PVA 센서를 이용한 에탄올의 수분 측정

박수정, 김병철, 김영한*
동아대학교 화학공학과
(yhkim@mail.donga.ac.kr*)

Measurement of Water Content in Ethanol Using PVA Coated Quartz Crystal Resonator

Su Jeong Park, Byoung Chul Kim and Young Han Kim*
Dept. of Chemical Engineering, Dong-A University
(yhkim@mail.donga.ac.kr*)

1. Introduction

The prospective use of ethanol for automobile application is expected to increase drastically, since the fuel is relatively clean and sustainable. Though chemical synthesis has been a major process of its production, the grain fermentation is a desirable process having sustain ability. The beer produced from the fermentation has low ethanol contents and a lot of suspended particles of solid waste. Due to the suspended particles and the formation of an azeotropic mixture with water, the common separation technique of distillation is not implemented for the dehydration of the fermented ethanol. Zeolites, a known adsorbent for the water removal, are developed for the adsorptive dehydration of the ethanol.

A quartz crystal resonator (QCR) has a thin quartz crystal plate with two metal electrodes on both sides that establish an alternating electric field across the plate, causing vibration of the plate at its resonant frequency. This frequency is sensitive to mass loading on the electrodes [1]. For example, a 9 MHz resonator detects mass variation with a sensitivity of 1.4 ng/Hz [2]. Quartz crystal microbalances utilize the characteristic of frequency variation with changed mass loading.

Instead of the direct measurements of surface loading, a modification of the electrode surface of a quartz crystal resonator has been utilized for the entrapment of target materials inducing a load change. In the determination of organic substances either in gas or liquid phase, organic film has commonly been coated on the surface of one of its electrodes [3,4]. Though polymer film coated sensors improved the stability of coated material and selectivity of the detected material, they have different characteristic with solid adsorbent coated sensors [5,6]. Carbon coated quartz crystal sensors have high stability for wide range of applications. Kim et al. investigated the stability of a carbon-coated sensor to find that it is very stable and easy to regenerate by simple thermal treatment [7].

In this study, a measurement device of water contents in ethanol is developed by applying PVA on the electrode surface of the QCR. For the performance evaluation, the 2 % to 10 % water contents are utilized to determine the frequency drop of the PVA coated QCR.

2. Experimental

2.1 Materials

Polyvinyl alcohol (Mw. 22,000) was from Junsei Chemical, and ethyl alcohol was from

Burdick & Jackson. The chemicals wereused as received. Quartz crystal resonators (Sunny Electronics Co., Korea) were purchased from a local store as capped state for electronic circuit use. The cap was removed before coated with PVA film.

2.2 Equipment

An AT-cut quartz crystal resonator having base frequency of 8 MHz was utilized in this experiment. The electrodes of the resonator were silver finished. PVA was dissolved in water at a concentration of 0.3 %, and the solution was stirred for an hour. A 1.8 μL of the completely dissolved PVA solution was applied on the one of electrode surfaces of the resonator. After briefly dried in air, the resonator was baked in an oven at a temperature of 120 ℃ for half an hour. The resonator was cooled in a Petri dish containing silica gel for 10 minutes. The PVA thin film was coated twice following the same procedure. Figure 1 describes the sensor preparing procedure. The cell module holding the resonator was built with polypropylene plates of which a schematic was illustrated in Figure 2. The thicknesses of two plates were 5 mm. The top plate has a hole to make one electrode of the resonator contact with the ethanol, and the other is sealed from the ethanol. To prevent leakage a thin silicone gasket and two o-rings are placed between the two plates. The sizes of the two plates were the same with a dimension of 30 mm by 45 mm. Six screws tighten the two polypropylene plates as shown in Figure 2.

2.3 Procedures

The PVA coated resonator was mounted in the cell, and placed vertically in a 50 mL beaker containing ethanol. While the ethanol was stirred mildly, the resonant frequency was measured as illustrated in Figure 2. The oscillation circuit provides a small amount of oscillating current to the resonator, and the resonant frequency of the resonator is determined by the load and rheological variation on the surface of the resonator electrode. The frequency is counted with a home-made counter connected to a PC. The measured frequency was stored I the PC for later data analysis. When the frequency is stable, water is added to ethanol to increase the water content by 2 % point each time up to 10 %.

3. Results and discussion

The variation of resonant frequency with increased water contents is shown in Figure 3. The step-wise decrease of the frequency indicates the elevation of water content by 2 % each. The measurement was conducted for about 8 minutes at each water contents. Figure 3 shows the frequency variation. The frequency of bare resonator is affected from the variation of water content, and it is demonstrated in Figure 3. For the compensation of the frequency variation the results of the blank tests are given with linear fitting of the results. The frequency variation of bare resonator is deduced from the actual measurement. Also the amount of PVA coating affects the frequency variation.

