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Potential Bleaching Techniques for Corn Distillers Grains

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Abstract: The ethanol industry is booming and extensive research is now being pursued to develop alternative uses for Distillers Dried Grains (DDG) and Distillers Dried Grains with Solubles (DDGS), coproducts of the ethanol production process. Currently, DDG and DDGS are used exclusively as livestock feed. The low starch, high protein and high fiber coproducts appear to be ideally suited for diets treating medical conditions such as diabetes and Celiac's disease by virtue of their chemical composition. Processing methods need to be investigated to create flours that can be used effectively. Modifying aspects such as color, odor and baking functionality may eventually hold the key to the use of distillers grains in food products.

Key words: Corn distillers grains, DDG, DDGS, bleaching

INTRODUCTION

Increased demand for ethanol gives researchers increased incentive to find value added uses for coproducts. This topic is currently undergoing a great deal of research in order to increase potential revenues from ethanol processing and utilization. Ethanol is commercially produced from corn through either a wet milling or dry-grind process. Wet milling is a more capital and equipment intensive process. The corn kernel is fractionated into different components, thus, resulting in many coproducts. Modern distilleries and processors can typically produce large volumes of ethanol. The other method of ethanol production is dry-grind processing. This process does not fractionate the entire corn kernel, thus, requiring less equipment and capital compared to the wet milling process. In general, smaller volumes of ethanol are produced. One benefit of dry-grind processing being less costly is that many plants can be producer-owned and directly benefit surrounding rural communities (Rausch and Belyea, 2006).

Overall, the number of corn ethanol plants is quickly escalating. At the beginning of 2008, the United States expects to produce approximately 7,230 million gallons of ethanol utilizing 134 manufacturing plants. Currently, another 77 plants are under construction or expansion and will be able to produce an additional 6,217 million gallons of ethanol (RFA, 2008).

Currently, livestock feed is the ethanol industry's only outlet for the non-fermentable residues, DDG and DDGS. Due to the high quantity of residues (approximately 1/3 of the original corn mass) produced from dry-grind processing, it may be ideal to use these coproducts as ingredients in human food products (Rosentrater and Krishnan, 2006). Distillers dried grains (DDG) are a good source of fiber (13%) and protein (27-30%), while remaining relatively low in total carbohydrate (46%) (Miron *et al*., 2001; Al-Suwaiegh *et al*., 2002; Davis *et al*., 1980). The nutritional composition of Distillers Dried Grains with Solubles (DDGS) can vary more, often containing 5-11% fiber, 27-34% protein, 5-6% starch and 39-62% carbohydrates (UMN, 2007; Belyea *et al*., 2004; Spiehs *et al*., 2002; NRC, 1998; 1982). The removal of fermentable carbohydrates, primarily starch, to produce ethanol leaves non-fermentable nutrients concentrated 3-9 fold in the coproduct streams (Rosentrater and Krishnan, 2006).

By virtue of distillers grains being low in starch, but high in protein and fiber, the nutritional content of DDG and DDGS appears to match the needs of therapeutic diets for medical conditions such as diabetes and Celiac diseases. Short-term studies completed by Arora and McFarlane (2005) concluded that a low carbohydrate diet resulted in lower HbA1c levels (7.6% +/- 0.3), greater glycemic control, lower postprandial glucose levels and improved insulin sensitivity when processed into viable food products for diabetic populations. Fiber was not a

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main concern of this study. Foods higher in starch increase postprandial glucose levels thus, increasing insulin dosage needs. To compensate, insulin dependent (Type I) diabetics would increase insulin injected, while non-insulin dependent (Type II) diabetics would merely restrict the quantity of high starch foods consumed.

Celiac disease is categorized by sensitivity to gluten, a protein in wheat, rye and barley. Oats may also need to be removed due to possible wheat contamination. A recent article from the Mayo Clinic (2006), states that the following starches are safe for consumption by individuals with Celiac diseases: cornstarch, potato starch, arrowroot starch, rice flour, quick-cooking tapioca, cornmeal and potato flour. The restrictive nature of this disease negatively impacts quality of life. In fact, approximately 1 in 133 persons in the United States is diagnosed (Mahan and Escott-Stump, 2004). A study completed by Lee and Newman (2003), concluded that 86% of respondents to a survey of Celiac patients considered themselves to be restricted in their ability to dine out. Perhaps the introduction of distillers grains into the food market will open up additional food choices for individuals with these medical conditions.

