WHITE PAPER

Improving the corn to ethanol fermentation process with near-infrared spectroscopy (NIRS)

The fermentation of corn starch to produce ethanol is a complex biochemical process that requires monitoring of many different parameters to ensure optimal production. Some of these quality parameters include solids (non-volatiles), dissolved solids, pH, the sugar profile, glycerol, lactic and acetic acid, water content, and of course ethanol itself.

Traditional laboratory analysis using primary methods (e.g. Karl Fischer titration) takes about an hour to complete and is a limiting step for increasing plant capacity and efficiency. As a fast and non-destructive analytical technique, near-infrared spectroscopy (NIRS) can replace routine laboratory analysis, decreasing operating costs and increasing plant efficiency and capacity.

This White Paper describes the capabilities of the modern analytical method near-infrared (NIR) spectroscopy for monitoring and improving the fermentation process of corn to ethanol. Analysis time of in-process fermentation samples is reduced from one hour to five minutes—nearly 90% Additional time savings by close monitoring of the fermentation process with NIRS also allows ethanol producers the ability to increase their manufacturing capacity by up to 10%.

Metrohm

ETHANOL AS A FUEL ADDITIVE

Ethanol is an increasingly important component in the global fuel market, with countries looking to secure domestic fuel supplies and reduce their greenhouse gas emissions relative to fossil fuels. Demand for corn to transform into ethanol is likely to rise as the United States increases adoption of E15 blends (15% ethanol in gasoline) [**1**]. Ethanol for export is also likely to increase in demand, with countries such as China implementing a E10 fuel standard for motor vehicles.

One of the primary ways to meet increasing product demand while maintaining price competitiveness is to increase plant capacity. However, the standard laboratory analytical workflow for monitoring the different parts of the fermentation process can be a limiting factor for growing a production site or improving its efficiency.

A report from the National Renewable Energy Laboratory estimated that nearly 40% of the production cost of fuel ethanol from corn comes from labor, supplies, overhead, and variable operating costs [**1**]. Optimization of these costs, which include routine quality checks of the fermentation broth, regular maintenance of the fermenters and distillation towers, and triaging process upsets in a timely manner, leads to higher profitability of the ethanol production facility.

To maximize bioethanol production and profitability, laboratory limitations must be overcome. Near-infrared (NIR) spectroscopy is a proven economical, rapid, and operator friendly way to overcome common laboratory limitations.

LAB ANALYSIS SHORTFALLS

The lab serves many functions, but one of the key ones is to monitor the progress of the fermentation in each fermentation tank. This typically requires many different technologies, because many different signals must be recorded to ensure that a fermentation is on track. Some of the most common analytical instruments and their use cases are listed in **Table 1**.

If all these properties are to be measured, it can easily take an hour using six different pieces of equipment. Factor in conditioning steps and reference scans to ensure proper calibration, and the time for a routine fermentation analysis increases. For a single corn fermentation, this can take upwards of 55 hours—one hour to perform the analysis and six hours between each measurement. However, increasing the number of concurrent fermentations to four or six means that measurements from the different tanks will begin to overlap.

The impact on measurement time is clear if we consider four production batches running concurrently in four fermentation tanks (**Table 2**). There should be 12 measurements per tank, but due to overlapping demand for lab equipment, none of these four tanks completed all 12 measurements.

Table 1. Typical instruments and properties that are measured during fermentation of corn to ethanol.

Property	Instrument / technology	Analysis time (min) including sample preparation
Dissolved solids (°Bx)	Refractometer	3–5
pH	pH meter	3–5
Solids (non-volatiles)	Infrared balance	15–20
Ethanol	HPLC	30–45
Sugar profile (DP2, DP3, DP4+, glucose, total sugar)	HPLC	30–45
Glycerol	HPLC	30–45
Lactic acid	Ion chromatography	30–45
Acetic acid	Ion chromatography	30–45
Water content	Karl Fischer titration	5–10

Table 2. Ethanol concentration values (%) measured by primary analysis method for four concurrent batches.

Timestamp	Batch			
	6377	6378	6379	6380
5			0.62	0.61
6	1.58	1.47	1.44	1.47
8		2.04	2.02	2.17
12	3.76	3.79	3.51	3.71
18	6.32	6.95	6.40	6.47
24	8.91	9.68	9.03	9.20
30	10.70	11.44	10.85	
36	12.06	12.94	12.18	12.11
42	13.14	14.16		
48	14.12	14.58		
54	14.69	14.75		14.68
Fermentation Drop				14.75

Overlapping instrument demand combined with long analysis times results in a number of different challenges for bioethanol producers. First, if scheduled sample pull times overlap, then pulls must either be delayed or samples must age while waiting for analysis. Both of these options reduce the utility of the data because one sample pulled at 18 hours after tank filling cannot be compared directly with another. Second, the long analysis time means that data is no longer current, but minimally one hour or older by the time it has made it to the plant control center, which decreases the ability to deal with deviations.

