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Effects of particle size distribution, compositional and color properties of ground corn on quality of distillers dried grains with solubles (DDGS)

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ABSTRACT

Oftentimes, corn processors believe that ground corn (raw material) and distillers dried grains with solubles (DDGS) are interrelated in certain quality parameters. Yet, previous studies, although rather limited, have not established this relationship. In this study, six ground corn samples and their resulting DDGS were analyzed for particle size distribution (PSD), using a series of six selected US standard sieves: Nos. 8, 12, 18, 35, 60, and 100, and a pan. The original sample and sieve sized fractions were measured for contents of moisture, protein, oil, ash and starch, and surface color. Total carbohydrate (CHO) and total non-starch CHO were also calculated. Results show that the geometric mean diameter (d_{gw}) of particles varied with individual corn and DDGS samples, and that d_{gw} of DDGS was larger than that of corn (0.696 vs. 0.479 mm, average values), indicating that during conversion of corn to DDGS, certain particles became enlarged. For d_{gw} and mass frequency of individual particle size classes, the relationship between ground corn and DDGS varied, but PSD of the whole sample was well correlated between them ($r = 0.807$). Upon conversion from corn to DDGS, on an average, protein was concentrated 3.59 times; oil, 3.40 times; ash, 3.32 times; and total non-starch CHO, 2.89 times. There were some positive correlations in contents of protein and non-starch CHO and in *L* value between corn and DDGS. Yet, variations in nutrients and color attributes were larger in DDGS than in corn. For either corn or DDGS, these variations were larger in sieved fractions than in the whole fraction. Raw material, processing method and addition of yeasts are among major factors considered for causing larger variations in these attributes among DDGS. The study partially supports the common belief by processors that quality attributes of corn affect those of DDGS.

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1. Introduction

Increase in the demand for ethanol as a fuel additive and a decrease in dependency on fossil fuels have resulted in a dramatic increase in the amount of corn used for ethanol production. A major process for making ethanol from corn is the dry-grind method. The basic steps of the method include grinding, cooking, liquefaction, scarification, fermentation, distillation, and co-product recovery. Grinding is done to reduce corn particle size by passing whole corn through a hammer mill containing screens with relatively small openings (3.2–4.8 mm diameter) (Bothast and Schlicher, 2005). The resulting ground corn consists of a mixture of particles of different sizes. The particle size of ground corn is reported to affect ethanol yield, energy efficiency, and concentration of soluble solids in thin stillage (Kelsall and Lyons, 2003; Naidu et al., 2007).

There are only two co-products generated from the dry-grind method, distillers dried grains with solubles (DDGS) and carbon dioxide. Marketing of DDGS is critical to sustainability of a dry grinding plant, while factors that affect quality of DDGS directly impact the price and end use of DDGS, and thus the economics of ethanol production. One major factor that affects quality of DDGS is variation in chemical and physical properties. The composition of DDGS can vary substantially (Belyea et al., 1998, 2004; Speihs et al., 2002; Liu, 2008). So do physical properties of DDGS (Rosentrater, 2006; Liu, 2008). Such variation reduces quality of DDGS and negatively impacts market value.

Like ground corn, DDGS is also a mix of particulate materials. Thus, the relative amounts of particles present, sorted according to size, commonly known as particle size distribution (PSD), is a characteristic of a particular DDGS sample. It affects handling characteristics and market value. Recently, a study was carried out in the author's lab to investigate PSD of DDGS and its relationships to composition of various nutrients and surface color in the original and sieve sized fractions (Liu, 2008). It was found that particle size of DDGS varied greatly within a sample and PSD varied greatly among samples. Although PSD and color parameters had little correlation with composition of whole DDGS samples, in sieved fractions distribution of nutrients as well as color attributes correlated well with PSD.

A new question is raised regarding relationships between ground corn, the starting material, and DDGS, a co-product of the

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ethanol production, with respect to particle size distribution, chemical and physical properties. Oftentimes, by intuition and common reasoning, corn processors believe that (1) PSD of ground corn affects that of DDGS, (2) the chemical and physical properties of ground corn and DDGS are related to each other, and (3) variation in the composition of corn is a major cause of variation in composition of DDGS. Yet, previous research, although still limited, has provided results contrary to these common beliefs. Rausch et al. (2005) compared PSD between ground corn and DDGS from dry-grind processing and found that the two were not significantly correlated with each other. Belyea et al. (2004) compared chemical composition of corn and DDGS produced in multiple years from a single plant and reported that variation in the composition of DDGS was not related to variation in corn composition.

In this study, particle size distribution, proximate composition and surface color of 6 ground corn samples and corresponding DDGS samples from different processing plants were measured, and compared symmetrically, not only in whole fractions, but also in sieve sized fractions, in order to gain better insights about relationships between ground corn and DDGS in these attributes. Such information would also help understand physical and chemical changes of corn during the ethanol production, and provide strategies to improve end product quality.

2. Methods

2.1. Materials

Six ground corn and resulting DDGS samples were collected from six dry-grind ethanol plants located in the states of Iowa and South Dakota, USA. These plants processed commodity yellow dent corn available locally.

2.2. Measurement and expression of particle size distribution

PSD was measured with a series of six selected US standard sieves (Nos. 8, 12, 18, 35, 60, and 100) and a pan, fitted into a sieve shaker (DuraTap, Model DT168, Advantech Mfg. Co. New Berlin, WS). The sieving procedure was according to a standard method (ASAE Standards, 2003). Basically, 100 g of DDGS sample, without any additional processing, was sieved by shaking for 10 min. In order to improve sieving efficiency, tapping option was used during shaking. The mass of material retained on each sieve as well as on the pan was determined and recorded. The test was duplicated. The mass frequency (%) for material retained on each sieve size was calculated and plotted against each particle size category. Geometric mean diameter (d_{gw}) and geometric standard deviation (S_{gw}) were also calculated for each sieving replicate based on the formula described in the ASAE Standards (2003).

