from each batch to determine solids concentration. Fisher's least significant difference method was used to determine if four batches were different on the total solid concentration (Table 3.5). Batch 3 had a higher dry matter concentration, though of effect solids concentration on fouling could not be determined from this study. Dry matter concentration varied from 7.23 to 8.93% prior to diluting thin stillage to 5 or 7% total solids.

### 3.2.4 Experimental Material for Experiment Two

Thin stillage and fresh wet cake were collected from a commercial DGC plant and stored at room temperature until tested. Batches (60 L) were collected at three times during one month with two tests conducted per batch. Each test used a 25 L sample and total solids concentrations of thin stillage and wet cake were measured with three replications before each test was conducted. Samples from each batch was analyzed for total solids concentration determined by standard oven method (AACC 2000).

To study the effects of added wet cake solids, dependent variables were the fouling rate at 90 min and maximum fouling resistance and the independent variable was the extra 2% total solids component of wet cake. The control treatment was thin still age adjusted to 7% total solids.

**Table 3.6. Experimental treatment for experiment two (% total solids).**

| Treatment | Raw Thin Stillage | Added Wet Cake |
|---|---|---|
| 1 | 7 | 0 |
| 2 | 5 | 2 |

**Table 3.7. Initial dry matter of thin stillage from a commercial DGC facility.**

| Sample | Dry Matter (%) | Mean ± SD |
|---|---|---|
| Batch 1 test 1 | 8.14 | |
| Batch 1 test 2 | 8.09 | 8.12 ± 0.001[a] |
| Batch 2 test 1 | 7.99 | |
| Batch 2 test 2 | 7.57 | 7.78 ± 0.088 [a] |
| Batch 3 test 1 | 7.63 | |
| Batch 3 test 3 | 7.97 | 7.80 ± 0.058 [a] |

### 3.3 Results and Discussion for Experiment One

Thin stillage with added starch had increased fouling rate compared to fouling thin stillage alone (Fig 3.3). In general, treatments with additional sucrose had lower rates of fouling. The treatment with additional sucrose showed similar fouling behavior compared to raw thin stillage with 7% total solids. For fouling rate calculated for 25 min of data, treatment STA had larger fouling rates than other treatments; there was no difference between SUC and TS. At intervals of 60 to 300 min, no differences in fouling rates were detected (Table 3.8).

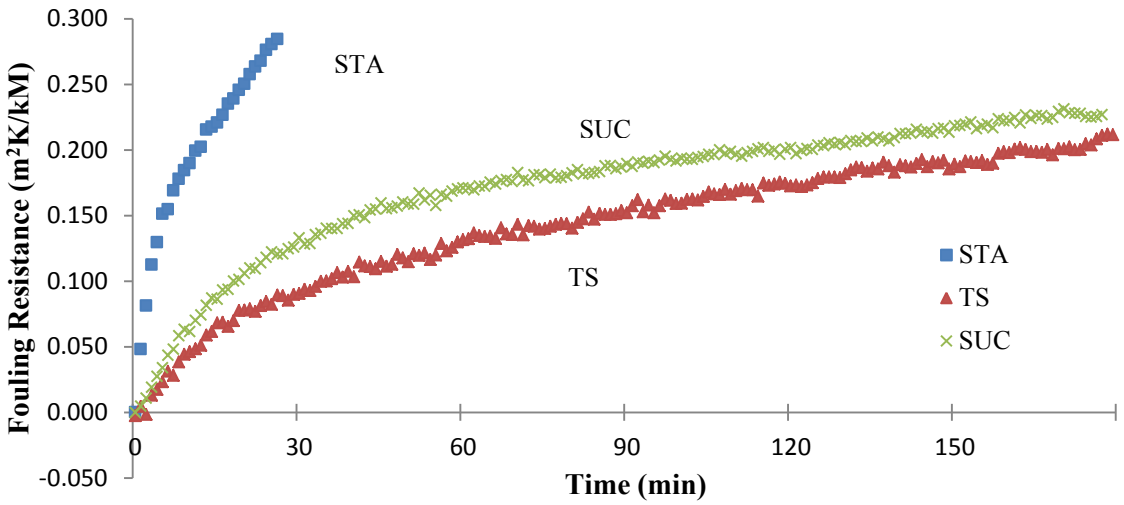


**Figure 3.3. Mean fouling resistances for commercial thin stillage (TS) and for thin stillage with added starch (STA) and added sucrose (SUC) at 7% (TS). Number of observations for each data point = 4.**

**Table 3.8. Linear fouling rates ($m^2K/kW/min$) calculated from 25 to 300 min for three treatments.**

| Treatment | 25 min | 60 min | 150 min | 300 min | Maximum Fouling Resistance ($m^2K/kW$) |
|---|---|---|---|---|---|
| STA | 0.0086[a] | - | - | - | 0.3000[a] |
| SUC | 0.0045[b] | 0.0019[a] | 0.0010[a] | 0.00068[a] | 0.2475[a] |
| TS | 0.0035[b] | 0.0025[a] | 0.0011[a] | 0.00077[a] | 0.2425[a] |

[1] Mean of four tests.

[2] Values with the same letter within same column are not different from one another ($P<0.05$).