This particular application for distillers grains research is new and has many unanswered questions. Efforts need to focus on determination of wholesomeness of these ingredients; development of optimal particle size, color and protein/fiber balance; increasing shelf life properties; potential applications in food products; determination of yeast fermentation metabolites (such as nucleic acids and vitamin E isomers) and other functional constituents (i.e., zein, carotenoids and xanthophylls pigments). Moreover, there is a need for more stringent regulation of the quality of the raw corn used as starting materials, all of which will ultimately impact final product quality (Rosentrater and Krishnan, 2006).

A sensory quality that heavily influences consumers' preference for a given product is color. As discussed by Rosentrater and Krishnan (2006), the replacement of distillers grains in flour blends generally has been found to result in darker-colored finished food products. Additionally, the functionality of foods including fibrous materials, such as resulting volume, expansion during baking, moisture absorption, texture and mouthfeel are also altered. Overall, higher substitution levels of DDG in traditional food products have been found to lead to reduced sensory traits. Additionally, performance of many DDGS-based food products was often marginally acceptable to not acceptable. Bleaching and deodorizing DDGS may be essential to its use in human foods, as these steps can decrease fatty acids and pigments content resulting in higher quality end products (Rosentrater and Krishnan, 2006).

To date, this type of research has not yet been pursued. Thus, the focus of this research was thus, to review the literature and assess possible bleaching agents and techniques that may be applicable for corn DDG and/or DDGS. Color removal applications should reduce pigments and improve the overall baking performance of DDG and DDGS in foods.

MATERIALS AND METHODS

Many bleaching processes will be reviewed; however, some methods appear to be more applicable to DDG and DDGS than others. It is hypothesized that a bleaching or color removal treatments applied to DDG and DDGS will improve color and alter baking functionality. Major types of methods investigated include enzymatic, chemical, extraction and colorants. A brief synopsis of previously-conducted studies is provided in Table 1.

Enzymatic treatments

Natural maturation: In general, pigments in flour slowly bleach during storage throughout 2-3 weeks (Mercier and Gelinas, 2001). This process is referred to as atmospheric oxidation. Used by millers for centuries, this phenomenon not only improves color, but also the baking quality of the flour. One drawback was the need for lengthy time periods for storage, which is much longer than millers today would allow. Nitrogen trichloride has been used to speed up the maturation process. Although, it has little effect on the color itself, it does accelerate the aging process (Ranum and DeStefanis, 1989). This agent produces a byproduct known as methionine sulfoximine (MSO). It has been hypothesized that an increased amount of MSO in the food system has led to an increase in neurodegenerative disorders in humans. The result of MSO was the inhibition of glutathione and glutamine production, thus, decreasing the body's ability to defend itself from increased levels of oxidative stress (Shaw and Bains, 1998). For DDG and/or DDGS, a waiting period of 2-3 weeks may be considered too long to be economical. Processing plants typically lack this quantity and type of storage volume. Since, nitrogen trichloride appears to result in negative health consequences, it is probably best to look at other possibilities for bleaching distillers grains.

Lipoxygenases: Lipoxygenase is an enzyme that accelerates the oxygenation of polyunsaturated fatty acids. This enzyme is commonly found in plant and animal sources (Hildebrand, 1989). Its function in plants has been connected to flavor and odor formation of fruits. In animals, this enzyme forms precursors for chemical messengers such as leukotrienes or lipoxins (Gaffney, 1996). Mercier and Gélinas (2001) investigated slightly

Table 1: Comparison of bleaching techniques discussed in literature that may be appropriate for distillers grains

