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Maa Ja Elintarviketalouden Tutkimuskeskus (MTT)

MTT Agrifood Research Finland

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D5.5 Potential for pressure-swing cell disruption as a biogas upgrading method

Lead contractor: **Maa Ja Elintarviketalouden Tutkimuskeskus (MTT)**

Main contributors

Satu Ervasti, Saija Rasi, Jukka Rintala (MTT)^a

^a Maa Ja Elintarviketalouden Tutkimuskeskus, H-Building, Jokioinen, FI-31600, Finland

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D5.5 Potential for pressure-swing cell disruption as a biogas upgrading method

1 Introduction

In this deliverable the laboratory trials on gas upgrading under pressure are reported. The experimental work on laboratory-scale pressure upgrading was carried out by MTT.

In deliverable D3.3 novel cell disruptor technology (ESI) (developed by VALORGAS partner ESI) was studied with respect to material treatment. Changes in absorbent characteristics were explored by chemical and microbiological analyses. The effects of CO₂ pressurisation on microbiological inactivation were detected clearly on *Salmonella enterica* serovar *typhimurium* pure culture samples. Cell disruption experiments were performed at 25 bar pressure. In saline water *Salmonella* inactivation was increased by extending the treatment time. A 2-hour treatment had no effect on concentration while 24-hour treatment decreased *S. enterica* concentration on average 6 logs. *Salmonella* pure culture in saline water was completely inactivated with a treatment time of 24 hours at 35 °C. Similar results with respect to the duration of treatment were reported by Mushtaq et al. (2012) for *Escherichia coli*.

Experiments reported in this deliverable were performed to explore the possibilities of using pressure cell disruption as a biogas upgrading method. The idea was to test solubilisation of carbon dioxide into a liquid material which would cause enrichment of methane in the headspace of the chamber. Methane enrichment could be performed simultaneously with cell disruption treatment.

Experiments included pre-trials where variation in methane content over pressure release period was tested. Gas upgrading experiments were done first with water and the effect of shaking the chamber was tested. Gas upgrading was tested also with digestate.

2 Materials and methods

2.1 Materials

Gas upgrading trials were carried out with a synthetic standard gas mixture of methane (CH₄) 60 % and carbon dioxide (CO₂) 40 %. Trials were carried out in a pressurisation unit made of a filter cartridge housing connected to a CH₄/CO₂ bottle (Figure 1). The system can be operated at pressures up to 28 bar.



Figure 1. Pressurisation unit connected to gas bottle.

Gas upgrading was tested using cold tap water and digestate as absorbents. The initial pH of tap water used in the pre trials varied between 6.32 and 7.15 and was on average 6.81 (Table 1). The initial pH of the water used in shaking experiments varied from 6.2 to 7.09 and was on average 6.69. Temperatures of water samples in pre trials and shaking experiments varied from 8.0 to 11.8 °C and from 6.1 to 10.2 °C, respectively.

Digestate from the Enviro Biotech Ltd Forssa plant, a mesophilic CSTR digesting biowaste and sewage sludge, was cooled and stored at 4 °C before using in trials. The TS content of the digestate was 6.13 % and VS 3.79 %. Digestate was used within one week of collection. The effects of pressure treatment on absorbent characteristics, etc solubilisation and bacterial inactivation were not analysed in these studies.

Table 1. Characteristics (pH and temperature) of the absorbent materials used.

Material	Tap water, pre trials	Tap water	Digestate
Initial pH	6.32 – 7.15 average 6.81	6.2 – 7.09 average 6.69	7.54 – 7.72 average 7.61
Initial temperature (°C)	8.0 – 11.8 average 9.9	6.1 – 10.2 average 7.7	5.5 – 10.6 average 7.9

2.2 Experimental set-up

The pressurisation unit was placed at room temperature, 20 °C \pm 2 °C. The amount of absorbent in each test was 1300 g and this was loaded into the pressurisation chamber at the beginning of the test. The head space of the chamber was 0.9 litres. The system was flushed with the CH₄/CO₂ gas mixture for one minute to replace air. After flushing the lid was sealed and the system connected to the gas bottle. Pressure readings were recorded at the beginning and the end of the treatment. pH and temperature of absorbents were measured before and after pressure treatment.