STA: thin stillage and 2% added starch; 7% total solids

SUC: thin stillage and 2% added sucrose; 7% total solids

TS: thin stillage; 7% total solids

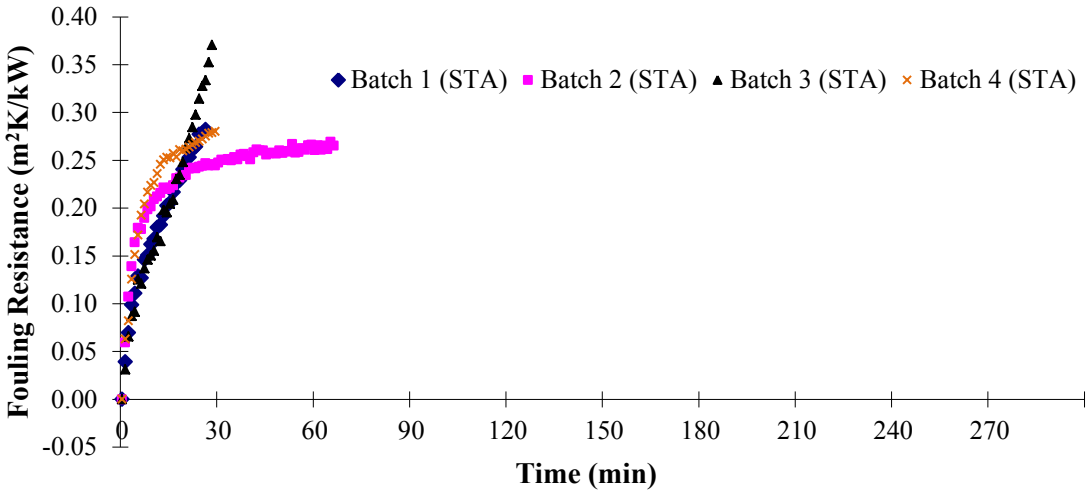


**Figure 3.4. Effects of starch addition on fouling resistance of four batches.**

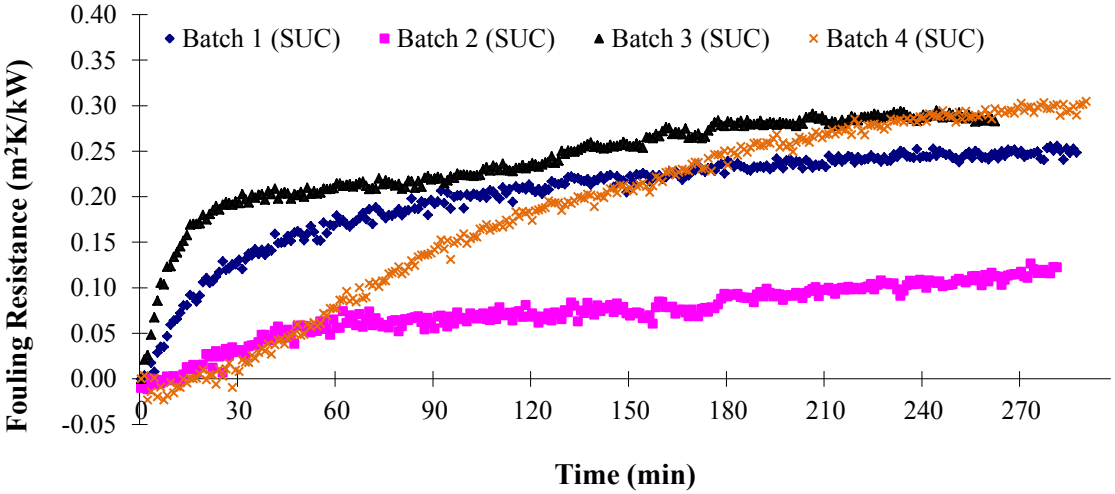


**Figure 3.5. Effects of sucrose addition on fouling resistance of four batches.**

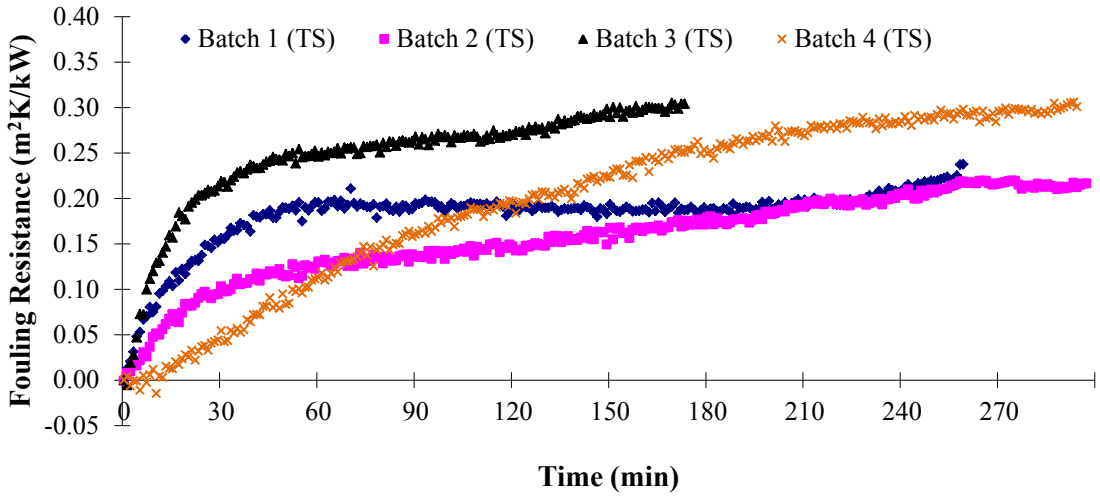


**Figure 3.6. Fouling resistance of four batches of raw thin stillage.**

Thin stillage with 5% total solids and 2% added starch had $R_f$ of 0.37 m² K/kW for batch 3, which had a larger maximum fouling resistance. For batches 1, 3 and 4, $T_c$ reached 170°C after 30 min. It took more than 1 hr for the $T_c$ of batch 2 to reach 170°C (Fig 3.4). Also, fouling deposits rapidly adsorbed onto the surface, resulting in reaching 170°C less than 2 hr for each of the four batches. For thin stillage with 2% added sucrose, the batch having the largest $R_f$ was batch 4. For all those four batches, $T_c$ had never reached 170°C within 300 min. After approximately 180 min, the rate of increase in fouling resistance (fouling rate) decreased sharply until 300 min (Fig 3.5). Batch 3 and batch 4 had a bigger maximum $R_f$ 0.31 m² K/kW compared to maximum of $R_f$ 0.23 m² K/kW for batch 1 and maximum of $R_f$ 0.22 m² K/kW for batch 2. Batch 3 reached 170°C after 160 min and the other batches did not reach 170°C within 300 min, as same as all the other sucrose treatments (Fig 3.6).

For the treatment with 2% of starch in total solids concentration, fouling rates calculated for 25 min data had larger fouling rates than the other treatments. After 25 min, no difference among treatments was detected. For the treatment with 2% added sucrose, fouling rates showed no difference compared to treatment with 7% total solids concentration of thin stillage for all time intervals.

Experiment one involving starch and sucrose addition was designed to evaluate the roles of these two components in fouling of heated surfaces. It provided an initial understanding of how starch based compounds affect fouling. Adding starch to thin stillage increased fouling rates and accelerated fouling; sucrose's effects on fouling behavior were not detected. Due to time and

equipment limitations, degree of polymerization was not quantified in this study. It also showed that suspended solids such as starch could increase production rate of solids that can deposit onto the surface and initiate fouling compared to soluble solids such as sucrose.

Variations in composition could be controlled by changes in the operation of the facility from which the thin stillage was obtained, such as acid addition rates, centrifuge conditions, enzyme loadings, temperatures, and fermentation conditions. Variability in composition of maize processing streams has been observed in other work (Rausch et al 2005). Observing fouling rates with different insoluble and soluble solids concentrations indicate that strict control of these factors may control thin stillage fouling behavior.

### 3.4 Results and Discussion for Experiment Two

Adding 2% wet cake to thin stillage increased fouling rates compared with thin stillage with 7% total solids (Fig 3.7 and Table 3.10). Thin stillage treatment showed similar fouling behavior among batches. Fouling rate of 90 min for treatments with 2% added wet cake was larger than the fouling rate for raw thin stillage and required less than 90 min to reach 170°C (Table 3.9).

