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Evaluation of Methods for Dry Matter Determination of Ethanol Byproducts

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Summary

Traditional wet distillers grains plus solubles, modified distillers grains, Dakota Bran Cake, and distillers solubles were sampled and replicates tested using oven drying (n = 8) at 105°C and 60°C, vacuum oven drying (n = 3) and toluene distillation process (n = 8). Two replicates were evaluated using Karl Fischer titration. Oven drying was compared to toluene distillation as the standard. Oven drying at 60°C for 24 hours resulted in the same DM (P > 0.10) as toluene distillation for wet byproducts.

Introduction

With the growing availability of wet ethanol byproducts, accurate determination of the DM content of these wet byproducts is important.

Many different methods are available for determining DM, but the most common are oven drying procedures because of their cost effectiveness. Our objective was to compare different methods of DM determination to obtain the most consistent and accurate DM procedure for an ethanol plant or producer using wet byproducts.

Procedure

Samples

Samples of wet distillers grains plus solubles (WDGS), modified wet distillers grains (MWDGS), Dakota Bran Cake (Dbran), and distillers solubles (solubles) were obtained. For the least variability possible, large 5 lb byproduct samples were taken and used for each method. Traditional wet distillers grains plus solubles (WDGS) has a DM of 31%-35% and is used widely in feedlot diets. Modified wet distillers grains (MWDGS) is partially dried to about 42%-48% DM. Dakota Bran Cake (Dbran), marketed by Poet Nutrition, has a DM of 50%-54% and is a bran and distillers solubles mix. Distillers solubles (e.g. solubles), is generally 25%-35% DM and is added back to wet grains, fed as a separate ingredient, or used in liquid supplements.

Oven Drying Methods

The 105°C and 60°C oven drying methods were conducted by weighing out 8 replications of each of the four products (5g wet weight). Weights were recorded at three different drying times of 3, 8, and 24 hours for the 105°C oven. The samples in the 60°C oven were weighed back at 24 and 48 hours.

Vacuum Oven Analysis

Vacuum oven analysis was conducted using the AOAC Official Method 934.01. Each product was replicated three times using approximately 5 g of wet byproduct. The samples were dried using a temperature of ≤ 70°C and pressure of ≤ 50 mm Hg.

Toluene Distillation Process

The toluene distillation procedure was based on AOAC Official Method 925.04,. The 90-minute procedure required 12-15 mL of moisture, therefore approximately 25 g (as-is) sample was used. The sample was weighed into a 250 mL Pyrex flask and toluene added to cover the byproduct sample. Toluene was then rinsed down the sides of the condenser into the collection trap and the trap was filled until it was slightly running over into the flask. Heat was applied so the toluene boiled at approximately 7 to 10 minutes. Measurements were taken at 30, 45, 60, 75, and 90 minutes. The condenser was rinsed after measuring at 45, 60, 75, and 90 minutes. After allowing time to cool, the condenser tube was rinsed to take a final reading. An aliquot of the distilled moisture was collected via syringe and analyzed for any volatiles using gas chromatography (GC). Four of 8 distillation replications were analyzed with the GC by preparing 2.0 mL of moisture collected with 0.5 mL 2-Ethylbutyrate.

The toluene heated faster than the solubles forcing the solubles to stick to the glassware. Therefore, to solve this challenge, dried bran (105°C for 24 hours) was added to the distillers solubles in a 1:3 ratio of bran to solubles. This allowed the solubles to remain within the toluene for the duration of the procedure. Amounts were then back-calculated to account for the bran.

Karl Fischer Titration

Karl Fischer titration, AOAC method 2001.12, was conducted in duplicate on all products.

Results

For WDGS, the DM determined from toluene distillation was 33.2%, which was not different (P > 0.10) from DM measured using 60°C oven for either 24 hours or 48 hours (Table 1). Also, no difference (P > 0.10) was observed between the 60°C oven for 48 hours and 105°C oven for 3 hours. It was determined that samples in the 105°C oven decreased in DM over time. The vacuum oven results were higher in DM content than all other methods for WDGS.

