# 혐기성 처리 **system** 에서 메탄올의 경로

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# Fate of Methanol in an Anaerobic Treatment System

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## Introduction

Packaging Corporation of America (PCA) operates a mill in Tomahawk, Wisconsin that presently uses a large anaerobic lagoon system to treat its wastewater. Concern has arisen, primarily on the part of the EPA, regarding introduction of methanol containing condensate into the treatment system, specifically anaerobic digester. The concern centers on the anaerobic biodegradability of methanol and by-products and potential stripping from the system. The University of Wisconsin-Madison conducted a series of laboratory-scale experiments and developed a mathematical model to evaluate the fate of methanol during anaerobic digestion.

BMP tests have been utilized to determine the degree of degradability for industrial wastes and individual compounds. The approach utilizes a series of inoculated serum bottles. The tests are performed in a batch, closed manner so that both liquid and gas samples can be analyzed. In the general BMP analysis the relative amount and quality of gas produced from the serum bottles is utilized to predict the degradability of the test material. In the proposed modified approach, chemical oxygen demand (or biochemical oxygen demand) and methanol will also be analyzed to evaluate the fate of methanol under the anaerobic condition.

The objective of the study was to provide reasonable (technically valid, quick, and appropriate) evaluation of samples from the PCA site to determine the fate of methanol from the condensate in an anaerobic system. A mathematical model was developed to assess the fate of methanol in anaerobic digester under various conditions.

**Experimental methods**

Methanol (also known as methyl alcohol and wood alcohol) is a colorless liquid that may explode when exposed to an open flame. It occurs naturally in wood and in volcanic gases. Methanol is also a product of decaying organic material. It is produced in large amounts (approximately 1.3 billion gallons in 1992) by thirteen companies in the United States (U.S.). U.S. demand for methanol is likely to increase over the next several years. The largest users of the methanol sold in the U.S. are companies that make methyl t-butyl ether, a gasoline additive. Companies also use methanol to make chemicals such as formaldehyde, acetic acid, chloromethanes, and methyl methacrylate. Companies add methanol to paint strippers, aerosol spray paints, wall paints, carburetor cleaners, and car windshield washer products. Methanol is also a gasoline additive and, in some cases, a gasoline substitute for use in automobiles and other small engines.

**BMP Tests**

A series of biochemical methane potential (BMP) was performed for 5 to 15 days to assess the degree of anaerobic degradation of condensate. The analysis utilized samples of current influent, condensate, and anaerobic mixed liquor from the PCA site. PCA collected 1 gallon of anaerobic sludge consisting of 1 qt. from each of the four anaerobic basins (head end) out of a sludge recirculation line. The sample is believed to be representative of the anaerobic sludge that will be in contact with the condensate stream. The samples were stored in a 4°C cold room until used.

In order to evaluate the effect of mixing on gas production, several samples were not mixed. The other samples were mixed in a constant temperature water bath equipped with a shaker. The temperature was maintained at 35±1°C. Since the PCA anaerobic digester is mixed by generated gas release and internal sludge recirculation without any mechanical mixing device, shaking was gentle enough to help the release of gas to the headspace. The total solids at various locations and depths of the PCA anaerobic digester were measured to be similar, indicating relatively good mixing. Since the anaerobic digester is covered and the oxygen that may exist in the influent is rapidly consumed, the effect of oxygen to the methanol anaerobic digestion is expected to be minimal.

**Analytical Methods**

COD and methanol in the liquid phase, and gas volume, $CH_4$ content in the gas phase were measured to perform a quasi-mass balance, determine effect of introduction of condensate on system, and verify removal from system. Gas volumes were measured frequently. Methanol in liquid phases was measured on days, 0, 1, 5, and 15. Total solids and volatile solids concentrations were obtained from 20-mL samples in accordance with Parts 2540B and 2540E, respectively, of Standard Methods (APHA et al., 1995). Suspended and volatile suspended solids concentrations were measured by following the procedure outlined in Parts 2540D and 2540G of Standard Methods (APHA et al., 1995) using between 15 and 40 mL sample. Total volatile, suspended, and volatile solids concentration values were computed to the nearest 10 mg/L. Chemical oxygen demand (COD) was determined by diluting all samples and following the method in Parts 5220C of Standard Methods (APHA et al., 1995). Samples were digested in an autoclave for 2 hours at 132°C. The digested sludge sample was diluted with 100 parts of DI water by volume to achieve the most reproducible result. A well-defined standard COD curve was obtained using the same COD procedure outlined above without any dilution for various concentrations of potassium hydrogen phthalate (KHP). The spectrophotometer used was a Milton Roy Spectronic 301. Each sample's absorbance was measured at a wavelength of 600 nm. Calculated COD values were rounded to the nearest 10 mg/L.

**Results**

Methanol, methyl ethyl ketone (MEK), and acetaldehyde in the liquid phase were analyzed using a gas chromatograph (GC) equipped with a flame ionization detector (FID). Gas composition and methanol in the vapor phase were determined with a GC equipped with a thermal conductivity detector (TCD). An aliquot of 10 mL of ASTM Type 1 water and 10 μL of sample were injected. The column temperature was 40°C, injection temperature was 50°C, and detector temperature was 250°C. Formaldehyde was not reliably detected with FID. For the vapor phase methanol analysis, a GC equipped with thermal detector was used.

The detailed operational conditions of PCA anaerobic digester are summarized in Table 1.

Table 1. Operational conditions of PCA anaerobic digester

| Parameters | Values |
|---|---|
| Influent flow | 5.146 MGD[1] |
| Influent $BOD_5$ | 2,046 mg/L |
| Condensate flow | 0.1224 MGD |
| Condensate BOD | 6,000 mg/L |
| Digester volume | 25.6 million gallon |
| Digester total suspended solids (TSS) | 26,000 mg/L |
| Digester volatile suspended solids (VSS)/TSS | 82% |
| Digester hydraulic retention time | 5 days |
| Digester mixed liquor estimated $BOD_5$[2] | 18,200 mg/L |

[1] MGD = million gallons per day

[2] Estimated $BOD_5 = 26,000 \times 0.82 \times 1.42$ COD/VS $\times 0.6$ $BOD_5$/COD $\approx$ 18,200 mg/L

Conclusions

1. More than 99% of methanol existing in condensate was biodegraded during anaerobic digestion.

2. From an anaerobic digester batch test, the second order biodegradation rate constant, $k_{b2}$, was estimated to range from $3.97 \times 10^{-3}$ $m^3/g\cdot day$ (when only condensate was fed) to $4.06 \times 10^{-2}$ $m^3/g\cdot day$ (when condensate was fed at the proposed rate).
3. The losses of methanol through the Styrofoam® cover and volatilization were estimated to be almost zero.
4. Byproducts from methanol degradation such as acetaldehyde and methyl ethyl ketone were degraded completely in 32 hours. Since the PCA anaerobic digester has the detention time of 5 days, condensate byproducts are thought to be completely biodegraded.
5. Since acetaldehyde and methyl ethyl ketone have one order of magnitude smaller Henry's law constants than methanol, the release of these byproducts to the atmosphere is expected to be much smaller than methanol, which was found to have almost zero loss through volatilization.
6. The introduction of condensate into the existing anaerobic digestion process improves the treatment efficiency, leading to more stable anaerobic digester operation and potential reduction of sludge from the wastewater treatment process.

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