

Effect of pH on Fouling Characteristics and Deposit Compositions in Dry-Grind Thin Stillage

M. R. Wilkins,¹ V. Singh,² R. L. Belyea,³ P. Buriak,² M. A. Wallig,⁴ M. E. Tumbleson,² and K. D. Rausch^{2,5}

ABSTRACT

Cereal Chem. 83(3):311–314

Dry-grind corn processing facilities produce ethanol, carbon dioxide, and distillers dried grains with solubles (DDGS). To produce DDGS, dry-grind corn processors concentrate thin stillage in multieffect evaporators. Concentration of thin stillage uses large amounts of energy, and efficient operation is important for long-term economic stability of the industry. Little data are available on fouling of evaporators during thin stillage concentration. We evaluated how thin stillage pH and acid type used during pH adjustment affected fouling as measured by induction period, fouling rate, and deposit composition. Using an annular fouling appa-

atus, fouling tests were conducted at pH 3.5, 4.0, and 4.5. In a second experiment, we used two types of acid, HCl or H₂SO₄, to adjust thin stillage to pH 3.5. Induction periods were shorter at pH 3.5 than at pH 4.0 or 4.5. As pH increased, fouling deposit protein decreased and ash increased. Concentrations of most elements, including P, Ca, Mg, Mn, and K, increased with an increase in pH. Phosphorus was the most abundant mineral element in fouling deposits. Induction periods were similar for the two acids. Thin stillage pH has an influence on deposit concentration, fouling rate, and induction period.

In the United States, fuel ethanol is produced primarily from corn by wet-milling and dry-grind (DG) processes. DG facilities require lower capital investment than wet-milling facilities, but they produce only one coproduct, distillers dried grains with solubles (DDGS). DDGS is sold as an animal food, primarily for ruminants. To meet growing demand for ethanol, farmer-owned cooperatives and others have built DG facilities throughout the corn-producing states of the United States. Decreased production costs are needed to make DG processing more competitive and stable.

Several strategies can be pursued to compensate for declining DDGS prices. One of these is to increase DG process efficiency. Concentration of thin stillage is one of the more energy-intensive unit operations in DG processing. Evaporation and drying operations account for 40–45% of thermal energy and 30–40% of electrical energy used in a DG facility (Meredith 2003). Thin stillage is the liquid fraction that results from centrifuging material left over after ethanol distillation (whole stillage) and is composed of soluble proteins, ash, lipids, and carbohydrates that were not converted into ethanol during fermentation. Thin stillage is concentrated from 4–6% (wb) solids to 25–30% (wb) solids using multieffect evaporators and combined with the insoluble fraction from whole stillage centrifugation (wet grains) to form DDGS (Singh et al 1999). Evaporators accumulate deposits on their surfaces that reduce heat transfer and increase pressure loss in a process known as fouling. Fouling decreases energy efficiency and increases operating costs through higher heating fluid temperatures and increased cleaning of evaporators.

The fouling of heated surfaces in fluid dairy processing has been reported in numerous studies. In dairy processing situations, pH and its relationship to the isoelectric point of dairy proteins have been shown to play key roles in fouling mechanisms (Belmar-Beiny and Fryer 1993; Visser and Jeurmink 1997). When solution pH is at or near a protein's isoelectric point, the protein has neutral charge and protein molecules aggregate due to a lack of electrostatic repulsion. Protein aggregates can then attach to a

heated surface (Visser and Jeurmink 1997). A similar effect has been observed with other proteins such as bovine serum albumin and gelatin (Fukuzaki et al 1995). The typical pH range for thin stillage is 3.7–4.7 (Jones and Ingledew 1994). Slurry pH is adjusted by H₂SO₄ and HCl addition before saccharification and fermentation for optimal yeast growth and glucoamylase enzyme activity (Kelsall and Lyons 2003; Russell 2003).

There are few publications regarding fouling of thin stillage evaporators. Singh et al (1999) found that thin stillage from corn wet milling fouled at a rate 67% less than DG thin stillage. There are few published data on fouling rate and deposit composition. This study was designed to determine effect of pH on thin stillage fouling behavior and fouling deposit composition.