Bleaching agent	Concentrations	Times	Measure of effectiveness	Safety concerns[1]	Other factors	Citations
Enzymatic						
Natural Aging	N/A	2-3 week	Improved color and baking quality of the flour	Addition of Nitrogen Trichloride leads to neurodegenera-tive disorders among humans; not listed as GRAS	Nitrogen Trichloride will speed up the but does not result in lighter flour itself	Mercier and Gélinas (2001), Ranum and DeStefanis (1989) Shaw and Bains, (1998)
Enzyme Lipoxygenases	1-2% enzyme active soy flour, pea flour, or broad bean flour	N/A	Increased mixing tolerance of dough	Enzyme Lipoxygenase: not listed as GRAS	Produced a lighter end product but did not change color of flour itself	Ranum and DeStefanis (1989)
	Oxidation of PUFA's high in linoleic (~2.25% flour basis)	6-10 h of forced oxidation	Fig. 1: Peroxide vs. Index (meq/kg oil) Oxidation time (h)	Linoleic GRAS acid: (CFR 182.5065)	Bleaching increased in combination with long mixing times	Mercier and Gélinas (2001)
	Soy flour at a 5% substitution level of CGM	30/20 min	65% carotenoids removed at pH 6.5 vs. 47% removal at pH 7.0	N/A	Vigorous stirring shortened reaction time and improved degree of bleaching	Cha *et al*. (2000)
Oxido-Reductases	100 g flour combinations of: peroxidase (3,000 U), lipase (815-1,630 U) and linoleic acid (0-300 mg)	Unknown	Completely bleached bread dough	Peroxidase: not listed as GRAS lipase: GRAS (§184.1420) Linoleic acid: GRAS (CFR 182.5065)	Worked best in combination than as separate entities; worked best at pH of 5.5 or 6.5	Gélinas (1998)
Chemical						
Benzoyl Peroxide (BPO)	Diluted: addition rate to flour was 50 ppm	1-2 days	Poorly bleached most materials other than wheat flour	BPO in purist powder form can be explosive; high conc. could induce allergic reactions not listed as GRAS, but allowed as a food additive; no more than 0.002% of the weight of dairy products; treatment of whey-max conc. 100 mg kg^{-1} poses no safety concern (JECFA/63/SC)	BPO could affect baking quality of end products; most effective if color was extractable via acetone	Ranum and DeStefanis (1989)
	Bleaching mixture: 30 mg benzoyl peroxide and 70 mg calcium carbonate and 50 g flour: Benzoyl Peroxide Conc. of 150 ppm Hydrogen peroxide	Sample extractions then every 4 for 24 h and once daily for 3 months	After 9 days, benzoic acid was non-detectable in the flour which was bleached	BPO in purist powder form can be explosive; high conc. could induce allergic reactions Not listed as GRAS, but allowed as a food additive; no morethan 0.002% of the weight of dairy products; treatment of whey -max conc. 100 mg kg^{-1} poses no safety concern (JECFA/63/SC)	Treatment was applied at room temperature	Saiz *et al*. (2001)
Hydrogen Peroxide	Acute toxicity tests: 10, 2, 0.1 and 0.02%	7 days	Toxicity reported at 10% level, resulting in fetal weight loss	Toxicity to fetal development at 10% Not listed as GRAS but allowed as a food additive; no more than 75 ppm for meat (Title 21, Sec 173.370)	Pregnant rats received food with varying HP levels	Moriyama *et al*. (1982)

Bleaching agent	Concentrations	Times	Measure of effectiveness	Safety concerns1	Other factors	Citations
	10-28 g L^{-1} hydrogen peroxide	1 h incubation	Evenly bleached, however, yield returns were <50%; low conc. of apple pomace resulted in more effective bleaching	Toxicity to fetal development at 10% Not listed as GRAS but allowed as a food additive; no more 100 mL) than 75 ppm for meat (Title 21, Sec 173.370)	pH (9-12); Temp. (60-80°C); apple pomace solid/liquid ratio (5-10g/	Renard*et al*. (1996)
Hydrogen peroxide Treated Lignocellulose	Lignocellulose substrates AHP treatment (pH 11.5)	Oven fried at 4°C or 24 h	Mixograph peak height increased as much as 40%; more water could be incorporated into product too fiber fractions	Toxicity to fetal development at 10%. Not listed as GRAS but allowed as a food additive; no more than 75 ppm for meat (Title 21, Sec 173.370)	Replacement up to 40% of flour with treated lignocellulose	Jasberg*et al*. (1989)
Chlorine or chlorine gas[2]	4,000 U of chlorine gas	N/A	Not effective in bleaching bran or	Safety levels have been established by the FDA (CFR 173.300)	Improved color and baking qualities of flour	Abdel-Aal *et al*. (1996) and Ranum and DeStefanis (1989)
Azodicarbonamide (ADA)	N/A	N/A	It does not bleach flour; a second bleaching agent would be necessary	Not listed as GRAS: restricted to 45 ppm	Has no actual bleaching effects on its own, rather it improves baking qualities	Ranum and DeStefanis (1989)
Sulfites or sulfating agents	N/A	N/A	Bleaches some foods but mostly preserves color a product already has	Sulfite sensitivity in individuals is increasing; allergic reactions result; not listed as GRAS, so must report if >10 ppm (was GRAS 1958-1982 when sulfite sensitivity increased)	The FDA has mandated that products with >10 ppm include it on the label; it also can't be used used on fresh fruits and vegetables	Lecos (2008)
Extraction						
Ethanol or Butanol	150 mL for 1st extraction; 100 mL for 2nd extraction	15 min	Ethanol: 54% removed after 1st extraction; 88% removed after 2nd extraction Butanol: 74% removed after 1st extraction; 94% removed after 2nd extraction	Ethanol: exception for Frito Lay: GRAS up to 3000 ppm or 17.1 mg ethanol/d (21 CFR 170.36 (f)); treatment of fresh produce with 10% ethanol and water appeared to extend shelf life	Room temperature (25+/ -1°C); filtered through Whatman No. 1 filter paper	Park *et al*. (1997)
Organic Solvents	Control WDG Petroleum ether n-butanol Acetone	2 h	(L: 49.2b, a: 3.0b, b: 15.0, ΔE: 30.6) L: 44.2c, a: 4.5a, b: 14.7b, ΔE: 35.7) (L: 57.3a, a: 3.0b, b: 14.5b, ΔE: 23.2c) (L: 58.7a, a: 2.3c, b: 15.7a, ΔE: 21.4c)	Petroleum ether: Not listed as GRAS n-butanol: Not listed as GRAS Acetone: GRAS: but restricted to 30 ppm (CFR 173.210)	Partially effective in pigment removal	Abdel-Aal *et al*. (1996)
Colorants						
Titanium Dioxide (TiO_2)	1.0 g L^{-1} of TiO_2	2 h	70% bleaching of the dye	Application on food products is unknown; TiO_2 is safe for coloring food products but cannot exceed 1% by weight of the food product (Title 21, Sec 73.575) Not listed as GRAS	Photobleaching with a 150W spotlight	Epling and Lin (2002)

