



CARBON DIOXIDE DEPLETION DURING H₂/CO₂ AND BIOGAS FERMENTATION IN CHEMOSTAT STIRRED TANK REACTORS: EFFECT OF HYDRAULIC RETENTION TIME

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ABSTRACT

Microorganisms are preferentially used in energy production from biomass because less expensive and normally more resistant to the gas contaminants such as hydrogen sulfide. In the present study, the stoichiometric relation of CO₂ conversion to methane in the presence of H₂, was used to investigate the effect of hydraulic retention time (HRT) on H₂/CO₂ fermentation aiming at evaluating the carbon dioxide depletion. Four chemostat stirred tank reactors operating at 37 °C in presence of fix amount of H₂/CO₂ gas (80:20; v/v) by means of 12L/reactor /day) were used. The carbon dioxide removal rate was found to increase when the hydraulic retention time increased. At HRT of 8; 10; 12; 14 days CO₂ removal rate were 82.2; 86.7; 90.7 and 92.8%, respectively. The food to Microorganisms (F/M) ratio was found to also be related to the hydraulic retention time; the Food to microorganism ratio decrease with the HRT. The replacement of mix H₂/CO₂ gas by the biogas from wastewater treatment plant obtain also a CO₂ depletion and the methane fraction enrichment in the biogas.

KEYWORDS: CO₂ depletion; H₂/CO₂; Biogas; food to microorganisms' ratio; gas recirculation; inorganic substrate.

1- INTRODUCTION

The carbon dioxide removal from biogas has been experimented in several ways such as absorption separation in liquid^{[1] [2]}, biogas purification using the membranes separation^[3], cryogenic separation as well as adsorption separation. The latter playing a vital role if suitable adsorbent material and adsorption-desorption devices are available. Cited technologies improve the biogas quality but did not enrich the methane amount in the biogas. In anaerobic degradation, microorganisms gain their energy by coupling the oxidation of hydrogen to the reduction of compound such as carbon dioxide. The small amount of energy available in anaerobic digestion involves an efficient syntrophic cooperation within all communities.^[4] Hence, microorganisms have their metabolic pathways potentially affected by the concentration of environmental hydrogen level^[5] and CO₂ constraints.^{[6] [7]} Therefore, the stoichiometric relation of conversion of CO₂ to methane in the presence of H₂ and the higher solubility of CO₂ in comparison to methane in liquids could open new approach.

In addition, within all operational parameters in anaerobic digestion, Hydraulic retention time (HRT) is known as an important factor which directly affects wastewater treatment characteristics, the operational design, and investment cost.^{[8] [9]}

Thus, in this research, we investigate H₂/CO₂ fermentation reactors conjointly with different HRT for carbon dioxide removal using chemostat reactor. Then, the Food to Microorganisms (F/M) ratio was estimated when the HRT varied. Finally, the mixture gas H₂/CO₂ was replace by a plant produced biogas to confirm previous results.

2- MATERIAL AND METHODS

2.1- Sample acclimation

Anaerobic sludge from a municipal waste water treatment plant was obtained and treated anaerobically under mix gas H₂/CO₂ (80:20, v/v) as sole carbon and energy source during seven months operating at mesophilic conditions (37 °C).

2.2- Experimental design

The obtained acclimated methanogens were filled in 4 Duran vials, each vial (500 mL with 250 mL working volume) connected to an air tight pump for H₂/CO₂ recirculation and anaerobic chemostat cultivation was done as in.^[10] Figure 1 presented the experimental set up.

The daily input carbon dioxide from the mix H₂/CO₂ (80:20, v/v) was fixed at 12 L by means of 107 mmol of CO₂ per aluminum gas pack. Four different hydraulic retention time (14; 12; 10 and 8 days) were applied using inorganic nutrients and trace metals^[11] until steady state cultivation was achieved. All experiment were done at 37°C with pH set at 7; all during one (1) week.

After the week experiment, a new aluminum gas pack was filled with 2.4 L biogas from a domestic wastewater treatment plant and completed with hydrogen (pure at 99.9%) to achieve a total volume fixed at 12 L as proposed in^[10] for the standard characteristics to design a chemostat reactor when H₂/CO₂ gas is used as substrate. Then, the same protocol was used as previous experiment.

Finally a new experiment was realized using the previous apparatus with 12 L biogas without H₂ addition.



Figure 1: Experimental incubation chamber with the four reactors systems.

2.3- The utilized raw biogas

The biogas was obtained from a wastewater treatment plant and an identical amount of biogas (2.4 L) was used no matter the carbon dioxide initial percentage in the gas.

Table 1: Measured Data for the biogas from a wastewater treatment plant before the experiment.

