Stability of Lipids in Distillers' Dried Grain Products Made from Soft White Winter Wheat

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ABSTRACT

The effect of different processing treatments on the stability of lipids in distillers' grain products made from soft white winter wheat was examined. Processing treatments included the method of drying, the level of soluble solids incorporated into the distillers' grain products, and the addition of antioxidants to the fermented mash prior to drying. Antioxidants—tertiary butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), or butylated hydroxytoluene (BHT)—did not significantly improve lipid stability in distillers' grain products. Lipid hydrolysis was greater in vacuum rotary dried distillers' dried grains than in the atmospheric drum-dried product. During an accelerated storage test, the effect on lipid stability of removing the soluble solids by filtration and washing was determined for drum-dried and lyophilized products.

Lipid oxidation has been implicated as a primary factor in the development of off-flavors in distillers' grains and brewers' spent grain products. Distillers' grains have a moisture content of <10%, and lipid oxidation is a common problem when attempting to increase the shelf life of such low-moisture foods. Distillers' dried grains with solubles (DDGS) are produced from wheat by concentrating and drying the solid residue remaining after the enzymic and yeast fermentation of whole grain to ethanol. The principal components of DDGS made from wheat are dietary fiber (approximately 35% dwb) (Dong and Rasco 1987, San Buenaventura et al 1987) and protein (approximately 35% dwb) (Wu et al 1984, Rasco et al 1987a). The crude lipid content of DDGS ranges from 2.5 to 4.5%, dwb (Rasco et al 1987a).

Very little is known about the storage stability of DDGS. Results from this laboratory on wheat and research by others on other cereal grains (Bookwalter et al 1984, Dawson et al 1984) indicate that oxidative rancidity does occur in distillers' dried grains. Oxidized lipids have been implicated as primary contributors to off-flavors in food products incorporating distillers' dried grains. Other forms of deterioration, including microbial spoilage and changes in texture or color upon storage, do not appear to be a problem with DDGS (Bookwalter et al 1984). Dawson et al (1984) examined the changes in the neutral lipid composition of distillers' grains from barley. These researchers found that the level of unsaturated fatty acids in distillers' grains decreased in relation to the level in the unfermented cereal grain. They also observed that free fatty acids were produced as a result of processing; Dawson et al (1984) observed that cookies containing delipidated, dried distillers' grains had sensory scores similar to the controls that contained no distillers' grains. Dawson et al (1985) found a higher preference score for muffins containing 15% delipidated distillers' grains than for those products containing untreated distillers' grains.

The primary objectives of this study were to determine whether incorporating the antioxidants tertiary butylhydroquinone (TBHQ), butylated hydroxyanisole (BHA), or butylated hydroxytoluene (BHT) into the mash prior to drying would improve the stability of the lipid component in DDGS during accelerated storage stability tests. The effects on lipid oxidation of the drying method used, the removal of soluble solids from distillers' grains by filtration, and water washing were also tested. A secondary objective was to develop a suitable analytical method for measuring peroxide values in small samples (<1 g) of grain with a low lipid content.

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MATERIALS AND METHODS

Production of Distillers' Dried Grain Products

DDGS from soft white winter wheat were produced using the procedure outlined in Rasco et al (1987a). The whole mash has approximately 10% solids. Distillers' grains (DDG) were produced by taking a portion of the whole mash and straining it through cheesecloth to make a semisolid product with a solids content of approximately 18% before drying. A washed distillers' grain product (WDG) was prepared by rinsing the semisolid residue four times with one volume of clean tap water each time. The WDG contained approximately 18% solids before drying. Products were dried by either an atmospheric drum dryer, which is described below, or a lyophilizer (Freezemobile 6, Virtis Co., Gardiner, NY).

The proximate composition of distillers' grains products from wheat are reported elsewhere (Wu et al 1984, Rasco et al 1987a), as are the dietary fiber content (San Buenaventura et al 1987) and fiber profile for DDGS (Dong and Rasco 1987).