For example, a high lactic acid concentration can indicate a lactobacilli infection in the fermentation tank. Each molecule of monomeric carbohydrate diverted to lactic acid production by the bacterial contamination results in the loss of two molecules of ethanol that could have been produced by yeast fermentation [**2**]. Therefore, faster detection of lactic acid presents an opportunity to intervene in the fermentation by adding antibiotics early in the process to increase ethanol production.

Similarly, an increased glycerol concentration indicates yeast stress. If the glycerol level is determined to be high early in the fermentation process, it is likely that ethanol production will be low. If detected at an early time, an intervention such as a urea rescue dose can be applied to boost yeast growth.

Long laboratory analysis times and infrequent measurements reduce the ability to perform interventions such as these, or to adjust other critical parameters (e.g., enzyme addition rate or process temperature). Additionally, such long wait times can impede the decision to end a fermentation early and begin anew if the batch is judged to be beyond recovery.

FASTER MEASUREMENTS, HIGHER PROFITABILITY

The most obvious way to overcome measurement time challenges is to increase the number of tools in the lab and/or to add automation. This is straightforward multiplexing—double the number of instruments and double the number of measurements that can be run simultaneously. However, this approach has costs in time; twice the sample preparation increases operating expenses and still fails to give high-speed feedback to the plant operations team.

A better way to overcome measurement time delays is to deploy NIR spectroscopy, which can make all of the traditional laboratory measurements with one piece of equipment, at the same time, in less than five minutes. In **Figure 1**, the average ethanol concentration from HPLC measurements during several fermentations from one plant is displayed. The data shows apparent discontinuities in the first 12 hours, with spikes in glucose, total sugars, and dissolved solids. It is also apparent that the total solids measurement at 48 hours is erroneous. However, because lab data requires so much time to collect, this spike is ignored instead of retested.

The NIR alternative to traditional measurements shown in **Figure 2** is of a single fermentation monitored in near real time. This high-speed analysis is possible because sample preparation is trivial. Simply pour corn mash into the sample cup and place it on the analyzer. Compared to the combination of HPLC and other analytical methods that consume about 60 minutes of operator time per sample, the NIR method measures the same parameters and produces a quality result in about a minute. The ability to collect many spectra in the early stages of the process provides a higher fidelity process picture, enabling more timely interventions to maximize production.

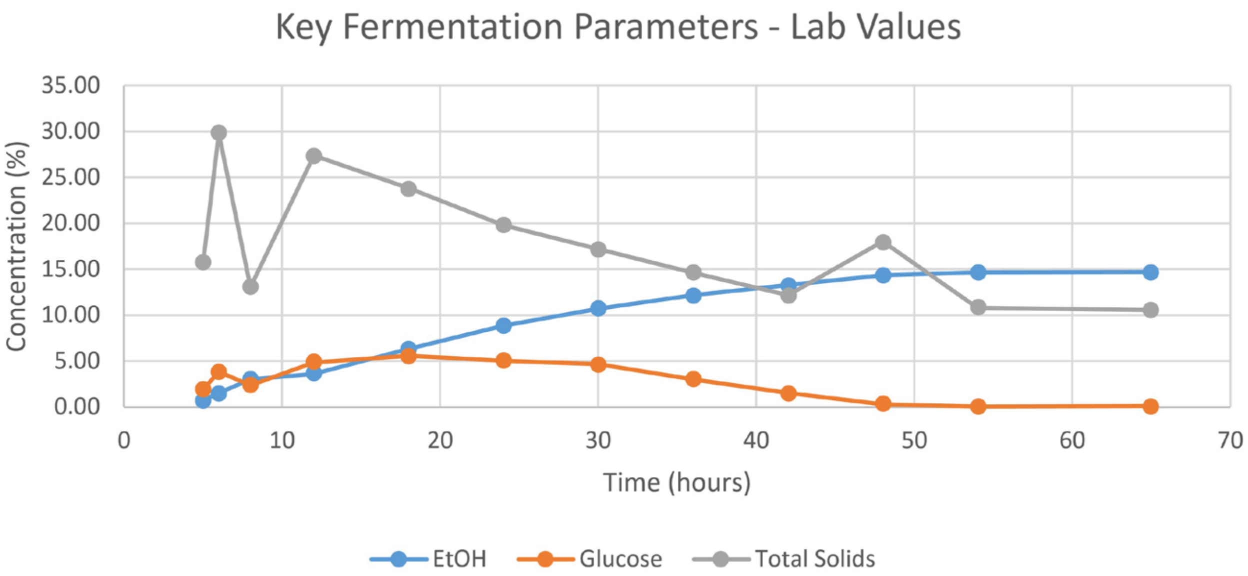

Figure 1. Key parameters measured for corn fermentation to ethanol as reported by the primary analysis methods listed in **Table 1**.