MATERIALS AND METHODS

Fouling Test Apparatus

The apparatus for measuring fouling characteristics was based on previous work (Fischer et al 1975; Singh et al 1999; Agbisit et al 2003; Wilkins et al 2006) and consisted of a stainless steel rod inserted into a cylindrical housing, creating an annulus (0.00042 m² cross-sectional area). Thin stillage flowed through the annular space between the concentric rod and cylindrical housing. The rod interior was equipped with an electrical resistance heater and four thermocouples arranged to heat a portion of the rod and to measure the interior surface temperature. Thin stillage was pumped through the testing loop at a linear velocity of 5.2 m/sec and bulk temperature (T_b) was maintained at 40 ± 2°C throughout each test.

When bulk temperature of thin stillage reached 40°C, power was supplied to the resistance heater within the rod; power was adjusted to an average initial temperature of 100°C within the rod, after which power was maintained constant (± 15 W). As material was deposited on the heated portion of the rod, the rate of heat transfer decreased due to the low thermal conductivity of the fouling deposit, and interior temperature (T_{ic}) increased. Each test was terminated when the interior rod temperature reached 200°C or when test time reached 8 hr, whichever occurred sooner.

Fouling resistance, R_f (m²·K/kW), was calculated from T_{ic} and heater power (Q) as testing progressed. Q was kept constant throughout each test. Rod surface temperature (T_s) was determined by:

$$T_s = T_{ic} - \left(\frac{x}{k}\right) \frac{Q}{A}$$

where x/k is the radial distance (m) of the thermocouple from the surface divided by the thermal conductivity (kW/m·K) of the rod metal, and A is the area (0.0034 m²) of the heated section of the rod based on the outside diameter of the rod and assumed to be constant (Singh et al 1999). Quantity x/k is determined for each

¹ Biosystems and Agricultural Engineering, Oklahoma State University, Stillwater, OK 74078.

² Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

³ Animal Sciences, University of Missouri-Columbia, Columbia, MO 65211.

⁴ Veterinary Pathobiology, University of Illinois at Urbana-Champaign, Urbana, IL 61801.

⁵ Corresponding author. Phone: 217-265-0697. Fax: 217-244-0323. E-mail: krausch@uiuc.edu

thermocouple by a calibration procedure described in Fischer et al (1975) and based on a graphical technique by Wilson (1915). The ratio x/k was 0.061, 0.091, and 0.10 $\text{m}^2\cdot\text{K}/\text{kW}$ for each of the three thermocouples. Because thermal conductivity of stainless steel is constant, the radial distance of each thermocouple from the rod surface varied, resulting in variations in x/k . Individual rod surface temperatures associated with each thermocouple were calculated using T_{tc} and x/k values for each thermocouple and averaged for each time interval to obtain a mean T_s . Using mean T_s , the overall heat transfer coefficient for the probe (U) ($\text{kW}/\text{m}^2\cdot\text{K}$) is determined by:

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

R_{ft} is calculated as:

$$R_{ft} = \frac{1}{U_t} - \frac{1}{U_0}$$

where U_0 is the overall heat transfer coefficient ($\text{kW}/\text{m}^2\cdot\text{K}$) at the beginning of the test and U_t is the overall heat transfer coefficient ($\text{kW}/\text{m}^2\cdot\text{K}$) at time t . The beginning of the test ($t = 0$) is defined as the time when mean T_{tc} reached 100°C .

Following each test, the rod surface and fouling analysis system were cleaned. To avoid scratching the rod surface, fouling deposits were removed using a plastic spatula. After most of the deposit was removed using the spatula, the rod was soaked at room temperature overnight in 5% (w/v) NaOH solution. After soaking, remaining deposits were removed using a wet sponge. The fouling analysis system (batch tank, tubing, heat exchanger, pump, and rod housing) was cleaned by recirculating 20 L of 1% (w/v) detergent solution (Alconox, New York, NY) for 20 min, followed by a cold water rinse (250 L).

