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Sulfate in Wet Distiller's Grain from the Kansas Ethanol, L.L.C., Plant

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ABSTRACT

With increased ethanol production comes increased production of distiller's grain, a byproduct of ethanol production. Distiller's grain can be used in many types of animal feed. The concentrated nutrients in distiller's grain due to the removal of starch for ethanol production can be beneficial as a feeding agent. However, some elements and salts can have adverse effects if fed in too high of a concentration. With high amounts of variation in distiller's grain, sulfur can be extremely dangerous. The purpose of this research was to determine the amount and variation of sulfate in wet distiller's grain from one ethanol plant. Samples were taken weekly from September 13 to December 1, 2009. Gravimetric analysis was used to determine the amount and percent sulfate of each wet distiller's grain sample on a dry weight basis. Variation was shown to exist with daily averages ranging from 0.37% to 1.27%. The overall average was 0.59% with a 43.42% coefficient of variation. The variation was supported by an independent lab. With more information about the variation of the contents of distiller's grain, more confidence can be gained and distiller's grain can be safely mixed into feed rations.

Keywords: *Animal feed, Distiller's Byproducts, Ethanol, Sulfate, Wet Distiller's Grains (WDG).*

INTRODUCTION

Ethanol is becoming an ever increasing form of alternative fuel. Distiller's grains are a byproduct of ethanol production that can be fed to animals, mostly ruminants. Distiller's grains are high in fiber, protein and fat, thus making them a fallback source of feed, especially as corn prices continue to rise due mostly to the production of ethanol. The high fiber, protein, and fat are selling points that the ethanol industry uses to promote the use of distiller's grain as cattle feed. The down side, seldom mentioned, is hidden in with the selling point. The starch from the grain, usually corn in the United States, has been removed. The starch is roughly two-thirds of the corn grain, making the remainder, the distiller's grain, three times more concentrated than the beginning corn grain (Uwituze, 2008). This is where an issue arises with the feeding of distiller's grains. The concentrated fiber, protein, and fat are great for cattle producers but the concentrated sulfur, phosphorus, various salts, and other nutrients are potentially harmful.

Even though ethanol production involves the same basic steps for all ethanol plants, the inconsistency and uncertainty of the nutrient content of the byproducts raise concerns to those who try to formulate beef diets containing distiller's grains with solubles (DGS), wet or dry (Uwituze, 2008). Buckner et al. (2008) analyzed wet distiller's grains with solubles (WDGS) from six ethanol plants in Nebraska for two separate months, one each summer 2006 and winter 2007, to determine nutrient variability. Sulfur as a percent of dry matter (%DM) varied, with the overall average from all of the plants being 0.79% with a coefficient of variation ranging from 3.5%-36.3%. The variation for sulfur was higher than any other nutrient tested, with the next highest amount of variation being up to 8.8% in fat. The major factors of variability are the type of grain, milling processes, grain quality, fermentation processes, drying temperatures and proportion of solubles blended back into the unfermented fraction at the time of drying. To accurately estimate the nutritional value of the ethanol byproducts, each load must be sampled and tested (Uwituze, 2008).