The repeated measurements of water content in ethanol using different resonators are summarized in Figure 4. Though there is some deviation with different resonators, the decrease of the frequency with the increased water content is demonstrated. The measurement of water content using a quartz crystal resonator is relatively simple compared with other measurement technique utilizing analytical instruments. In addition, the proposed measurement technique can be applied for in-line measurement.

4. Conclusion

Quartz crystal resonators coated with PVA are utilized to determine water contents in ethanol. The PVA is easily dissolved in water, but is insoluble to ethanol. When the PVA coated quartz crystal resonator is dipped in the ethanol containing small amount of water, the water is absorbed in the PVA increasing the load on the PVA coating to result in frequency drop. The determination performance of PVA coated resonator is examined by measuring frequency decreases in 2 % to 10 % water contained ethanol. The measurements indicates that the higher water content is the more the frequency reduction is, though some variation in the measurement is observed. The blank test using the bare QCR yields the insignificant drop of frequency.

References

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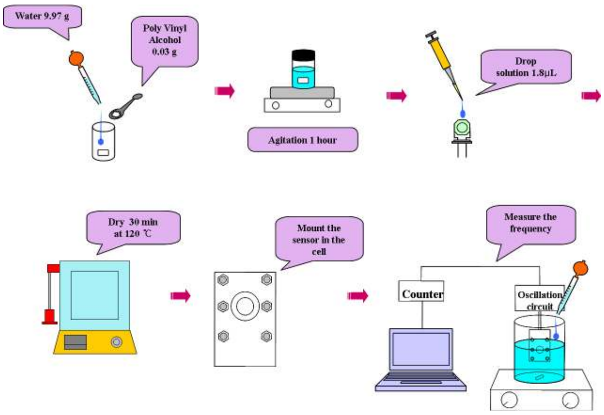

Figure 1. A schematic of QCR preparation procedure.

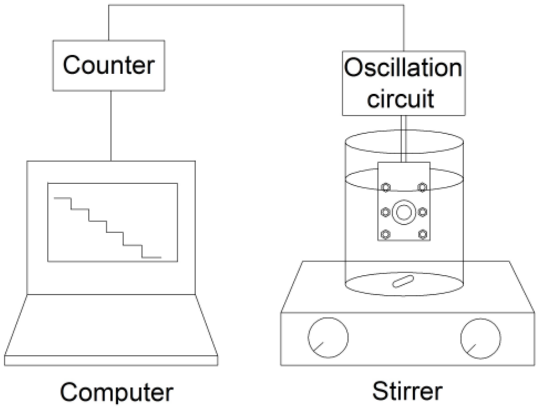

Figure 2. A schematic diagram of experimental setup.

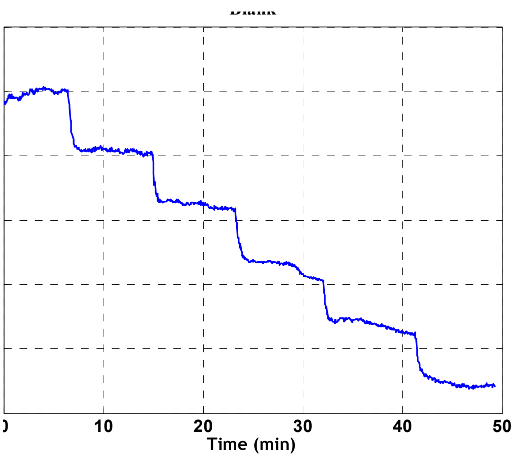

Figure 3. Frequency variation of blank QCR at different water contents.

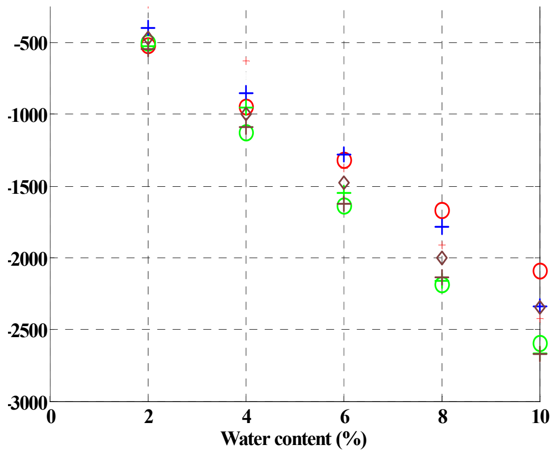

Figure 4. Frequency shifts of PVA coated QCR at different water contents.