2.3. Chemical analysis and surface color measurement

The ground corn and DDGS samples, as well as their sieve sized fractions were measured for contents of moisture, protein, oil, ash and starch, and surface color. The original corn or DDGS sample is termed as "whole" fraction, in contrast to sieved fractions. For corn samples, the material retained on No. 8 mesh was too small to measure all the attributes. So, data for the particle size of 2.36 mm category were mostly unavailable. Details on chemical analysis and surface color measurement were described elsewhere (Liu, 2008).

2.4. Data treatments and statistical analysis

Data were treated with JMP software, version 5 (JMP, a business unit of SAS, Cary, NC, USA), for calculation of means and standard deviation of measured attributes, and correlation coefficients of attributes between ground corn and DDGS, and for analysis of variance. The Tukey's HSD (honestly significant difference) test was also conducted for pair comparisons when there was a significant effect at $p < 0.05$ based on analysis of variance.

3. Results and discussion

3.1. Particle size distribution

How the particle size of a powder material is expressed is usually defined by the method by which it is determined. In this study, a sieve analysis was used (ASAE Standards, 2003), where ground corn or DDGS powder was separated by sieves of different sizes, and particle size distribution (PSD) was defined in terms of mass frequency over discrete size ranges. Based on this method, the geometric mean diameter ($d_{gw)}$ of particles for the 6 ground corn samples had an average value of 0.479 mm, ranging from 0.430 to 0.516 mm, while d_{gw} of the corresponding 6 DDGS samples had an average value of 0.696 mm, ranging from 0.483 to 0.894 mm (Table 1). Furthermore, d_{gw} of each ground corn sample was significantly lower than that of corresponding DDGS. Similar trends were also observed for geometric standard deviation (S_{gw}), but to a lesser degree. These observations suggest that during conversion of ground corn to ethanol and DDGS, certain particles became enlarged. Perhaps, it was due to agglomeration of particles during the drying of mixed wet distillers grains and condensed solubles may actually.

Rausch et al. (2005) reported a mean d_{gw} value of 0.94 mm for 9 ground corn samples and 0.92 mm for 9 resulting DDGS samples. The two were not significantly different from each other. The result of this study disagrees with their report. Furthermore, the particle size of both corn and DDGS were found much larger, in terms of mean d_{gw} values, in the Rausch et al. study than in the current study. Change or improvement of processing methods over the last few years, as well as use of different sieve series for the particle

Table 1
Geometric mean diameter and geometric standard deviation (S_{gw}) of particle diameter (d_{gw}) by mass for 6 corn samples and resulting DDGS samples[a].

Samples	d_{gw}	S_{gw}
Corn		
C1	0.430 ± 0.002 g	0.342 ± 0.001 e
C2	0.446 ± 0.001 fg	0.439 ± 0.004 c
C3	0.469 ± 0.008 efg	0.427 ± 0.002 cd
C4	0.514 ± 0.011 e	0.401 ± 0.003 d
C5	0.516 ± 0.006 e	0.422 ± 0.001 cd
C6	0.503 ± 0.001 e	0.416 ± 0.001 cd
Minimum	0.430	0.342
Maximum	0.516	0.439
Mean	0.479	0.408
Range	0.087	0.097
S.D.	0.037	0.034
DDGS		
D1	0.636 ± 0.006 d	0.420 ± 0.006 cd
D2	0.894 ± 0.027 a	0.549 ± 0.021 a
D3	0.750 ± 0.001 b	0.438 ± 0.001 c
D4	0.483 ± 0.004 ef	0.337 ± 0.003 e
D5	0.716 ± 0.025 bc	0.481 ± 0.007 b
D6	0.699 ± 0.013 c	0.432 ± 0.006 c
Minimum	0.483	0.337
Maximum	0.894	0.550
Mean	0.696	0.443
Range	0.411	0.213
S.D.	0.135	0.070

Column means with different letters differ significantly at $p < 0.05$.

[a] Mean value of duplicate measurements ± standard deviation.

size analysis in the two studies, might explain the discrepancy between the studies.

Geometric mean diameter is an effective way of expressing and comparing PSD on a statistical basis (ASAE Standards, 2003) but expression in the proportion of material retained on (or pass through) each sieve size (mass frequency) can be more easily understood by processors. When using the selected series of 6 sieves (US standard Sieve Nos. 8, 12, 18, 35, 60, and 100) and a pan, the 6 ground corn and corresponding DDGS samples had varying curves of particle size distribution (Fig. 1). All corn curves were bimodal except for C5 sample which had a unimode. The mode is the center of the size class that contains most of the material. For the samples with a bimode, the PSD had a major mode in the center of size class between 0.5 and 1.0 mm (the material retained in No. 35 sieve but passed through No. 18 sieve). The minor mode changed with samples but all were in the finer particle size classes. For the sample having a unimode, the PSD had a mode the same as the major mode of the bimodal samples. In contrast, all DDGS had unimodal PSD, with the same mode. Furthermore, this same mode overlapped the mode or major mode of ground corn samples, that is, in the center of the size class between 0.5 and 1.0 mm. Although the height of the peaks varied among samples, the PSD peaks of ground corn samples were generally lower than these of DDGS. Again, the data in Fig. 1 also suggest that during conversion of ground corn to DDGS, certain particles became enlarged.

