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Current and Potential Applications of Distiller's Spent Grain

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ABSTRACT Distiller's spent grain (DSG) is the major by-product of the distilleries. Recently, due to the high demand of bio-fuels there is a significant expansion of the ethanol distilleries globally. This major increase in the bio-fuel production has resulted in a substantial increase in the volume of distiller's grain generated. Currently, livestock industries are the major market for the distiller's grains, but the necessity of alternative markets for DSG is becoming very essential due to an increase in their production. However, recent research has shown that DSG has a potential to be used as a supplement and/or ingredient in human food products and in industrial sectors. Processing techniques, such as drying, play a substantial role in determining the quality of the DSG obtained, especially for human consumption.

Keywords: distiller's spent grain, applications, foods, drying, superheated steam, color

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INTRODUCTION Distiller's spent grain (DSG) is the major by-product of the distilleries, where starchy materials such as cereal grains are fermented and distilled to yield ethanol. There are two types of ethanol processing methods, i.e. dry milling and wet milling (Belyea et al., 2004). In dry milling process, the starchy grain is first ground into flour (meal) and then processed without separating out the various components of the grain. Whereas in wet milling process, the starchy grain is first soaked in water and dilute sulfuric acid, and then separated into constituent fractions. Dry milling process is less capital intensive and is more common among ethanol plants (Belyea et al., 2004). During dry milling process three major co-products are produced: ethanol, carbon dioxide and DSG. During the fermentation process starch is converted to alcohol and other fermented products, whereas nutrients such as protein, fiber, fat, vitamins and minerals remains in DSG.

Production of ethanol tripled in the last decade and recent estimates indicate a continued high growth (UNEP, 2009). Due to an increase in ethanol production there has been a greater availability of distiller's grains. The marketability of DSG is dependent on its quality which has a direct impact on the economics of the ethanol production process (Singh et al., 2001). Currently, livestock industries are the major market for the distiller's grains, but the alternative markets for DSG are in a great need due to an increase in its production. Recent research has shown that DSG has potential to be used as a supplement and/or ingredient in human food products, industrial and agricultural sectors (Liu et al., 2011; Tavasoli et al., 2009). This paper discusses the potential applications, and the issues associated with the use of DSG in cattle feed, human consumption, and industrial applications.

CURRENT USES AND CONCERNS WITH DSG The presence of highly digestible fiber, high protein content, less starch content and fairly high concentration of fat compared to feed grains, makes DSG an excellent replacement for cattle feed. Oba et al. (2010) reported that DSG can replace canola meal or soybean meal in the diets of lactating dairy cows without effecting the production adversely. There are some advantages of using spent grains in cattle feed due to their low starch content. For dairy cows the high energy diets, which are typically high in starch content, can increase the risk of ruminal acidosis (Yang and Beauchemin, 2006). Low starch content in DSG can reduce the chances of acidosis and can serve as an excellent replacement for corn (Larson et al., 1993). In addition, the presence of fairly high amounts of fat makes it a high-energy feed for animals (Kleinschmit et al., 2006). There are, however, some practical issues related to the usage of DSG. Due to the high temperature used in drying DSG, damage of protein molecules are common among dried DSG (Kleinschmit et al., 2006). Lysine, tryptophan and arginine present in proteins of DSG are the amino acids that are susceptible to heat damage (Schwab, 1995; Nichols et al., 1998; Nakamura et al., 1994; Whitney et al., 2000).

The dark color of DSG is an indication of heat damaged protein molecules. Powers et al. (1995) observed less milk yield when dairy cows were fed with diets containing dark colored DSG than when fed with diets containing golden colored DSG. The quality of the cattle feed can be improved by blending DSG diet with other protein supplements that contain more lysine, tryptophan and arginine (Nichols et al., 1998). The mycotoxins present in DSG can be of another risk for the cattle. It was reported by Applegate and Adeola (2008) that if corn used in fermentation is contaminated with mycotoxins, the DSG will contain three to four times the concentration of mycotoxins, as the removal of starch lowers the mass of the product after fermentation.