At the end of the treatment time the pressure was released and gas was collected in aluminium gas bags. Composition of gas was analysed from the gas bag and the gas volume was measured.

The pre-trials on the gas release method were done only with water. Pre-trials were performed using treatment pressures of 5, 10, 15 and 20 bar and a treatment time of 30 minutes (Table 2). The gas chamber was not shaken during these trials and no duplicate treatments were performed. Two different gas release methods were tested:

- One-stage pressure release, where gas was released to aluminium gas bag until the over pressure in the pressure chamber went down to 0 bars.
- Two-stage pressure release, where the first gas release cycle was stopped and the gas valve closed when the over pressure in chamber went to 2 bars. The gas bag was changed and the remaining pressure was released into a second gas bag.

Gas upgrading trials with tap water were performed by the one-stage gas release method. Tests were performed in triplicate and the treatment time was 15 minutes. The gas valve was closed immediately after pressurising. Tests were performed with and without shaking; with shaking the gas chamber was manually shaken in a vertical position for a one minute at 0, 5 and 10 minutes from the pressure set up. For the rest of the treatment time the gas chamber was kept in its holder.

Pressures of 5, 10 and 15 bars were used in tests comparing effects of shaking and the 20 bar pressure treatment was tested only with shaking.

Trials with digestate were performed by same procedures as gas upgrading tests with water. Experiments were done with the one pressure release method with a total treatment time of 15 minutes and the chamber was shaken three times in one minute. Treatment pressures of 10 and 15 bars were tested and four parallel treatments were performed in each condition.

Gas upgrading with digestate was also tested at conditions near to those used in the *S. enterica* inactivation experiments where 24 hour treatment at 35 °C showed promising inactivation results, total inactivation of *S. enterica* in saline water pure culture (see D3.3). In the gas upgrading experiments the treatment time was 24 hours, temperature was maintained at 35 °C in a water bath and the treatment pressure in the beginning of the treatment was 19.5 bars. The chamber was manually shaken for one minute at the beginning of the treatment and then placed in the water bath.

Table 2. Experimental set-ups of pre trials and gas upgrading trials with water and digestate as absorbent.

	Pre-trials	Gas upgrading with water	Gas upgrading with digestate
Absorbent material	tap water	tap water	digestate
Treatment time	30 minutes	15 minutes	15 minutes, 24 hours
Pressure (bar)	5, 10, 15 and 20	5, 10 and 15, 20 only with shaking	10, 15 and 19.5
Shaking	no	both tested	yes
Number of parallel samples	1	3	4 (1 in 19.5 bar trial)

2.3 Analytical methods

TS and VS were determined according to SFS 3008 (Finnish Standard Association, 2002). Gas volumes were measured with a drum type gas meter based on water displacement (Ritter TG1/5) and gas composition analysed using a portable Combimass GA-m gas analyzer (Binder Engineering GmbH, Germany). pH and temperature were determined using VWR pH100 and VWR pH110 pH-analyzers (VWR International).

2.4 Calculations

Incoming gas volume to chamber was calculated using equation 1. The chamber headspace volume is 900 ml as the volume of the filter housing is 2.2 litres and the sample amount is 1300 g.

$$V_{in} = [(p_{treatment} * V_{head\ space}) / p_{atm}] - V_{head\ space} \quad (1)$$

where
 V_{in} is volume of in fed gas (l) in p_{atm}
 $p_{treatment}$ is pressure during treatment (bar)
 $V_{head\ space}$ is head space volume (l)
 p_{atm} is atmospheric pressure (bar)

The out-coming gas volume was measured from the gas bag with a drum type gas meter and the gas volume used for gas analysis was added to the volume given by gas meter. The gas analysers aspiration rate is approximately 400 ml min⁻¹ and the gas analyser was used from 2 min to 3.16 min per sample.

Solubilisation was determined from the reduction in volume of the out-coming gas component compared to the volume of the in-fed gas component.