Experiment 1: Effect of pH on fouling

During production of ethanol, DG processors have the ability to adjust pH. If it were known that certain pH would reduce fouling rates, cost of operating evaporators could be reduced and energy efficiency increased. Effect of pH was determined on fouling by thin stillage using three pH levels (3.5, 4.0, and 4.5). These are typical pH of thin stillage in the DG process (Jones and Ingledew 1994). Three batches (90 L each) of thin stillage were collected from a typical commercial DG facility located in the midwestern United States and stored at 4°C . Each batch was divided into three samples (30 L); samples were adjusted to pH 3.5, 4.0, or 4.5 using solutions of 5.0% (w/v) NaOH and 37.5% (w/v) HCl.

A subsample (500 mL) of thin stillage was collected from each batch and analyzed for initial pH and protein, ash, and mineral contents. Following each test, fouling deposits were collected and removed from the rod surface with a plastic spatula. Deposits

were dried overnight at 49°C and stored at room temperature. Deposits from each replicate test at each pH were combined to obtain sufficient material for compositional analyses. Total nitrogen (TN) content was measured using nitrogen combustion (Approved Method 46-30, AACC International 2000); protein content was calculated as $\text{TN} \times 6.25$. Ash content was measured using a dry ash method (Approved Method 08-01, AACC International 2000). Mineral contents (Ca, Cu, Fe, K, Mg, Mn, Na, P, S, Zn) were determined using an inductively coupled plasma (ICP) (Approved Method 40-75, AACC International 2000).

A randomized complete block experimental design was used, with each batch of thin stillage representing a block. Linear regression was performed on R_{ft} versus time data for each test. The slope of each regression line ($\text{m}^2\cdot\text{K}/\text{kW}/\text{hr}$) was defined as the average fouling rate. For some treatments, R_{ft} versus time data were found to be nonlinear; average fouling rate was not reported for these treatments. Induction period, the initial period where no fouling occurred, was defined as the time when the 1 min moving average of $R_{ft} < 0.01 \text{ m}^2\cdot\text{K}/\text{kW}$, beginning with activation of the resistance heater. Effects of pH were determined on induction period and fouling rate using a general linear model (v. 8.0, SAS Institute, Cary, NC). When effects were significant ($P < 0.05$), Fisher's least significant difference method was used to compare means.

Experiment 2: Effect of Acid Type to Adjust pH

Commercial DG facilities use varying acids, including HCl and H_2SO_4 , to adjust pH of process streams. The effect of using either acid on fouling of heated surfaces was unknown. One batch (180 L) of thin stillage was divided into six 30-L samples that were analyzed for fouling characteristics (fouling rate and induction period). Three samples were adjusted to pH 3.5 using 37.5% (w/v) HCl and three were adjusted using 95.9% (w/v) H_2SO_4 . Testing was conducted in random order. Parameters for the fouling apparatus (bulk fluid temperature, flow rate, test sample volume) were the same as in Experiment 1. Deposits from each replicate test using each acid type were collected and combined to obtain sufficient material for compositional analysis as in Experiment 1, except that no ICP analyses were conducted. Effects of acid type on induction period were determined using the general linear model. When effects were significant ($P < 0.05$), Fisher's least significant difference method was used to compare means.

RESULTS AND DISCUSSION

Experiment 1: Effect of pH

Thin stillage composition varied in solids, protein, and ash concentrations, similar to previous work (Wilkins et al 2006) (Table I). Mean protein concentration ($\text{TN} \times 6.25$) of thin stillage was 20.6% (db) and mean ash concentration was 10.4% (db). Ranges in composition for thin stillage solids, protein and ash were 7.3–9.5%, 18.2–23.3% (db), and 8.2–11.9% (db), respectively; there can be considerable variation in thin stillage composition. This variation contributes to variation in processing requirements (i.e., needs for water removal) and is a source of variation in DDGS composition, and presumably affects fouling characteristics.