Antioxidant Treatments

Either butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) or tertiary butylhydroquinone (TBHQ) (UOP, Inc., Des Plaines, IL) was added to the DDG or DDGS immediately before drying. Antioxidants were solubilized in 95% ethanol before addition. The final antioxidant concentration was 0.01% (w/w) of the lipid content of the DDG or the DDGS. The crude lipid content was determined using standard AOAC (1984) methods. The mash was dried using either an atmospheric drum dryer (model ALC-4 standard atmospheric double drum dryer 6× 8 in., Blaw-Knox Food and Chem. Equip. Div., Buffalo, NY) or a rotary batch vacuum dryer (University of Washington) where product temperature was approximately 140° F. Contact time of the product on the drum dryer was 50–90 sec; residence time in the rotary vacuum dryer was approximately 4 hr. The low solids content (9.5–11%) of the whole mash made it extremely difficult to dry using the rotary batch vacuum dryer; therefore, a rotary vacuum dried DDGS product was not treated with antioxidants. Triplicate analyses for two samples from two separate batches of product were tested in these experiments.

Storage Stability Tests

Accelerated storage tests (Jacobs 1958) were conducted to determine the effects of adding antioxidants and the drying method on the development of rancidity and production of lipid oxidation products in DDG or DDGS. Samples were incubated in sealed glass jars at 63° C in a forced-air convection oven (Precision Mechanical Convection Oven, model 625, GCA Corp., Chicago, IL) for 34 days. Samples were removed at regular intervals as suggested by Cox and Pearson (1962). The presence of a detectable rancid odor was used to determine the onset of rancidity (Jacobs 1958, Dugan 1976). Peroxide values (Buege and Aust 1978), free fatty acids (AOAC 1984, method 14-069), and thiobarbituric acid

reactive substances (TBARs) (Ke et al 1984) were measured. Analyses were conducted in triplicate on two batches of distillers' grain product. Data were analyzed using one-way analysis of variance (Zar 1984).

Color Measurement

Color parameters were measured using a Hunterlab color meter, model D25M-2, a standard tan color tile ($L = 78.3$, $a = -2.7$, $b = 21.6$), and standard light source luminescence C, true to daylight for DDG and DDGS products dried by atmospheric drum and rotary vacuum dryers. Duplicate samples from two batches of each product were analyzed.

RESULTS AND DISCUSSION

Effect of Antioxidants on Lipid Stability in DDG and DDGS

The incorporation of antioxidants did not appear to improve the stability of lipids in either drum-dried or rotary vacuum dried distillers' grain products (Figs. 1 and 2). The levels of TBARs were not significantly different ($P > 0.05$) in DDG or DDGS that received the same antioxidant treatment. The concentrations of TBARs in antioxidant-treated samples were not significantly different from the controls. There were also no significant differences in TBA values between products dried by a rotary vacuum dryer and products dried using a drum dryer. The concentration of TBARs for the rotary vacuum dried DDG and for the drum-dried DDG treated with TBHQ or BHT peaked at day 4 and then decreased. TBA values for the untreated (control) and BHA treated drum-dried DDG were highest at day 0 and then decreased over the course of the accelerated storage study. These data suggest that the addition of antioxidants has little effect on the lipid stability of DDG, and inclusion of antioxidants at this level did not significantly improve shelf life.

The fat acidity values for drum-dried DDGS, drum-dried DDG, or rotary vacuum dried DDG remained relatively constant after day 4 (Fig. 2), indicating that the degree of lipid hydrolysis did not