3.2. Relationships in particle size and PSD between ground corn and DDGS

Many corn processors attribute particle size of DDGS to that of ground corn. However, Rausch et al. (2005) concluded that the particle size distributions of DDGS were not correlated to that of ground corn. Their conclusion was based on linear regression of d_{gw} value as well as mass frequency of individual particle size categories between ground corn and DDGS ($r < 0.35$). In this study, linear regression was made not only for these two sets of data (d_{gw} values between ground corn and DDGS, as well as the mass frequency of individual particle size categories between ground corn and DDGS) but also on data of mass frequency over the entire particle size ranges (that is, the particle size distribution data). Results showed that the correlation coefficient (r value) for d_{gw} of whole fraction between ground corn and DDGS was −0.423, while r values for mass frequency of individual particle size classes between ground corn and DDGS ranged from −0.623 to 0.758 (Table 2). Since the r value for d_{gw} was negative while r values for mass frequency between the two types of samples was negative or positive, depending on individual particle size categories, the overall correlation was difficult to define.

However, if one looks at PSD curves across the entire particle size categories (Fig. 1), the ground corn and DDGS showed very similar changing patterns. In particular, as noticed before, the two shared the same mode (either the unimode or the major mode). Indeed, the particle size distribution of DDGS was very positively correlated to that of ground corn based on linear regression of mass frequency across the entire particle size ranges ($r = 0.807$). This last conclusion confirms the common belief by the processors, but disagrees with conclusion of Rausch et al. (2005). The reason is that the two studies draw conclusions from regression of different data sets, as discussed above. It is believed that regression of mass frequency over the entire particle size range (all sieved fractions) is the correct way to draw a conclusion, since it describes a relationship in particle size distribution rather than mass frequency of a

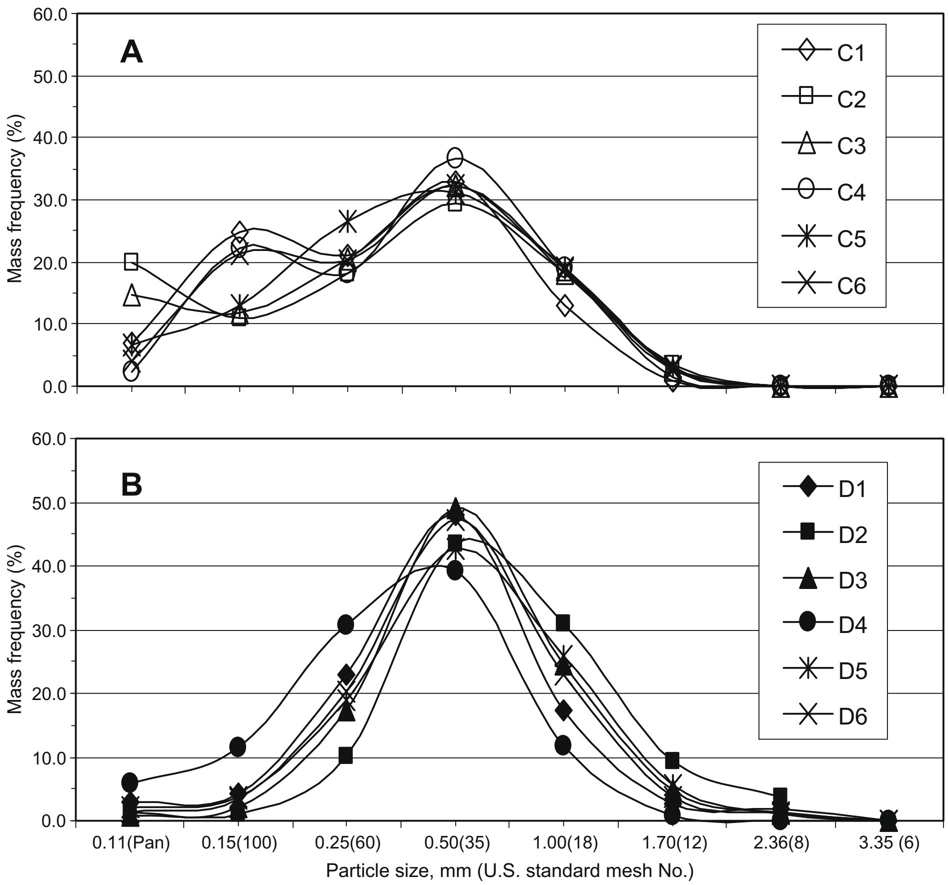

Fig. 1. Particle size distribution of the 6 ground corn (A) and corresponding DDGS (B) samples collected from the US Midwest region. Mass frequency was based on the proportion of material retained on each sieve size, by weight.

Table 2
Correlation coefficients (r value) of parameters of whole and sieved fractions between corn and resulting DDGS[a].

	Whole	Particle size (mm)							All sieved fractions
Parameters		>2.36	1.70–2.36	1.00–1.70	0.50–1.00	0.25–0.50	0.15–0.25	<0.15	
d_{gw}	−0.423								
S_{gw}	0.481								
Mass frequency %		−0.327	0.758	0.239	−0.368	−0.047	0.580	−0.623	0.807
Protein %	0.710	−0.409	0.361	0.306	0.550	0.384	0.217	0.605	−0.362
Oil %	−0.100		0.256	0.380	−0.638	0.364	−0.153	−0.661	0.359
Ash %	−0.784		−0.044	0.036	−0.069	−0.167	−0.198	−0.321	−0.519
Starch %	0.583		0.724	0.091	0.353	0.322	−0.422	0.759	−0.112
Total carbohydrate %	−0.032		0.428	0.653	−0.175	0.528	−0.599	0.320	−0.748
Total non-starch CHO %	0.776		0.269	0.229	0.049	0.476	0.459	−0.202	0.832
L value	0.499		−0.195	0.734	0.549	0.761	−0.700	0.663	0.436
a value	−0.918		−0.605	−0.572	−0.702	−0.109	−0.506	−0.388	0.273
b value	−0.183		−0.114	0.014	−0.128	0.411	0.818	0.775	−0.057