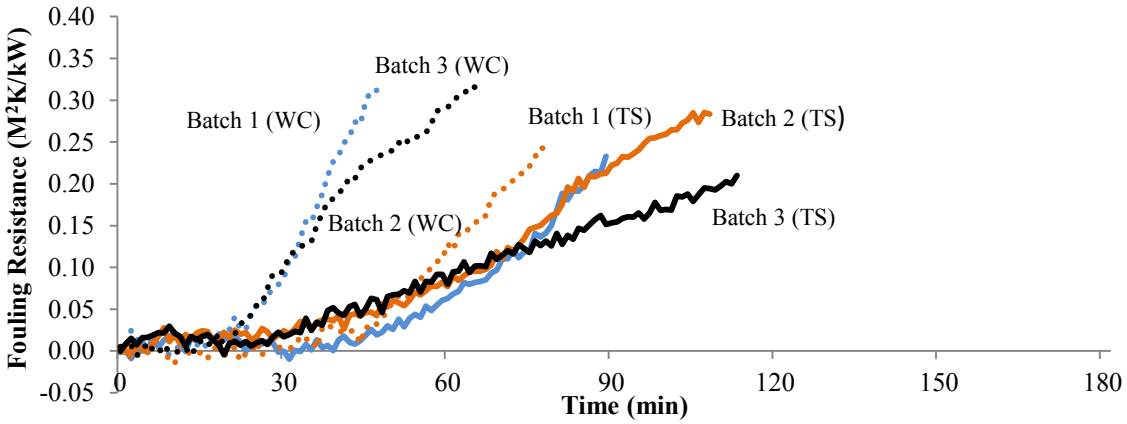


**Figure 3.7. Fouling resistance of thin stillage with (WC) and without (TS) added wet cake. TS: thin stillage, WC: thin stillage and 2% added wet cake; 7% total solids.**

**Table 3.9. Maximum fouling resistance ($m^2K/kw$) at 300 min.**

| | Thin stillage | Added wet cake |
|---|---|---|
| Batch 1 | 0.233 | 0.312 |
| Batch 2 | 0.215 | 0.245 |
| Batch 3 | 0.210 | 0.317 |
| Mean ± SD | $0.219 \pm 1.46\times10^{-4}$ a | $0.291 \pm 1.61\times10^{-3}$ b |

[1] Values with the same letter are not different from one another ($P<0.05$).

**Table 3.10. Fouling rates ($m^2K/kw/min$) at 90 min.**

| | Thin stillage | Added wet cake |
|---|---|---|
| Batch 1 | $2.16\times10^{-3}$ | $6.75\times10^{-3}$ |
| Batch 2 | $2.18\times10^{-3}$ | $3.05\times10^{-3}$ |
| Batch 3 | $1.79\times10^{-3}$ | $5.77\times10^{-3}$ |
| Mean ± SD | $2.04\times10^{-3} \pm 4.82\times10^{-8}$ [a] | $5.19\times10^{-3} \pm 3.67\times10^{-6}$ [b] |

[1] Values with the same letter are not different from one another ($P<0.05$).

Wet cake increased fouling. Therefore, in DGC processing, it is essential to make sure whole stillage centrifugation separates completely wet cake from thin stillage.

### 3.5 Conclusions

Fouling rates increased with starch addition, as well as with wet cake addition. At equal total solids contents, insoluble starch had larger effect than soluble sucrose on fouling. Sucrose alone did not increase fouling. At equal total solids contents, wet cake can increase fouling rate and accelerate fouling. Fouling among batches showed large variability.

# CHAPTER 4. FUTURE WORK

1. Study the effects of bulk temperature as well as Reynolds number and the interactions among those two on thin stillage fouling. In this study, bulk thin stillage temperatures and flow rate were set to a constant value due to equipment limitations. In DGC facilities, the temperature of thin stillage was 75 to 80°C. Using other heating systems to increase the temperature could more closely approximate fouling conditions for thin stillage. Using a different pump or using a control valve to direct a portion of thin stillage flow back to the sample tank could control the flow rate.
2. More work needs to be done to analyze the fouling deposition and the order each component of fouling deposit may adsorb onto the probe surfaces.
3. In this study, only starch and sucrose were studied in their roles in thin stillage fouling. But these compounds are only a part of a complex mixture that comprises thin stillage, steepwater and distillers soluble streams. Other compositions such as fiber, acid, oil, protein and inorganic components could contribute to fouling or interacting with one another.
4. Replicate data need to be collected to support all conclusions.
5. For thin stillage aging studies, a longer storage period must be applied.

# APPENDIX

## A.1. Thin Stillage Aging Study

Fuel ethanol is produced mainly from corn in the US. by corn wet milling (CWM) and dry grind corn (DGC) processing. CWM produces several coproducts but the facilities involve considerable capital investment to build. DGC facilities require much lower capital investment, but it produces primarily one coproduct, distillers dried grains with solubles (DDGS). DDGS is sold as an animal diet, primarily for ruminant animals. During DGC processing, after distillation, the remaining nonfermented material is known as whole stillage which includes starch, protein, fiber, oil and minerals. Whole stillage is centrifuged to produce two products; wet cake (30 to 35% solids) and thin stillage (5 to 10% solids).

Thin stillage is concentrated from 4 to 6% solids to 25 to 30% solids in multiple effect evaporators (Singh et al 1999). Evaporation and drying operations account for 40 to 45% of thermal energy and 30 to 40% of electrical energy used in a DGC facility that is recovered from distillation (Meredith 2003). Evaporators accumulate deposits on their surfaces that reduce heat transfer and also increase pressure loss in a process known as fouling. Fouling decreases energy efficiency and increases operating costs. Many approaches have been made to decrease the cost in DGC processing in thin stillage evaporations. However, little is known about fouling in corn processing, particularly with regard to thin stillage evaporation.

Singh et al (1999) found that thin stillage from DGC fouled at a rate 67% more than did CWM thin stillage. They suggested this was due to higher oil content in DGC thin stillage than CWM thin stillage. No reproducibility of the fouling probe technique using DGC thin stillage was evaluated.

Agbisit et al (2003) evaluated fouling behavior of steepwater from wet milling and found microfiltration membrane (0.1 micron nominal pore size) of CWM steep water reduced fouling rate by 80% as opposed it unfiltered steep water.

Wilkins et al (2006) studied the effect of pH on fouling behaviors of thin stillage and found at pH 3.5 it had a shorter induction period and a greater initial fouling rate than did thin stillage adjusted to pH 4.0 and 4.5. Also, as pH increased, protein contents of fouling deposits decreased and ash content of fouling deposits increased. Adjusting thin stillage pH to 4.0 or 4.5 resulted in reduced fouling as opposed to thin stillage pH 3.5.

Arora et al (2010) investigated fouling characteristics of thin stillage (7.0% TS) from a dry grind facility, filtered thin stillage (FTS, 3.5% TS) and diluted thin stillage (DTS, 3.5% TS). At 10 hr of fouling, a 50% reduction in fouling resistance was observed when solids level decreased from 7.2 to 3.5%, with no change in composition. Microfiltration of thin stillage resulted in a 90% reduction of the fouling resistance value for the same reduction in total solids content.

Research on fouling of maize processing streams is limited and effects of process stream variation on evaporator efficiency are not well known. One of the questions to be answered was if the age of thin stillage sample would affect fouling. Objectives were to 1) study effects of sample age on fouling characteristics in thin stillage and 2) study the variability of thin stillage fouling.

DGC thin stillage was collected from a commercial DGC facility and stored at room temperature until tested. Three batches were collected at three times over two months. Three tests were conducted for batch one and batch three; five tests were conducted for batch two. A batch size of 30 L thin stillage was used for each test at 1, 5, 7, 15 and 20 days after sampling. Only two samples were collected from days 5, 7, 15 and 20, and three samples were collected from day 1, no aging differences were detected over 20 days. Dry matter concentrations were not measured.

