The Applications of Rate Constants in Commercial Methane Digesters

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Key Terms

- **Anaerobic digestion** - the decomposition of organic matter in an oxygen-free environment

- **Semi-Continuously Fed Methane Digester** - a closed tank into which organic matter is added at regular intervals for the purpose of producing methane gas

- **Organic Loading Rate** - the amount (kg) of organic matter added to the digester; may include sewage, slaughterhouse waste, or glycerin (byproduct of industrial processes)

- **Acetotrophic methanogens** – microorganisms that produce methane from acetate

- **Methanogenesis** - the formation of methane by microorganisms

- **Hydrolysis** – the formation of mono- or oligomers from organic matter by enzymes
Methane: The other greenhouse gas

- Methane gas is produced in huge quantities by a number of industrial and agricultural processes.  
- If allowed into the atmosphere, it is more than 25 times more harmful than CO$_2$. 
- In order to do the least damage possible, methane should be burned rather than released into the atmosphere.
- When captured for use by a methane digester, it is a versatile energy source, being easily converted to vehicle, cooking, or heating fuel, as well as electricity!
Methane: The other greenhouse gas

2015 U.S. Methane Emissions, By Source

- Natural Gas and Petroleum Systems: 31%
- Enteric Fermentation: 25%
- Landfills: 18%
- Manure Management: 10%
- Coal Mining: 9%
- Other: 7%

Here is a diagram of a rural Nigerian family’s methane digester. Cow dung from the family’s cattle and lemongrass from their fields are fed into the tank, and methane gas is produced. The methane is fed through a pipe directly into their kitchen, where it can be safely lit on a stove and used for cooking. ¹
Overview

• Commercially, methane gas can be produced using such materials as municipal sewage, industrial waste, and slaughterhouse waste. ³

• The most efficient form of production is a continuously-fed methane digester, rather than production by batches. ³

• In order to maximize productivity, we must be able to monitor the rate of production and detect instability. There are already several ways to identify such bottlenecks, but most of these methods are time-consuming and result in long response-times. Rate constants may provide a solution ³
The main goal of this study was to see if rate constants could be used to detect process interruption or process instability more quickly than standard methods.  

A secondary goal of this study was to test the effects of trace minerals on the individual steps of digestion.

The microorganisms involved in these four steps have previously been found to be positively affected by the daily addition of Co\textsuperscript{2+}, Ni\textsuperscript{2+}, and Cu\textsuperscript{2+} supplements.

Since there are multiple microorganisms involved in multiple steps, and each microorganism prefers different trace elements, the addition or absence of these trace minerals could also be a viable method of controlling this process.
The 4 steps of a methane digester

- **Step 1: Hydrolysis**
  - Fermentative bacteria produce hydrolytic enzymes, which convert organic matter to mono- or oligomers.

- **Step 2: Acidogenesis**
  - Said mono- or oligomers are then converted to volatile fatty acids, alcohols, hydrogen, and carbon dioxide by the same fermentative bacteria.

- **Step 3: Acetogenesis**
  - The various products of step 2 are converted to acetate, carbon dioxide, and hydrogen by different (secondary) fermentative bacteria.

- **Step 4: Methanogenesis**
  - Acetate is converted to methane and carbon dioxide by a third type of microorganisms, acetotrophic methanogens. ³
In order to test their hypothesis regarding rate constants, experimenters needed to observe the digester when stressed. For the first 89 days, they increased the organic loading rate above what the digester was supposed to tolerate, but the trace elements counteracted the efforts and kept the process stable (see table below).

Finally, they succeeded in disrupting the digestion process by ceasing the addition of nickel supplements.

| Table 1. Schedule of changes to organic loading rate (slaughterhouse waste, the organic fraction of municipal solid waste (OFMSW) and glycerin) and hydraulic retention time (HRT) in the semi-continuously fed anaerobic digester during the experimental period. |
|---|---|---|---|---|
| Period (days) | OLR Slaughterhouse Waste (kg·VS·m⁻³·d⁻¹) | OLR OFMSW (kg·VS·m⁻³·d⁻¹) | OLR Glycerin (kg·VS·m⁻³·d⁻¹) | HRT (Days) |
| -25 to -15 | 0.8 | 2.8 | 0 | 21 |
| -14 to 25 | 0.8 | 3.9 | 0 | 18 |
| 26 to 39 | 0.8 | 3.9 | 0.5-1.6 | 18 |
| 40 to 168 | 0.8 | 3.9 | 1.8 | 18 |
This graph depicts total volume of the various gases produced on day 89, when Ni$^{2+}$ was removed from the daily trace element supplement. Graphs like this one were made every day, and measurements were taken every 5 minutes. Note that gas production is initially steep (high productivity), but gradually slows down (low productivity).
Researchers calculated the methane production rate constant ($K_m$) according to the following first-order equation:

$$\text{CH}_4\text{spec}(t) = \text{H}_4\text{max}(1 - e^{kmt})$$

After analyzing the daily graphs and $K_m$ values together, researchers noted that $K_m$ value changed immediately and proportionally at every step of the process. These calculations were completed long before standard methods detected any changes.³

Furthermore, researchers noted that methane production generally decreased after they stopped adding nickel, but the other gases’ production levels were hardly affected at all.³

This shows that nickel affects the final step of methane production (methanogenesis) most strongly. Without nickel, methanogenesis is the rate-limiting step.³

K$_m$ values throughout the experiment (red dots). Note the sharp decline around when nickel supplements ceased.³
Carbon dioxide rate constants (acidogenesis: $K_{c1}$, acetogenesis: $K_{c2}$) were derived from another first-order equation

$$[CO_{2\text{spec}}(t)=CO_{2\text{max}}(x(1-e^{-kc_1t})+(1-x)(e^{-kc_2t}))]$$

After analyzing the $K_{c1}$ and $K_{c2}$ values for acidogenesis and acetogenesis, researchers could confirm that they were not affected by the absence of nickel. 3

When analyzed together, this data shows that rate constants (especially $K_m$) can be used to measure stability and productivity in a methane digester. 3

$K_{c1}$ values (blue dots) and $K_{c2}$ values (yellow dots) throughout the experiment. Note, there is no decrease after nickel supplements cease. 3
Conclusion

- By measuring total gas volumes under differing conditions and fitting them to first-order equations, this study proved its hypothesis that rate constants can be used to identify disruptions in commercial methane digesters. ³

- It also showed that nickel supplements have a large effect on rate constants, and especially on the methanogenesis step of production. ³

- Utilizing rate constants can help make methane order an economically viable energy option by ensuring peak production as often as possible. ³

- If rate constants are used to their potential, methane could make green energy more available to the general public while also decreasing greenhouse gas emissions.³
References


3. Moestedt, J; Malmborg, J; Nordell, E; *Enrgs*. [Online] **2015**, 8 (1) 645-655