[a] The three color values were measured triplicate. For each color attribute, the total number of paired samples (corn and DDGS) was 18 for the whole and individual sieved fractions, 126 for all sieved fractions, and 144 for all whole and sieved samples. The rest parameters were measured duplicate. For each parameter, the total number of paired samples (corn and DDGS) was 12 for the whole and individual fractions, 84 for all sieved fractions, and 96 for all whole and sieved samples.

particular size class. In other word, for mass frequency of a particular size class, the relationship between ground corn and DDGS varied and was hard to define, but in terms of particle size distribution of the entire sample lot, the two were well correlated.

Particle size of ground corn has been shown to affect ethanol yields and amounts of solids in thin stillage (Naidu et al., 2007). Fineness of ground corn influences amounts of sugars formed due to variation in surface area. Reducing particle size of ground corn increases ethanol yield, but at the same time increases solids in thin stillage and reduces efficiency of centrifugation and evaporation steps (Kelsall and Lyons, 2003). Therefore, there is a need for optimization of particle size of ground corn. In this study, in terms of particle size distribution pattern, ground corn and DDGS correlated positively with each other. However, analysis of variance showed that the type of material and processing plant had significant effects on d_{gw}, S_{gw}, and mass frequency of individual particle size classes. Comparing means of mass frequency between ground corn and DDGS for each particle size category indicates significant difference between ground corn and DDGS samples except for the fraction of the largest particle size. Furthermore, based on particle size distribution (Fig. 1), although all the DDGS samples shared the same mode, there was great variation in mass frequency within each particle size class. In contrast, for ground corn samples, except for some finer particle size classes, variation in the mass frequency within each particle size class was much less than that of DDGS. These observations indicate that during processing, some factors other than the particle size of ground corn also determined the particle size of DDGS and thus were partially responsible for larger variation of particle size of DDGS among processors. Mechanical, thermal, chemical and biological stresses and shocks on the original corn particles, addition of new particles (such as yeast cells) during the processing and agglomeration of particles during the drying of mixed wet distillers grains and condensed solubles are among factors expected to cause particle size breakage, clumping, regrouping and thus re-distribution. The net effect would lead to larger particle size of DDGS over ground corn and bigger variation among DDGS samples from different processing plants than among ground corn samples. All these factors may actually alter the particle size distribution of DDGS independently of the hammer milling of the corn and/or the bioprocessing of ethanol production.

3.3. Protein, oil and ash contents in whole and sized fractions

Protein content in the whole fraction of ground corn varied from 7.05% to 8.75% (dry matter basis) among samples collected from different processors, with a mean value of 7.63% (Table 3). Upon sieving, its content was reduced slightly in the finer fractions (Fig. 2A). As the particle size increased, the protein content in sized fractions increased slightly. Thus, fractions of finer particle size had lower protein content than those of larger particle size.

Table 3
Variations in attributes measured in the whole lot of ground corn and DDGS samples[a].

	Protein	Oil	Ash	Starch	NS CHO	T CHO	*L*	*a*	*b*
Ground corn									
Mean	7.63	3.43	1.33	69.75	17.87	87.61	84.68	0.80	31.95
Minimum	7.05	2.64	1.25	67.76	16.28	86.26	83.54	0.38	30.67
Maximum	8.75	3.70	1.42	71.68	20.15	88.16	86.16	1.49	32.92
Range difference	1.70	1.06	0.17	3.92	3.86	1.90	2.62	1.12	2.25
Standard deviation	0.63	0.39	0.05	1.44	1.37	0.69	1.20	0.48	0.79
Relative range difference (%)	22.27	30.79	12.44	5.62	21.62	2.17	3.09	139.97	7.03
Relative standard deviation (%)	8.27	11.35	4.01	2.06	7.64	0.78	1.42	60.70	2.46
DDGS									
Mean	27.41	11.67	4.42	4.85	51.66	56.51	54.68	9.69	41.50
Minimum	25.79	11.00	4.00	3.21	50.31	55.74	44.89	8.27	30.98
Maximum	29.05	12.15	4.88	5.72	54.72	57.93	59.59	11.36	46.38
Range difference	3.26	1.15	0.87	2.52	4.41	2.18	14.69	3.10	15.40
Standard deviation	1.09	0.46	0.34	1.24	1.65	0.88	5.40	1.17	5.93
Relative range difference (%)	11.91	9.84	19.78	51.96	8.54	3.86	26.87	31.96	37.12
Relative standard deviation (%)	3.99	3.95	7.79	25.65	3.20	1.56	9.88	12.09	14.29
Ratio of DDGS to Corn	3.59	3.40	3.32	0.07	2.89	0.64	0.65	12.15	1.30

[a] NS CHO, non-starch carbohydrates; T CHO, total carbohydrate.