Sulfur in too high of a concentration can be toxic and even lethal to animals (Kandylis, 1983). Signs of toxicity include muscle twitching, abdominal pain, fast labored breathing, diarrhea, respiratory distress, vasculitis and necrosis of rumen and abomasal wall, reduced gain, reduced feed intake, reduced growth rate, polioencephalomalacia, lower water consumption, and death (Kandylis, 1983). Large amounts of hydrogen sulfide generated in the rumen may depress ruminal activity and cause severe strain on the nervous and respiratory systems. When excess sulfur is ingested, the microbes of the rumen produce too much hydrogen sulfide. The hydrogen sulfide gas fills the rumen cap as it accumulates. It is then absorbed into the blood stream and the high levels interfere with cellular energy production, thus increasing the possibility of severe damage to the brain. Hydrogen sulfide in the rumen increases as the rumen pH decreases. Two forms of polio can result from the sulfur, acute and subacute. Once the diet reaches this state, cattle producers can only hope for the subacute form, as the acute form causes sudden death. The subacute form shows a range of signs; if caught soon enough, the animals may return to normal (Ensley and Engelken, 2007). Ruminal infusions, single or multiple, of high amounts of sulfur in the forms of sulfate or sulfide cause harmful effects. *In vitro* studies indicate that high sulfate concentrations reduce cellulose digestion by ruminal microorganisms (Kandylis, 1983). Also, dry matter intake of dairy cattle was reduced when sulfur was 0.35% of diet or above (Kandylis, 1983). Rumsey (1978) showed that 9.8 g of sublimed sulfur/kg of diet noticeably reduced the feed intake and weight of steers on high concentrate diets. It has been found that ruminal infusion of 6 g sulfur as sodium sulfate per day results in complete lack of appetite (Kandylis, 1983).

The use of sulfuric acid to control the pH and to clean fermentation equipment in the ethanol process results in S levels of 0.6 to 1.0% or greater in DGS (Uwituze, 2008). While ruminal microorganisms require S, high levels (above 0.4% DM) may cause polioencephalomalacia, reduce dry matter intake and average daily gain, and reduce liver Cu stores in cattle (Uwituze, 2008).

With the increased costs of feed for ranchers, they are quickly turning away from corn grain to the less expensive distiller's grains. The cheaper option may in reality not be cost effective, considering all of the possible side effects of distiller's grain consumption. Sulfur content and variation in distiller's grain needs to be documented so that cattle feeders may make an educated decision on the continued use of this product. The purpose of this study was to measure the amount and variation of sulfate in wet distiller's grains.

MATERIALS AND METHODS

Wet distiller's grain samples were collected weekly from September 13 to December 1, 2009 from the Kansas Ethanol, L.L.C. plant in Lyons, Kansas. Samples were collected by scooping the sample directly into a zipper-seal type bag. The samples were taken from approximately (~) 3 inches below the surface of the wet distiller's grain pile and sealed immediately, folding over the excess portion of the bag to reduce the amount of trapped air. The samples were taken directly to the lab (~ 45 minutes away), where ~ 60-70 g was weighed out into a drying pan and dried in a drying oven at 105°C. At ~ 24 hours the sample was removed, ground through a 1 mm screen and placed back into the drying oven. An additional ~ 2 g sample was weighed and placed separately into the drying oven to calculate percent dry matter (%DM) and percent moisture at 24 hours using the formula dry weight / wet weight= %DM. 100 - %DM = % moisture. The excess of each sample was dated and frozen immediately. At ~ 48 hours the sample would then be divided into three ~ 2.5 g samples with the leftover being disposed.