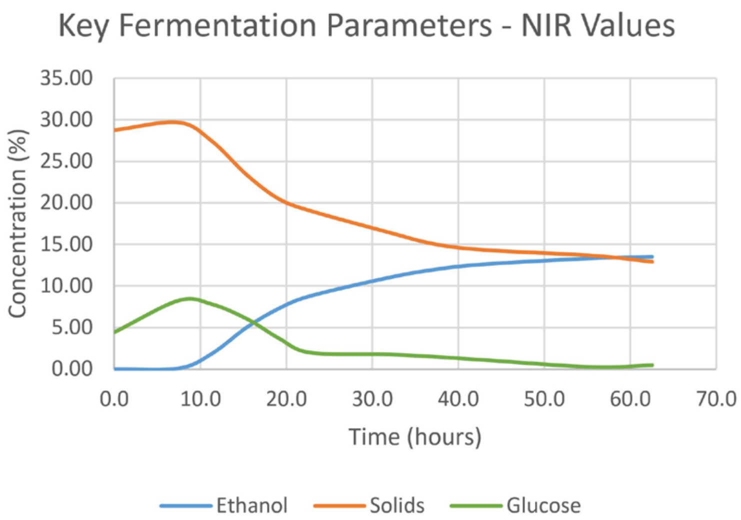

Figure 2. (Left) Ethanol fermentation as measured by NIR spectroscopy. (Right) Sample of corn mash ready for NIRS measurement.

The higher speed NIR analysis can be used to increase total plant throughput by growing the number of batches and revenue, as shown in **Table 3**. With the traditional analysis, the fermentation is allowed to run 62–65 hours, depending on the final laboratory results. With NIR analysis, this fermentation is complete in around 56 hours. Reducing fermentation time by six hours expands the potential number of batches by 13 over the course of a year, representing a potential plant capacity increase of 10%.

Table 3. Comparison of the apparent fermentation time based on primary lab analyses vs NIRS analysis.

	Traditional Lab Analysis	NIRS Analysis
Total measurement time	12 hours	5 hours
Number of measurements	12	62
Fermentation end point	~62 hours	56 hours
Batch capacity	37,850 L	37,850 L
Batches per year	129	142

CLOUD BASED NEAR-INFRARED SOLUTION

While the benefits of NIRS for ethanol production are clear, NIRS methods typically require extensive method development to relate the spectral signatures to the lab measurements—something most production sites do not have the time nor expertise to do on their own. To bring the advantages of NIR spectroscopy to the ethanol industry, Metrohm uses cloud technology to optimize NIR models for each site remotely.

This begins with deploying a DS2500 Solid Analyzer and precalibrations for fermentation monitoring, selected from those available listed in **Table 4**. These precalibrations are installed locally on the DS2500 with Vision Air software [**3**], where they can be left as is. To achieve even better results, connect the instrument to a secure Vision Air Server for remote method improvement, illustrated in **Figure 3**. This allows for optimization over time without the associated expenses for in-person support, as well as adjustments that may be necessary due to seasonal changes in the raw materials.

For cloud-based optimization, laboratory reference data is associated with the NIR spectral data and then transmitted to the Vision Air Server over a secure internet connection. Metrohm incorporates that data into the model that runs on the analyzer, validates it, and pushes the updated model back to the instrument remotely. This approach gives two benefits: (1) as soon as the instrument is installed, it begins producing useful data, and (2) the analysis will improve with use as the model is continually customized to the local site.

Table 4. Available Metrohm NIRS precalibrations and ranges for corn ethanol fermentation monitoring.