3 Results and discussion

Effect of gas release method

In the pre-trials the effect of the pressure release system was tested with tap water. Treatment time was 30 minutes and there was no shaking of the chamber during the tests. There was no remarkable difference detected in methane content between the first and second gas release batch, as the difference in methane content was less than 0.4 % (Table 3). Methane contents in pre trials varied from 59.8 % to 64.2 %. The temperature of water samples before treatment was on average 9.9 °C varying from 8.0 to 11.8 °C. Initial water pH was an average 6.81 and varied from 6.32 to 7.15.

Table 3. pH values of water after pressurisation and methane content after one and two stage pressure release.

pressure (bar)	one stage pressure release		two stage pressure release			Weighted average CH ₄ (%)
	pH after	CH ₄ (%)	pH after	CH ₄ (%) 1st	CH ₄ (%) 2nd	
5	5.34	62.7	5.31	59.8	60.1	60.0
10	5.01	59.8	5.03	59.8	60.1	60.0
15	4.82	61.1	5.50	64.2	64.2	64.2
20	4.76	62.5	4.80	61.8	61.4	61.7

There was some variation between CH₄ contents in one and two stage pressure release methods. This may have been due to air remaining in the system despite gas flushing: the effect of this could not be assessed as no duplicate trials were performed.

As there was no observation of differences in gas quality between gas releasing methods, all further tests were done with one pressure release only.

Gas upgrading tests

Shaking improved gas upgrading remarkably compared to the samples that remained stationary. The CH₄ content rose up to 70 % in 10 and 15 bar treatments with shaking (Table 4). The 20 bar treatment with shaking gave a slightly lower CH₄ content, 69.4 %. Tests performed with no shaking caused only minor enrichment of CH₄ and for example in 10 bar treatment the methane content was only 61.4 %. The average pH of tap water used as absorbent was 6.69 (6.2-7.09) and average temperature 7.7 °C (6.1-10.2).

Table 4. pH values of water and CH₄ and CO₂ contents in gas after pressure treatments with and without shaking. Numbers are averages of triplicates.

pressure (bar)	pH after treatment		CH ₄ (%)		CO ₂ (%)	
	no shaking	shaking	no shaking	shaking	no shaking	shaking
5	5.81	4.95	59.0	66.4	36.7	27.1
10	5.37	4.65*	61.4	70.7*	38.4	30.0*
15	5.27	4.64	62.1	70.7	38.7	30.0
20		4.81		69.4		29.5

* four parallel experiments

There was a correlation between CH₄ enrichment and pH decrease (Figure 2). pH decreased most in samples that were shaken. Similarly from 5 to 15 bars pH decreased more with higher treatment pressures. Changes in pH indicated solubilisation of CO₂ which was seen also in enrichment of CH₄.

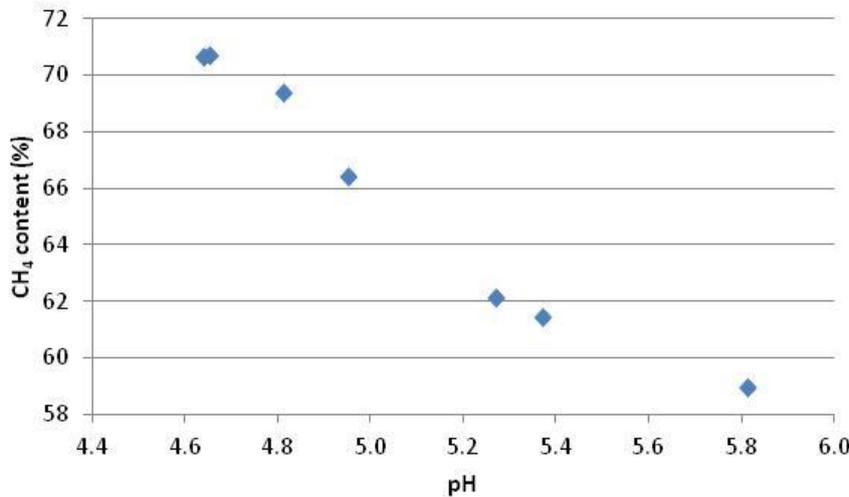


Figure 2. Correlation between absorbent pH after treatment and CH₄ content of gas in experiments performed with water.

As the lower pH values and CO₂ contents in out-coming gas indicated (Table 2), the proportion of solubilised CO₂ was higher in treatments performed with shaking. Solubilisations of gas components (CH₄ and CO₂) are given in Table 5.

