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Abstract. *The ethanol industry is booming. And extensive research is currently 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. previous research has shown promising avenues for the use of DDG and DDGS in human foods. The low starch, high protein and high fiber grains seem ideally suited for medical conditions such as diabetes and Celiac's disease. Processing methods need to be investigated to create functional flours that can be used effectively. Refining aspects such as color, odor, and baking functionality will eventually hold the key to the use of distillers grains in food products. The objective of this paper was to examine previous research on bleaching various food products, and to discuss their potential applicability for distillers grains. No research has yet been completed on bleaching distillers grains. This will be the topic of future research, and will be reported at a later date.*

Keywords. *Bleaching, distillers grains, DDGS, ethanol, food, processing.*

Introduction

Throughout the past several years, increased demand for fuel ethanol and use of its coproducts has expanded. This topic is currently undergoing a great deal of research in order to increase potential revenues from ethanol processing and utilization. Ethanol is produced from corn via 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. Large volumes of ethanol can be produced, typically by corporate-owned distilleries and processors. The other method of ethanol production is dry-grind processing. This process does not fractionate the entire corn kernel, and thus requires less equipment and capital compared to the wet milling process. In general, smaller volumes of ethanol are produced. One benefit of dry-grind processing is that many plants are producer-owned and directly benefit surrounding rural communities (Rausch and Belyea, 2006).

Overall, the number of corn ethanol plants is quickly climbing. At the beginning of 2007, the United States produced approximately 5.6 billion gallons of ethanol per year with 114 manufacturing plants. Currently, another 87 plants are under construction or expansion. Upon completion, an additional 6.4 billion gallons will be produced yearly (RFA, 2007).

As of now, 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). Distillers dried grains with solubles (DDGS) nutritional content varies more, often containing 5-11% fiber, 27-34% protein, 5-6% starch, and 39-62% carbohydrates (UMN, 2006; Belyea et al., 2004; Spiehs et al., 2002; NRC, 1998; NRC, 1982). The removal of fermentable carbohydrates, primarily starch, to produce ethanol leaves nonfermentable nutrients concentrated three to nine fold in the coproduct streams (Rosentrater and Krishnan, 2006).

Because distillers grains are low in starch, but high in protein and fiber, the nutritional content of DDG and DDGS appears to match the needs of 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. Foods higher in starch increase postprandial glucose levels thus increasing insulin needs. To compensate, an insulin dependent (Type I) diabetic would increase insulin injected, while a non-insulin dependent (Type II) diabetic would restrict the quantity of high starch foods consumed. Celiac disease, on the other hand, is categorized by sensitivity to gluten, which is a protein in wheat, rye, and barley. Research has speculated that 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 Celiac consumption: 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 are 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 negatively impacted on the 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.

The fact that the field of alternative distillers grains research is so new leaves many questions unanswered. Efforts need to focus on determination of wholesomeness of these ingredients; development of optimal particle size, color, and protein/fiber composition; 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. carotenoids, zein, and xanthophylls). 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).

Color is a sensory quality that heavily impacts consumers' preference for a given product. In terms of color, distillers grains generally result in darker-colored finished food products. Additionally, the functionality of foods using these materials, such as resulting volume, expansion during baking, moisture absorption, texture, and mouthfeel are altered as well. Overall, a negative impact is generally seen for products to which high substitution percentages of distillers grains have been added. Additionally, performance of many DDGS-based food products is often marginally acceptable to not acceptable, according to several sensory studies. Bleaching and deodorizing DDGS will be essential to its use in human foods, as these steps will neutralize fatty acids and pigments, and should result in higher quality end products (Rosentrater and Krishnan, 2006).

To date, this work has not yet been pursued. Thus the focus of this paper is to review the literature, investigate, and assess possible bleaching techniques and agents that may be applicable for DDG and/or DDGS. Bleaching applications should reduce pigments and improve the overall baking performance of DDG and DDGS in foods.