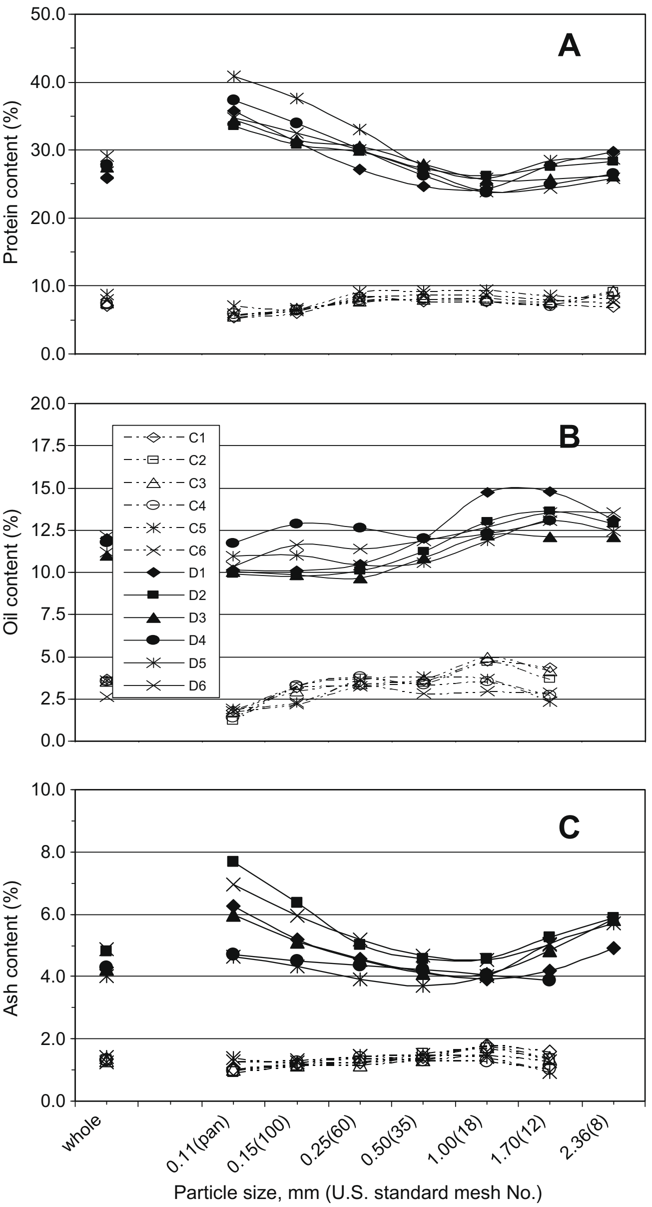

Fig. 2. Protein (A), oil (B) and ash (C) contents (%, dry matter basis) in the original (whole) and sieve sized fractions of the 6 ground corn and corresponding DDGS samples.

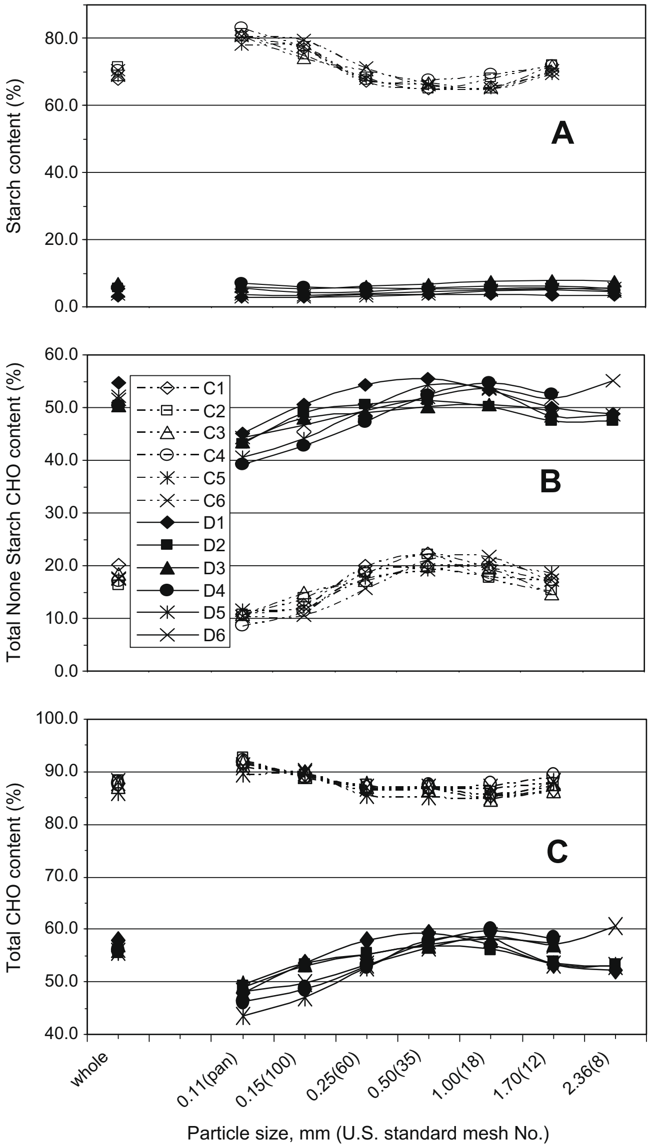

Fig. 3. Starch (A), total non-starch carbohydrate (B), and total carbohydrate (C) contents (%, dry matter basis) in the original (whole) and sieve sized fractions of the 6 ground corn and corresponding DDGS samples.

The protein content of whole DDGS samples varied from 25.79% to 29.05%, with a mean value of 27.41% (Table 3). In contrast to ground corn, upon sieving the protein content of DDGS was increased significantly in finer fractions (Fig. 2A). As the particle size increased from 0.11 to 2.36 mm, protein content in sized fractions of all the DDGS samples followed a general decreasing pattern, reached a bottom value at 1.00 mm and then started to increase. Thus, for DDGS, finer fractions generally had higher protein content than coarser fractions. Overall, protein content in sieved fractions of DDGS had much larger variation than that of corn. The observation indicated that protein content in DDGS fractions with smaller particle size become more concentrated than fractions with larger particle size during ethanol production. Particle size re-distribution and addition of other protein sources such as yeast as a result of processing may be possible explanations.

