On-line Monitoring of Volatile fatty acids and Hydrogen During Anaerobic Digestion

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H_2 Introduction

Current methods for on-line calculation of dissolved H_2 concentration in anaerobic biogas production involve detection of the fraction of H_2 in the gas phase of the digester. Although this measurement is straight forward, the limited H_2 mass-transfer coefficient suggests a significant delay in H_2 concentration equalization between the liquid and gas phases of the digester. This is a severe limitation to maintaining optimal control of the biogas production process [1]. Furthermore, off-line dissolved H_2 monitoring requires extraction methods that are both time consuming and disadvantageous to continuous process control. Although many electrochemical sensors that can measure dissolved H_2 have been developed, some require the use of H_2 permeable membranes that are susceptible to fouling resulting in a short sensor lifetime, low selectivity, low signal-to-noise, and are therefore are not in use by the industry [2]. This research intends to address the lack of on-line monitoring of the dissolved H_2 concentration. A new optical fiber based sensor system allowing the live monitoring of H_2 during the biogas production process will be pursued. This will be in the form of a some-what indiscriminate optical sensor. If successful, the on-line measurement of H_2 will allow continuous manipulation of externally produced H_2, increasing the productivity of the biogas production process.

Why Fiber Optics?

- Fiber optic (FO) sensor systems have the potential to offer small sized, real time, label free sensing with high sensitivity.
- Previous work has shown that surface plasmon resonance (SPR) can give sensitive real-time monitoring of specific H_2.
- SPR H_2 sensors can be manufactured by sputtering gold (Au), silicon dioxide (SiO_2), and palladium (Pd) on a cladding-less multi-mode fiber.

Sensing Principle

The plasmonic sensing principle is shown in figure 1, where the refractive index on the surface of the Au layer is measured as a function of the SPR frequency that Au exhibits when illuminated with light.

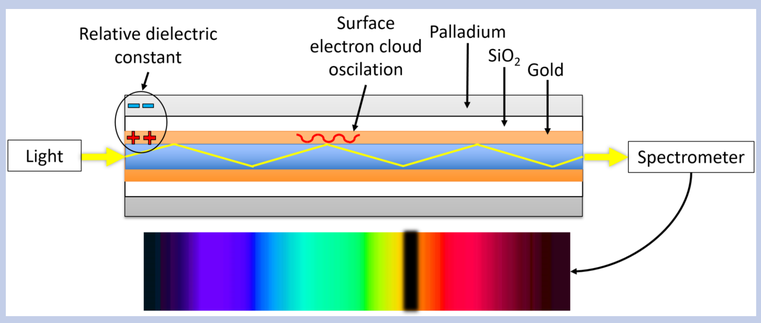

Figure 1: Illustration of the surface plasmon resonance of Au sensing the refractive index surrounding their surface. Here, the Au exhibits SPR, the Pd is the hydrogen sensitive component, while changing the thickness of the SiO_2 allows tuning of the plasmon resonance wavelength.

Fiber Optic Sputtering

The SPR is determined by measuring the transmission of light through a fiber. The Tefzel jacket, and hard polymer cladding of the fiber was removed to allow sputtering (figure 2). Deposition of Au (35 nm), SiO_2 (150 nm), and Pd (5 nm), on to a small section (about 50 mm) of ThorLabs multimode step-index fiber (FT200EMT, Thorlabs), was performed using an AJA magnetron sputtering system (figure 3).

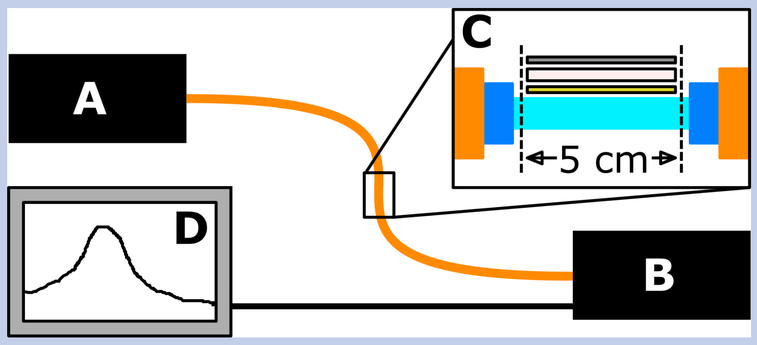

Figure 2: Sensor set-up using a halogen light source (**A**), and a spectrometer (**B**). **C** shows the section of fiber (light blue) without Tefzel jacket (orange), and hard polymer cladding (dark blue) spliced into the patch cable. The fiber has layers of Au (35 nm; yellow), SiO_2 (150 nm; off-white), and Pd (5 nm; grey). The relative transmitted light that is detected by the spectrometer can be displayed on a PC (**D**).