[1]Food Additives List-FDA CFSAN (http://www.cfsan.fda.gov/~dms/opa-appa.html); [2]Chlorine, as calcium hypochlorite, not to exceed 0.036% of dry starch; The finished food starch-modified is limited to use only as a component of batter for commercially processed foods; Chlorine, as sodium hypochlorite, not to exceed 0.0082 pound of chlorine per pound of dry starch; Chlorine, as sodium hypochlorite, not to exceed 0.055 pound of chlorine per pound of dry starch; 0.45% of active oxygen obtained from hydrogen peroxide and propylene oxide, not to exceed 25%; Residual propylene chlorohydrin not more than 5 parts per million in food starch-modified; Sodium hydroxide, not to exceed 1%; 21CFR172.892 http://www.cfsan.fda.gov/~lrd/FCF172.html

oxidized fats and long dough mixing times to replace the use of benzoyl peroxide for the flour bleaching process. Oxygen intake by dough can be accelerated in the presence of polyunsaturated fatty acids (i.e., linolenic and linoleic acids) that have unconjugated double bonds (Smith and Andrews, 1957). Supplementing dough with linoleic acid has been shown to accelerate pigment discoloration (Hawthorn and Todd, 1955). Oils high in linoleic acid (sunflower) versus those low (colza) were more effective in bleaching dough after being oxidized for 6-10 h. Mercier and Gélinas (2001) found that free linoleic acid and highly oxidized sunflower oil have major dough bleaching potential, especially in combination with long dough mixing times. Unfortunately, this was proven under intense mixing conditions that can be too long for standard or commercial dough development. While, the process of oxidizing oils high in polyunsaturated fatty acids appears ideal, this process has only been tested in the dough stage. Effects of bleaching on distillers grains are yet unknown. Perhaps this is a process that can result in improved color and be completed at bakeries.

A bleaching effect has also been accomplished when 1-2% of an enzyme-activated soy flour, pea flour, or broad bean flour was utilized. It was important to note that these mixtures will not necessarily produce lighter colored flour, rather a whiter breadcrumb upon baking (Ranum and DeStefanis, 1989). The addition of soy flour also improved the nutritional value of the overall product due to its high levels of the amino acids lysine and tryptophan (Park *et al*., 1997). Another study involved altering carotenoids in corn gluten meal (CGM) with soy flour (5%) as a lipoxygenase source. Results revealed that 65% of the carotenoids were bleached at a pH of 6.5, compared to only 47% bleached at a pH of 5.0. The ideal pH range for carotenoid reduction of CGM was 6.5-7.0. Higher mechanical energy for stirring optimized bleaching, while decreasing reaction time needed to achieve maximum bleaching (Cha *et al*., 2000). The use of enzyme-activated flour produced a reaction that could be suitable for distillers grains. It is imperative to create a bleaching process involving only a few key steps; process simplification could allow uniform color for distillers grains, regardless of the processing plant. Standardized procedures for distillers grains will result in more consistent and reliable end products for consumers.

Oxido-reductases: Oxido-reductases have been used to replace benzoyl peroxide as a dough-bleaching agent. Results from a study completed by Gelinas (1998) found peroxidases to be most efficient in bleaching activity for dough. Catalases were found to have potential for bleaching liquid systems, but were not effective in bread dough. This suggests that those enzymes have limited application for dough. This study tested 100 g of flour with combinations of peroxidases (3,000 U), lipase (815-1,630 U) and linoleic acid (0-300 mg). This combination was shown to completely bleach bread dough. One interesting point to note was that the bleaching action occurred during the dough stage. While, this may be one option for producing a lighter end product, other methods may be more applicable to distillers grain flour color, prior to the dough stage.