The pH of thin stillage affected fouling responses. In contrast to treatments at other pH, fouling deposits rapidly adsorbed onto the surface at pH 3.5, resulting in induction periods of less than 10

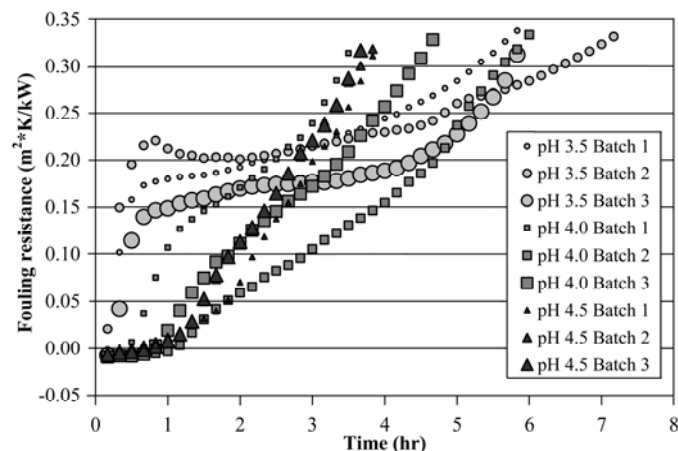


Fig. 1. Fouling resistance curves for thin stillage at pH 3.5 to 4.5.

TABLE I

Solids, Protein, and Ash Concentrations of Three Thin Stillage Batches from a Commercial Facility Used in Experiment 1

Batch	Solids (% wb)	Protein (% db)	Ash (% db)
1	7.3	18.2	11.9
2	7.7	20.2	11.2
3	9.5	23.3	8.2

min (Fig. 1, Table II). After ≈ 40 min, the rate of increase in fouling resistance decreased sharply until ≈ 4 hr. After 4 hr, fouling rate increased, though not at the rate observed during the first 40 min. Wilkins et al (2006) observed similar behavior in a batch of thin stillage at pH 3.8. Because changes in fouling resistance at pH 3.5 were not linear (Fig. 1), average fouling rates for this pH were not reported. At pH 4.0, a mean induction period of 50.2 min was observed (Table II). The induction period at pH 4.5 was similar to pH 4.0. After the induction period, fouling resistance increased linearly until an interior rod temperature of 200°C was reached. Induction period was highly variable among tests at pH 4.0. There was no correlation observed between thin stillage batch solids, protein, and ash concentrations and induction period or fouling rate for pH 4.0 tests. Similar variability in induction period was observed in a previous study among tests using thin stillage at pH 4.0 (Wilkins et al 2006). It was not possible to obtain enough fouling deposit from each individual fouling test to do compositional analysis. The composition of deposits from individual tests may have helped explain the variability in tests at the same pH.

Protein contents of fouling deposits decreased and ash contents increased as pH increased (Table III). Mean protein concentrations of deposits from tests at pH 3.5, 4.0 and 4.5 were 1.5, 1.0, and 0.5 times the mean protein concentration of thin stillage, respectively. Mean ash concentration of deposits from tests at pH 3.5, 4.0, and 4.5 were 1.5, 3.6, and 5.7 times the mean ash concentration of thin stillage, respectively. As the pH of thin stillage was increased, the composition of the resulting fouling deposit changed from high protein and low ash to low protein and high ash. This resulted in different responses for different elements. Calcium (Ca), iron (Fe), magnesium (Mg), manganese (Mn), sodium (Na), potassium (K), phosphorus (P) and zinc (Zn) concentrations in fouling deposits increased as pH increased (Table III). The ash content of fouling deposits increased by a factor of ≈ 2 from pH 3.5 to 4.0 and increased another factor of 2 from pH 4.0 to 4.5. P had the highest concentrations of the elements measured (32,000 to 121,000 ppm, db). Corresponding increases in P, Ca, Mg, Mn, and K concentrations in fouling deposits with increasing pH were suggestive that phosphate salts of Ca, Mg, Mn, and K may have been present in the fouling deposits. Cu, S, and protein concentrations decreased with increasing pH. Element concentrations in fouling deposits were suggestive that the ash components in fouling deposits contained more Ca, Mg, and Mn salts and fewer K salts as pH increased. Therefore, processing conditions that result in low pH of thin stillage can have adverse effects on fouling rate and fouling deposit composition.

