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# Fouling characteristics of model carbohydrate mixtures and their interaction effects

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## ABSTRACT

Fouling resistances of carbohydrate mixtures were measured using an annular probe at bulk fluid temperature of 75 °C and initial probe surface temperature of 120 °C. Induction period, maximum fouling resistance and mean fouling rates were determined. Two experiments were performed with two varieties of starch (waxy and high amylose) and short chain carbohydrates, corn syrup solids and glucose. Interaction effects of glucose with starch varieties were studied. In the first experiment, short chain carbohydrates individual and interaction effects with starch were studied. Glucose and corn syrup solids showed no fouling, whereas starch, a long glucose polymer, showed marked fouling. Corn syrup solids and glucose mixed with pure starch decreased the mean fouling rates and maximum fouling resistances. Between corn syrup solids and glucose, starch fouling rates were reduced with addition of glucose. Induction periods of pure mixtures of either glucose or corn syrup solids were longer than the test period (5 h). Pure starch mixture had no induction period. Maximum fouling resistance was higher for mixtures with higher concentration of longer polymers. Waxy starch had a longer induction period than high amylose starch. Maximum fouling resistance was higher for waxy than high amylose starch. Addition of glucose to waxy or high amylose starch increased induction period of mixtures longer than 5 h test period.

*Keywords:* Evaporation; Maize processing; Fouling; Thin stillage; Ethanol production; Biorefining

## 1. Introduction

Fouling is the result of deposit formation on a heat transfer surface that increases resistance to heat transfer and fluid flow (Taborek et al., 1972). These deposits are thermally insulating and decrease the heat transfer efficiency of processing equipment such as evaporators. Fouling and cleaning related losses include cleaning chemicals, reduced productivity due to plant shut downs, maintenance and operating costs, and capital costs from oversized heat transfer equipment to accommodate fouling. Evaporation is one of the key unit operations used to remove water in the food industry. During evaporation, components in the bulk fluid form deposits on evaporator surfaces. The rate of deposit formation depends on many variables, including bulk fluid temperature, flow velocity and stream composition.

Fouling of evaporators is a chronic problem during maize starch and ethanol production. In the US, more than 200 plants use multiple effect evaporators to remove water from the thin stillage and steepwater processing streams from dry grind and wet milling processes, respectively. In the maize ethanol industry, evaporator fouling is encountered during thin stillage concentration to condensed distillers solubles. Thin stillage fouling is caused by the deposition of proteins, fat, ash, fiber and carbohydrates on evaporator surfaces during ethanol production using the dry grind process. Fouling

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decreases evaporator efficiency, increases steam consumption and therefore, increases ethanol production costs. Despite these well known issues, fundamental causes of increased fouling in maize processes are not well understood. 1 L of ethanol produced by the dry grind process can generate up to 5–6 L of whole stillage (Rasmussen et al., 2014); upon centrifugation, whole stillage is separated into thin stillage and wet grains. In the US, fuel ethanol production from corn increased from 34.1 billion liters (9 billion gallons) in 2008 to 50.3 billion liters (13.3 billion gallons) in 2012 (RFA, 2010).

One fouling mitigation strategy not requiring capital investment is to delay fouling by maintaining optimal processing conditions. There is limited research on evaporator fouling caused by thin stillage. Although earlier studies on thin stillage fouling reported composition, induction period, fouling resistance and fouling rates (Arora et al., 2010; Singh et al., 1999; Wilkins et al., 2006a,b), it is unknown whether protein, fiber, lipid, carbohydrates or a combination accelerate evaporator fouling. Singh et al. (1999) reported fouling rates of thin stillage from dry grind and distillers solubles from wet milling. Thin stillage had fouling rates 3× higher than distillers solubles. Wilkins et al. (2006) measured effects of Reynolds number (Re) in the laminar region and pH on thin stillage fouling rates and deposit composition. When Re increased from 440 to 880, thin stillage fouling rates decreased. As pH increased, ash content in fouling deposits increased, indicating a pH effect on mineral deposition. Phosphorus was the most abundant mineral in the deposits. Arora et al. (2010) used microfiltration to reduce solids, protein and fat contents of thin stillage and measured effects of total solids on thin stillage fouling tendencies. Solids removal decreased mean fouling rates but it was not determined whether the decrease was from reduced protein, fat or ash content. Also, effects of carbohydrates such as unconverted starch on thin stillage fouling were not determined in earlier studies.