Chemical treatments

Benzoyl peroxide: Benzoyl peroxide (BPO) was used in industry by many wheat millers due to its ability to bleach flour within 24 h (Mercier and Gelinas, 2001). By oxidizing conjugated double bonds of carotenoid pigments, BPO was able to neutralize color. Benzoic acid (BA) was a byproduct of this bleaching process. BPO is oil soluble; therefore, it can be extracted via methanol or other solvents (Ranum and DeStefanis, 1989).

The oxidation of flour accelerated the natural aging process through, the oxidation of sulfhydryl groups on flour gluten proteins. Benzoyl peroxide, a free radical initiator, changed the double bonds of carotenoids to less conjugated double bonds, which produced a less colored product and generally does not inhibit baking functionality (Fennema, 1985). Experiments completed by Saiz *et al*. (2001) resulted in bleached wheat flour through, the use of benzoyl peroxide (30 mg) and calcium carbonate (70 mg to stabilize the mixture). This bleaching mixture was added to 50 g of flour, which resulted in a final benzoyl peroxide concentration of 150 ppm. The treatment was applied at room temperature with sampling every 4 for 24 h and then once daily for 3 months. It was found that benzoyl peroxide reached non-detectable levels after 9 days, by decomposing into benzoic acid, which then acted as a food preservative. The literature shows that that BPO could impact baking quality of end products. Also, excessive concentrations of BPO remaining in flour could induce allergic reactions, as well as destroy vitamin E and other nutrients. The United States regulates maximum concentrations of BPO use to 0.05 g kg^{-1} (Wei *et al*., 2006).

BPO in its pure powder form is dangerous due to its explosive nature. Diluting it in solution to approximately 50 ppm, reduces the danger (Ranum and DeStefanis, 1989). They showed that other than wheat flour, BPO poorly bleached other food materials including: apple fiber, corn bran, oat fiber, rice flour, soy flour and wheat fiber. They concluded that BPO's bleaching action was most effective on materials whose color was extractable via acetone.

Abdel-Aal *et al.* (1996) also, indicated that BPO (up to 400 μg g^{-1}) as not effective in bleaching bran of fiber fractions from wheat, corn, rice, apple, or sugar beet. Presently, it is not known if color from DDGS can be extracted via acetone. However, it is known that DDGS contains high dietary fiber contents (24-40%) (San Buenaventura *et al.*, 1987; UMN, 2007; Belyea *et al.*, 2004; Spiehs *et al.* 2002; NRC, 1998, 1982). Moreover, these studies have also indicated that BPO is not efficient in the removal of color pigments from corn products. These findings indicate that bleaching methods that have better results with corn products should be examined instead.

Hydrogen peroxide: Abdel-Aal *et al.* (1996) investigated the use of Alkaline Hydrogen Peroxide (AHP) and its effects on wheat stillage (both with and without solubles). Their findings indicated that alkaline (pH 11.5) hydrogen peroxide treatment (0.3 mol L^{-1}) of cereal straw, stalks, husks, or other lignocellulosic materials resulted in a whiter fiber color and enhanced functional baking properties when combined with the stillage. The AHP technique greatly eliminated the yeasty taste and dark colors shown in wheat distillers grains. The alkaline hydrogen peroxide technique proved to be most effective when pH treatment solutions were adjusted before and after the hydrogen peroxide bleaching. Bleaching apple pomace (a byproduct of apple juice and cider production) with alkaline peroxide has also proved to be very effective (Renard *et al.*, 1996). Treatment conditions were as follows: pH (9-12), hydrogen peroxide concentration (10-28 g L^{-1}), temperature (60-80°C) and solid/liquid ratio of the pomace (5-10 g/100 mL). The alkaline treatment evenly bleached the pomace, even though yield returns (<50%) were lower than other treatments tested (80-90%). Efficiency of bleaching depended on whether a high or low concentration of apple pomace was used. Low concentrations had superior bleaching results versus high concentrations. Finally, a pH of 12 resulted in the most effective bleaching versus the other pH levels.

Hydrogen peroxide is a widely used food additive that acts as a bleaching agent, but it can also have negative effects. Moriyama *et al.* (1982) tested acute toxicity with hydrogen peroxide orally administrated to pregnant rats at 0.02, 0.1, 2 and 10% levels. Results indicated no pathological changes were exhibited, except when hydrogen peroxide was administered at the 10% level. At this dose, a significant decrease in body weight in the fetus resulted. Therefore, it is important to carefully monitor hydrogen peroxide levels in food products so that negative health effects can be avoided. It appeared that the AHP treatment of lignocellulose could result in a whiter fiber color. DDGS is very high in fiber with ranges between 25.0-51.3% (neutral detergent fiber) (Rosentrater and Muthukumarappan, 2006). Thus, the AHP treatment could possibly effectively bleach DDGS. This method appears very promising, however, yield efficiency will xneed to be closely monitored and managed.