As noted earlier, several investigations have shown that adsorption of protein onto a variety of surfaces, including stainless steel, latex, and metal oxides, is at a maximum when pH is near the isoelectric point of a protein (Norde and Lyklema 1978; Bagchi and Birnbaum 1981; Koutsoukos et al 1983; Norde et al 1985; Fukuzaki et al 1995). Thin stillage proteins include water-soluble corn proteins, α -amylase, and glucoamylase. Corn proteins insoluble in water, such as zein and yeast, are generally part of the wet grains portion, which is the other fraction from whole stillage centrifugation. Peplinski et al (1994) observed that water-soluble proteins in corn had an isoelectric point of pH 4.8 after being subjected to temperatures $>70^\circ\text{C}$ during corn drying. However, the soluble protein concentration isoelectrically focused at pH 4.8 decreased with increasing drying temperature, presumably due to denaturation. Proteins in thin stillage experience temperatures $>100^\circ\text{C}$ during processing, so the concentration of corn proteins in thin stillage with an isoelectric point of pH 4.8 is probably low. Thermostable α -amylase enzymes from *Bacillus amyloliquefaciens* and *B. licheniformis*, which are commonly used in DG processes, have reported isoelectric points of pH 6.25 and 6.5, respectively (Kochhar and Dua 1990; Maasen 1991; Power 2003). Previous

studies have reported isoelectric points of glucoamylase enzymes from *Aspergillus* to be between pH 3.5 and 4.15 (Amirul et al 1996; Sauer et al 2001). *Aspergillus* fungi are a common source of glucoamylase enzymes for saccharification in DG processing. The sources and isoelectric points of the α -amylase or glucoamylase enzymes used by the facility from which thin stillage was sampled are not known. The rapid rate of fouling in the early stages of tests at pH 3.5 indicates that proteins with isoelectric points at \approx pH 3.5 may have been responsible for the rapid development of a fouling deposit layer, similar to observations with other proteins (Bagchi and Birnbaum 1981; Norde and Lyklema 1978; Koutsoukos et al 1983; Norde et al 1985; Fukuzaki et al 1995). Tests at pH 4.0 and 4.5 may have been farther from the isoelectric point of the aggregated protein, resulting in greater induction periods, decreased initial fouling, and decreased protein concentrations in fouling deposits than what was observed for pH 3.5 tests. Because some glucoamylase enzymes commonly used in DG processes have isoelectric points near pH 3.5, these proteins may have been partially responsible for fouling observed at pH 3.5.

In dairy processing, heat transfer fouling has been the result of reactions that form protein aggregates that eventually adsorb onto the heated surface (Belmar-Beiny and Fryer 1993; Visser and Jeurink 1997). After the surface is covered with a monolayer of protein, other components such as mineral salts and additional protein aggregates, build up on the surface and increase fouling resistance (Visser and Jeurink 1997). In thin stillage, deposit adsorbed onto the stainless steel surface of the fouling rod for each test was dark brown in color at all pH. Amino groups in proteins react with reducing sugars when heated to form brown compounds called melanoidins in a reaction called Maillard browning (Damodaran 1996). At pH 3.5, deposit layers above the surface layer were also dark brown in color. At pH 4.0, the surface layer was

TABLE II
Fouling Rates and Induction Periods of Fouling Tests at Varying pH Levels in Experiment 1^a

pH	Fouling Rate (m ² ·K/kW/hr) ^b	Induction Period (min) ^c	Initial pH ^d
3.5	na ^e	9.6a	3.65
4.0	0.0741a	50.2b	3.68
4.5	0.0937b	56.6b	3.66

^a Mean values of three tests. Means followed by the same letters in the same column are not different ($P < 0.05$ unless noted).

^b SE = 0.0063 ($P < 0.10$).

^c Period of time between start of test and time $R_t = 0.01$ m²·K/kW; SE = 3.8; LSD = 13.1.

^d No differences detected ($P < 0.05$); SE = 0.089.

^e Not applicable (nonlinear).

TABLE III
Composition of Protein, Ash, and Selected Elements in Fouling Deposits and in the Ash Component of the Deposit in Experiment 1

	pH Concentration in Deposit (ppm, db)			
	3.5	4.0	4.5	TS ^a
Protein (% db)	31.2	20.1	10.1	20.6
Ash (% db)	15.5	37.3	59.6	10.4
Ca	1,670	6,290	13,900	
Cu	586	138	58	
Fe	10,100	20,900	17,900	
K	6,380	14,500	21,200	
Mg	11,600	33,500	65,900	
Mn	293	1,520	3,110	
Na	603	1,960	1,470	
P	32,200	85,300	121,000	
S	4,200	2,350	1,250	
Zn	5,590	9,490	8,750	

^a Thin stillage.