The oil content in ground corn samples was in 2.64–3.70% range, with a mean value of 3.43% (Table 3). In sized fractions, it increased with an increase in particle size (Fig. 2B). There was detectable variation in oil contents among samples from different plants, particularly in sieved fractions of larger particle size classes. The oil content in most DDGS samples was in the range of 11.00–12.15%, about 3.40 times of ground corn. Similar to ground corn fractions, oil content in sized fractions for most DDGS samples had a slight upward trend as the particle size increased. This was in contrast to the change of protein content in sized fractions of DDGS samples, which had a decreasing trend. Again, oil content in sieved fractions of DDGS had much larger variation than that of corn.

In ground corn, ash was around 1.33%. As the particle size increased, ash content increased slightly (Fig. 2C). In whole DDGS samples, ash varied from 4.00% to 4.88%. In sized fractions, ash content decreased as the particle size increased from 0.11 to 1.00 mm, and then increased with particle size. This trend was similar to that of protein in the sieved fractions. Like protein and oil, ash content in sieved fractions of DDGS also had much larger variation than that of corn.

3.4. Starch, total non-starch CHO, and total CHO contents in whole and sized fractions

Starch in ground corn had a mean value of 69.75% (Table 3). Upon sieving, starch content was highest in the finest fraction (Fig. 3A). As the particle size increased, it decreased up to the 1.00 mm size class and then increased slightly. Starch is the main component for ethanol production. During ethanol production, unlike other components which are concentrated, it is depleted. However, since conversion is typically incomplete, there is still residual starch in DDGS. In this study, residual starch content in DDGS samples had a mean value of 4.85%. This value matches that reported by Belyea et al. (2004). However, in the previous report (Liu, 2008) with 11 DDGS samples, three of them had unusually high concentration of starch, ranging from 11.1% to 17.6%. The high residual starch in the DDGS samples was attributed to unconventional processes. In sieved fractions, starch changed very little as the particle size increased. The variation of starch among ground corn was similar to that among DDGS samples.

Total non-starch carbohydrate in corn refers to all the carbohydrates excluding starch. This includes soluble sugars, cellulose, hemicellulose, and lignin. The last three are also known as fiber. Since soluble sugars are mostly absent in DDGS and relatively lower in raw corn tissue (about 2.6**%**, as reported by Gulati et al., 1996), the total non-starch CHO is almost equivalent to total fiber, which is considered non-fermentable in the starch-based biofuel conversion. In ground corn, starch was a major portion of total CHO. Therefore, the total non-starch CHO was around 17% of dry matter (Fig. 3B). This value changed from about 10% to about 20% in sized fractions when the particle size increased from less than 0.11 to 0.50 mm, and then decreased slightly from 0.50 to 1.70 mm. In other words, sieved corn fractions with finer particle sizes had lower non-fermentable CHO and higher fermentable CHO (starch, Fig. 3A). This is expected since corn fibrous material tended to be larger in particle size than other ground components, and thus ended more in coarse fractions upon sieving.

During ethanol fermentation, soluble sugars are completely converted and starch is mostly converted to ethanol, leaving non-fermentable fiber in DDGS. Most DDGS samples had non-starch CHO content around 52%. Like in ground corn, upon sieving, the content of non-starch CHO was reduced in the fractions with finer particle size. As the particle size increased, it increased up to the 1.00 mm size class and then decreased slightly. Again this is due to visual observation that fibrous materials left in DDGS samples, such as seed coat, tended to be larger in particle size.

In earlier discussion, protein content in fractions with smaller particle size was found concentrated more than fractions with larger particle size during ethanol production (Fig. 2A). Besides particle size re-distribution and addition of other protein sources such as yeasts as a result of processing, the observation that fractions with finer sizes of ground corn were lower in non-starch CHO but higher in starch content would be another possible explanation since higher concentration of starch and lower content of non-fermentable CHO in finer fractions would allow more complete conversion of CHO to ethanol during processing, resulting in higher concentration of protein.

The total CHO in ground corn was between 86.26% and 88.16% for 6 samples collected (Table 3). Upon sieving, its content was increased in the fractions with finer particle size (Fig. 3C). With increasing particle size, it showed a slight yet visible decreasing trend. DDGS samples had a content of total CHO in the range of 55.74–57.93%. In contrast to ground corn, upon sieving, the total CHO content was reduced in the fractions with finer particle sizes. As the particle size increased, it increased and then decreased.

3.5. Surface color attributes in whole and sieved fractions

The surface color of ground corn samples did not vary much (Table 3). The value ranges of the three color spaces were: *L*, 83.54–86.16; *a*, 0.38–1.49; and *b*, 30.67–32.92, indicating that the corn used as raw material for all 6 plants had similar color - slightly yellowish. Upon processing into DDGS, their color changed dramatically, toward darker, yellower and redder color since *L* decreased to a range of 44.89–59.59; *a* value increased to a range of 8.27–11.36, and *b* value increased to a range of 30.98–46.38 (Fig. 4). Furthermore, DDGS from different plants varied greatly in color, some were darker, more yellow or more red than others. There were also some noticeable changes in surface color of sized fractions among ground corn and DDGS samples. For corn samples, the changing patterns for the three color values were similar; as the particle size increased, the *L* value decreased, *a* and *b* values increased. This shows that fractions of smaller particle size were relatively lighter, less red and less yellow than fractions with larger particle size. For DDGS samples, most showed decrease in *L* value and slight increase in a value as the particle size increased. These