**Table A.1. Experiment design.**

| | Day 1 | Day 5 | Day 7 | Day 15 | Day 20 |
|---|---|---|---|---|---|
| Batch 1 | 30 L | 30 L | 30 L | - | - |
| Batch 2 | 30 L | 30 L | 30 L | 30 L | 30 L |
| Batch 3 | 30 L | - | - | 30 L | 30 L |

The annular fouling probe used in this study was the same one used in Chapter 3 as well as in previous research (Agbisit et al 2003; Arora et al 2010; Wilkins et al 2006a; Wilkins et al 2006b).

$T_b$ was adjusted to 48°C and the heater activated. When $T_s$ reached 100°C, data collection began. Power was shut down when $T_C$ reached 170°C or after 300 min. The fouling resistance

obtained at 170°C was considered the maximum fouling resistance. Details of the equipment can be found in Chapter 3.

$R_f$ vs. time was plotted for each test and a linear regression line was fitted to the data. The slope of each regression line was defined as the fouling rate for that test. $R_f$ at t = 300 min were used to measure the variability of thin stillage batches. Analysis of variance (ANOVA) was calculated (SAS Release 9.2, Cary, NC) with fouling rate and max fouling resistance as dependent variables and batch as the independent variables. Fisher's least significant difference method was used to determine if batches were different from one another.

Fouling rates and maximum fouling resistances were measured to determine how aging could affect the thin stillage fouling as well as the variability of three batches.

**Table A.2. Maximum fouling resistances of three batches after 300 min ($m^2$•K/kw).**

| | Day 1 | Day 5 | Day 7 | Day 15 | Day 20 |
|---|---|---|---|---|---|
| Batch 1 | 0.2144 | 0.0587 | 0.3079 | - | - |
| Batch 2 | 0.1788 | 0.2206 | 0.2074 | 0.1085 | 0.2557 |
| Batch 3 | 0.0880 | - | - | 0.1804 | 0.0281 |
| Mean | 0.1604[a] | 0.1397[a] | 0.2577[a] | 0.1445[a] | 0.1419[a] |

**Table A.3. Fouling rates for t = 0 to 300 min ($m^2$•K/kw/min).**

| | Day 1 | Day 5 | Day 7 | Day 15 | Day 20 |
|---|---|---|---|---|---|
| Batch one | 0.0005 | 0.0002 | 0.0008 | - | - |
| Batch two | 0.0004 | 0.0004 | 0.0003 | 0.0003 | 0.0006 |
| Batch three | 0.0002 | - | - | 0.0004 | -0.0002 |
| Mean | 0.00037[a] | 0.00030[a] | 0.00055[a] | 0.00035[a] | 0.0002[a] |

Negative $R_f$ values observed in Fig A.1 were a result of an increase in the heat transfer coefficient after start of the test. Negative $R_f$ has been measured by others (Agbisit et al 2003; Wilkins et al 2006a; Wilson and Watkinson 1995) and is thought to be caused by particles disrupting the thermal boundary layer (Crittenden and Alderman 1988) and power fluctuations and/or deposition that produces roughness (Panchal and Watkinson 1993).

Thin stillage had been stored for 7 days showed the larger maximum fouling resistance (Table A.1.2) and larger fouling rate over 300 min (Table A.1.3). Fouling rates within batches of thin stillage showed large variability. The causes of variation in fouling behavior were unclear; variations among replicates from the same aging time were relatively small. Sample size was too small to detect differences in fouling rates and fouling resistances.

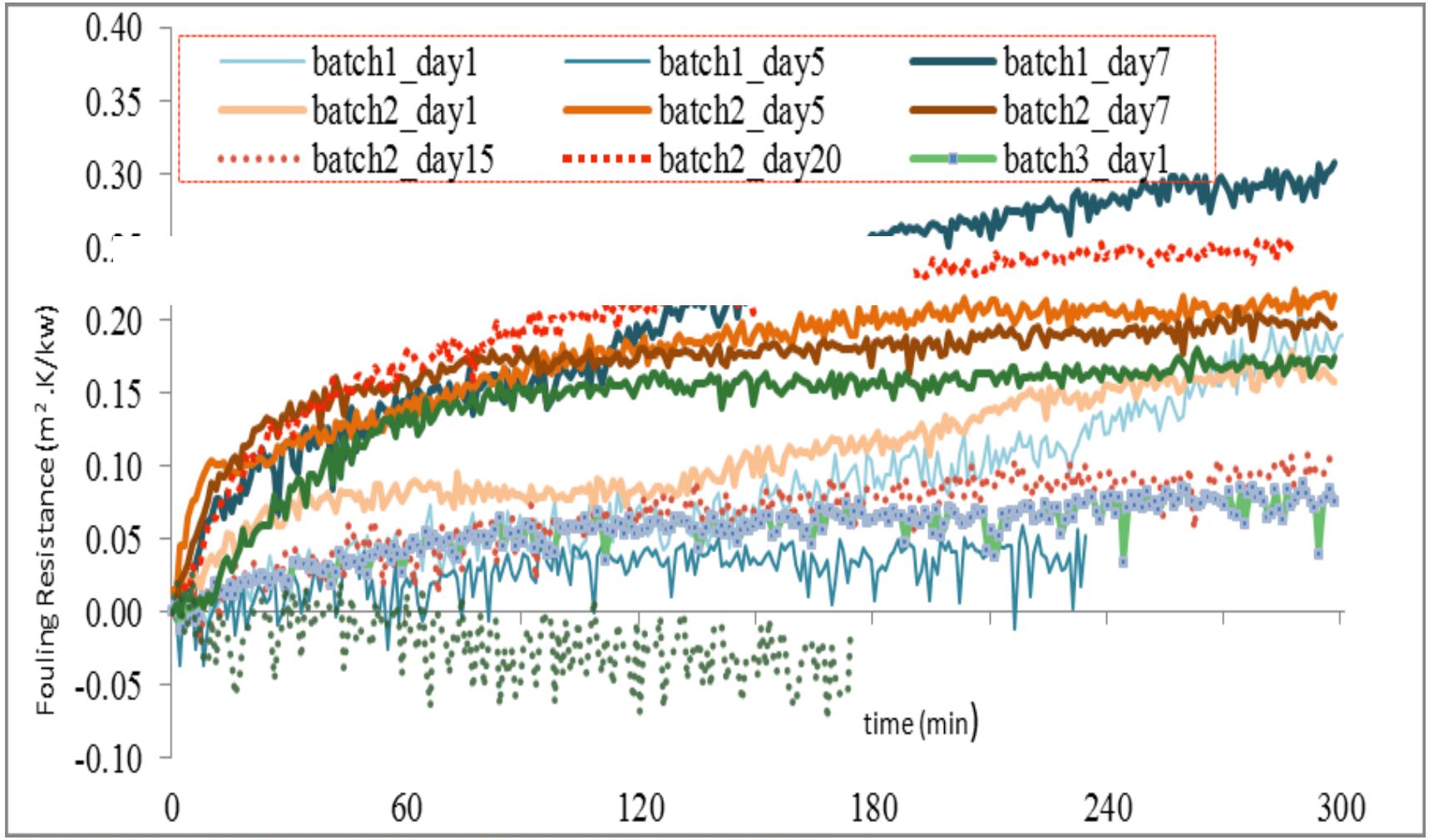


Figure A.1. Fouling resistance of three batches over 300 min.