Data available from thin stillage fouling studies were generated at bulk fluid temperatures of 40–60 °C (Arora et al., 2010; Singh et al., 1999; Wilkins et al., 2006a,b) which are lower than operating temperatures (75 °C) in a typical dry grind plant evaporator. Thin stillage composition, as reported in literature, varies with corn variety and operating conditions at dry grind facilities (Belyea et al., 2004). Process streams are biological in origin, are perishable and have variable compositions. In the dry grind process, starch is hydrolyzed to dextrin and then to glucose before fermentation to ethanol. Residual sugars from fermentable and unfermentable starch components in thin stillage may increase evaporator fouling. The possibility exists that starch hydrolysis was incomplete and carbohydrate in thin stillage remains as starch, dextrin or glucose and may affect thin stillage fouling rates. The extent of hydrolysis is expressed in terms of the dextrose equivalent (DE), a measure of total reducing power of sugars present in a carbohydrate mixture on dry basis relative to a dextrose (glucose) standard. Degree of polymerization (DP) is an indicator of the degree of hydrolysis and is inversely proportional to DE.

Earlier work with starch and sucrose showed increased starch content had larger effects on fouling than sucrose alone (Rausch et al., 2013). The same authors also found that ungelatinized starch in model thin stillage caused heat transfer fouling. It is unknown whether gelatinized starch alters fouling characteristics of starch mixtures. With continued heating, a starch granule swells many times from its original volume, loses crystallinity and solubilizes amylose polymers (Morris, 1990). Maize starch is a mixture of two polysaccharides, amylose and amylopectin. Amylose is a linear polymer whereas amylopectin is a branched molecule. In both polymers, glucose is the building block. In an amylose molecule, about 99% of glucose units are linked by α-1,4 bonds and few by α-1,6 bonds (<1%). The amylopectin polymer has at least 95% of glucose molecules linked by α-1,4 bonds and 5% by α-1,6 bonds. Regular maize starch contains 20–30% amylose and 70–80% amylopectin. However, there are other corn varieties that contain various amylose/amylopectin ratios. Waxy maize starch primarily contains amylopectin (>95%) and less than 5% amylose; high amylose maize starch contains >35% amylose (Tester et al., 2004). Starch gelatinization temperature is altered with amylose/amylopectin ratio; high amylose starches had higher gelatinization temperatures (Shi et al., 1998). It has been shown that amylose content influences starch thermodynamic parameters and functional properties (Jenkins and Donald, 1995; Sievert and Würsch, 1993). However, there is no evidence that amylopectin gets released into slurry even above 100 °C. Since maize starch is composed of varying amylose and amylopectin contents, it is possible that heat transfer fouling is influenced by starch variety. The objectives of this study were to (1) investigate the fouling characteristics of carbohydrate mixtures (starch, corn syrup solids and glucose) and (2) study the fouling tendencies of high amylose and waxy starch and their interactions with glucose.

**Table 1 – Carbohydrate composition (%, w/w).**

| Material | Glucose | Maltose | DP3 | DP4+ |
|---|---|---|---|---|
| Glucose | 99.7 | 0.3 | – | – |
| Corn syrup solids | 3.0 | 9.0 | 11 | 77 |

## 2. Materials and methods

### 2.1. Carbohydrate mixtures

Regular yellow dent maize starch (STA) and glucose (GLU) samples were obtained from Tate & Lyle (Decatur, IL, USA). Corn syrup solids (CSS) were obtained from Grain Processing Corporation (Muscatine, IA, USA). Typical dextrose equivalent (DE) of starch is zero and that of glucose is 100. DE of CSS is 20 or higher. Glucose (DP1), maltose (DP2), DP3 and DP4+ were measured using standard HPLC methods. Starch was assumed to have 100% (w/w) DP4+ (Table 1).

### 2.2. High amylose and amylopectin starches

Commercially available high amylose and waxy corn starches were used for the study. Waxy corn starch was food grade and mostly contained amylopectin (93%). Amylose starch contained a maximum of 70% amylose. Table 2 lists the characterization of waxy and high amylose starches provided by the manufacturers.

**Table 2 – Amylose and amylopectin contents of maize starches (manufacturer's analysis).**

| Starch source | Water content (%) | Amylopectin content (% db) | Amylose content (% db) |
|---|---|---|---|
| Waxy | 10 | 93 | – |
| High amylose | 11 | 30 | 70 |

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