To analyze the sulfate content the three ~ 2.5 g well mixed, ground samples were placed into 125 mL Erlenmeyer flasks using a Denver Instrument Company TR-104 analytical balance. Then ~ 5 mL of deionized (D.I.) water was added to each flask. Each ~ 2.5 g sample was gently digested on a hot plate in 10 mL concentrated hydrochloric acid. Five glass beads were added immediately with ~ 10 mL of D.I. water and boiled for 30 minutes. After 30 minutes, each flask was removed from the hot plate and placed on ceramic tiles. Each sample was then filtered though a Whatman (125 mm, No. 2) filter-papered glass funnel into a 250 mL beaker, rinsing the flask several times to rinse in all the sample. Each beaker was covered with a watch glass and brought to a boil on a hot plate. Three aliquots of 10% barium chloride ($BaCl_2$) measuring 5 mL each (a total of 15 mL) were then added, allowing the samples to return to a boil between additions of $BaCl_2$. The beakers were then removed from the hotplate and placed back on the ceramic tiles, allowing the samples to cool for 45 minutes in the beaker with the watch glass covering. While cooling, three small gooch crucibles with a small micro-fiber filter paper (Whatman 934-AH) lining the bottom of each were placed in a drying oven at 105° C for 25 minutes. After 25 minutes the crucibles were removed and placed into a dessicator and allowed to cool for 15 minutes. The weight of each crucible was determined on the analytical balance and recorded. The samples from the beakers were poured through the crucibles using vacuum filtration, rinsing to ensure complete sample transfer. The crucibles were returned to the drying oven (105ºC) for 30 minutes and then moved directly to the muffle oven and ashed for 20 minutes at 650ºC. The crucibles cooled on ceramic tiles briefly (two minutes) then finished cooling in a dessicator. The weight of the crucibles was determined and recorded. Grams of barium sulfate was then determined for each sample by subtracting the beginning weight of the dry crucible and filter from the final weight of the crucible containing the barium sulfate precipitate. The weight of the barium sulfate was then multiplied by 41.22% (g SO_4^{2-} / g $BaSO_4$) to get g SO_4^{2-}. Grams SO_4^{2-} was then divided by the beginning weight of the sample (~ 2.5 g) to get the percent sulfate in each sample.

RESULTS

The amount of sulfate as a percent had a downward trend for the sample period; however, variation did exist, ranging from 0.37% to 1.27%. The largest variation was seen from November 10 to November 24. The drastic change from November 10 to November 17 was supported by an independent lab. Sulfate varied, with an overall average of 0.59% on a dry matter basis, with a coefficient of variation being 43.42%. The highest average of 1.27% sulfate was seen November 17. Percent dry matter ranged from 45.80% to 53.79% with an average of 51.13%.

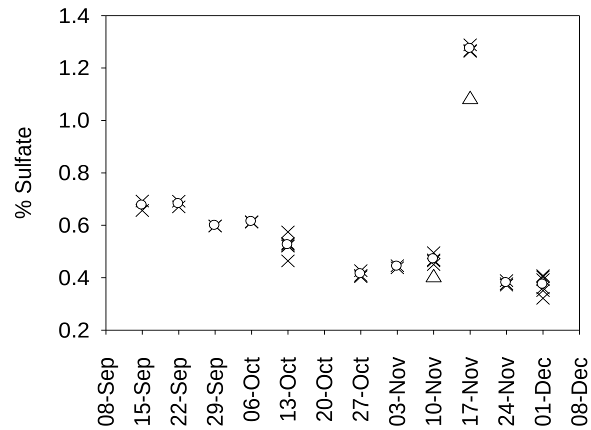

Figure 1. Percent sulfate on a dry basis. Individual sample values (X), daily average values (circles), and independent lab values (triangles) are all shown.

DISCUSSION

This experiment resulted in a higher coefficient of variation than Buckner et al. reported for sulfur (2008). The significant variation seems to be only partially based on the use of sulfuric acid to clean the evaporators used during ethanol processing. The production lag time for the ethanol plant where the samples were taken was approximately 75-80 hours from start to finish. This lag time along with the unknown time necessary to rinse all sulfuric acid residue from the evaporators could add to the variation. By measuring only sulfate, more information could be gained about how and from where the additional sulfur concentrations can arise; however, some forms of sulfur where not measured. For individuals interested in using distiller's grain as a feedstuff, total sulfur should be considered when formulating a feed ration.

Recommendations for future experiments would be to document the exact time the evaporator cleaning process was started and how much sulfuric acid was used to control the pH in each batch of yeast during the fermentation process. With variation shown to exist within a single ethanol plant, a more confident correlation may arise if the time frame for sulfuric acid lag could be documented and verified. A correlation may also be found by documenting how much sulfuric acid is used in controlling the pH during fermentation. Also, by gathering samples on a daily basis the variation could be better explained.

As more knowledge is gained about the inconsistencies in the byproducts of ethanol production, users will be able to become more confident in their animals' safety as safe rations may be determined and reliably used.

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