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Publisher's version / Version de l'éditeur:

Proceedings Venice2016, Sixth International Symposium on Energy from Biomass and Waste, 14-17 November 2016, Great School of St. John the Evangelist, Venice, Italy, 2016-11-14

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MAXIMIZING THE BIOMETHANE YIELD FROM ALGAL BIOMASS BY INTEGRATING HYDROTHERMAL POSTTREATMENT OF THE ANAEROBIC SOLID DIGESTATE

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ABSTRACT: As an alternative to applying the hydrothermal treatment to the raw algal feedstock before the anaerobic digestion (i.e. pre-treatment), one considered a post-treatment scenario where anaerobic digestion is directly used as the primary treatment while the hydrothermal treatment is thereafter applied to the digestate. Hydrothermal treatments such as wet oxidation (WetOx) and hydrothermal carbonization (HTC) were compared at a temperature of 200°C, for initial pressure of 0.1 and 0.82 MPa, and no holding time after the process had reached the temperature setpoint. Both WetOx and HTC resulted in a substantial solids conversion (47% with HTC; 64-83% with WetOx) into soluble products, while some carbon loss was observed (20-33%). This generated high soluble products concentrations (from 6.2 to 10.9 g soluble chemical oxygen demand/L). Biomethane potential tests showed that these hydrothermal treatments allowed for a 4-fold improvement of the digestate anaerobic biodegradability, with a methane potential of about 200 L_{STP} CH₄/kg volatile solids when based on the organic content of the untreated digestate.

KEYWORDS: *microalgae, degradation, wet oxidation, hydrothermal carbonization, biomethane, anaerobic digestion*

1. INTRODUCTION

Microalgae can be an attractive feedstock for biogas production as it contains biodegradable compounds such as carbohydrates (4-57% of total solids (TS)), lipids (2-40% of TS) and proteins (8-71% of TS) (Prajapati et al., 2013). These compounds can be converted into methane. However in practice, the methane yield from anaerobic digestion (AD) of algae (0.1-0.4 L_{STP} CH₄/g volatile solids (VS) (McGinn et al., 2012; Marsolek et al., 2014)) is much lower than the methane potential based on the theoretical yields of cellular components, estimated at 0.42, 0.50, and 1.01 L_{STP} CH₄/g, for carbohydrates, proteins and lipids, respectively (Guiot and Frigon, 2012). A number of factors may contribute to the lower than anticipated methane yield. Cellulose and pectin are the main components of the cell walls of algae, and such rigid cell walls resist hydrolysis (Passos et al., 2015). Non-hydrolysable aliphatic biopolymers called algeanans are also present in the outer wall of many green microalgae (Schwede et al., 2011). Moreover polyphenols, found commonly in brown algae, inhibit alginate lyase activity and methane production during anaerobic digestion of algae (Marsolek et al., 2014). Therefore, thermal treatments can be applied to the raw algae before anaerobic digestion, to disrupt the structure of algae, increase the availability of substrates, and hereafter improve the biogas yield.

Thermal treatment increases the solubilisation of particulate organic fractions and the hydrolysis of the polymeric organic molecules. Heat disrupts the hydrogen bonds in crystalline cellulose and lignocellulose complexes. The temperature used in thermal pretreatment methods can range from below 100°C, at atmospheric pressure (0.1 MPa) to up to 300°C at higher pressure. Amongst them, the hydrothermal treatment refers to technologies involving reactions carried out in an aqueous solvent at elevated temperatures (above 100°C), with the subsequent increase of pressure (Rodriguez et al., 2015). Hydrothermal treatment includes, amongst others, wet oxidation and hydrothermal carbonization.

Wet oxidation (WetOx) can break down the large polymers and convert them to low molecular weight biodegradable compounds (Malik et al., 2014) with air or oxygen as oxidant (Collado et al., 2013) at 125-320°C and 0.1–6 MPa (Padoley et al., 2012). The wet oxidation has been reported to have significant advantages over other thermal treatment technologies such as lower production of toxic degradation products, decrease of cellulose crystallinity, and high delignification potential (Arvanitoyannis, 2010).

Hydrothermal carbonization (HTC) is operated at 180-280°C for a few minutes up to several hours without oxygen (Wirth et al., 2015). Biomass is heated in water under autogenous conditions and produces a carbonaceous fraction (hydrochar) (Sabio et al., 2016). The dissolved organic products (e.g. fatty acids, soluble proteins) and nutrients (e.g. NH₄⁺, P, K⁺) from the hydrothermal carbonization can be used as substrate and nutrients for anaerobic digestion (Erdogan et al., 2015).