Replacement with Treated Lignocellulose: The desire to use high fiber additives (such as brans, seed hulls, or purified cellulose) in food products has been faced with several challenges associated with cellulose content. When hydrated, the outer surface of these particles softens while, the interior often remains intact and can reduce gluten strands, thus, degrading baking quality (Dubois, 1978). Applying an Alkaline Hydrogen Peroxide (AHP) treatment to fiber additives can result in higher water absorption, improved softening and the ability to swell into dough easily (Jasberg *et al.*, 1989; Gould *et al.*, 1989).

A study completed by Jasberg *et al.* (1989) compared the height of mixograph peaks for doughs consisting of flour alone versus a mixture of flour and AHP-treated lignocellulose (from corn stalks). Results indicated that 10% substitution of the flour with AHP-treated corn stalks caused significant increases in the height of the mixograph peak for the dough. Not only was peak height increased, but also, the amount of water incorporated into the dough without causing reductions in dough tensile strength. This avenue of bleaching should be evaluated in concurrence with Alkaline Hydrogen Peroxide (AHP) treatment, as discussed earlier. Studies indicated many potential benefits, especially the enhancement of baking properties.

Chlorine: Chlorine gas has been commonly used in the wheat flour industry as a means to bleach and improve baking functionality. The United States has placed chlorine on the GRAS list (Generally Regarded as Safe) for food products such as bottled water, cereal flours, poultry process water and anti-microbial agents used to wash produce (CFR 173.300). It was considered a food additive; therefore, safety levels have been established by the FDA and are illustrated in Table 1 (Fukayama *et al.*, 1986). Tsen *et al.* (1971) also studied the effect of chlorine on wheat flour by varying treatments of 1-16 oz of chlorine per cwt. Results indicated that chlorine effectively bleached flour pigments up to 2.0 oz cwt^{-1}. Any additional levels of chlorine did not reduce the pigments of the flour further. The grain, texture and color of cakes prepared with the treated flour were enhanced up to 4.0 oz cwt^{-1} treatment. Johnson *et al.* (1979) tested baking

functionality of cakes prepared from chlorine-treated flour compared to its untreated counterpart. Higher volumes and enhanced quality resulted from the chlorine-treated flour. However, untreated flour resulted in a collapsed cake volume, thick grain and flat contour.

Often, the bleaching of food products can result in other consequences. The use of chlorine for bleaching not only improves the color of the product, but also many baking qualities of the flour. Unfortunately, chlorine gas treatment (up to 4000 μg) has not been effective for bleaching bran or fiber fractions from wheat, corn, rice, apple or sugar beet (Ranum and DeStefanis, 1989). Bleaching flour with chlorine has resulted in many positive attributes, such as enhanced color and baking functionality. However, DDG and DDGS are materials high in corn bran and fiber. Chlorine has been shown to not be effective for bleaching these types of products. This method of bleaching may not be appropriate for distillers grains. Other avenues should be investigated instead.

Azodicarbonamide: Azodicarbonamide (ADA) is a bleaching technique that replaced the common use of chlorine dioxide in the 1950's and 1960's. It was found to be an easier and more effective bleaching method. However, ADA has no actual color removing or whitening effects on its own. Its only function was to improve the baking qualities of the flour. Historically, ADA was linked with bleaching agents and consequently was still classified as a bleaching agent under the U.S. Food and Drug Regulations (Ranum and DeStefanis, 1989). It is unclear why azodicarbonamide is still classified as a bleaching agent when it does not have the ability to bleach. This method is probably not appropriate for distillers grains for the purpose of color modification. If the only goal was to enhance baking functionality, this might be a suitable treatment.

Sulfating agents: Sulfites have been used in the food industry for a number of purposes. Benefits of their use included inhibition of enzymatic browning, inhibition of non-enzymatic browning, antimicrobial actions, dough conditioning effects, antioxidant purposes and bleaching of some food components. When sulfites are used, sulfur dioxide is liberated under certain conditions (Simon, 1992). Low-moisture foods do not require pre-treatment of sulfites for color stability (Ling *et al*., 2005). This suggests that DDG and DDGS should not require sulfite treatment, due to low water activity levels, in order to maintain color.