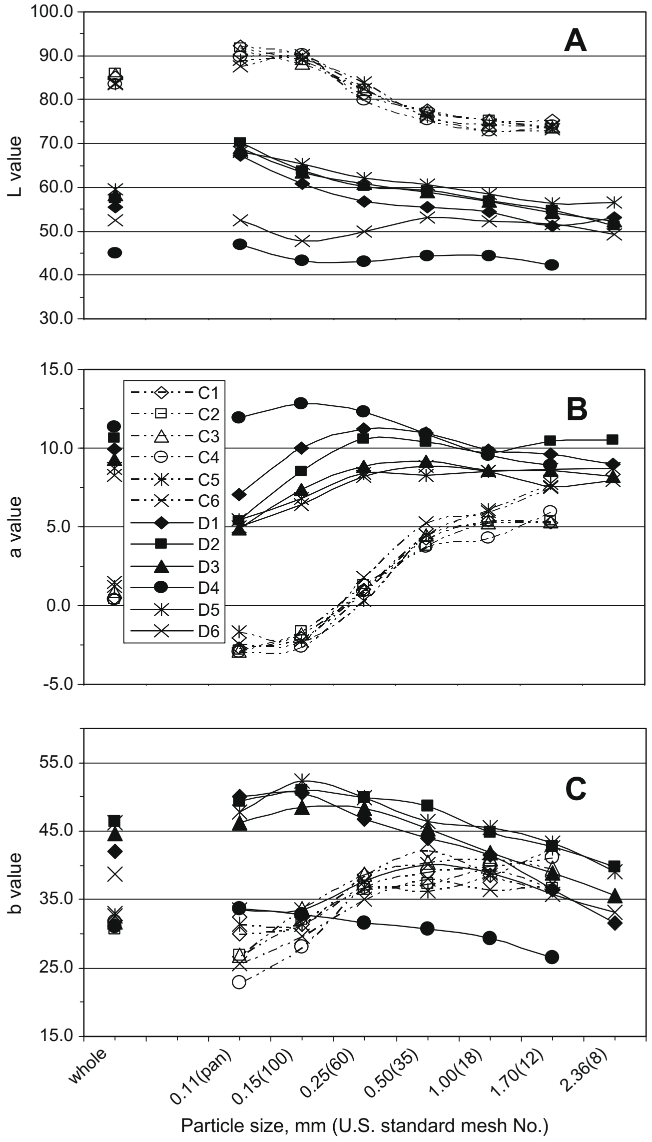

Fig. 4. Surface color, expressed in *L* (A), *a* (B), and *b* (C) color space, in the original (whole) and sieve sized fractions of the 6 ground corn and corresponding DDGS samples.

trends were similar to those of corn. However, with increasing particle size, *b* value decreased in DDGS but increased in corn samples. In other words, for DDGS samples, fractions of smaller particle size were relatively lighter and less red, but more yellow. The largest variations in the three color attributes among DDGS samples were found in fractions of smaller particle sizes.

3.6. Variations in chemical components and color attributes of whole and sieved fractions

Variation in nutrient concentrations can be expressed in different ways. A range difference (that is, actual difference between the highest and lowest values) is a simple way of expressing variation. Another measurement of variation is the standard deviation, a statistical parameter, measuring a degree of variation from a mean of a sample population. In addition, to reflect magnitudes of variation relative to the mean value, relative range difference and relative standard deviation (also known as coefficient of variation) are also used. Depending upon which measurement of variation is used, different interpretations can be obtained. As shown in Table 3, in whole fractions, the range difference and standard deviation in protein content of corn samples was 1.70% and 0.63% units, respectively, compared to 3.26% and 1.09% units, respectively, for DDGS. On the basis of these two parameters, variation for DDGS was about 2 times greater than for corn. However, based on relative range difference and relative standard deviation, variation in protein was even higher in corn than DDGS. The reason is that protein was concentrated in DDGS. When the range difference and standard deviation increased from corn to DDGS, so did the mean value. This is true for other nutrients. Since the actual variation (range difference) is easier to calculate, and commonly used, and has direct impact on quality of corn and end products, it will be used hereafter in this study. It should be pointed out that the range differences of the chemical compositions of several nutrients (protein, oil, starch, and ash) in the whole DDGS samples observed in this study generally agree with previous reported range differences (Belyea et al., 2004).

Variations in nutrients and surface color of sieved fractions were larger than of the whole fraction. This was particularly true for DDGS (Figs. 2–4). Corn kernels have four distinct structural parts: hull, germ, endosperm, and tip cap. These parts have different cellular structures and physical texture, and thus would have different behavior during grinding or milling. This may contribute in part to variation in particle size of ground corn. Furthermore, according to Gulati et al. (1996), most of the starch and protein is contained in the endosperm, while the germ contains most of the lipids and soluble sugars. Over 50% of the fiber (hemicellulose, cellulose, and lignin) is present in the hull. The heterogeneous distribution of nutrients and apparent difference among the structural parts in color and resistance to break during milling explain well the observed differences in composition and color among sieved fractions of ground corn. Yet, regardless of the observed difference among sieved fractions from the same corn sample, the differences in composition and color attributes among corn samples in the whole fraction was relatively small. One major reason was that majority of ethanol plants in the Midwest used commodity varieties of yellow dent corn as their major raw material.

The increase in variation of nutrients upon sieving into sized fractions (as compared with that of the whole sample) was larger in DDGS than in corn. Therefore, larger variation in DDGS sieved fractions was noticeable as compared to that of corn sieved fractions. As for color values, DDGS samples had much larger variations than that of corn. This was true not only in the whole fraction, but also in sieved fractions.