Review of Bleaching Techniques

Throughout the course of this discussion, many bleaching agents and processes will be reviewed; however, some methods appear to be more applicable to DDG and DDGS than others. It is hypothesized that a bleaching treatment applied to DDG and DDGS will improve color and baking functionality because physiochemical properties may change. Major types of bleaching methods to be examined include: enzymatic, chemical, extraction, and colorants. A brief synopsis of previously conducted studies is also provided in Table 1 for reference.

Enzymatic

Natural Maturation

Pigments in flour typically exhibit slow bleaching during storage throughout a 2 to 3 week time period (Mercier and Gelinas, 2001). This process can be 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 is the need for lengthy time periods for storage, which is generally much longer than millers today would allow. To overcome this dilemma, the use of nitrogen trichloride was adopted due to its ability to extensively speed up the maturation process. Nitrogen trichloride has little effect on the color itself; however it does accelerate the aging process (Ranum and DeStefanis, 1989). The use of nitrogen trichloride produces a byproduct known as methionine sulfoximine (MSO). It has been hypothesized by researchers that an increased amount of MSO in the food system has led to an increase in neurodegenerative disorders among humans. The result of MSO is 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 to 3 weeks is probably too long to be economical, because processing plants typically lack this type of storage volume. And because the addition of 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 oxidized fats and long dough mixing times to replace the use of benzoyl peroxide for the flour bleaching process, as 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 (such as sunflower) versus those low (like colza) were more effective in bleaching dough after being oxidized for 6-10 hours. Mercier and Gélinas (2001) found that free linoleic acid and highly oxidized sunflower oil do 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 be completed at the bakery scale, and will result in an improved color.

A bleaching effect can also be accomplished when 1-2% of an enzyme-activated soy flour, pea flour, or broad bean flour is utilized. It is important to note that this mixture will not necessarily produce lighter colored flour; rather a whiter bread crumb will result upon baking (Ranum and DeStefanis, 1989). The addition of soy flour can also improve 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 altered 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 to produce a bleaching reaction appears to be a very promising avenue to pursue for distillers grains. It is imperative to create a bleaching process comprised of only a few key steps; process simplification will allow uniform color for distillers grains, regardless of which processing plant the grains came from. And 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. 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 these enzymes have limited application for dough. The study tested 100g of flour with combinations of peroxidases (3,000 U), lipase

(815-1,630 U), and linoleic acid (0-300mg). This combination was shown to completely bleach bread dough. One important element to note is 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

Benzoyl Peroxide

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

The oxidation of flour accelerates the natural aging process through the oxidation of sulfhydryl groups present on flour gluten proteins. Benzoyl peroxide, a free radical initiator, changes the double bonds of carotenoids to less conjugated double bonds, which produces 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 (30mg) and calcium carbonate (70mg to stabilize the mixture). This bleaching mixture was added to 50g of flour, which resulted in a final benzoyl peroxide concentration of 150 ppm. The treatment was applied at room temperature with sample extractions every 4 hours for 24 hours, and then once daily for 3 mo. It was found that benzoyl peroxide reached non-detectable levels after 9 d, by decomposing into benzoic acid, which then acted as a food preservative. Literature has indicated that BPO could affect 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 (Wei et al., 2005).

It is important to be careful when using BPO in its pure powder form, due to its explosive nature. By diluting it in solution to approximately 50 ppm, it becomes less dangerous (Ranum and DeStefanis, 1989). A study completed by Ranum and DeStefanis (1989) 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) was not effective in bleaching bran of fiber fractions from wheat, corn, rice, apple, or sugar beet. At this point in time it is unknown 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). 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) 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 (10-28g/L), temperature (60-80ºC), and solid/liquid ratio of the pomace (5-10 g/100mL). 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. (2002) 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 appears that the AHP treatment of lignocellulose can result in a whiter fiber color. DDGS are very high in fiber and cellulose, thus the AHP treatment could possibly bleach DDGS effectively. This method appears very promising, however yield efficiency will need 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 is faced with several challenges associated with cellulose content. When hydrated, the outer surface of these particles softens; however, the interior often remains intact, and can cut gluten strands, thereby degrading baking quality (Dubois, 1978). Applying an alkaline hydrogen peroxide (AHP) treatment to fiber additives can result in higher water absorbency, 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 did peak height increase, but so did 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 indicate many potential benefits, especially the enhancement of baking properties.