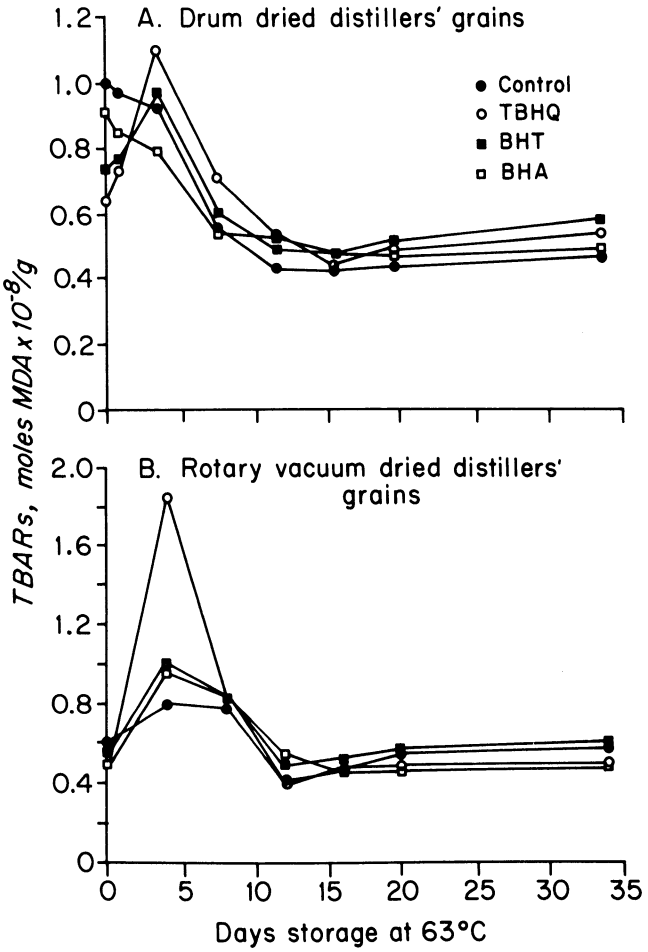

Fig. 1. Concentration of thiobarbituric acid reactive substances (TBARs) as malondialdehyde (MDA) for (**A**) atmospheric drum-dried and (**B**) rotary vacuum dried distillers' dried grains with solubles from soft white wheat treated with antioxidants during the course of an accelerated storage stability test. Antioxidants (butylated hydroxyanisole [BHA], butylated hydroxytoluene [BHT], or tertiary butylhydroquinone [TBHQ]) were added at a concentration of 0.01%, w/w, of the lipid content of the distillers' grains. The control contained no added antioxidant. Products were subject to an accelerated storage test with samples taken at regular intervals. Each data point represents the mean of triplicate analyses for duplicate samples from two batches of distillers' dried grains.