3.7. Correlations of chemical components and color attributes between ground corn and DDGS

Just like for particle size, processors also tend to believe that variation of various nutrient contents in DDGS results from variation in corn. A question is, to what degree does the corn material affect quality of DDGS? To answer this question, linear regression was performed on all attributes between corn and DDGS in whole fraction and individual sieved fractions. In this case, only positive *r* values could be meaningfully interpreted. When *r* values were near zero or entered into the negative side, correlations were considered non-existing or hard to define. Results indicate that for protein content, there were some positive correlations between the two in the whole sample ($r = 0.710$) and in all sieved fractions except for the fraction of >2.36 mm class (Table 2). For non-starch CHO, there were also some positive correlations in the whole sample ($r = 0.776$) and in most sieved fractions. For ash, oil, and total carbohydrate, little or even negative correlations were noticed in the whole sample between corn and DDGS. Among three color attributes, only *L* value showed some positive relationship in the whole fraction ($r = 0.499$).

Belyea et al. (2004) reported no significant correlations between components of corn and components of DDGS in the whole sample, and thus concluded that there was no scientific basis for the assumption that variation of various nutrient contents in DDGS results from variation in corn. Results in this study do not totally agree with their finding, since protein and non-starch CHO were found to have some correlations between corn and DDGS. The effect of raw material on variation of DDGS quality parameters was apparently through concentration effect that simply resulted from depletion of soluble sugars and starch during processing. For example, upon conversion from corn to DDGS, on an average, protein was concentrated 3.59 times, oil, 3.40 times, ash, 3.32 times, and total non-starch CHO, 2.89 times (Table 3). As the value of nutrients increased from corn to DDGS, so did variation among samples.

In the Belyea et al. study only the whole sample was measured. In this study, linear regression was also made for nutrients in all sieved fractions between ground corn and DDGS. The resulting *r* values indicate the degree of correlations between the corn and DDGS in the distribution pattern of each compositional and color attribute measured across the entire particle size ranges. For example, protein distribution of ground corn over the range of particle size classes was negatively correlated with that of DDGS ($r = -0.362$). In other word, as the particle size increased, the change of protein content in sieved fractions was generally opposite to that of DDGS. This was evident in Fig. 2A, as the two clusters of curves, one for corn and one for DDGS, moved into opposite direction with changing particle size. Similarly, distribution of ash and total CHO were negatively correlated while that of oil, total non-starch CHO and *L* value were positively correlated between ground corn and DDGS. It is interesting to note that for some attributes, such as protein, correlation between corn and DDGS was positive in whole sample as well as most sieved fractions, but negative in its distribution over the range of particle sizes. This reflects the complex change of protein during conversion of corn to ethanol and DDGS. Partial dissolution and hydrolysis of protein and addition of yeast proteins in the whole bioprocess may partially explain the observed changes.

3.8. Other possible factors affecting variations of nutrients and surface color in DDGS

Although there are some correlations in protein and non-starch CHO between corn and DDGS, what was found in this study is that differences in composition as well as color attributes, either among sieved fractions of the same sample or among whole samples (in whole fraction and sieved fractions) were larger in DDGS than corn samples. This indicates that beside raw material, there are other factors which are responsible for the larger variation in chemical attributes and color properties of DDGS. One such factor would be variation in methods among plants. Even a small change would lead to variation of DDGS quality. For example, one aspect of method variation, as suggested by Belyea et al. (2004), would relate to the final stage of ethanol processing. DDGS is formed by mixing two processing streams, wet grains (WG) and condensed distillers' solubles (DS) (also known as syrup). The composition of WG and DS was found varying significantly and among plants and even from batch to batch (Belyea et al., 1998). This variation plus variation in proportion of WG and DS during mixing could have contributed to greater variation in concentration of nutrients in DDGS.

Variation in color of DDGS was not only visible but also measurable, as shown in this study as well as in previous ones (Rosentrater, 2006; Liu, 2008). It is also a major factor that determines the perceived value of DDGS by purchasers. Results show that color of raw material had little effect on the color of DDGS. Apparently it is complex interactions of many factors during processing, which determine the color of DDGS. Since surface color of DDGS results mostly from Mallard browning, small variation in processing methods, such as drying temperature and duration, and in composition of intermediate products, such as residual sugar contents in WS and DS, etc. would lead to big difference in color attributes. This would explain well the usual larger variation of DDGS 4 sample from the rest DDGS in color attributes even though its original material had similar color (Fig. 4).

Another factor for large variation in DDGS quality is the addition of yeast cells. During fermentation, as yeasts grow, they ferment starch, and at the same time produce cell mass which contains about 60% of protein on dry matter basis. Thus, the protein in DDGS is assumed to derive from two main sources, corn and yeasts. Since yeasts lack proteolytic enzyme and cannot degrade corn protein, a significant portion of the protein in DDGS could be corn protein. The proportion of yeast protein to corn protein in DDGS is not well documented in the literature, but based on the ratio of amino acid composition between DDGS to yeast protein, Belyea et al. (2004) suggested that yeast protein may make up as much as 50% of the protein in DDGS.

4. Conclusion

This study showed that in terms of geometric mean diameter (d_{gw}) of particles of the whole fraction and mass frequency of individual particle size classes, the relationship between ground corn and DDGS varied, but in term of PSD, the two had a highly positive correlation ($r = 0.807$). There also were some positive correlations in contents of protein and non-starch carbohydrate and in L value between corn and DDGS, but variations in nutrients and color attributes were larger in DDGS than in corn. Thus raw material affected DDGS quality to some extent, but other factors, such as processing method and contribution of yeasts, were also considered responsible for large variations in DDGS quality attributes. The results disagree with previous reports and provide scientific basis to partially support the common belief expressed by processors regarding relationships in quality parameters between corn and DDGS. The study also contributes better understanding of the physical and chemical changes of corn during ethanol production, which may lead to strategies for improving end product quality.

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