DSG can also be used for the partial replacement of swine diets due to its high phosphorous content and low cost (Whitney et al., 2001). Phosphorous and calcium are the two most abundant minerals in swine, and they play a key role in the development and maintenance of the skeletal system, muscle contraction, blood clotting, and many other regulatory functions in pigs (Crenshaw,

2001). It was reported that DSG from corn has at least two to three times greater phosphorous content when compared to corn before fermentation (Parsons et al., 2006; Whitney et al., 2001).

DSG can be a source of nutrient for the poultries. Current recommended maximum dietary inclusion levels for corn DSG are 10% for broilers and 15% for chicken layers (Shurson and Noll, 2005). A Study conducted by Pettersson et al. (1987) showed that the addition of up to 20% of DSG into broiler rations did not significantly affected the growth rate of the birds. Corn DSG contains about 40 ppm of xanthophylls which significantly increases egg yolk color and increases skin color of broilers (Applegate and Adeola, 2008). Skin color, which is associated with feed choices of broilers, plays a significant role in consumer acceptance of broilers especially in United States and Mexico (Bunell and Bauernfeind, 1962). Some of the issues related to the usage of DSG in poultry are: presence of mycotoxins, and variability in factors such as amino acid content (a mixture of amino acids extracted from vegetative origin with the help of enzymatic hydrolysis), energy, phosphorous availability, sodium content and particle size (Applegate and Adeola, 2008). If particle size of DSG is overly fine (i.e., 300-400 microns) it will lower the nutrient digestibility in the bird as fine particles of feed pass quickly through the gizzard of the bird (Applegate and Adeola, 2008).

Variability in nutrition Researches reported a significant variation in nutrient profile of DSG among various ethanol plants and even within plants (Spiehs et al., 2002; Belyea et al., 2004). This creates a challenge in using DSG as feed for cattle and poultry as information regarding its nutrient profile and amino acid digestibility is not reliable (Shurson and Noll, 2005). There are substantial differences in nutrient composition between soluble and solid fractions of spent grain. Because the ratio of blending of these two fractions to produce distiller's dry grain with soluble (DDGS) varies among plants, the end product may have a different nutrient composition (Reese and Lewis, 1989; Shurson and Noll, 2005). As the solubles have a higher fat content DDGS has a relatively high fat content because of the added solubles. The solubles are obtained by the evaporative concentration of thin stillage, which is the separated liquid fraction from the spent grain after fermentation. Some ethanol plants partially remove the germ of the corn before fermentation (Singh and Eckhoff, 1996, 1997). As the germ contains high fat content the DDGS produced from de-germed corn has a lower fat content.

POTENTIAL USES AND PROBLEMS ASSOCIATED WITH DSG

HUMAN FOODS There are many indications that the expansion of biofuel industries will lead to food insecurity and food price hike (FAO, 2011). Studies conducted by International Food Policy Research Institute (IFPRI) suggested that the number of food-insecure people in the world will rise by over 16 million for every percentage increase in the real prices of staple foods (Runge and Senauer, 2007). The utilization of bio-fuel by-products for human consumption can reduce the existing gap between the bio-fuels and food insecurity.

Various studies done by researchers proved that DSG has fairly good potential for commercial food uses, especially in baked foods (Bookwalter et al., 1984; Wall et al., 1984; Abbott et al., 1991; Maga et al., 1989; Prentice, Kissell et al., 1978; Rasco et al., 1987a; Rasco et al., 1989; Reddy et al., 1986). Incorporation of DSG into human foods could add value to the traditional baked food market in terms of favorable nutritional profile, lower glycemic effect and higher dietary fibers (Liu et al., 2011). Brochetti and Penfield (1989) studied the effect of varying levels of distillers dried grain (DDG) addition on the sensory characteristics of bakery products. Corn muffins, hush puppies, spiced doughnuts, and molasses-raisin cookies were the products selected for the study. It was observed that compared with baked foods made with all-purpose flour, supplementing the flour with DDG increased absorption of water and oil, increased food acidity, and caused a darker color for the food products. The study showed that about 10 to 20% DDG can be added to the products without adversely affecting the appearance, flavor, and texture of the products.