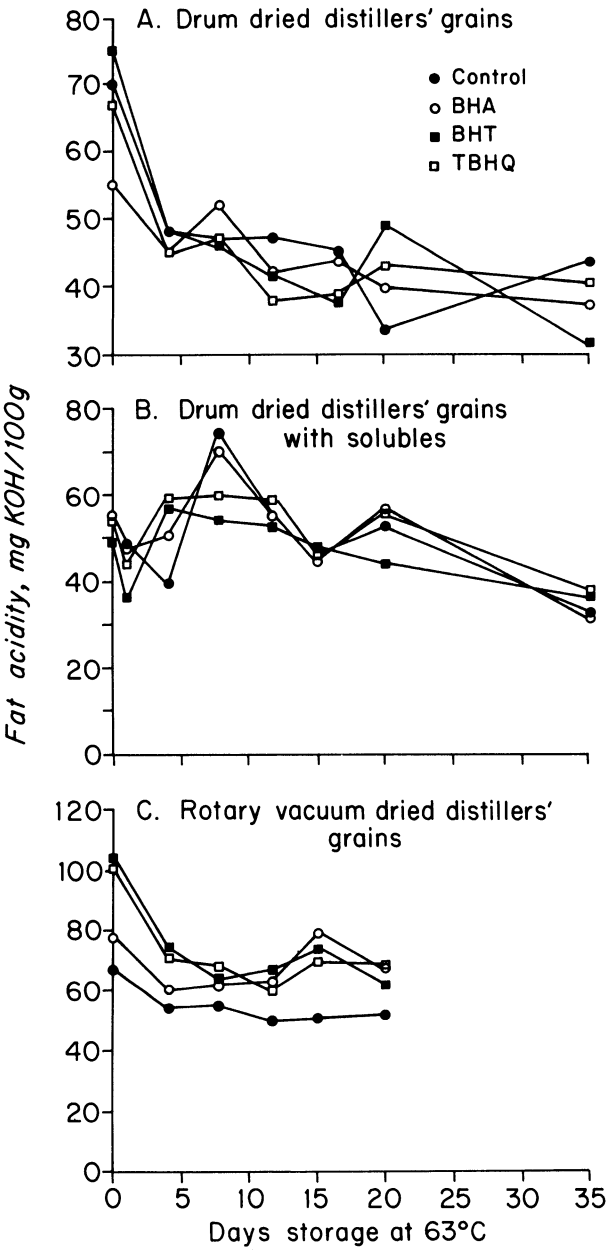

Fig. 2. Fat acidity values for (**A**) drum-dried distillers' grains, (**B**) drum-dried distillers' grains with solubles, or (**C**) rotary vacuum dried distillers' grains from soft white wheat. Antioxidants (butylated hydroxyanisole [BHA], butylated hydroxytoluene [BHT], or tertiary butylhydroquinone [TBHQ]) were added at a concentration of 0.01%, w/w, of the product lipid content. The control contained no added antioxidant. Products were subjected to an accelerated storage test with samples taken at regular intervals. Each data point represents the mean of triplicate analyses for duplicate samples from two batches of distillers' dried grains and distillers' dried grains with solubles.

increase further during the accelerated storage test. The fat acidity values tended to be high at day 0. This was most likely due to the presence of residual organic acids that were produced during the fermentation and were not volatilized during drying, but were lost from samples heated at 63° C for one to four days.

Effects of Drying Technique on Lipid Stability of DDG Products

Rotary vacuum dried DDG had significantly higher fat acidity values ($P < 0.05$) than the corresponding drum-dried DDG product after four days (Fig. 2). Vacuum rotary drying, which is a harsh drying method compared to drum drying, increased lipid hydrolysis in the product. Although the lipid in the vacuum rotary dried DDG was hydrolyzed to a greater extent, both the rotary vacuum dried and atmospheric drum-dried DDG had detectable rancid odors within eight days under the conditions of the accelerated storage test.

Effect of Removing Soluble Solids on Lipid Stability in DDG Products

The fat acidity values for drum-dried DDG and drum-dried DDGS receiving the same antioxidant treatments were not significantly different. Because most of the soluble solids were removed, including prooxidant metals and organic acids that would accelerate lipid hydrolysis, one might also predict that the