## A.2. SAS Programs

### A.2.1 Program for Variability of Reynolds Number of Three Treatments

```
Note: "……": example data
options ls=74 ps=50 nodate nocenter pageno=1;
data A;
input rep trt Reynolds;
cards;
1 1 1522
……
4 3 1775
;;;
proc sort data=A; by trt; run;
proc means data=A mean var;
var Reynolds; by trt; run;
proc glm;
class trt;
model Reynolds = trt/ss1;
means trt/LSD Tukey lines alpha=0.05 hovtest=bf; run;
```

### A.2.2 Program for Variability of Total Solids Concentration of Batches for Experiment One

```
options ls=74 ps=50 nodate nocenter pageno=1;
data A;
input rep batch solids;
cards;
1 1 7.99
……
3 4 8.22
;;;
proc sort data=A; by batch; run;
proc means data=A mean var;
```

```
var solids; by batch; run;
proc glm;
class batch;
model solids = batch/ss1;
means batch/LSD Tukey lines alpha=0.05 hovtest=bf; run;
```

### A.2.3 Program for Variability of Total Solids Concentration of Batches for Experiment Two

```
ptions ls=74 ps=50 nodate nocenter pageno=1;
data A;
input rep batch solids;
cards;
1 1 8.14
……
2 3 7.97
;;
proc sort data=A; by batch; run;
proc means data=A mean var;
var solids; by batch; run;
proc glm;
class batch;
model solids = batch/ss1;
means batch/LSD Tukey lines alpha=0.05 hovtest=bf; run;
```

### A.2.4 Program for Effect of Starch and Sucrose on Fouling Behavior of Thin Stillage

Note: This program is an example for fouling rates at 25, 60, 150 and 300 min fouling.

```
options ls=74 ps=50 nodate nocenter pageno=1;
data A;
input rep treatment rate;
cards;
```

```
1 1 0.0092
…….
4 3 0.0017
;;;
proc sort data=A; by treatment; run;
proc means data=A mean var;
var rate; by treatment; run;
proc glm;
class treatment;
model rate = treatment/ss1;
means treatment/LSD Tukey lines alpha=0.05 hovtest=bf; run;
```

### A.2.5 Program for Effect of Wet Cake on Fouling Behavior of Thin Stillage

```
options ls=74 ps=50 nodate nocenter pageno=1;
data A;
input rep treatment rate;
cards;
1 1 0.00216
…….
3 2 0.00577
;;;
proc sort data=A; by treatment; run;
proc means data=A mean var;
var rate; by treatment; run;
proc glm;
class treatment;
model rate = treatment/ss1;
means treatment/LSD Tukey lines alpha=0.05 hovtest=bf; run;
```

### A.3. F and T Tables

#### A.3.1 F and T Tables for Variability of Reynolds Number of Three Treatments

Dependent Variable: Reynolds

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 2 | 462390.1667 | 231195.0833 | 57.97 | <.0001 |
| Error | 9 | 5890.7500 | 3987.8611 | | |
| Corrected Total | 11 | 498280.9167 | | | |

| R-Square | Coeff Var | Root MSE | Reynolds Mean |
|---|---|---|---|
| 0.927971 | 3.853125 | 63.14951 | 1638.917 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| trt | 2 | 462390.1667 | 231195.0833 | 57.97 | <.0001 |

The GLM Procedure
Brown and Forsythe's Test for Homogeneity of Reynolds Variance
ANOVA of Absolute Deviations from Group Medians

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| trt | 2 | 4998.2 | 2499.1 | 0.69 | 0.5265 |
| Error | 9 | 32623.8 | 3624.9 | | |

The GLM Procedure
t Tests (LSD) for Reynolds
NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 9 |
| Error Mean Square | 3987.861 |
| Critical Value of t | 2.26216 |
| Least Significant Difference | 101.01 |

Means with the same letter are not significantly different.

| t Grouping | Mean | N | trt |
|---|---|---|---|
| A | 1786.50 | 4 | 3 |
| A | | | |
| A | 1768.75 | 4 | 2 |
| B | 1361.50 | 4 | 1 |

### A.3.2 F and T Tables for Variability of Total Solids Concentration of Batches for Experiment One

Dependent Variable: solids

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 3 | 1.96286667 | 0.65428889 | 8.84 | 0.0064 |
| Error | 8 | 0.59213333 | 0.07401667 | | |
| Corrected Total | 11 | 2.55500000 | | | |

| R-Square | Coeff Var | Root MSE | solids Mean |
|---|---|---|---|
| 0.768245 | 3.309733 | 0.272060 | 8.220000 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| batch | 3 | 1.96286667 | 0.65428889 | 8.84 | 0.0064 |

The GLM Procedure
Brown and Forsythe's Test for Homogeneity of solids Variance
ANOVA of Absolute Deviations from Group Medians

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| batch | 3 | 0.1186 | 0.0395 | 0.63 | 0.6155 |
| Error | 8 | 0.5013 | 0.0627 | | |

The GLM Procedure
t Tests (LSD) for solids
NOTE: This test controls the Type I comparisonwise error rate, not the
experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 8 |
| Error Mean Square | 0.074017 |
| Critical Value of t | 2.30600 |
| Least Significant Difference | 0.5122 |

Means with the same letter are not significantly different.

| Mean | N | batch |
|---|---|---|
| A | 8.8700 | 3 | 3 |
| B | 8.2300 | 3 | 4 |
| B | | | |
| B | 7.9733 | 3 | 1 |
| B | | | |
| B | 7.8067 | 3 | 2 |

### A.3.3 F and T Tables for Variability of Total Solids Concentration of Batches for Experiment Two

Dependent Variable: solids

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 2 | 0.14123333 | 0.07061667 | 1.44 | 0.3647 |
| Error | 3 | 0.14725000 | 0.04908333 | | |
| Corrected Total | 5 | 0.28848333 | | | |

| R-Square | Coeff Var | Root MSE | solids Mean |
|---|---|---|---|
| 0.489572 | 2.804992 | 0.221548 | 7.898333 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| batch | 2 | 0.14123333 | 0.07061667 | 1.44 | 0.3647 |

The GLM Procedure

t Tests (LSD) for solids

NOTE: This test controls the Type I comparisonwise error rate, not the experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 3 |
| Error Mean Square | 0.049083 |
| Critical Value of t | 3.18245 |
| Least Significant Difference | 0.7051 |

Means with the same letter are not significantly different.

| Mean | N | batch |
|---|---|---|
| A | 8.1150 | 2 1 |
| A | | |
| A | 7.8000 | 2 3 |
| A | | |
| A | 7.7800 | 2 2 |

### A.3.4 F and T Tables for Effect of Starch and Sucrose on Fouling Rate within 25 min of Thin Stillage

Dependent Variable: yield

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 2 | 0.00005823 | 0.00002912 | 4.38 | 0.0470 |
| Error | 9 | 0.00005986 | 0.00000665 | | |
| Corrected Total | 11 | 0.00011809 | | | |

| R-Square | Coeff Var | Root MSE | yield Mean |
|---|---|---|---|
| 0.493116 | 46.81853 | 0.002579 | 0.005508 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 2 | 0.00005823 | 0.00002912 | 4.38 | 0.0470 |