Rasco et al. (1987a) conducted studies by incorporating, 0, 12.5 or 25% distillers' dried grains with solubles (DDGS) obtained from soft white winter wheat to make baguettes, cinnamon rolls, and chocolate chip cookies. Their results showed that the sensory panelists were unable to differentiate cookies containing 12.5% DDGS from control cookies. The cinnamon rolls and chocolate chip cookies obtained from the study were rated as highly acceptable. But the baguettes containing DDGS showed stronger flavor and/or off-flavor and were found to be less acceptable than the control ones. In another study Liu et al. (2011) showed that supplementing corn flour with 20 to 25 g/100 g DDGS produced corn bread of acceptable quality and processability.

It was reported by Bookwalter et al. (1984) that the soluble component in DSG is considered to be the main source of off-flavors for the distillers' products. Morad et al. (1984) removed a major portion of the solubles from the DDGS and incorporated 25% DDG obtained from white sorghum into molasses cookies. The cookies obtained were rated higher by a consumer panel than the control cookies. DDGS can be used for preparing batter mixes for fried foods. DDGS obtained from either red wheat, white wheat, or corn was added to batter mixes in the amount of 25%. The results showed that all the products were acceptable with the highest sensory rating given to batter mixes prepared with corn DDGS (Rasco et al., 1987b).

Studies done by Reddy et al. (1986) showed that DDG can be incorporated up to 10% in wheat muffins without affecting the appearance, texture, flavor, and overall acceptability. It was reported that the addition of either raisins or blueberries to wheat muffins allowed to increase the DDG level up to 15%. As the DDG level increased, loaf volume of the bread decreased (Brochetti et al., 1989). Breads made with wheat distiller's grain (WDG) had the poorest crumb grain. But when the fiber fractions were ground, crumb grain improved in many cases. A decrease in stability of the dough was observed by substituting 10 and 20% DDG from corn for wheat flour in a high-protein bread formula (Tsen et al., 1983). Morad et al. (1984) observed an increased water absorption by the addition of DDG from sorghum in a white-pan bread formula. When the soluble solids were removed from WDG the baking performance decreased (Fiasco et al., 1990). Brochetti et al. (1989) showed that the quality of breads containing 5, 10, and 15% DDG were comparable with that of control bread containing 50% whole-wheat flour. There were only few differences observed in the mixing and baking properties of wheat distillers' grains (DDGS or DDG) irrespective of which drying method was employed i.e. whether the WDG was dried using steam or drum dryers (Fiasco et al., 1990). Also, DSG can be used in the production of bran. Sodium bicarbonate, aminoacids, or mixture of aminoacids and potato starch are added to the WDG or DDGS, and then the residue-additive mix is blended and dried to form a type of nutritious bran (Reddy and Stoker, 1991). This bran can be used on a 50-50 weight basis with wheat flour, and can be used for making noodles or baked foods.

Problems related to inclusion of DSG into human foods Consumer acceptability of food products containing DSG is one among the main issue. Therefore, poor flavor, darker color, oxidative rancidity, odor, poor texture and loaf volume of the food products developed are of a major concern for their marketability (Tsen et al., 1982; Dresse and Hosene, 1982; Morad et al., 1984; Prentice & D'Appolonia, 1977; Murphy et al., 2006; Dawson et al., 1984). When utilizing DDGS for human consumption distilleries must meet food safety standards and good manufacturing practices (Murphy et al., 2006). Contamination of DSG with mycotoxins is one of the concerns (Applegate and Adeola, 2008). After harvesting, food grains must be dried to reduce the moisture content to safe levels of storage. Delay in drying to safe moisture levels may increase the risk of mould growth and mycotoxin production. Faulty storage conditions may also increase the risk of microbial attack and production of mycotoxins (Semple et al., 1989).

DRYING Drying is used for increasing the shelf life of DSG and for increasing its ease of handling and transportation capabilities. DSG must be dried to about 10% moisture content (wet basis, wb) (Woods et al., 1994). Drying also has an impact on the nutritive value and physical characteristics

of DSG. In turn, it has a direct impact on the economics of ethanol production process, as it can be a source of substantial income for the distilleries (Singh et al., 2001). Air-drying, oven-drying or steam-drying are the technologies employed in drying of DSG.