An increasing percentage of the human population has developed a sulfite sensitivity, which can negatively impact health. The use of sulfites needs to be closely regulated to prevent further health complications in sulfite-sensitive people. All sulfite use must be declared on food labels. In 1986, the Food and Drug Administration banned the use of sulfites from fresh fruits and vegetables (excluding potatoes) (Simon, 1992). From that point, the FDA has enforced regulations to protect sulfite-sensitive individuals. Current regulations included not using sulfites on fresh fruits and vegetables and any foods containing more than 10 ppm of sulfites must label it on the ingredient list. The FDA has also taken steps to identify prescription drugs containing sulfites, which can be used to maintain drug potency and stability (Lecos, 1986).

Sulfites have been primarily used for color stability, however, due to the increased number of sulfite sensitivity allergies, the use of sulfites in DDG and DDGS should be avoided.

Extraction treatments

Ethanol and butanol: A study completed by Park *et al*. (1997) showed that carotenoids in Corn Gluten Meal (CGM) could be eliminated via extraction with ethanol and butanol. Extractions were completed using wet corn gluten meal and 150 mL of ethanol or butanol by stirring the solution for 15 min at room temperature and then filtering. The remaining slurry was suspended in another 100 mL of ethanol or butanol, stirred for 15 min at room temperature and filtered a second time. Results showed that the carotenoids in the CGM were rapidly extracted into ethanol with no additional increase in carotenoid extraction after 5 min. In contrast, butanol extracts gradually increased the absorbance of carotenoids for up to 1 h. The difference in extraction rates was readily explained by CGM having a greater dispersibility in ethanol. Surface area contact can be improved with vigorous stirring or agitation, thus, resulting in greater carotenoid extraction. Total solids loss after the second filtration was greater with butanol (24%) than ethanol (11%). The majority of solid losses occurred after the first extraction. This method of bleaching appears to be effective, even if only 2 extractions are performed, however, the amount of solids lost needs to be taken into consideration.

Other organic solvents: A study completed by Abdel-Aal *et al*. (1996) found the use of organic solvents to be only partially effective in pigment removal and color improvement. The removal of grey pigments in Wheat Distilled Grains (WDG) was effective with the extraction of n-butanol and acetone. However, the use of petroleum ether (an extremely non-polar solvent) resulted in a darker color of the WDG. Overall, treatment with pH's between 8 and 12 resulted in progressively darker WDG.

Previous studies have been completed using wheat distilled grains, which is similar to corn-based DDG and DDGS. This is an excellent measure of how this process might work on corn-based products. Results showed that the use of organic solvents for color removal purposes have not been shown to be very effective. Ethanol, in particular, is a more polar solvent than petroleum ether. Ethanol is efficient in disrupting hydrogen bonds, electrostatic interactions and hydrophobic interactions with proteins. Phospholipids, glycolipids and steroids are polar lipids that can be removed with the ethanol solvent. Non-polar ethers (such as petroleum ether) breaks Van der Waal forces and can remove hydrocarbons, sterol esters, acylglycerols and carotenoid lipids. These 2 different solvents are equipped to remove different lipids and therefore, depending on the material analyzed, have different levels of efficiency (Sikorski and Kolakowska, 2003). Therefore, this method using petroleum ether may not be appropriate to be tested on DDG or DDGS. As already discussed, other more promising methods should be pursued instead.

Colorants

Titanium dioxide: Titanium dioxide (TiO_2) has been used as a photocatalyst for the degradation of organic pollutants. However, TiO_2 has also been shown to be an effective catalyst for the photobleaching of organic dyes in aqueous solutions with the use of visible light (UV or sunlight). A study completed by Epling and Lin (2002) suggested that both TiO_2 and a light source are necessary to produce the photobleaching of the dye. Approximately 70% of the dye tested was bleached within a 2 h time period. While, the literature surrounding photobleaching appears to be promising, the scope of this literature review did not find any studies testing TiO_2 and photobleaching on food products. Most literature supported the use of sunlight as a source to bleach the dyes. However, this is not practical to use at ethanol plants in the United States. Each location has various environmental differences, which would result in uncontrolled variations in the bleaching.

Possibilities for distillers grains

Enzymatic treatments: Enzymatic bleaching agents discussed in this study, include the natural maturation process, lipoxygenases and oxido-reductases. Natural maturing of flour that could contain various substitutions of DDG/DDGS (through, the aging process) may not appropriate. Nitrogen trichloride has the ability to speed up the natural maturation process, but has many negative health consequences. Oxido-reductases are commonly used during the dough stage, but not the flour stage.Bleaching abilities are utilized in the bakery to form a whiter final product. In order to bleach DDG and DDGS during the flour stage, the use of oxido-reductases must be eliminated from further consideration. Lipoxygenase appears to be a promising enzymatic method of bleaching DDG and DDGS. Enzyme activated flour can produce a bleaching reaction when combined into the matrix. The reaction does not appear during the flour stage but occurs when final baking products are produced. Lipoxygenases appeared more promising than oxido-reductase in that the enzyme-activated flour can be used at the bakery. Thus, the preparation step could be readily accomplished at the plant, not by the baker.

