Rapid Measurement of Residual Ethanol in Corn Stillage (Beer) during Distillation

I. Introduction

Ethanol concentrations in complex matrices such as stillage (beer bottoms) from the base of distillation columns can be measured in about one minute with minimal preparation using the YSI 2700 SELECT. YSI's unique enzyme electrode technology provides for specific ethanol measurements in the range of 0.004% to 0.32% w/v. Measurements are virtually unaffected by color, turbidity, density, pH, or the presence of chemical substances.

When configured with YSI 'alcohol' buffer and the YSI alcohol oxidase enzyme membrane, the YSI 2700 analyzer measures ethanol after aspiration of just 10 microliters of sample. Some samples may need filtered; and for ethanol concentrations that exceed 0.32% w/v, dilution of sample may be required. Results are displayed and printed. The sample is automatically flushed from the electrode chamber within 30 seconds after the displayed result and the YSI 2700 is ready to measure the next sample. Turn around time is under two minutes.

In the study described ethanol was measured in both beer bottoms in an early distillation stage and again in side stripper bottoms later in the distillation process. The target value in both stages was 0.05% w/v ethanol. Samples were collected and measured over a six week period using the YSI 2700 and an HPLC system for comparison. The 40 MMGY bioethanol plant used corn-based fermentation to produce fuel-grade ethanol[1].

II. Materials and Setup

Sample Collection

Collection container (500 ml flask)

Drip coffee filter paper or equivalent to filter particulates

Collection tube (5 ml, to collect filtrates)

YSI 2700S or 2700D, configured for ethanol measurement

YSI 2700 Instrument Setup

See the YSI 2700 user's manual for general setup and safety information.

Chemistry electrode and reagent configuration depends on single or dual channel operation. The information below outlines ethanol configuration for a single channel. If you have a 2700D version then assign 'None' to the electrode that you are not using when you set up the electrodes in the menu.

Under Menu choose Setup, and then choose MeasParam to access the electrode assignment configuration. Set or confirm the following parameters.

Sample Size	10 microliters
Cal Method	One Station
Black Probe Parameters	
Chemistry	Ethanol
Unit	% (w/v)
Calibrator	0.20% (2.00 g/L)
End Point	45 seconds
CalStation#	2
White Probe Parameters	
Chemistry	None
Unit	N/A
Calibrator	N/A
End Point	N/A
CalStation#	N/A
Autocal Parameters[2]	
Sample Error	ON
Temperature	1°C
Time	60 Min[3]
Sample	0 Sam
Cal Shift	2%
Calibration Station	#2
Sample Station	#3 (or #4 if turntable)

III. Method

A. Calibrate the YSI 2700 by entering Run Mode or, if in Run Mode, by pressing the Calibrate key.

B. Each day, prior to runs, perform the FCN membrane test using YSI 2363 solution.

C. Each day, prior to runs, test the linearity of the system with 0.32% w/v ethanol from YSI 2790 calibration kit.

D. When idle for more than 15 minutes during sampling, initiate a calibration to ensure greatest accuracy.

E. Collect about 200 ml of sample from the base of the distillation tank, ensuring a representative sample.

F. For beer bottoms mix well and pour through filter paper to capture particulates; then sample the filtrate.

G. For side stripper bottoms (no particulates) collect and run samples without the filtration step.

[1] YSI gratefully appreciates the contributions of Amanda Huber (Process Manager) and her staff at Front Range Energy, LLC, Windsor, CO.

[2] Enter AutoCal menu from RunMode under Setup Menu.

[3] Calibration is automatically updated hourly. To ensure best accuracy, manually update calibration (press Calibrate key) a few minutes prior to measuring a sample.

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H. Immediately present the sample to Station #3 of the YSI 2700 for aspiration; then record the ethanol concentration when it is displayed.

I. If the ethanol reading exceeds the linear maximum 0.32% w/v or other specified limit, collect another sample and dilute appropriately with reagent water to bring the concentration within the measurement range.

J. Repeat measurement steps (F or G, then H).

K. Record the concentration, adjust with calculations as necessary, and compare to your reference range values.

IV. Calculations

Samples that were compensated for dilution must be back-calculated by the dilution factor.

Example: Assume you have about 5 ml of filtrate. If this solution measures 0.60% w/v ethanol with the YSI 2700, you might consider a 4-fold dilution (1 ml sample; 3 ml water) to bring the value near the calibration value. You might expect a number near 0.15% w/v (0.60% ÷ 4). In this example let us assume the diluted sample now measures 0.22% w/v. Corrected for dilution, the undiluted sample concentration is 0.88% w/v (4 x 0.22%). This means that the system was significantly under-linear with undiluted filtrate. The correct number to record is 0.88% w/v.

V. Results

Samples of beer bottoms and side stripper bottoms were collected on thirty (30) different days over a six week period. Each sample was measured with the YSI 2700 and with an HPLC system[4] commonly used in bioethanol production. YSI 2700 results were obtained within 2 minutes after filtration. HPLC results were determined approximately 35-40 minutes after filtration.

Data tables for each study are displayed on the next page while correlation graphs are shown in the right column of this page.