TABLE IV
Protein and Ash Contents of Fouling Deposits
and Thin Stillage in Experiment 2

Batch	Induction Period (min) ^a	Protein (% db)	Ash (% db)
Thin stillage (pH 4.1)	na	19.6	10.0
HCl added	10.4	31.0	8.3
H ₂ SO ₄ added	11.8	30.2	6.7
pH 3.5 ^b	9.6	31.2	15.5

^a Mean values of three tests; SE = 2.2; no differences detected ($P < 0.05$).

^b Experiment 1 results for comparison (HCl added).

covered by a lighter brown layer that appeared to also contain grey deposits, indicative of ash. At pH 4.5, the surface layer was covered with a gray colored layer that appeared to contain mostly ash. Though it was impossible to separate the layers of deposit from each other for compositional analysis, the visual observations follow the trend of the overall deposit compositions. From these qualitative observations and the overall deposit compositions, it appears that thin stillage fouling follows a model similar to that described for dairy fouling, with aggregated proteins adsorbing to the stainless steel surface, followed by additional protein aggregates or mineral salts adsorbing to the surface adsorbed protein. At pH 3.5, fouling was primarily due to protein aggregation and deposition. As pH increased, initial adsorption of aggregated protein occurred at a slower rate, probably because of increased differences between protein isoelectric points and thin stillage pH, which decreased electrostatic repulsion between protein molecules and subsequent aggregation. After a protein layer formed on the heated surface, additional layers adsorbed to the surface layer that contained increasing amounts of mineral salts as pH increased. From the shape of the fouling curves at each pH, the build up of additional layers that contained predominantly protein after the initial coating of the surface occurred at a slower rate (pH 3.5) than did build up of layers that contained higher concentrations of ash (pH 4.0 and 4.5) (Fig. 1).

Experiment 2: Effect of Acid Type

The R_{ft} versus time data were nonlinear for Experiment 2; therefore, fouling rates were not reported. Induction periods for tests from both acid types were not different from one another. Thin stillage protein and ash contents were similar to mean contents of thin stillage in Experiment 1 (Table IV). Although no statistical inferences can be made, protein contents of fouling deposits from tests with both acids were similar to protein contents of fouling deposits from previous tests conducted at thin stillage pH 3.5. Based on these data, acid type appears to have little effect on fouling characteristics and deposit compositions.

CONCLUSIONS

Fouling rates were greater at pH 4.5 than at pH 4.0. Thin stillage adjusted to pH 3.5 had a shorter induction period and a greater initial fouling rate than thin stillage adjusted to pH 4.0 or 4.5. As pH increased, protein contents of fouling deposits decreased and ash contents of fouling deposits increased. Phosphorus was the most abundant mineral in fouling deposits. Greater protein concentrations of fouling deposits from tests at pH 3.5 and previous studies were suggestive that glucoamylases in thin stillage may have aggregated and adsorbed onto the fouling probe more rapidly at pH 3.5 than pH 4.0 or 4.5, causing shorter induction periods. Induction periods for tests using HCl and H₂SO₄ to adjust pH were not different. Further testing between pH 4.0 and 4.5 is necessary to determine the best pH for the lowest fouling rate and greatest induction period. Lower fouling rates and increased induction periods would allow evaporators to operate for longer time periods without cleaning.

ACKNOWLEDGMENTS

Partial funding provided by the USDA Cooperative State Research, Education and Extension Service through the USDA CSREES Science and Education Resources Development program.