As an alternative to applying the hydrothermal treatment to the raw feedstock before AD (i.e. pre-treatment), one can consider a post-treatment scenario where AD is directly used as the primary treatment of the raw algae while the hydrothermal treatment is thereafter applied to the digestate. The rationale behind such post-treatment approach is 1) to save energy as thermal treatment energy is spent only to recalcitrant compounds, what the solid digestate is in essence (as opposed to conventional pre-treatment where both easily biodegradable and recalcitrant compounds use the treatment energy indistinctly, and unnecessarily in the case of the biodegradable ones); 2) to return the liquid products recovered from the thermally treated digestate back to the digester, improving that way the overall methane yield; and 3) to reduce the digestate volume. Figure 1 is illustrating the post-treatment concept (B) in comparison with the conventional AD scheme with pre-treatment (A).

The objective of this study was to determine under which temperature, pressure and retention conditions the conversion of an algal solid digestate into liquid compounds would be maximized, then to compare WetOx and HTC under the optimal conditions as determined above, namely with respect to their impact on the biomethane potential improvement of the digestate after such a post-treatment.

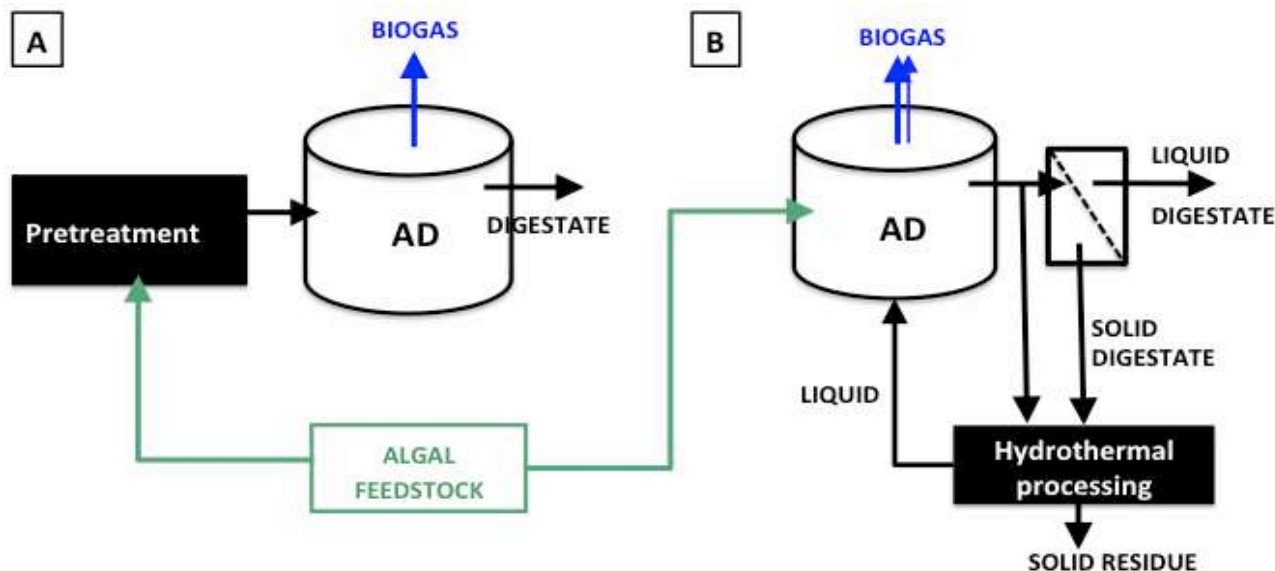


Figure 1. Schematic illustration of the post-treatment concept (B) in comparison with the conventional anaerobic digestion (AD) approach with pre-treatment (A).

2. MATERIALS AND METHODS

2.1 Feedstock

The digestate was obtained from an upflow anaerobic sludge blanket (UASB) reactor treating raw *Scenedesmus* microalgae at an organic loading rate (OLR) of 3 g VS/L reactor.d. Liquid and solid fractions were separated by centrifugation (10,000 rpm at 10°C for 10 min). The solid fraction (128 ± 1.5 g TS/kg and 124 ± 1.5 g VS/kg), referred to as algal digestate, served as the feedstock for this study and was stored at 4°C until further use.