YSI 2700 Precision for Bottoms' Samples

Samples MR01 and MR02 (beer bottoms) and MR06S (side stripper bottoms) were arbitrarily selected for precision studies. Ten (10) replicates of each sample were performed.

Sample	Replicates	Mean % w/v	STD % w/v
MR01	10	0.027	0.0011
MR02	10	0.028	0.0016
MR06S	10	0.002	0.0013

The standard deviation (STD) was determined for each replicate series. YSI precision was well within the specified limits of 2% CV or 0.004% w/v, whichever the greater.

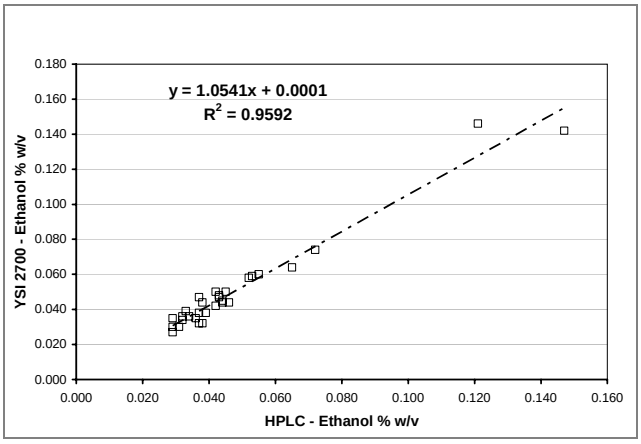
[4] Shimadzu modular HPLC system with autoinjector, 10 uL sample injection, Phenomenex Rezex ROA column (300 x 7.8 mm), 0.02-0.05 N sulfuric acid mobile phase, 0.60 ml/min flow, 60°C, RI detector. Analytes detected: DP4+, DP3, maltose, glucose, lactic acid, glycerol, acetic acid and ethanol.

Accuracy: YSI 2700 vs. HPLC

The mean ethanol concentration (n=30) studied was 0.050% w/v and 0.048% w/v, respectively for the YSI and HPLC systems. The mean bias for the YSI 2700 vs. HPLC for beer bottoms was 0.003% w/v ethanol. Refer to data in Table 1 (next page).

Correlation of YSI 2700 ethanol and HPLC results proved to be very good in the concentration range of interest. The target value in both beer bottoms and side stripper was 0.05% w/v. This value had been determined to be optimal for the distillation process.

Figure 1: Ethanol in Beer Bottoms



Later in the distillation the side stripper bottoms result from the last distillation step of a very low proof steam. Again the target ethanol concentration is 0.05% w/v. Early in the study relatively high ethanol concentrations (above the YSI reportable range) were observed on six different days (see Table 2), and although lower than HPLC results, the information was useful to operators indicating the need to adjust operations controls of the distillation process.

The mean concentration (n=24) was 0.036 % w/v and 0.034% w/v, respectively for the YSI and HPLC systems. The mean bias was 0.002% w/v, which is well within the expected bias of the two methods.

Figure 2: Ethanol in Side Stripper Bottoms

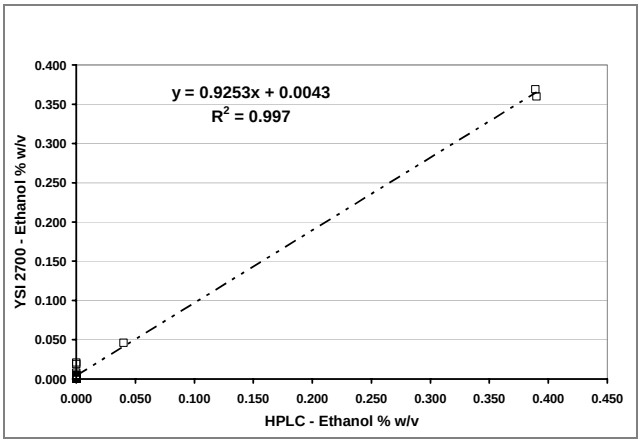


Table 1: Ethanol in Beer Bottoms

YSI 2700 vs. HPLC

Sample	YSI Ethanol % w/v	HPLC Ethanol % w/v	Bias
JA29	0.044	0.044	0.000
JA30	0.044	0.046	-0.002
JA31	0.058	0.052	0.006
FE01	0.074	0.072	0.002
FE02	0.035	0.029	0.006
FE05	0.142	0.145	-0.005
FE06	0.060	0.055	0.005
FE07	0.048	0.043	0.005
FE08	0.050	0.042	0.008
FE09	0.036	0.034	0.002
FE12	0.032	0.038	-0.006
FE14	0.146	0.121	0.025
FE15	0.036	0.032	0.004
FE20	0.039	0.033	0.006
FE21	0.030	0.029	0.001
FE22	0.032	0.037	-0.005
FE23	0.064	0.065	-0.001
FE26	0.038	0.039	-0.001
FE27	0.045	0.044	0.001
FE28	0.050	0.045	0.005
MR01	0.027	0.029	-0.002
MR02	0.030	0.031	-0.001
MR05	0.047	0.043	0.004
MR06	0.035	0.036	-0.001
MR07	0.034	0.032	0.002
MR08	0.038	0.037	0.001
MR09	0.059	0.053	0.006
MR12	0.047	0.037	0.010
MR13	0.044	0.038	0.006
MR14	0.042	0.042	0.000
MEAN	**0.050**	**0.048**	**0.003**
N=30	YSI	HPLC	Bias