The GLM Procedure

Brown and Forsythe's Test for Homogeneity of yield Variance
ANOVA of Absolute Deviations from Group Medians

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 2 | 1.202E-6 | 6.008E-7 | 0.48 | 0.6313 |
| Error | 9 | 0.000011 | 1.241E-6 | | |

The GLM Procedure
t Tests (LSD) for yield
NOTE: This test controls the Type I comparisonwise error rate, not the
experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 9 |
| Error Mean Square | 6.651E-6 |
| Critical Value of t | 2.26216 |
| Least Significant Difference | 0.0041 |

Means with the same letter are not significantly different.

| Mean | | N | treatment |
|---|---|---|---|
| | A | 0.008575 | 4 1 |
| | A | | |
| B | A | 0.004450 | 4 3 |
| B | | | |
| B | | 0.003500 | 4 2 |

### A.3.5 F and T Tables for Effect of Starch and Sucrose on Fouling Rate within 60 min of Thin Stillage

Dependent Variable: rate

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 1 | 1.125E-6 | 1.125E-6 | 2.78 | 0.1466 |
| Error | 6 | 2.43E-6 | 4.05E-7 | | |
| Corrected Total | 7 | 3.555E-6 | | | |

| R-Square | Coeff Var | Root MSE | yield Mean |
|---|---|---|---|
| 0.316456 | 27.37188 | 0.000636 | 0.002325 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 1.125E-6 | 1.125E-6 | 2.78 | 0.1466 |

The GLM Procedure
Brown and Forsythe's Test for Homogeneity of yield Variance
ANOVA of Absolute Deviations from Group Medians

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 2E-8 | 2E-8 | 0.29 | 0.6122 |
| Error | 6 | 4.2E-7 | 7E-8 | | |

The GLM Procedure
t Tests (LSD) for rate
NOTE: This test controls the Type I comparisonwise error rate, not the
experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 6 |
| Error Mean Square | 4.05E-7 |
| Critical Value of t | 2.44691 |
| Least Significant Difference | 0.0011 |

Means with the same letter are not significantly different.

| | Mean | N | treatment |
|---|---|---|---|
| A | 0.0027000 | 4 | 2 |
| A | | | |
| A | 0.0019500 | 4 | 1 |

### A.3.6 F and T Tables for Effect of Starch and Sucrose on Fouling Rate within 150 min of Thin Stillage

Dependent Variable: yield

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 1 | 0 | 0 | 0.00 | 1.0000 |
| Error | 6 | 1.24E-6 | 2.0666667E-7 | | |
| Corrected Total | 7 | 1.24E-6 | | | |

| R-Square | Coeff Var | Root MSE | yield Mean |
|---|---|---|---|
| 0.000000 | 43.29581 | 0.000455 | 0.001050 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 0 | 0 | 0.00 | 1.0000 |

The GLM Procedure
Brown and Forsythe's Test for Homogeneity of yield Variance
ANOVA of Absolute Deviations from Group Medians

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 5E-9 | 5E-9 | 0.07 | 0.8027 |
| Error | 6 | 4.4E-7 | 7.333E-8 | | |

The GLM Procedure
t Tests (LSD) for yield

NOTE: This test controls the Type I comparisonwise error rate, not the
experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 6 |
| Error Mean Square | 2.067E-7 |
| Critical Value of t | 2.44691 |
| Least Significant Difference | 0.0008 |

Means with the same letter are not significantly different.

| Mean | N | treatment |
|---|---|---|
| A 0.0010500 | 4 | 1 |
| A | | |
| A 0.0010500 | 4 | 2 |

### A.3.7 F and T Tables for Effect of Starch and Sucrose on Fouling Rate within 300 min of Thin Stillage

Dependent Variable: rate

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 1 | 1.25E-9 | 1.25E-9 | 0.01 | 0.9264 |
| Error | 6 | 8.075E-7 | 1.3458333E-7 | | |
| Corrected Total | 7 | 8.0875E-7 | | | |

| R-Square | Coeff Var | Root MSE | yield Mean |
|---|---|---|---|
| 0.001546 | 53.36087 | 0.000367 | 0.000688 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 1.25E-9 | 1.25E-9 | 0.01 | 0.9264 |

The GLM Procedure

Brown and Forsythe's Test for Homogeneity of rate Variance
ANOVA of Absolute Deviations from Group Medians

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 1.125E-8 | 1.125E-8 | 0.24 | 0.6394 |
| Error | 6 | 2.775E-7 | 4.625E-8 | | |

The GLM Procedure

t Tests (LSD) for rate

NOTE: This test controls the Type I comparisonwise error rate, not the
experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 6 |
| Error Mean Square | 1.346E-7 |
| Critical Value of t | 2.44691 |
| Least Significant Difference | 0.0006 |

Means with the same letter are not significantly different.

| | Mean | N | treatment |
|---|---|---|---|
| A | 0.0007000 | 4 | 2 |
| A | | | |
| A | 0.0006750 | 4 | 1 |

### A.3.8 F and T Tables for Effect of Starch and Sucrose on Maximum $R_f$ of Thin Stillage

Dependent Variable: yield

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 2 | 0.00811667 | 0.00405833 | 0.82 | 0.4709 |
| Error | 9 | 0.04455000 | 0.00495000 | | |
| Corrected Total | 11 | 0.05266667 | | | |

| R-Square | Coeff Var | Root MSE | yield Mean |
|---|---|---|---|
| 0.154114 | 26.71756 | 0.070356 | 0.263333 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 2 | 0.00811667 | 0.00405833 | 0.82 | 0.4709 |

The GLM Procedure

Brown and Forsythe's Test for Homogeneity of yield Variance
ANOVA of Absolute Deviations from Group Medians

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 2 | 0.00302 | 0.00151 | 0.62 | 0.5616 |
| Error | 9 | 0.0221 | 0.00245 | | |

The GLM Procedure
t Tests (LSD) for yield

NOTE: This test controls the Type I comparisonwise error rate, not the
experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 9 |
| Error Mean Square | 0.00495 |
| Critical Value of t | 2.26216 |
| Least Significant Difference | 0.1125 |

Means with the same letter are not significantly different.

| | Mean | N | treatment |
|---|---|---|---|
| A | 0.30000 | 4 | 1 |
| A | | | |
| A | 0.24750 | 4 | 3 |
| A | | | |
| A | 0.24250 | 4 | 2 |

### A.3.9 F and T Tables for Effect of Wet Cake on Fouling Rate of Thin Stillage

Dependent Variable: rate

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 1 | 0.00001485 | 0.00001485 | 7.98 | 0.0476 |
| Error | 4 | 0.00000745 | 0.00000186 | | |
| Corrected Total | 5 | 0.00002230 | | | |

| R-Square | Coeff Var | Root MSE | rate Mean |
|---|---|---|---|
| 0.666071 | 37.72463 | 0.001364 | 0.003617 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 0.00001485 | 0.00001485 | 7.98 | 0.0476 |

The GLM Procedure
Brown and Forsythe's Test for Homogeneity of rate Variance
ANOVA of Absolute Deviations from Group Medians