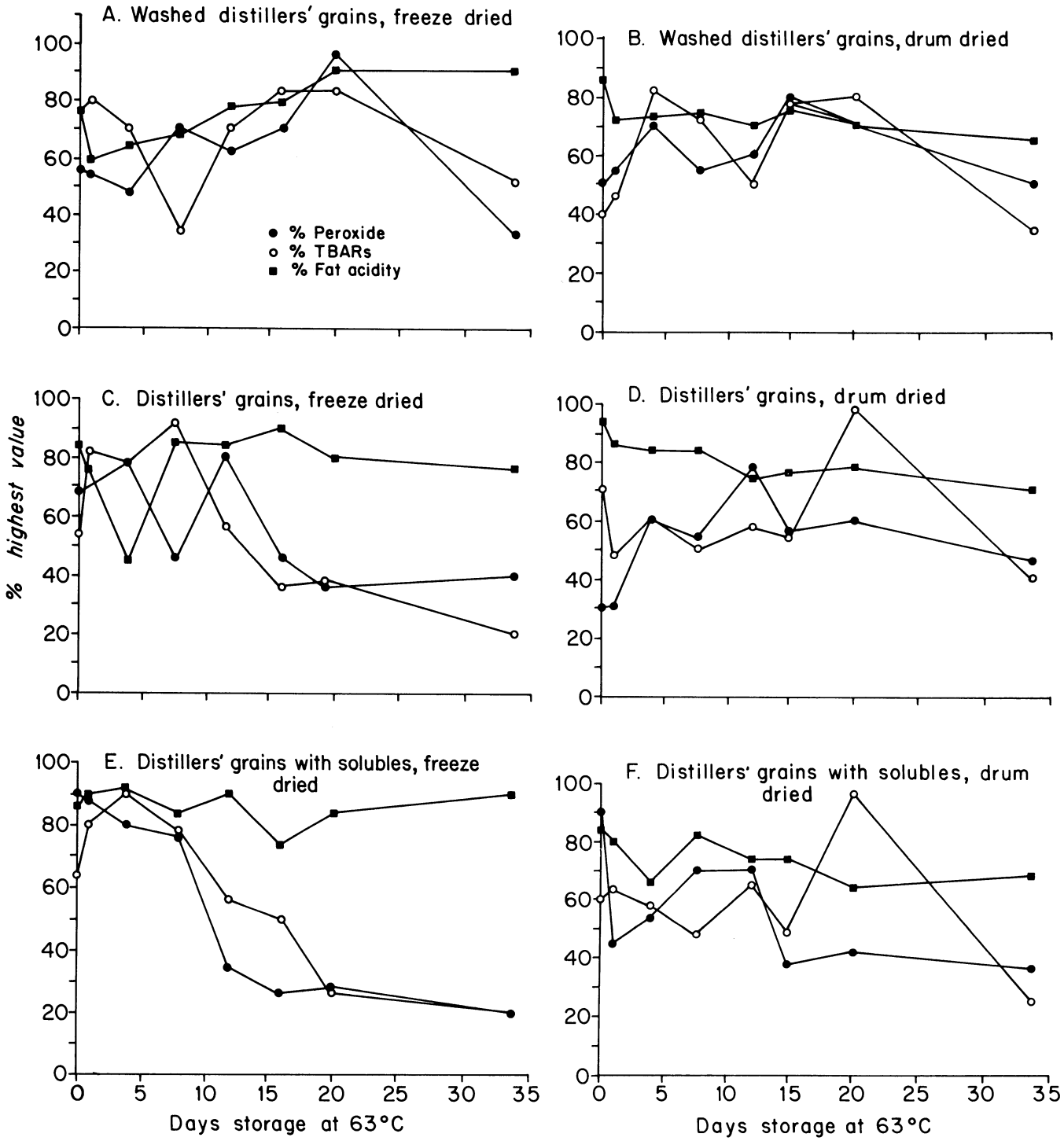

Fig. 3. Oxidative test values for freeze-dried and drum-dried distillers' grain products. Reported values are expressed as a percentage of the highest measured value for each test for separate experiments and are based on the mean and standard deviation of triplicate analyses from two batches of drum-dried or freeze-dried material. Distillers' grain products tested were washed distillers' grains (**A** and **B**), distillers' dried grains (**C** and **D**), and distillers' dried grains with solubles (**E** and **F**).

TABLE I
Highest Measured Values (100%) for Oxidative Test Data in Figure 3[a]

Sample[a]	Peroxide Value (μmol of hydroperoxide as cumene hydroperoxide/100 g)	TBA[b] Value (μmol of TBARs/100 g)	Fat Acidity Value (mg of KOH/100 g)
Drum-dried			
Washed distillers' grain	26 ± 17	38.7 ± 8.3	137 ± 24
Distillers' grains	27 ± 16	32.2 ± 7.6	137 ± 64
Distillers' dried grains with solubles	21 ± 17	27.3 ± 7.8	143 ± 44
Freeze-dried			
Washed distillers' grain	38 ± 24	25.5 ± 13.3	178 ± 36
Distillers' grains	17 ± 7	15.0 ± 2.2	230 ± 39
Distillers' dried grains with solubles	14 ± 5	26.5 ± 6.9	228 ± 70

[a] All data are mean and standard deviations for triplicate analyses from two batches of drum-dried or two batches of freeze-dried materials expressed on a dry weight basis.
[b] TBA = Thiobarbituric acid; TBARS = thiobarbituric acid reactive substances.

fat acidity values for WDG would be less than those for DDG or DDGS.