The use of DSG is limited by the presence of off-flavors and specific aroma. Using appropriate drying technology, its off-flavors and aroma can be reduced to a large extent (Ezhil, 2010). Some of the results obtained from the drying experiments conducted at our lab are discussed here. The spent grain samples were obtained from a local distillery (Mohawk Canada Limited, a division of Husky Oil Limited, Minnedosa) of Manitoba, Canada. The raw material used was a mixture of corn and wheat in the ratio 90:10. The material was dried at 150 °C for both oven-drying and superheated steam (SHS) drying methods. For air-drying, samples were dried at 45 °C in a convection oven. All the drying experiments were carried out until the moisture content of the samples reached 10% (db) or less.

The color parameters (CIE L*, a*, and b*) of the dried DSG samples were determined using the Minolta CR-410 Chroma Meter (Minolta Co. Ltd., Osaka, Japan) in three duplicate runs after grinding the samples. The L* value gives a measure of the lightness of the product color from 100 for perfect white to zero for black. The value 'a*' measures redness when positive, gray when zero, and greenness when negative, whereas the 'b*' value measures yellowness when positive, gray when zero, and blueness when negative. Before measuring the color of DSG samples, the colorimeter was calibrated with the standard white calibration plate provided with the instrument. The color parameters (L*, a*, b*) obtained for different drying methods are shown in Table 1. From the values it can be observed that, air-dried samples have a lighter color (Higher L* value) compared to other two samples. The SHS dried samples are the darkest among the samples, as high temperatures of steam can possibly damage the protein molecules. But SHS dried samples have very less off-flavors and aroma compared to oven-dried and air-dried samples. The values of the color parameters obtained were in agreement with the values reported by Kingsly et al. (2010) for corn DDGS.

Superheated steam-drying technology is a promising technology which has the potential to remove and/or prevent the off-flavors and aroma in food products (Speckhahn et al., 2010). SHS drying technique has significant benefits over hot air drying process, which includes: higher drying rates, better quality of the dried products, energy savings and moreover, an environmentally friendly technology (Shibata and Mujumdar, 1994; Taechapiroj et al., 2003; Tang and Cenkowski, 2000). The SHS drying technology utilizes steam under superheated conditions to remove moisture out of the materials. No oxidative reactions are possible due to lack of presence of oxygen during the process (Mujumdar, 1991). Also, due to the fact that moisture evaporates within the product as a result of the superheated surrounding, products dried with superheated steam have a higher porosity compared with other drying techniques (Ezhil, 2010).

Table 1. Average color parameter values of DSG samples.

Treatments	Average Color Parameters		
	L*	a*	b*
Air-Drying	62.29 (±0.02)	4.84 (±0.07)	33.33 (±0.02)
Oven-Drying	53.94 (±0.03)	8.59 (±0.03)	30.3 (±0.03)
Superheated Steam-Drying	51.88 (±0.01)	10.76 (±0.04)	31.01 (±0.02)

Values in parenthesis indicate standard deviations (n=3).

Drying technique plays a key role in increasing the marketability of DSG. The selection of drying technique also depends on the end use of DSG. For example, DSG used for cattle feed can be of low quality, as odor, color and off-flavours are not a problem animal feeding, but DSG used for human consumption must be of high quality. Thus, drying method plays a key role in improving the quality of DSG as well as for increasing the profitability of distilleries.

INDUSTRIAL APPLICATIONS DSG has high fibre content and a molecular structure suitable for binding, therefore it can be used as fillers for plastics (Rosentrater, 2008). DSG can be used as a potential alternative to bio-based fillers such as bamboo, corn stover and soybean hulls (Rosentrater, 2008). As DDGS are complex oxygenated hydrocarbons they have a high potential to produce hydrogen, syngas (H_2+CO) and hydrocarbons using processes such as pyrolysis, gasification and catalytic reforming reaction (Tavasoli et al., 2009).