Chemical Treatments: Many chemical bleaching agents have been identified during this discussion. Agents reviewed include benzoyl peroxide, chlorine, hydrogen peroxide, lignocellulose replacement, azodicarbonamide and sulfating agents. Some chemical agents appear to be more promising for bleaching DDG and DDGS than others. Azodicarbonamide (ADA) is currently classified as a bleaching agent, even though, it has no bleaching properties. The main use for ADA is to enhance baking functionality. Sulfating agents are commonly used to maintain color in food products; however, an increasing percentage of the population was acquiring an allergenic sensitivity to sulfites. If this method is utilized for DDG and DDGS, the potential consumer population would immediately be reduced. Previous studies on benzoyl peroxide (Abdel-Aal *et al*., 1996) and chlorine (Ranum and DeStefanis, 1989) have not proven to be effective in pigment removal for fibrous materials similar to DDG and DDGS. Therefore, it is unlikely that these bleaching agents will be successful if applied to distillers grains. Of all the chemical agents discussed, hydrogen peroxide appears to be most promising for bleaching DDG and DDGS. An alkaline environment should exhibit high bleaching ability in addition to other positive benefits, such as improved water absorbency and baking functionality.

Extraction treatments: Ethanol, butanol and other organic solvents used pigment extraction to accomplish bleaching. Organic solvents have not proven to be effective bleaching agents for materials similar to DDG and DDGS; therefore, they may not be appropriate methods to use either. Conversely, ethanol and butanol extractions appear to be promising for the bleaching of DDG and DDGS, however, extraction losses must also be considered. This method will not be appropriate if a significant portion of DDG and DDGS are lost during extraction, which will merely forms another waste product for processors to find a use for.

Colorants: Titanium dioxide was the only colorant discussed; unfortunately it did not appear to be practical for use with distillers grains. Titanium dioxide is used in conjunction with a photobleaching process that relied on sunlight as the major source of energy to bleach. The literature did not mention its use in food products; rather it is mostly used for the bleaching of dyes.

Need for further study: Based upon this review of literature, it was believed that the following methods may not be appropriate for bleaching DDG or DDGS: natural maturation, oxido-reductases, benzoyl peroxide, chlorine, azodicarbonamide, sulfating agents, organic solvents, or titanium dioxide. They are typically ineffective for bleaching fibrous materials, may have harmful health consequences, or may not prove to be applicable for bleaching corn-based DDG and DDGS during the flour stage before utilization in food products.

Methods that do show promise included hydrogen peroxide, ethanol/butanol extraction and lipoxygenases. Hydrogen peroxide appears to be extremely successful when used in an alkaline environment. Ethanol and butanol have proven bleaching abilities. However, it is important to monitor extraction losses and perhaps analyze additional methods of extraction that can increase product yield. Finally, lipoxygenases, such as those found in enzyme-activated soy flour, appear to have high bleaching potential for these products. An advantage to this process would be the ability to assemble appropriate substitutions of DDG and DDGS flour with the enzyme-activated flour prior to packaging for consumers or food processors. Flours may appear darker in color; however, their color improvement should be viewed in finished baked products. Although not previously studied, perhaps a mixture of treatments, such as lipoxygenase and hydrogen peroxide treated flour could result in a more highly bleached, functional product. It is hypothesized that alkaline hydrogen peroxide treated flour, combined with enzyme activated flour might produce a superior product when used in combination and is thus, a potential avenue that needs to be investigated in future studies.

CONCLUSION

DDG and DDGS hold great potential to be used in food products, particularly for use in diets for people with medical conditions such as diabetes and Celiac's disease. Distillers grains are low in starch and high in protein and fiber. Thus, they may potentially provide appropriate food components for diabetics. Distillers grains, a coproduct of the ethanol process, are appropriate for Celiac's disease since, they are gluten free. Individuals with Celiac's disease are restricted from barley, rye and wheat, which does not leave many other grain options available for consumption. Research to create appropriate processing procedures for DDG and DDGS needs to be pursued before these products can reach potential consumers. Aspects such as color, odor and baking functionality need to be examined, as they will eventually hold the key to the use of distillers grains in food systems. The objective of this research was to review the literature and to discuss previous studies regarding various bleaching processes. No research has been conducted on bleaching corn-based distillers grains yet. Hydrogen peroxide, ethanol/butanol extraction and lipoxygenases appeared to be the most promising bleaching agents that should be pursued.

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