

# Bioconversion of CO<sub>2</sub> to CH<sub>4</sub> and biogas upgrading using anaerobic granular sludge and Zero Valent Iron.

Maria Andronikou <sup>1</sup>, Ioannis Vyrides <sup>1</sup>

<sup>1</sup>Department of Chemical Engineering, Cyprus University of Technology, Limassol, 3036, Cyprus

Keywords: CO<sub>2</sub> utilization, methane, biogas upgrading, zero valent iron.

Presenting author email: [mi.andronikou@edu.cut.ac.cy](mailto:mi.andronikou@edu.cut.ac.cy)

## Introduction

Carbon dioxide (CO<sub>2</sub>) can be considered as one of the main reasons of climate change and global warming. The intense fossil fuel consumption due to industrial processes and energy production activities, considered to be the major cause of CO<sub>2</sub> elevated atmospheric levels (Daglioglu et al., 2019). Thus, any exploitation of CO<sub>2</sub> into various chemicals and other fuels not only will be an attractive solution to global warming but also will lead to fossil fuels replacement (Yang et al., 2017).

Up to date, most of the technologies that are mainly proposed for CO<sub>2</sub> mitigation, are physicochemical methods such as physical absorption using water scrubbing systems, physical absorption using organic solvents, chemical absorption using amine solutions, pressure swing adsorption (PSA) etc that involve high value materials or even intense conditions such as high temperature, pressure etc., (Saeidi et al., 2014).

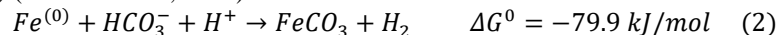
The same technologies that mention above, are also used for biogas upgrading to biomethane. Biogas synthesis is mainly methane (40-60%) and carbon dioxide (60-40%) (Aryal et al., 2018) and achieving biogas upgrading to biomethane (> 95% CH<sub>4</sub>) is essential primarily because it increases its calorific value and hence it can be easily stored or transported (Muñoz et al., 2015), (Angelidaki et al., 2018).

Several recent studies have examined an alternative process for CO<sub>2</sub> to CH<sub>4</sub> and biogas upgrading at mild conditions based on the utilization of CO<sub>2</sub> and H<sub>2</sub> by hydrogenotrophic methanogens according to Eq. (1).



In recent years, research in the addition of zero valent iron (ZVI) to anaerobic digestion process in order to enhance the biodegradation of waste and wastewater has become very popular. Particularly, ZVI contributed to higher chemical oxygen demand (COD) removal and methane production compared to no addition of ZVI (Hu et al., 2015). Up to date however, little research has been done on the use of ZVI and anaerobic granular sludge for the conversion of CO<sub>2</sub> as a sole carbon substrate to CH<sub>4</sub> and biogas upgrading.

ZVI under anaerobic aquatic condition (non-sulfidic, carbonate-buffered, pH~6) produced H<sub>2</sub> and oxidized according to Eq. (2) (Palacios et al., 2019).



## Material and methods

Batch laboratory-scale anaerobic fermentation experiments were conducted using anaerobic granular sludge (3g of wet weight was added in 80 ml). For CO<sub>2</sub> conversion to CH<sub>4</sub>, ZVI (fine powder) was added in various concentrations 25 g L<sup>-1</sup>, 50 g L<sup>-1</sup>, 75 g L<sup>-1</sup> and 100 g L<sup>-1</sup>. For biogas upgrading, ZVIS (zero valent iron scrap) was used in concentrations 100 g L<sup>-1</sup>, 200 g L<sup>-1</sup> and 300 g L<sup>-1</sup>. The remaining volume (up to 80 ml) was filled with media (Angelidaki et al., 2009). Initial pH 6, CO<sub>2</sub> as a sole carbon source, triplicates serum bottles were done for each condition. For creating anaerobic conditions, CO<sub>2</sub> gas was introduced to each serum bottle for 10 min to remove oxygen, and then, the bottles were capped and sealed with butyl septa and aluminum crimps and stirred in a shaking incubator (100 rpm) at 33 °C. For biogas upgrading same procedure was followed using synthetic biogas (60% CH<sub>4</sub> – 40% CO<sub>2</sub>). Gas composition (CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>, N<sub>2</sub>, and O<sub>2</sub>) was analyzed over time via a GC-TCD.

## Results and discussion

The results for CO<sub>2</sub> utilization shown that the highest CH<sub>4</sub> production over time was found at 75 g L<sup>-1</sup> of ZVI (69.2 % CH<sub>4</sub> in 18 days) followed by ZVI concentrations of 50 g L<sup>-1</sup> and 100 g L<sup>-1</sup> (around 53.8 % CH<sub>4</sub> in 18 days). For 25 g L<sup>-1</sup> the concentration was considerably lower. The biogas upgrading shows that 200 g L<sup>-1</sup> and 300 g L<sup>-1</sup> of ZVIS in anaerobic granular sludge resulted in CH<sub>4</sub> composition of 95.5 % and 95.3%, respectively after 21 days. Interestingly, very little H<sub>2</sub> was detected in the headspace and this could be due to slow release of H<sub>2</sub> by ZVIS followed by immediate consumption by hydrogenotrophic methanogens.

## Conclusions

This study tested a new approach for CO<sub>2</sub> conversion to CH<sub>4</sub> by using ZVI and anaerobic granular sludge under mild environmental conditions with CO<sub>2</sub> representing the sole carbon source. Importantly, due to the anaerobic

oxidation of ZVI, H<sub>2</sub> was produced and it was shown that hydrogenotrophic methanogens present in anaerobic granular sludge were the biocatalysts for the conversion of CO<sub>2</sub> to CH<sub>4</sub>.

The optimum batch conditions for CO<sub>2</sub> conversion to CH<sub>4</sub> by anaerobic granular sludge were set at initial pH of 6 under daily pH regulation, with 75 g L<sup>-1</sup> ZVI. Under these conditions, it was concluded that CO<sub>2</sub> is fully utilized from the headspace in 4 days and the maximum production of CH<sub>4</sub> is reached in around 6 days. The biogas upgrading to biomethane can be achieved in a batch system of anaerobic granular sludge and 200 g L<sup>-1</sup> zero valent scrap iron in 21 days.

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