2.2 Pressure hydrothermal treatment

The algal digestate was treated using a 300 mL pressure vessel (PV) reactor (Series 4560 Mini Bench Top Reactor System, Parr Instrument Company, Moline, IL). Five grams of the digestate with 45 mL of demineralized water were transferred into the reactor. The system was tightly sealed to ensure no leakage. Oxygen or nitrogen gas was used to achieve the WetOx or HTC treatments, respectively. The PV reactor initial air content was flushed with the gas for 2 min. After that, all the lines of the reactor were closed and then the gas (N_2 or O_2) was supplied again so to reach the pressure initial setpoint (0.1, 0.69 and 0.82 MPa). The reactor was stirred using an impeller rotating at 150 rpm. After the temperature had reached the setpoint (120, 170 or 200°C) at a rate of about 7°C/min, the PV reactor was cooled down to 30°C, which is hereinafter referred to as a holding times of 0 min. Otherwise, the PV reactor was kept at the temperature setpoint for a holding time of 60 min before to be cooled down.

Then, the volume of the gas produced was released and measured at atmospheric pressure. The gas composition was measured by gas chromatography (H_2 , O_2 , N_2 , CO , CH_4 and CO_2).

The treated digestate samples were then analyzed for TS, VS, suspended solid (SS), volatile suspended solid (VSS), total chemical oxygen demand (tCOD), soluble chemical oxygen demand (sCOD), according to the Standard Methods (Rice et al., 2012).

2.3 Biomethane potential (BMP) assays

The assays were performed in 500 mL serum bottles, as described in Frigon et al. (2013). Briefly, 5 g of raw algal digestate and 15.3 g of anaerobic sludge were added to the bottles for measuring the residual methane potential of the untreated digestate. The substrate to inoculum ratio was 1:2, based on the VS concentration. The algal digestate treated as described in section 2.2 was integrally transferred to the serum bottles with the same amount of inoculum sludge for measuring the methane potential of the so-treated digestate. Each bottle contained 0.5 mL of 1.25% cysteine-sulfide reducing solution, 2 mL of defined media and 2 mL of bicarbonate buffer. The final volume was adjusted to 100 mL with boiled demineralized water. Each bottle was prepared under a constant flow of a gas mix (80% N_2 and 20% CO_2) and closed with a butyl rubber seal. The bottles were incubated at 35°C with agitation at 100 rpm. To measure the endogenous methane production, the substrate was replaced with deoxygenated water. All tests were conducted in triplicate. The biogas production was measured by a water-displacement system, built from a volumetric glass burette, graduated every 0.2 mL. To measure biogas composition (H_2 , N_2 , CH_4 and CO_2), three hundred μ L of gas were taken from the bottle headspace and injected into an Agilent 6890 (Santa Clara, CA) gas chromatograph (GC) equipped with a thermal conductivity detector (TCD) and a 5 m x 2.1 mm Carboxen-1000 column (Supelco, Bellefonte, PA) with argon as a carrier gas, as described in (Frigon et al., 2012). Values of gas production are given at standard temperature (273 K) and pressure (1 atm). The maximum methane production rate (MMPR) was calculated by a least-squares-based linear regression over the four to six initial values of the CH_4 accumulation time-courses. The specific rate was obtained by dividing the production rate by the VS content in the serum bottle, and expressed in mL CH_4 per gram of VS added per day.

2.4. Analytical methods

The pH was measured on an Accumet AP61 portable pH meter equipped with a micro-probe (Fisher, Fairlawn, NJ), within one minute of sampling. The volatile fatty acids (VFA) and solvents were measured on an Agilent 6890 GC equipped with a flame ionization detector (FID) as described previously (Guiot et al., 2011). Cations (Na^+ , NH_4^+ , K^+) were measured by injecting a sample volume of 20 μ L into a high-performance liquid chromatograph (HPLC) (Alliance e2695 separations module, Waters Chromatography division, Milford, MA) equipped with an Hamilton PRP-X200 cation resin-based column (250 x 41 mm O.D.), a conductivity detector (Waters Millipore model 432) and an Empower2 data station. The mobile phase was a 4 mM solution of nitric acid with 30% methanol, flowing at a rate of 1.8 mL/min and a temperature of 40°C.

3. RESULTS AND DISCUSSION

3.1 Effect of temperature, pressure and holding time on the digestate wet oxidation performance

In the first part of this study, the solid algal digestate was treated by wet oxidation (WetOx) at pressures of 0.1, 0.69 and 0.82 MPa, at maximum temperatures (T_{\max}) of 120, 170 and 200°C, with 0 and 60 min holding times at T_{\max} . Figure 2 shows the performance of WetOx in terms of VSS conversion efficiency and tCOD loss, for a variety of combined temperature, pressure and holding time conditions.