Chlorine

Chlorine gas is 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 antimicrobial agents used to wash produce (CFR 173.300). It is 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 to 16 oz of chlorine per cwt. Results indicated that chlorine effectively bleached flour pigments up to 2.0 oz per cwt. Any additional levels of chlorine did

not reduce the pigments of the flour further, however. The grain, texture, and color of cakes prepared with the treated flour were enhanced up to 4.0 oz per cwt 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 of the 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 De Stefanis, 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. And 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 is to improve the baking qualities of the flour it is added to. Historically, ADA is linked with bleaching agents and consequently is still classified as a bleaching agent itself under the U.S. Food and Drug Regulations (Ranum and De Stefanis, 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 include 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, they liberate sulfur dioxide under certain conditions (Simon, 1992). Low-moisture foods do not require a 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, to maintain color.

An increasing percentage of the human population has developed a sulfite sensitivity, which can produce negative health effects. That is why 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 to help protect sulfite sensitive individuals. 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 include not using sulfites on fresh fruits and vegetables, and any foods containing more than 10 ppm of sulfites must include it in 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, 2006).

Because sulfites are primarily used for color stability, not bleaching per se, and due to the increasing number of sulfite sensitivity allergies, the use of sulfites in DDG and DDGS should be avoided.

Extraction

Ethanol and Butanol

A study completed by Park et al. (1997) indicates that carotenoids in corn gluten meal (CGM) can be eliminated via extraction with ethanol and butanol. Extractions were completed using wet corn gluten meal and 150mL of ethanol or butanol by stirring the solution for 15 min at room temperature and then filtering. The remaining slurry was suspended in another 100mL of ethanol or butanol, stirred for 15 min at room temperature, and filtered a second time. Results indicate 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. While this method of bleaching appears to be effective, the amount of solids lost needs to be taken into consideration. This method appears to be very effective, even if only one or two extractions are performed. This method should be investigated further, and process losses monitored, and other possible extraction methods that might produce less loss should also be pursued.

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 acid pH has no bleaching effect, while a pH between 8 and 12 resulted in progressively darker WDG. Previous studies have been completed using wheat distilled grains, which is somewhat similar to corn-based DDG and DDGS. This is an excellent measure of how this process might work on corn-based products. Results indicated that the use of organic solvents for bleaching purposes have not been shown to be very effective in pigment removal ability. Therefore, this method may not be appropriate to be tested on DDG or DDGS. Many other more promising avenues should be pursued instead.

Colorants

Titanium Dioxide

Titanium dioxide (TiO_2) is 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) suggests 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 hr 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 grains or any other food products. Most literature supported the use of sunlight as a source to bleach the dyes. However, this is not practical to use at the ethanol plants in the United States. Each location has various environmental differences, which would result in uncontrolled variations in the bleaching of the grains.

Possibilities For Distillers Grains

Enzymatic

Enzymatic bleaching agents discussed in this paper include the natural maturation process, lipoxygenases, and oxido-reductases. Naturally maturing of flour (through the aging process) is not appropriate for DDG or DDGS due to the prolonged waiting time of 2-3 weeks. Nitrogen tricholoride 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, we must eliminate oxido-reductases as an appropriate bleaching agent. Lipoxygenase appears to be the most 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 appear more promising than oxido-reductase in that the substitution of enzyme activated flour can be assembled prior to use at a bakery. Thus, the preparation step could be readily accomplished at the plant, not by the baker.

Chemical

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 is acquiring an allergenic sensitivity to sulfites. If this method were utilized for DDG and DDGS, a fraction of the potential consumer population could immediately be eliminated. Previous studies on benzoyl peroxide and chlorine 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. Grains that are kept in an alkaline environment should exhibit high bleaching ability in addition to other positive benefits, such as improved water absorbency and baking functionality.