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 1.826E-6 | 1.826E-6 | 1.88 | 0.2421 |
| Error | 4 | 3.882E-6 | 9.705E-7 | | |

The GLM Procedure
t Tests (LSD) for rate

NOTE: This test controls the Type I comparisonwise error rate, not the
experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 4 |
| Error Mean Square | 1.862E-6 |
| Critical Value of t | 2.77645 |
| Least Significant Difference | 0.0031 |

Means with the same letter are not significantly different.

| | Mean | N | treatment |
|---|---|---|---|
| A | 0.005190 | 3 | 2 |
| B | 0.002043 | 3 | 1 |

### A.3.10 F and T Tables for Effect of Wet Cake on Maximum $R_f$ of Thin Stillage

Dependent Variable: MAX

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| Model | 1 | 0.00777600 | 0.00777600 | 8.82 | 0.0411 |
| Error | 4 | 0.00352533 | 0.00088133 | | |
| Corrected Total | 5 | 0.01130133 | | | |

| R-Square | Coeff Var | Root MSE | MAX Mean |
|---|---|---|---|
| 0.688060 | 11.62686 | 0.029687 | 0.255333 |

| Source | DF | Type I SS | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 0.00777600 | 0.00777600 | 8.82 | 0.0411 |

The GLM Procedure

Brown and Forsythe's Test for Homogeneity of MAX Variance
ANOVA of Absolute Deviations from Group Medians

| Source | DF | Sum of Squares | Mean Square | F Value | Pr > F |
|---|---|---|---|---|---|
| treatment | 1 | 0.000400 | 0.000400 | 0.54 | 0.5028 |
| Error | 4 | 0.00296 | 0.000740 | | |

The GLM Procedure

t Tests (LSD) for MAX

NOTE: This test controls the Type I comparisonwise error rate, not the
experimentwise error rate.

| | |
|---|---|
| Alpha | 0.05 |
| Error Degrees of Freedom | 4 |
| Error Mean Square | 0.000881 |
| Critical Value of t | 2.77645 |
| Least Significant Difference | 0.0673 |

Means with the same letter are not significantly different.

| | Mean | N | treatment |
|---|---|---|---|
| A | 0.29133 | 3 | 2 |
| B | 0.21933 | 3 | 1 |

## LITERATURE CITED


AACC. 2000. Approved Methods of the American Association of Cereal Chemists. 10th edition. Methods 44-15A, 44-19. AACC International: St. Paul, MN.

Agbisit, R. M., Singh, V., Valenti, J. J., Kakleas, M., Tumbleson, M. E. and Rausch, K. D. 2003. Technique to measure surface-fouling tendencies of steepwater from corn wet milling. Cereal Chem. 80:84-86.

Arora, A., Dien, B. S., Belyea, R. L., Singh, V., Tumbleson, M. E. and Rausch, K. D. 2010. Heat transfer fouling characteristics of microfiltered thin stillage from the dry grind process. Biores. Technol. 101:6521-6527.

Asomaning, S. and Watkinson, A. 1992. Heat exchanger fouling by olefin - kerosene mixtures. Can. J. Chem. Engr. 70:444-451.

Awad, M. M. 2011. Fouling of heat transfer surfaces in: Heat Transfer - Theoretical Analysis, Experimental Investigations and Industrial Systems. InTech: Vienna.

Bansal, B. and Chen, X. D. 2006. A critical review of milk fouling in heat exchangers. Comp. Rev. Food Sci. Food Safety 5:27-33.

Belmar-Beiny, M., Gotham, S., Paterson, W., Fryer, P. and Pritchard, A. 1993. The effect of Reynolds number and fluid temperature in whey protein fouling. J. Food Eng. 19:119-139.

Belmar-Beiny, M. T. and Fryer, P. J. 1993. Preliminary stages of fouling from whey protein solutions. Journal of Dairy Research 60:467-483.

Blanpain, P. and Lalande, M. 1997. Investigation of fouling mechanisms governing permeate flux in the crossflow microfiltration of beer. Filtr. Sep. 34:1065-1069.

Bohnet, M. 1987. Fouling of heat transfer surfaces. Chem. Eng. Technol. 10:113-125.

Bothast, R. and Schlicher, M. 2005. Biotechnological processes for conversion of corn into ethanol. Appl. Microbiol. Biotechnol. 67:19-25.

Bott, T. R. 2001. Heat transfer to foul or not to foul-that is the question. Chem. Eng. Prog. 97:30-37.

Burton, H. 1968. Section G. Deposits from whole milk in heat treatment plant—a review and discussion. J. Dairy Res. 35:317-330.

Butterworth, D. 2002. Design of shell-and-tube heat exchangers when the fouling depends on local temperature and velocity. Appl. Therm. Eng. 22:789-801.

Butzen, S. 2006. Best management practices for corn-after-corn production. Crop Insights. 16:71-92.

Bylund, G. 1995. Dairy Processing Handbook, Tetra Pak Processing Systems AB: Sweden.

Changani, S., Belmar-Beiny, M. T. and Fryer, P. J. 1997. Engineering and chemical factors associated with fouling and cleaning in milk processing. Exp. Therm Fluid Sci. 14:392-406.

Chen, X. and Bala, P. 1998. Investigation of the influences of surface and bulk temperatures upon fouling of milk components onto a stainless steel probe. Proceedings of Fouling and Cleaning in Food Processing, Jesus College, Cambridge, England:25-32.

Chen, X. D., Li, D. X. Y., Lin, S. X. Q. and Özkan, N. 2004. On-line fouling/cleaning detection by measuring electric resistance—equipment development and application to milk fouling detection and chemical cleaning monitoring. J. Food Eng. 61:181-189.

Chenoweth, J. M. 1988. Liquid fouling monitoring equipment. Pages 49-65 in: Fouling Science and Technology. Springer.