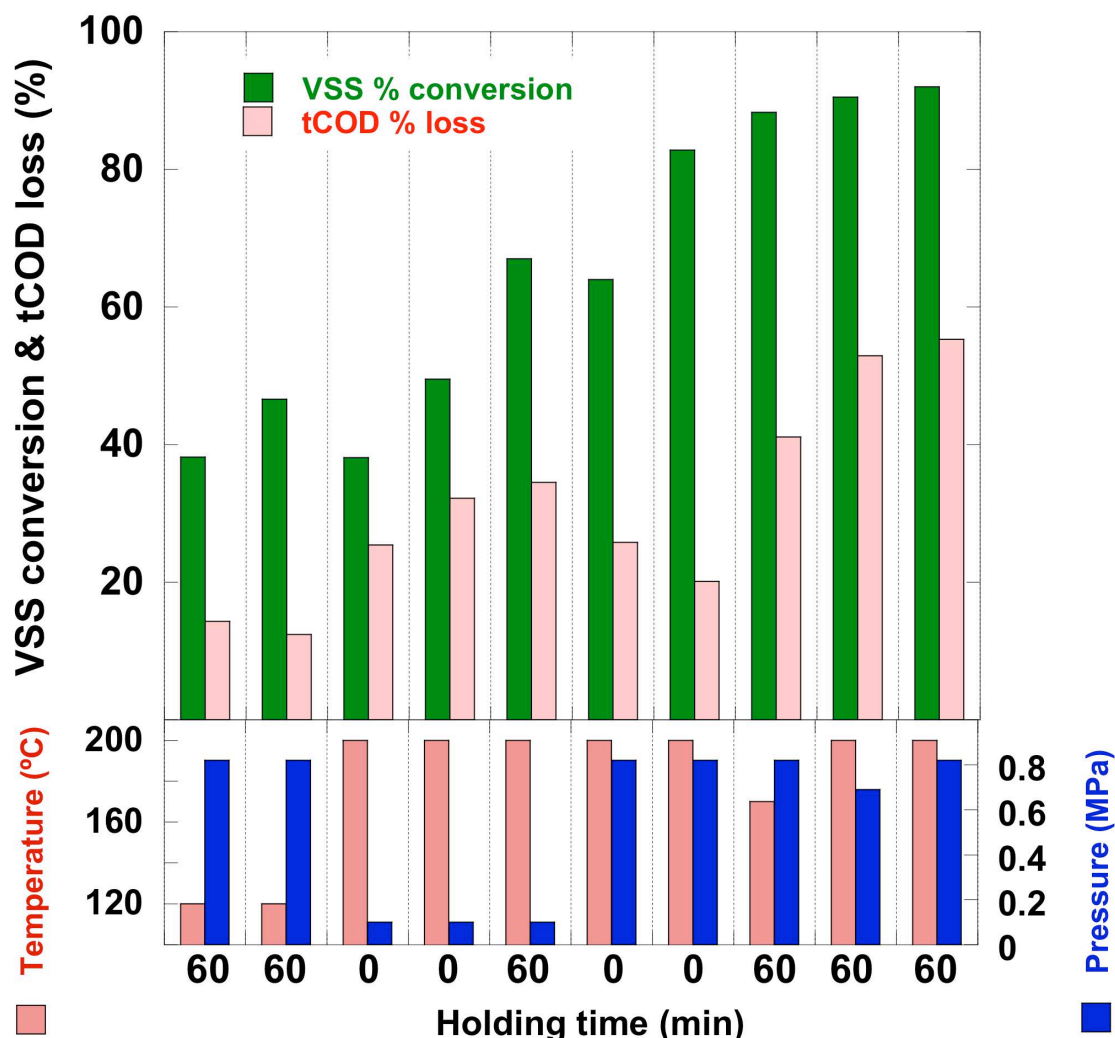


Figure 2. WetOx performance in terms of organic solids (VSS) conversion efficiency and total chemical oxygen demand (tCOD) loss, for a variety of combined temperature, pressure and holding time conditions.