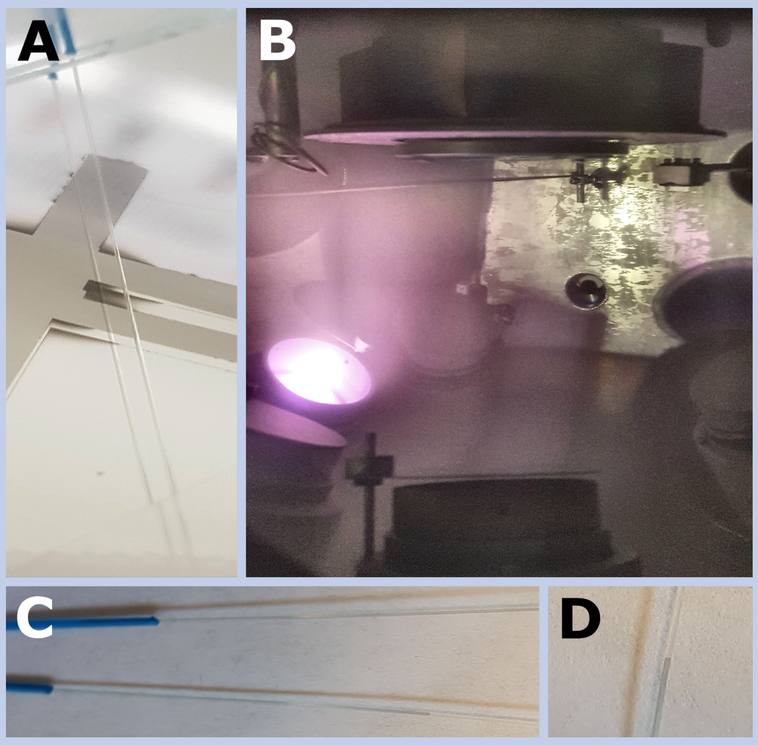

Figure 3: FT200EMT optical fiber section. **A:** Prior to AJA sputtering, **B:** during Au and SiO_2 sputtering, **C:** after sputter layers applied, and **D:** magnification of contrast between sputtered, and non-sputtered fiber. (still waiting for the Pd to be added due to problems with the AJA sputtering system).

VFA Introduction

Titrimetry and various gas chromatography techniques are commonly used methods for assessing VFA's, but are susceptible to biofouling and are time-consuming measurements. Alternative methods include using NIR- and IR-spectrometry techniques, but the required automation and sample processing needs advanced systems to maintain sufficiently rapid (< 2h) measurements [3]. The use of chemical sensors (including electrochemical, electronic, and optical technologies) appears to be ideal for monitoring of the bioprocess, but their limited selectivity, robustness, consistency, and stability may prove to be challenging for use in bioreactors [4, 5].

VFA Introduction continued

Therefore, the application of chemometric sensors (array of multiple chemical sensors where each sensor is only partially selective) may be a solution [4, 6]. Although there has been attempts to apply technologies to biogas production [7, 8], the complexity and low reproducibility of the process media composition can lead to sensor contamination [7].

Why Chemometrics

- Chemometrics sensor systems offer sensitive, real time, label free sensing for complex systems.
- These sensors can be manufactured by adding various indicators to a silicon matrix. These can then be used together with an camera to monitor changes in indicator colors over time.

Sensing Principle

Optical chemosensor systems consist of a matrix-embedded indicator that reacts to a specific analyte. The interaction of the indicator with the analyte can cause a change in the optical properties of the indicator (e.g., changes in absorption, reflection, or photoluminescence), which can be correlated to the concentration of the analyte (figure 4). This requires the use of principle component computation to analyze the cause of the color change.

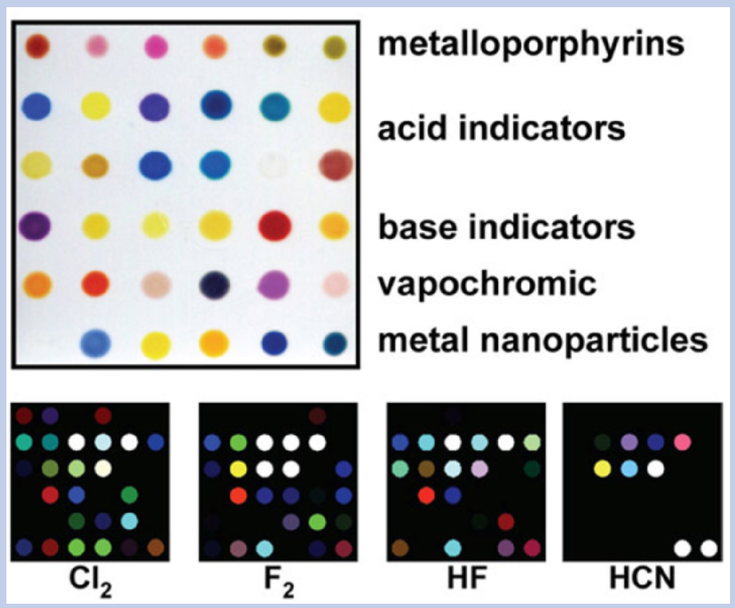

Figure 4: Illustration adapted from [6], showing indicator types and colour changes observed in relation to various analytes.

References

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