Table 2: Ethanol in Side Stripper Bottoms

YSI 2700 vs. HPLC

Sample	YSI Ethanol % w/v	HPLC Ethanol % w/v	Bias
JA29S	0.019	0.000	0.019
JA30S	0.360	0.390	-0.030
JA31S	0.046	0.040	0.006
FE01S	0.841*	1.243	-0.402
FE02S	0.369	0.389	-0.020
FE05S	0.005	0.000	0.005
FE06S	1.140*	2.500	-1.360
FE07S	0.588*	0.724	-0.136
FE08S	0.004	0.000	0.000
FE09S	1.000*	1.588	-0.588
FE12S	0.917*	2.522	-1.605
FE14S	1.640*	7.660	-6.020
FE15S	0.021	0.000	0.021
FE20S	0.008	0.000	0.006
FE21S	0.003	0.000	0.001
FE22S	0.001	0.000	-0.005
FE23S	0.000	0.000	-0.001
FE26S	0.002	0.000	-0.001
FE27S	0.003	0.000	0.001
FE28S	0.002	0.000	0.005
MR01S	0.000	0.000	-0.002
MR02S	0.000	0.000	-0.001
MR05S	0.000	0.000	0.004
MR06S	0.003	0.000	-0.001
MR07S	0.003	0.000	0.002
MR08S	0.001	0.000	0.001
MR09S	0.005	0.000	0.006
MR12S	0.002	0.000	0.010
MR13S	0.005	0.000	0.006
MR14S	0.000	0.000	0.000
MEAN	**0.036**[5]	**0.034**	**0.002**
N=24	YSI	HPLC	Bias

[5] Data pairs were excluded for results outside of the determined YSI reportable range (> 0.40% w/v). See the asterisks (*****) in the data table.

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VI. Discussion

The loss of ethanol to waste (by-product) from distillation bottoms in bioethanol production plants can significantly affect the efficiency of fuel-grade ethanol production. Monitoring residual ethanol levels during distillation allows operators to adjust control parameters to minimize ethanol to waste and improve energy efficiency in plant operation.

In the ethanol production plant laboratory HPLC is typically used to measure dextrose polymers, sugars, organic acids, glycerol and ethanol concentrations. Monitoring and controlling the fermentation reactions are especially important to maximize the ethanol concentration in the beer. However, once the beer is pumped to the distillation stage, ethanol that is not distilled off may be lost to waste by-product (beer bottoms). Frequently this mix of yeast and bacteria cells, along with various metabolites, is converted to livestock feed. Any ethanol lost at this stage cannot be returned to the process. Measurement of beer bottoms' ethanol during distillation not only provides valuable information related to controlling distillation parameters, but also alerts the operator to distillation maintenance needs. The sooner that reliable information on ethanol levels is gathered, the sooner the operator can tweak parameters to maximize ethanol production.

The YSI 2700 has proven to be a valuable tool in providing accurate ethanol readings from beer bottoms in near real time. The one minute ethanol readings in the concentration range of interest (~ 0.05% w/v) compare well with HPLC results and provide information nearly 30 minutes sooner than HPLC. According to operators the YSI 2700 is easier to use and easier to maintain than HPLC while providing timely results to help reduce the loss of final product (ethanol).

In addition to ethanol in beer bottoms, frequently the rectifier bottoms (where 190-proof ethanol is distilled) are pumped to a side stripper to retrieve the last bit of ethanol from a very low proof steam. In this study the side stripper bottoms were measured over a six week period (30 daily samples total). Periodically the distillation equipment requires cleaning. One indicator for the need to clean is the ethanol concentration in the side stripper bottoms. Note that ethanol concentrations were relatively high and sporadic from samples JA29S to FE14S. This signaled to the process manager that it was time to clean the side stripper. Once cleaned the ethanol concentrations in the bottoms decreased dramatically and returned to a level where control of physical parameters became more effective. This indicated a successful cleaning and improved efficiency in the process.

Although the YSI 2700 ethanol readings were out of the reportable range in several samples, the operators know to use the HPLC data in these cases. In this particular case an accurate value is not as important as knowing that ethanol levels are unusually high.

In conclusion the YSI 2700 used in beer bottoms and side stripper bottoms analyses provide valuable information relevant to recovering residual ethanol in the distillation process. The measurements allow the process manager to make timely decisions thus improving plant efficiency and reducing costs.

VII. Ordering Information

YSI Part Numbers:

2700S Biochemistry Analyzer or;
2700D Biochemistry Analyzer
2786 Alcohol Oxidase Membrane Kit
2787 Buffer Kit
2790 Ethanol Calibration Kit (2.00 g/L ethanol)
2790 Ethanol Linearity Test Standard (3.20 g/L)
2363 Potassium Ferrocyanide Test Solution
2392 NaCl Solution (for membrane installation)