Sample		D1	D2	D3	D4
Biogas composition	CO ₂ (%)	38	36	37	38
	Methane (%)	61	63	60	60
	H ₂ S (%)	0.055	0	0.006	0.012

2.4- Analysis methodology

The composition of the gas produced was determined using a GC-14B (Shimadzu) equipped with a thermal conductivity detector connected to a C-R8A data analyzer. A high performance column packed with 50/80 mesh Porapak Q was used. The temperatures of the injection, column and detector were set to 100, 50, 100

°C, respectively. Argon was used as the carrier gas at a pressure of 0.5 MPa. The volatile suspended solids (VSS) were determined with five duplicate analyses according to the Standard Methods for Examination of Water and Wastewater.^[12] The data were subsequently averaged; the deviations obtained were found to be less than 4%.

3- RESULTS AND DISCUSSION

3.1- Effect of HRT on carbon dioxide removal in H_2/CO_2 fermentation

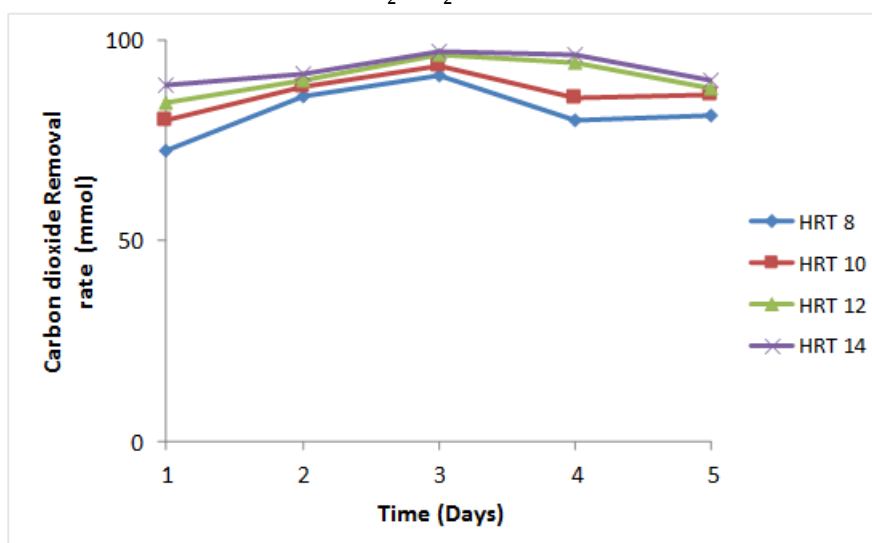


Figure 2: Carbon dioxide removal rate at different hydraulic retention time.

Under different HRTs as presented in Figure 1, the carbon dioxide removal efficiency, from the vial headspace and the gas bag, increase with the HRT. The average carbon dioxide removal was improved from 82.2% to 92.8% with HRT increase from 8 to 14 days. The results were similar when the COD removal rate was investigated at the organic loading rate variation.^[13]

Moreover,^[6] have shown the potential CO_2 reduction of 8-34% for sewage sludge and 3- 11% for food waste when CO_2 enrichment was done in anaerobic digestion treating sewage sludge or food waste. The present experiment results showed a higher CO_2 removal rate as considering the potential of carbon dioxide sequestration for renewable energy production.

3.2- Effect of HRT on microorganisms' activity

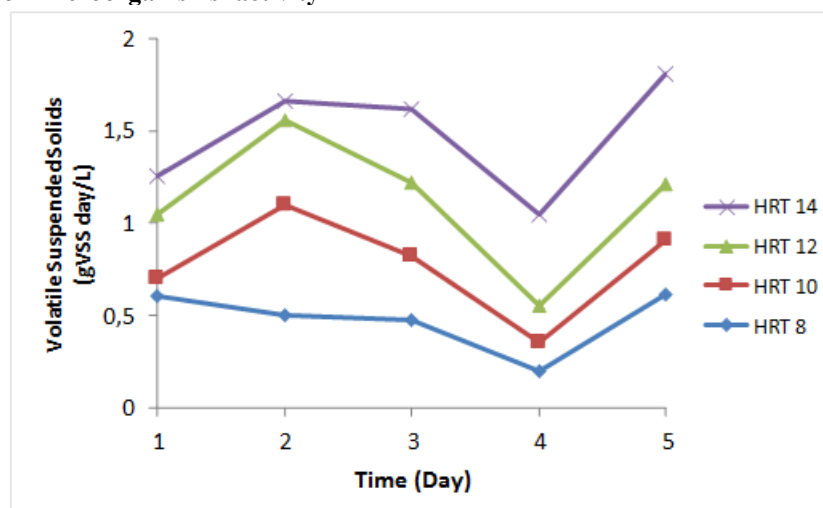


Figure 3: Volatiles Suspended Solids evolution at different hydraulic retention time.

The time course of microorganisms' activity is presented in Figure 3. It shows a relation between the Volatiles Suspended Solids (VSS) and the hydraulic retention time (HRT); when HRT increase more organic materials by means of VSS is produced. Authors have shown the importance of HRT on Archaea activity in organic substrate degradation; although the present study utilize mix gas H_2/CO_2 as substrate^[14], similar results are obtain. Hence, the microorganism's amount was higher at high

HRT; increasing the consumption rate of the gas affect undoubtedly the growth yield then the anaerobic digestion performance.