Further investigations involving the levels of soluble solids in the distillers' grain products and type of dryer used (atmospheric drum dryer vs. lyophilization) were also conducted. In addition to fat acidity values, TBARs and peroxide values were determined during the course of an accelerated storage stability test and are expressed as relative percent in Figure 3. The highest measured values, those set at 100% in Figure 3, are reported in Table I. There were no significant differences in oxidative test values between freeze-dried and drum-dried DDGS or between WDG and DDGS by one-way analysis of variance. The lipid contents of the three products were similar: 3.59 ± 0.23% lipid (dwb) for DDGS, 4.09 ± 0.18% for DDG and 4.30 ± 0.35% for WDG.

Fat acidity values for the lyophilized WDG increased during the 34-day accelerated storage stability test. Values for drum-dried WDG decreased from day 0 to day 1 and remained relatively constant. No clear trends were observed in fat acidity values during the accelerated storage stability test for either drum-dried or freeze-dried DDG or DDGS (Fig. 3).

TBARs reached their highest level for freeze-dried DDG at day 8 and for freeze-dried DDGS at day 4 and decreased upon further storage. TBARs were relatively stable for drum-dried DDG and DDGS for the first 16 days of an accelerated storage stability test, peaked at day 20, and then decreased. Data for freeze-dried and drum-dried WDG suggest that TBA values peak between days 16 and 20 (Fig. 3).

Peroxide values were measured using the iodometric procedure of Buege and Aust (1978) as an oxidative index of lipid stability in drum-dried and freeze-dried DDGS, DDG, and WDG products. This method is widely used in studies of membrane lipid peroxidation and was selected because of its sensitivity in detecting lipid peroxides in small samples ($\leq$ 1 g) with a low lipid content ($\leq$ 4.5%). This is substantially less lipid than that required for standard AOAC (1984) methods. However this procedure is technically difficult to run, and standard deviations within and between experiments were high.

The peroxide values for the freeze-dried WDG increased from day 0 to day 20 and decreased thereafter. There were no clear trends in the data for peroxide values for the drum-dried WDG material. The peroxide values for freeze-dried and drum-dried DDG and DDGS were also somewhat difficult to interpret. The peroxide values for the freeze-dried DDG remained stable through day 12 and then decreased, whereas the peroxide values for the drum-dried product increased from day 0 to day 4 and remained relatively constant throughout the rest of the storage study. Peroxide values for the freeze-dried DDGS decreased from day 1.

The soluble fraction contains a relatively high concentration of prooxidant metals such as iron (approximately 80 mg/ 100 g, dwb) in the DDG and DDGS products, which presumably is present in substantially lower quantities in the WDG. This should cause the DDG and DDGS to be more susceptible to lipid oxidation than the WDG. Lower peroxide values for DDG and DDGS materials would indicate that secondary oxidation products had already formed.

The type of dryer used was found to greatly affect the color, flavor, and texture of the distillers' grain product. Drum-dried DDGS or DDG were light tan flakes ($L = 62.8 \pm 1.2, a = 3.8 \pm 0.8, b = 1.95 \pm 1.5$) with a slightly sour, metallic-soapy flavor and a slight aftertaste (Rasco et al 1987b). Vacuum rotary dried DDG were granular and dark brown ($L = 47.7 \pm 0.8, a = -18.3 \pm 0.4, b = 20.8 \pm 0.1$) with a slight metallic-soapy, malty flavor and a musty aftertaste. Drum-dried DDG had less flavor than drum-dried DDGS. The drum-dried WDG had a bland flavor.

Information on oxidative deterioration of wheat distillers' grain products will be helpful in formulating low moisture foods containing this ingredient. Although some data on the oxidative stability of corn distillers' grain products have been reported (Bookwalter et al 1984), little is known about wheat distillers' grain products. The findings reported here on the effect of different drying techniques and the incorporation of various antioxidants on product stability will aid in process design and assist with further product development.

CONCLUSION

Antioxidants, at the level tested, do little to improve the stability of the lipid fraction in distillers' grain products from wheat. The major factor that influenced lipid stability was the drying technique used. Fat acidity may be a useful index for monitoring lipid stability; however, TBA and peroxide values appear to be of limited use.

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