Addition of lower-cost materials (fillers and reinforcements) to plastic resins has accelerated rapidly over the past decade. This can decrease the overall material manufacturing costs and increase stiffness of the composite material (Gurram et al., 2002). But the result of the study conducted by Julson et al. (2004) showed that, DSG may not be an acceptable filler as it has poor mechanical properties as well as problems with grinding of the raw material. Rosentrater (2008) prepared a compression moulded blend of DDGS and phenolic resin (ranging from 0% to 90% DDGS) for using as fillers for plastics. The result of his preliminary study showed that DDGS concentration between 25% and 50% produced excellent fillers for plastics.

Gasification is a technologically advanced and environmental friendly way for generating energy from biomass resources as conditions in the process are non oxidative. Tavasoli et al. (2009) studied the production of hydrogen and syngas using gasification of the corn and wheat DDGS. The results showed that corn DDGS gasification produced gas of higher H_2 and CO concentrations (11 and 56.5%) whereas gasification of wheat DDGS produced 10.5 and 51.5% of H_2 and CO concentrations, respectively. Also gasification of corn DDGS gave higher gas yield ($0.42\text{ m}^3/\text{kg}$), LHV ($10.65\text{ MJ}/\text{m}^3$) and carbon conversion efficiency (44.2%) compared to wheat DDGS gasification.

Fractionation There are a number of nutritionally essential components present in DSG, such as phytosterols, tocopherols, zein, etc. These components can be extracted and can be used for industrial purposes or can be incorporated into various food items for nutrient enrichment. Screening is considered as a simple procedure for fractionating spent grains. There can be a shift in the nutrient content depending on the particle size. A fine fraction obtained after sieving has a reduced fiber content and elevated protein level (Wu and Stringfellow, 1982). The major benefits for separating fibres from DSG are: (i) to enhance the nutritional characteristics of DDGS, and (ii) to use the separated fibres along with the solubles for energy generation by combustion (Srinivasan et al., 2008).

The economic value of DSG can be enhanced by extracting the lipid compounds from DSG. The oil obtained from corn DSG has similar properties compared to corn oil and can be used in food industries or as a bio-fuel (Xu et al., 2007). The lipid portion of DSG mainly contains considerable amounts of long-chain fatty acids, fatty aldehydes, fatty alcohols (policosanols), triacylglycerols, and other valuable components such as phytosterols, tocopherols and diacylglycerols (Hwang et al 2002 a, b; Singh et al., 2003; Cheryan, 2002). Lipid compounds such as phytosterols, tocopherol, policosanols and unsaturated fatty acids found in DSG have the potential to play a preventive role in many diseases, such as cardiovascular diseases, cancer and diabetes (Singh et al., 2003).

DDGS also contains zein, one of the major proteins present in corn. Zein is suitable for various industrial applications such as binders needed in paints, films and in binding fibers (Lawton, 2002).

Various researchers studied the possibility of using cellulose obtained from DDGS for developing films and fibers (Yamashiki et al., 1992 ; Zhang et al., 2001). Cellulose obtained from DDGS may also be used for applications such as films, composites, paper, water absorbents, lubricant and nutritional supplements (Xu et al., 2009).

As energy consumption in the world is increasing and fossil fuels are depleting at a fast rate, alternative sources of energy using biomaterials like DDGS will gain more attention in the future. Extraction of bioactive compounds and other nutritionally essential compounds from DDGS and utilizing it for nutraceutical and pharmaceutical industries can increase the value of DDGS.

FUTURE RESEARCH DIRECTION In future, more research must be directed towards finding alternative uses of DSG. Economical and less energy intensive techniques for drying bulk quantities of DSG must be developed. More studies must be carried out to increase the incorporation of DSG into human food products. Also, techniques must be developed for easy and economical extraction of different nutraceutical components from DSG. There is a need for more affordable technologies for increasing its use as fillers for plastics in industries, as well as for the generation of energy using DSG.

CONCLUSION The reuse of industrial by-products is gaining more importance in the recent years in terms of both economic and environmental viewpoints. DSG is one of such agro-industrial by-product generated in huge quantities from the distilleries globally. But the use of DSG is still limited to feeding cattle's, in spite of all potential applications mentioned. More studies must be encouraged to develop alternative uses of DSG, which enables to generate new knowledge/technology base for increasing the value of DSG.

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