3.3- Effect of HRT on F/M ratio

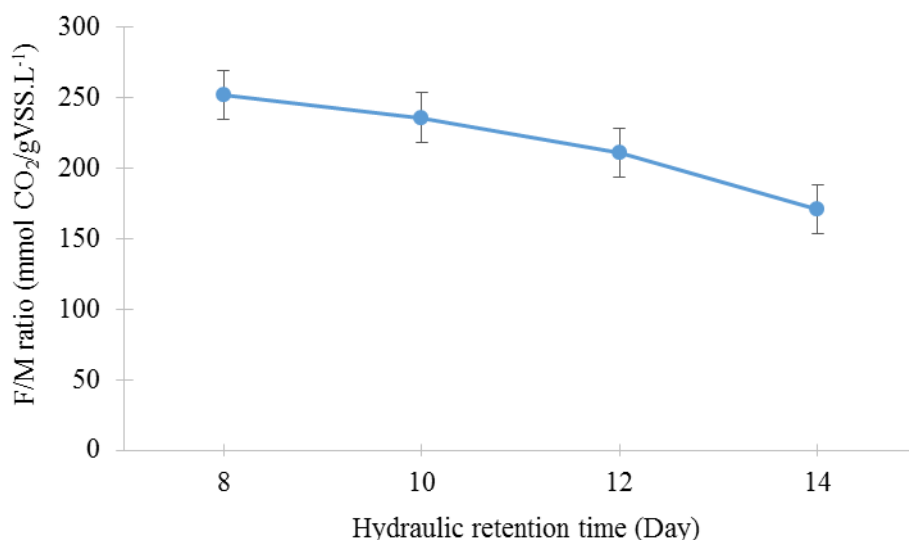


Figure 4: Food to microorganisms' average ratio at different hydraulic retention time.

Figure 4 shows the F/M ratio decrease when the HRT increase using inorganic substrate. The considerable influence of F/M ratio in anaerobic digestion for biogas production have been demonstrated.^[15] Figure 3 shows the F/M ratio decrease when the HRT increase using inorganic substrate. When^[16] increased the F/M ratio, better was the anaerobic digestion for organic substrate. We could assume that organic as inorganic anaerobic digestion need similar monitoring and control parameters.

3.4- Carbon dioxide removal from biogas at different HRT

As presented in Tab 1, the content of used biogas in CO₂ is found to be 38; 36; 37 and 38% variable values for different samples 1; 2; 3; 4 respectively, before each carbon dioxide removal process. When H₂ is added to biogas to achieve the 12 L, after HRT of 8; 10; 12 and 14 application, results are shown in Tab 2.

Table 2: Measured Data after biogas/H₂ mixture treatment at different HRT.

Sample		D1	D2	D3	D4
Applied HRT		8	10	12	14
Biogas Composition after treatment	CO ₂ (%)	27.03	28.87	27.76	20.44
	Methane (%)	62.4	64.6	63.5	65.77

As shown in Tab 2, CO₂ reduction and methane content enrichment can be observed in comparison to respective initial percentage shown in Tab1; all despite the CO₂ initial content in the biogas sample at various HRT. The carbon dioxide removal rate from biogas/H₂ mixture and the methane content enrichment are low in comparison to the mix H₂/CO₂ gas results. When pure biogas from a wastewater treatment plant is used (Tab 3), the carbon

dioxide depletion is critical and a very low methane enrichment in the biogas. The purity of the biogas could be a limiting factor and the used pressure couldn't be increased^[17] because of methanogenic strains constraints (data not shown). It is also important to notice that only gas phase content of carbon dioxide and methane were measured.

Table 3: Measured Data after raw biogas treatment at different HRT.

Sample		D1	D2	D3	D4
Applied HRT		8	10	12	14
Biogas Composition after treatment	CO ₂ (%)	33.2	30.08	31.14	30.3
	Methane (%)	59.4	60.6	60.5	61.1

4- CONCLUSION

The effects of HRT on gas (H₂/CO₂ mixture or biogas) recirculation in an anaerobic digester were investigated. The results showed the HRT influence on the carbon

dioxide depletion during H₂/CO₂ recirculation, and the microorganisms' activity in the anaerobic fermentation for biogas production. A depletion of 82.2; 86.7; 90.7 and 92.8%, of carbon dioxide was found at HRT of 8;

10; 12; 14 days, respectively. The food to Microorganisms (F/M) ratio was also related to the hydraulic retention time; low HRT increase the Food to microorganism ratio. Hence, HRT is a parameter that influence the performance and stability in H_2/CO_2 fermentation. When the biogas was used instead of mix H_2/CO_2 gas, the CO_2 removal rate and the methane content increased and were better at high HRT; but lower compared to H_2/CO_2 mix gas results. In the present study, the biogas purity was not extensively check during the experiment to better understand whether there is some limiting factor. Hence, the carbon dioxide removal in biogas using microorganisms could be an alternative to enrich the methane content in the biogas.

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