Extraction

Ethanol, butanol, and other organic solvents use pigment extraction to accomplish bleaching. Organic solvents have not proved to be effective bleaching agents for materials similar to DDG and DDGS; therefore they may not be appropriate methods to use. Conversely, ethanol and butanol extraction appears to be promising for the bleaching of DDG and DDGS. Bleaching ability is high, 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 form another coproduct for processors to find a use for.

Colorants

Titanium dioxide is the only colorant discussed; unfortunately it does not appear to be practical for use with distillers grains. Titanium dioxide is used in conjunction with a photobleaching process that often uses 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 is 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. As discussed, these methods may be ineffective for bleaching fibrous materials, may have negative 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 include 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 is 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 improvement should be viewed in 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.

Conclusions

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 are appropriate for Celiac's disease since the grains are a coproduct of corn, which is gluten free. Individuals with Celiac's disease are restricted from barley, rye, and wheat; this 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 the food system, and are currently barriers to utilization. The objective of this study was to review the literature and to analyze previous studies on various bleaching processes and agents. Unfortunately, no research has been conducted on bleaching of corn-based distillers grains yet. Hydrogen peroxide, ethanol/butanol extraction, and lipoxygenases appear to be promising bleaching agents that should be pursued. These goals are, in fact the topic of ongoing research and will be reported at a later date.

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Table 1. Comparison of bleaching techniques 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 wks	Improved color and baking quality of the flour	Addition of Nitrogen Trichloride leads to neurodegenerative disorders among humans; not listed as GRAS.	Nitrogen Trichloride will speed up the natural aging process 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 hrs of forced oxidation	Fig.1: Peroxide Index (meq/kg oil) vs. Oxidation time (hrs)	Linoleic Acid: GRAS (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	100g flour combinations of: peroxidase (3,000U), lipase (815-1,630 U) and linoleic acid (0-300mg)	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 50ppm	1-2 d	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. 100mg/kg 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: 30mg benzoyl peroxide and 70mg calcium carbonate and 50g flour: Benzoyl Peroxide Conc. of 150 ppm	Sample extractions every 4 hrs for 24 hrs and then once daily for 3 mth	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 more than 0.002% of the weight of dairy products; treatment of whey – max conc. 100mg/kg 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 d	Toxicity reported at 10% level, resulting in fetal weight loss	Toxicity to fetal development at 10%	Pregnant rats received food with varying HP levels	Moriyama et al. 1982

				Not listed as GRAS but allowed as a food additive; no more than 75 ppm for meat (Title 21, Sec. 173.370)		
	10-28g/L hydrogen peroxide	1 hr 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 than 75 ppm for meat (Title 21, Sec. 173.370)	pH (9-12); Temp. (60-80ºC); apple pomace solid/liquid ratio (5-10g/100ml)	Renard et al 1996
Hydrogen Peroxide Treated Lignocellulose	Lignocellulose substrates AHP treatment (pH 11.5)	Oven dried at 40ºC for 24hrs	Mixograph peak height increased as much as 40%; more water could be incorporated into product too	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 fiber fractions	Safety levels have been established by the FDA (CFR 173.300)	Improved color and baking qualities of flour	Abdel-Aal et al. 1996; 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 45ppm	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 >10ppm (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 on fresh fruits & vegetables	Lecos 2006
EXTRACTION						
Ethanol or Butanol	150mL for 1st extraction; 100mL 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 +/- 1ºC); filtered through Whatman No. 1 filter paper	Park et al. 1997
Organic Solvents	Control WDG Petroleum ether n-butanol Acetone	2 hrs	(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 of TiO_2	2 hrs	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 percent 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 percent of active oxygen obtained from hydrogen peroxide; and propylene oxide, not to exceed 25 percent. (Residual propylene chlorohydrin not more than 5 parts per million in food starch-modified.) Sodium hydroxide, not to exceed 1 percent. 21CFR172.892 (http://www.cfsan.fda.gov/~lrd/FCF172.html)