LITERATURE CITED

- 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.
- AACC International. 2000. Approved Methods of the American Association of Cereal Chemists, 10th Ed. Methods 08-01, 40-75, and 46-30. The Association: St. Paul, MN.
- Amirul, A. A., Khoo, S. L., Nazalan, M. N., Razip, M. S., and Azizan, M. N. 1996. Purification and properties of two forms of glucoamylase from *Aspergillus niger*. *Folio Microbiol.* 18:1347-1360.
- Bagchi, P., and Birnbaum, S. M. 1981. Effect of pH on the adsorption of immunoglobulin G on anionic poly(vinyltoluene) model latex particles. *J. Colloid Interface Sci.* 83:460-478.
- Belmar-Beiny, M. T., and Fryer, P. J. 1993. Preliminary stages of fouling from whey protein solutions. *J. Dairy Res.* 60:467-483.
- Damodaran, S. 1996. Amino acids, peptides, and proteins. Pages 321-429 in: *Food Chemistry*, 3rd Ed. O. R. Fennema, ed. Marcel Dekker: New York.
- Fischer, P., Sutor, J. W., and Ritter, R. B. 1975. Fouling measurement techniques. *Chem. Eng. Prog.* 71:66-72.
- Fukuzaki, S., Urano, H., and Nagata, K. 1995. Adsorption of protein onto stainless-steel surfaces. *J. Ferment. Bioeng.* 80:6-11.
- Jones, A., and Ingledew, W. M. 1994. Fermentation of very high gravity wheat mash prepared using fresh yeast autolysate. *Bioresource Technol.* 50:97-101.
- Kelsall, D. R., and Lyons, T. P. 2003. Grain dry milling and cooking procedures. Pages 9-21 in: *The Alcohol Textbook*, 4th Ed. Nottingham University Press: Nottingham, UK.
- Kochhar, S., and Dua, R. D. 1990. Thermostable liquefying alpha amylase from *Bacillus amyloliquefaciens*. *Biotechnol. Lett.* 12:393-396.
- Koutsoukos, P. G., Norde, W., and Lyklema, J. 1983. Protein adsorption on hematite (α -Fe₂O₃) surfaces. *J. Colloid Interface Sci.* 95:385-397.
- Maassen, A. 1991. Comparison of two alpha amylases from *Bacillus amyloliquefaciens* and *Bacillus licheniformis*. *Biomedica Biochimica Acta* 50:213-217.
- 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, England.
- Norde, W., and Lykema, G. 1978. The adsorption of human plasma albumin and bovine pancreas ribonuclease at negatively charged polystyrene surfaces. *J. Colloid Interface Sci.* 66:257-265.
- Norde, W., MacRitchie, F., Nowicka, G. and Lyklema, G. 1985. Protein adsorption at solid-liquid interfaces: reversibility and conformation aspects. *J. Colloid Interface Sci.* 112:447-456.
- Peplinski, A. J., Paulus, J. W., Bietz, J. A., and Pratt, R. C. 1994. Drying of high-moisture corn: Changes in properties and physical quality. *Cereal Chem.* 71:129-133.
- Power, R. F. 2003. Enzymatic conversion of starch to fermentable sugars. Pages 23-32 in: *The Alcohol Textbook*, 4th Ed. Nottingham University Press: Nottingham, UK.
- Russell, I. 2003. Understanding yeast fundamentals. Pages 85-120 in: *The Alcohol Textbook*, 4th Ed. Nottingham University Press: Nottingham, UK.
- Sauer, J., Christensen, T., Frandsen, T. P., Mirgorodskaya, E., McGuire, K. A., Driguez, H., Roepstorff, P., Sigurskjold, B. W., and Svensson, B. 2001. Stability and function of interdomain linker variants of glucoamylase 1 from *Aspergillus niger*. *Biochemistry* 40:9336-9346.
- Singh, V., Panchal, C. B., and Eckhoff, S. R. 1999. Effect of corn oil on thin stillage evaporators. *Cereal Chem.* 76:846-849.
- Visser, J., and Jeurnink, T. J. M. 1997. Fouling of heat exchangers in the dairy industry. *Exp. Thermal Fluid Sci.* 14:407-424.
- Wilkins, M. R., Belyea, R. L., Singh V., Buriak, P., Wallig, M. A., Tumbleson, M. E. and Rausch, K. D. 2006. Analysis of heat transfer fouling by dry-grind maize thin stillage using an annular fouling apparatus. *Cereal Chem.* 83:121-126.
- Wilson, E. E. 1915. A basis for rational design of heat transfer apparatus. *Trans. ASME* 37:546-551.

[Received July 21, 2005. Accepted January 26, 2006.]