Parameter	Range
Ethanol	0.51–14.96 %
Total solids	9.96–30.24 %
Total sugar	0.49–26.62 %
Brix	9.90–28.10 °Bx
Glucose	0.04–8.84 g/L
DP2	0.05–7.99 g/L
DP3	0.04–4.98 g/L
DP4+	0.28–14.46 g/L
Glycerol	0.10–3.21 g/L
Lactic acid	0.02–0.61 g/L

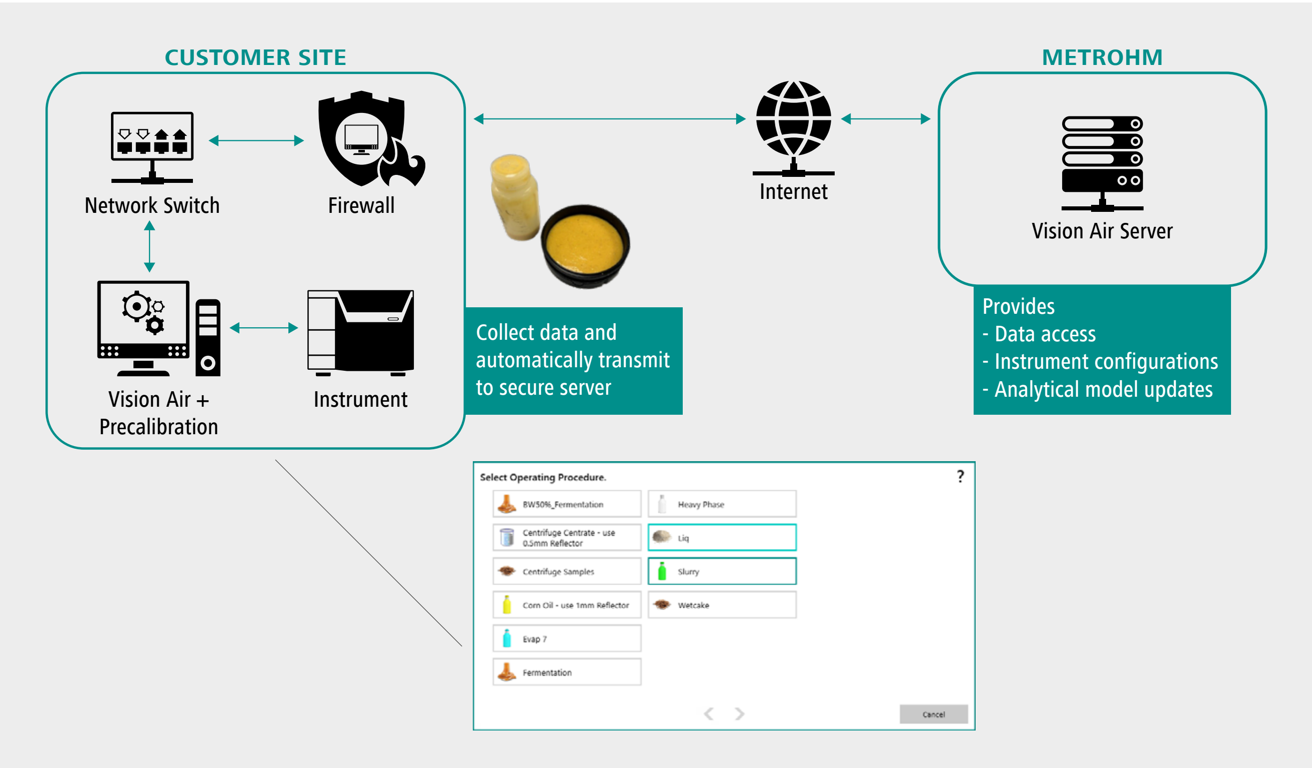

Figure 3. (Top) Cloud-based NIR model update schematic. (Bottom) Operating procedures for different areas of interest at an ethanol production site. Each operating procedure can have multiple NIR models.

This remote management strategy is not limited to fermentation monitoring alone [**4**]. The DS2500 analyzer can be used to analyze other parts of the fermentation process and byproducts such as DDGS (Distiller's Dried Grains with Solubles) and corn oil, or to reduce ethanol giveaway by more tightly controlling the water content in dried ethanol. **Figure 3** shows operating procedures (OP) for ten different areas of interest at one production site. Each of these OPs is optimized specifically for the site and remotely managed, enabling end-to-end facility analysis and optimization.

SUMMARY

Near-infrared analysis decreases measurement time for in-process fermentation samples by approximately 90%, from one hour to five minutes. Faster measurements allow the fermentation process to be followed much more closely, saving operator time to reduce costs and to optimize process conditions and plant operations. Capacity improvements of 10% are possible by being able to stop the fermentations based on rapid determination of the different parameters in the fermenter with NIRS rather than by slower traditional laboratory methods.

A cloud-based approach to deploying NIR spectroscopy eliminates the difficulties associated with building, maintaining, or modifying NIRS methods. This also allows the NIR instrument to be ready and running within a few hours of installation, producing useful data almost immediately without having to go through extensive operator training.

NIR methodology can provide benefits across the ethanol plant beyond fermentation monitoring to measure the performance of other plant components such as a centrifuge or dryer, making it a valuable tool to improve operations across the facility.

References

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