The MWDGS toluene distillation DM was 43.3% and was not different (P > 0.10) from the 105°C oven for 3 hours. The 60°C oven for 24 hours and 48 hours were not different

Table 1. Average DM percentages and CV between replicates of four different ethanol byproducts evaluated by different methods.

Sample	60°C		105°C			Toluene	Vacuum
	24 h	48 h	3 h	8 h	24 h		
WDGS	33.2[a]	33.0[ab]	32.7[b]	32.2[c]	31.6[d]	33.2[a]	35.2[e]
CV%	1.35	1.57	0.99	1.09	1.14	1.36	0.49
MWDGS	44.1[a]	43.7[a]	42.9[b]	42.2[c]	41.3[d]	43.3[b]	45.0[e]
CV%	0.22	0.42	0.59	0.78	0.51	0.47	0.34
Dbran	54.0[a]	53.7[a]	52.8[b]	52.1[c]	51.3[d]	53.7[a]	55.4[e]
CV%	0.56	0.42	0.54	0.57	0.63	0.46	0.34
Solubles	35.6a	34.9[b]	33.5[c]	32.2[d]	31.1[e]	35.9[a]	35.8[a]
CV%	1.53	1.96	3.13	3.87	3.28	2.00	0.26

[a,b,c,d,e]Means with different superscripts differ ($P < 0.10$).

($P > 0.10$) from each other. A reduction in DM was observed with drying MWDGS in the 105°C oven over time. The vacuum oven DM was 45.0%, which was greater than other methods discussed.

Dry matter was not different ($P > 0.10$) between the toluene distillation and 60°C oven (24 hours or 48 hours) for Dbran. The DM for Dbran was 53.7% for toluene distillation. Drying at 105°C decreased DM ($P < 0.10$) compared to toluene distillation or 60°C oven drying for Dbran, which is similar to what was observed with WDGS and MWDGS. Dry matter determined from the vacuum oven was also greater than oven drying at 60°C or toluene distillation.

Distillers solubles DM was 35.9% for toluene distillation (Table 1). No differences ($P > 0.10$) between toluene distillation, 60°C oven, and vacuum oven were observed. The only byproduct with the vacuum oven method being similar ($P > 0.10$) to toluene distillation was distillers solubles. The same decreases in DM occurred with the 105°C oven over time. This sample, averaged across methods, had the highest calculated coefficient of variation (CV).

The vacuum oven offered the most consistent CV as a method across all samples followed by the 60°C oven for 24 hours and toluene distillation. The 105°C oven was the least consistent especially with distillers solubles.

Less than 0.03% volatiles were present for water distilled from the 4 replications of toluene distillation suggesting the distillation removed only moisture For this reason, only 4 of the 8 replications for toluene distillation were completed.

Results from the Karl Fischer analysis were a DM of 37.3% for WDGS, 45.6% for MWDGS, 54.8% for Dbran, and 35.7% for distillers solubles. Coefficients of variation were 2.85%, 0.31%, 0.77%, and 2.38%, respectively. Because only 2 replicates were evaluated using Karl Fisher, the reader is cautioned to not compare the variation from Karl Fisher to other methods. No statistical comparisons were made due to less runs using Karl Fisher. However, the values are consistently greater than all other methods and for all byproducts except for vacuum oven. Interestingly, the solubles DM were consistent across all methods except for the 105°C oven method suggesting that the solubles can be measured using multiple methods.

Conclusions and Implications

Toluene distillation DM values were similar to 60°C oven for 24 hours. The 60°C oven is more cost effective and more easily completed than toluene distillation. With the decrease in DM over time in the 105°C oven, it could be implied that volatiles are lost due to more intense heat. However, loss of volatiles with the forced-air 60°C oven method was not observed given the close agreement with toluene distillations. Karl Fischer titration provides similar DM values to the vacuum oven method, and result in higher DM calculations than oven drying and toluene distillation. It is recommended that the 60°C for 24 hours be used as the standard for DM determination of wet byproducts because it is less tedious and costly than toluene distillation.

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