Crittenden, B. and Alderman, N. 1988. Negative fouling resistances: The effect of surface roughness. Chem. Eng. Sci. 43:829-838.
Delplace, F., Leuliet, J. and Leviex, D. 1997. A reaction engineering approach to the analysis of fouling by whey proteins of a six-channels-per-pass plate heat exchanger. J. Food Eng. 34:91-108.
Enrique, N. S. 2010. Efficacy of different antifouling treatments for seawater cooling systems. Biofouling 26: 923-930.
Fetissoff, P., Watkinson, A. and Epstein, N. 1982. Comparison of two heat transfer fouling probes. Pages 391-396 in: Proc. 7th Int Heat Transfer Conf., Munich.
Flint, S., Bremer, P. and Brooks, J. 1997. Biofilms in dairy manufacturing plant - description, current concerns and methods of control. Biofouling 11:81-97.
Garrett-Price, B. A., Smith, S. A. and Watts, R. L. 1985. Fouling of heat exchangers: Characteristics, costs, prevention, control and removal. Noyes Publications: Park Ridge, NJ.
Georgiadis, M. C., Rotstein, G. E. and Macchietto, S. 1998. Modeling and simulation of shell and tube heat exchangers under milk fouling. AlChE J. 44:959-971.
Jenner, H. A., Whitehouse, J. W., Taylor, C. J. L. and Khalanski, M. 1998. Cooling water management in European power stations biology and control of fouling. Hydroecologie Appliquee 10.
Karabelas, A. J., Yiantsios, S. G., Thonon, B. and Grillot, J. M. 1997. Liquid-side fouling of heat exchangers: An integrated R&D approach for convention and novel designs. Appl. Thermal Eng 17.
Katzen, R., Madson, P. and Moon, J., GD. 1999. Ethanol distillation: the fundamentals. by Jacques, K, Lyons, T. P, Kelsall, D. R. Nottingham University Press, Nottingham, UK:269-288.
Kern, D. and Seaton, R. 1959. A theoretical analysis of thermal surface fouling. British Chem. Eng. 4:258-262.
Kim, Y., Mosier, N. S., Hendrickson, R., Ezeji, T., Blaschek, H., Dien, B., Cotta, M., Dale, B. and Ladisch, M. R. 2008. Composition of corn dry-grind ethanol by-products: DDGS, wet cake, and thin stillage. Biores. Technology 99:5165-5176.
Knudsen, J. G. 1981. Apparatus and techniques for measurement of fouling of heat transfer surfaces. Pages 57-81 in: Fouling of Heat Transfer Equipment: Washington, DC.
Kuppan, T. 2000. Heat exchanger design handbook. Marcel Dekker: New York.
Lewis, M. and Heppell, N. 2000. Fouling, cleaning, and disinfecting. Institution of Chemical Engineers: Gaithersburg.
Lyons, T. 2003. Ethanol around the world: rapid growth in policies, technology, and production. Pages 1-7 in: The Alcohol Textbook, 4th ed. Nottingham University Press: Nottingham, UK.
Macchietto, S., Hewitt, G., Coletti, F., Crittenden, B. D., Dugwell, D., Galindo, A., Jackson, G., Kandiyoti, R., Kazarian, S. and Luckham, P. 2011. Fouling in crude oil preheat trains: a systematic solution to an old problem. Heat Transfer Eng. 32:197-215.
McDonald, A. G. and Magande, H. L. 2012. Fundamentals of Heat Exchanger Design. Pages 127-211 in: Introduction to Thermo-Fluids Systems Design. John Wiley & Sons: Chichester, UK.

Meredith, J. 2003. Understanding energy use and energy users in contemporary ethanol plants. Pages 355-361 in: The Alcohol Textbook, 4th ed. Nottingham University Press, Nottingham, UK.
Metaxas, A. and Meredith, R. J. 1983. Industrial microwave heating. Peter Peregrinus Ltd: London, United Kingdom.
Moran, M. J., Clawges, R. M. and Zogorski, J. S. 2000. Identifying the usage patterns of methyl tert-butyl ether (MTBE) and other oxygenates in gasoline using gasoline surveys. Pages 209-213 in: American Chemical Society: Wastington, DC.
Mueller, S. 2010. 2008 National dry mill corn ethanol survey. Biotechnol. Lett. 32:1261-1264.
Müller-Steinhagen, H. 2011. Heat transfer fouling: 50 years after the kern and seaton model. Heat Transfer Eng. 32:1-13.
Nema, P. K. and Datta, A. K. 2005. A computer based solution to check the drop in milk outlet temperature due to fouling in a tubular heat exchanger. J. Food Eng. 71:133-142.
Panchal, C. and Watkinson, A. 1993. Chemical reaction fouling model for single-phase heat transfer. ACS Symp. Ser. 295:323-333.
Paterson, W. and Fryer, P. 1988. A reaction engineering approach to the analysis of fouling. Chem. Eng. Sci. 43:1714-1717.
Pritchard, A. 1988. The economics of fouling. Fouling Sci.and Technol. 12:31-45.
Pugh, S., Hewitt, G. and Müller-Steinhagen, H. 2005. Fouling during the use of seawater as coolant—The development of a user guide. Heat Transfer Engineering 26:35-43.
Rausch, K. D. and Belyea, R. L. 2006. The future of coproducts from corn processing. Appl. Biochem. Biotechnol. 128:47-86.
Rendleman, C. M. and Shapouri, H. 2007. New technologies in ethanol production. Rep No. 842. US Department of Agriculture, Office of the Chief Economist, Office of Energy Policy and New Uses: Washington, DC.
RFA. 2012. Industry Statistics. <www.ethanolrfa.org/industry/statistics>. Renewable Fuels Association: Washington, DC.
Riverol, C. and Napolitano, V. 2005. Estimation of fouling in a plate heat exchanger through the application of neural networks. J. Chem. Technol. Biotechnol. 80:594-600.
Santos, O., Nylander, T., Rizzo, G., Müller-Steinhagen, H., Trägårdh, C. and Paulsson, M. 2004. Study of whey protein adsorption under turbulent flow. Page 24 in: Heat Exchanger Fouling and Cleaning: Fundamentals and Applications. Engineering Conferences International: Santa Fe, NM.
Singh, V., Panchal, C. B. and Eckhoff, S. R. 1999. Effect of corn oil on thin stillage evaporators. Cereal Chem. 76:846-849.
Skudder, P. J., Brooker, B. E., Bonsey, A. D. and Alvarez-Guerrero, N. R. 1986. Effect of pH on the formation of deposit from milk on heated surfaces during ultra high temperature processing. J. Dairy Res. 53:75-87.
Steinhagen, R., Müller-Steinhagen, H. and Maani, K. 1993. Problems and costs due to heat exchanger fouling in New Zealand industries. Heat Transfer Eng. 14:19-30.
Van Asselt, A., Vissers, M., Smit, F. and de Jong, P. 2005. In-line control of fouling. Proceedings of Heat Exchanger Fouling and Cleaning-Challenges and Opportunities, Engineering Conferences International, Kloster Irsee, Germany.
Visser, J. and Jeurnink, T. J. 1997. Fouling of heat exchangers in the dairy industry. Exp. Therm Fluid Sci. 14:407-424.

Wallhäußer, E., Hussein, M. and Becker, T. 2012. Detection methods of fouling in heat exchangers in the food industry. Food Control 27:1-10.
Wilkins, M., Belyea, R., Singh, V., Buriak, P., Wallig, M., Tumbleson, M. and Rausch, K. 2006a. Analysis of heat transfer fouling by dry-grind maize thin stillage using an annular fouling apparatus. Cereal Chem. 83:121-126.
Wilkins, M., Singh, V., Belyea, R., Buriak, P., Wallig, M., Tumbleson, M. and Rausch, K. 2006b. Effect of pH on fouling characteristics and deposit compositions in dry-grind thin stillage. Cereal Chem. 83:311-314.
Wilson, D. I. and Watkinson, A. P. 1995. Model experiments of autoxidation reaction fouling, part I: mechanisms. Chem. Engr. 73:59-68.
Wilson, D. I. and Watkinson, A. P. 1996. A study of autoxidation reaction fouling in heat exchangers. Can. J. Chem. Engr. 74:236-246.
Withers, P. 1994. Ultrasonic sensor for the detection of fouling in UHT processing plants. Food Control 5:67-72.
Xiong, Y. L. 1992. Influence of pH and ionic environment on thermal aggregation of whey proteins. J. Agric. Food. Chem. 40:380-384.