Table 5. Solubilisation of CO₂ and CH₄ to water: Incoming gas volumes, out-coming gas volumes and calculated proportions of solubilised components. Solubilisations are given as % of incoming gas.

Pressure (bar)	Total gas in (l)	Total gas out (l)		Solubilised CH ₄ (%)		Solubilised CO ₂ (%)	
		no shaking	shaking	no shaking	shaking	no shaking	shaking
5	4.44	3.14	2.60	30.6	35.3	35.2	60.3
10	8.88	6.09	5.16	29.8	31.7	34.2	56.3
15	13.32	9.08	7.45	29.4	34.1	34.0	58.0
20	17.76		10.36		32.6		57.0

Solubilisation of CO₂ in shaken samples is remarkably higher than in non shaken samples. In addition also solubilisation of CH₄ increases with shaking which reduces the upgrading efficiency.

Gas upgrading with digestate as an absorbent

Using digestate as absorbent enriched CH₄ only a little. CH₄ content rose to 62.2 % in 10 bar treatment and to 61.7 % in 15 bar treatment (Table 6). pH decreased during treatments by approximately 0.5 units. The initial pH of digestate was on average 7.61, varying from 7.54 to 7.72. The temperature of the digestate was on average 7.88 °C (variation 5.5 to 10.6 °C). Higher treatment pressure (19.5 bar) and temperature (35 °C) did not enhance the CH₄ enrichment to a useful degree. The CH₄ content was 64.1 % and pH was reduced only to 7.22. The temperature after 19.5 bar treatment was 33 °C, as the sample was taken from a 35 °C water bath.

Table 6. pH values of digestate after pressurisation, CH₄ and CO₂ contents in out-coming gas and calculated proportions of solubilised components. Solubilisations are given as % of incoming gas.

Pressure (bar)	pH after	CH ₄ (%)	CO ₂ (%)	Solubilised CH ₄ (%)	Solubilised CO ₂ (%)
10	7.11	62.2	37.2	31.6	38.7
15	7.01	61.7	37.0	31.7	38.4
19.5	7.22	64.1	35.9	25.9	37.8

The pH decrease for digestate was also low compared to that with water. This may indicate that the CO₂ did not solubilise in digestate so effectively, although digestate may also offer additional buffering capacity. The digestate was freshly stored and may have produced a small quantity of gas itself during the test period. The heterogeneous structure and solids in the digestate may also affect the dissolution process. In the 35 °C treatment the higher temperature may have promoted gas production from the digestate itself.

For gas upgrading purposes the absorbent material had a considerable influence on CH₄ enrichment efficiency. At 10 and 15 bar treatment pressures the CH₄ content with digestate as absorbent was considerably lower than with water as absorbent. Higher temperature (35 °C), pressure (19.5 bars) and treatment time (24 h) were not very effective in enhancing the enrichment process with digestate as the absorbent. Similarly in the cell disruption experiments reported in deliverable D3.3 effects of pressurisation on hygienic quality were lower with heterogeneous material (biowaste) than with water. Cell disruption seemed to require a longer treatment time with biowaste. Similar results were found in trials with sewage sludge, another complex matrix (Mushtaq et al., 2011; Mushtaq, 2013).

The test duration in the gas upgrading trials was 15 minutes, very short compared to the most effective treatment times in cell disruption (24 hours). Also the pressure levels tested in gas upgrading were lower than in the cell disruption trials. For gas upgrading with water, pressures 10 and 15 bars showed the best results. Gas enrichment did not show an increase with higher treatment pressure at 20 bars. Increasing treatment pressure does not necessarily improve CH₄ enrichment as the absorbent becomes saturated with CO₂.

4 Conclusions

Shaking (increasing the contact area between liquid and gas) improves CO₂ solubilisation to liquid and further CH₄ upgrading. The highest methane contents in these studies were still quite low, at approximately 71 %. Increasing the liquid to gas rate and contact area between phases could be tested, for example by bubbling gas through the liquid. Pressurisation of water gave some indications of potential for gas upgrading but connecting gas upgrade to material handling may have challenges, as gas upgrading with digestate was not promising in this experiment set-up.

5 References

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