The temperature increase from 120 to 200 °C improved the VSS destruction from 38 to 92%, at the highest initial pressure (0.82 MPa) and holding time (60 min). However, a carbon loss was also observed, based on the diminution of tCOD (from 14 to 55% losses) and the carbon dioxide production (from 13 to 234 mL/bottle). The sCOD of the treated digestate increased to 9.8 g/L with the temperature increase up to 170°C, with no noticeable difference

at above temperature. The WetOx treatment lowered the pH (between 4.6 and 6.9) compared to 8.3 for the untreated digestate. This is related to the acid production by WetOx. The acid production in the WetOx-treated digestate increased with the temperature: a VFA total of 2140 mg/L at 200°C against 320 mg/L at 120°C. Acetic acid was the main product at 200 °C, followed by lactic acid. Formic acid was only detected at 170 and 120°C (600 and 150 mg/L, respectively). Ammonium production also increased with temperature: from about 200 to 640 to 970 mg/L at 120, 170, and 200°C, respectively.

The initial pressure increase from 0.1 to 0.69 to 0.82 MPa improved the VSS destruction from 67 to 90 to 92%, at the highest temperature (200°C) and holding time (60 min). An increase in the carbon loss was also observed with the pressure increase, with an increase of the tCOD loss from 35% at 0.1 MPa to 55% at 0.82 MPa. The pressure change did not affect significantly the sCOD: 8.6, 10.2 and 9.4 g/L at 0.1, 0.69 and 0.82 MPa, respectively. The pH decreased from 8.3 to 6.3 – 6.9. Total VFA production also increased with pressure increase, from 600 to above 2100 mg/L. Acetic acid was the main product at all pressures tested, and as well, formic acid was only detected at 0.69 and 0.1 MPa (540 and 150 mg/L, respectively). Ammonium production also increased with pressure: from 280 to 880 to 970 mg/L at 0.1, 0.69 and 0.82 MPa, respectively, at 200°C with a holding time of 60 min. However such relatively high amounts of ammonium are still below the inhibition threshold for AD microbial populations (Chen et al., 2008).

The holding time had a mitigated effect on the VS conversion, at both low and high pressure. When the holding time was extended from 0 to 60 min, the VSS conversion efficiency increased from between 38 and 50% to 67% at a pressure of 0.1 MPa, and from between 64 and 83% to 92% at a pressure of 0.82 MPa. However the carbon loss more than doubled when the holding time was extended from 0 to 60 min at high pressure and temperature (tCOD loss increasing from 20-26% to 55%).

When comparing these results (Figure 2), considering the two most important selection criteria would be to maximize the solid conversion and minimize carbon losses, it appears that WetOX optimal conditions were high temperature, high pressure, with a minimum holding time (i.e. 200°C, 0.82 MPa, 0 min). Those conditions have been adopted in the next part of the study, where WetOx was compared to hydrothermal carbonization (HTC).

3.2 Comparison of WetOx and HTC

The digestate from a UASB digester fed with *Scenedesmus* biomass was processed using WetOx and HTC. The two compared treatments differ only by the initial gas environment (O₂ for WetOx and N₂ for HTC). Two initial gas partial pressure were tested: 0.1 and 0.82 MPa. The digestate treatment tests were all conducted in the same 300 mL ParrTM PV reactor, which was heated up to 200 °C and immediately cooled down (at a rate of 7°C/min), what we called a holding time of 0 min. The so-treated digestates were characterized (Table 1) as well as tested for their respective biochemical methane potential (BMP) (Table 2).

Characterization results showed that all treatments reduced the amount of suspended solid compared to raw algal digestate (Table 1). The suspended solids (SS), which appeared to be mostly composed of volatile suspended solids (VSS), were at the lowest levels following higher pressure conditions (0.82 MPa). The VSS decreased particularly under high-pressure O₂ conditions (WetOx), which appears to be consistent with the highest sCOD observed under the same conditions (10.2-10.9 g/L, Table 1). It is also consistent with gas production that was followed during treatments in the PV reactor and led to higher CO₂ gas production at these conditions (36-61 mL/bottle for WetOx at 0.82 MPa against 0-6 mL/bottle for WetOx at 0.1 MPa and HTC). In addition to these reported characteristics, the high pressure-WetOx treated

digestate led to higher VFA content (640-710 mg VFA/L) than the 3 other conditions (60-350 mg VFA/L). Solvent components were also measured and highest levels were observed once again under higher pressure (0.82 MPa) conditions containing mostly acetone and methanol (21 and 25 mg/L, respectively). Ammonium was also produced with values up to 425 mg/L.

The WetOx at a pressure of 0.82 MPa clearly gave the best results in terms of VSS conversion: 64-83% against 47% with HTC. This is correlated to the highest soluble COD with up to 10.9 g/L for WetOx against 9 g/L for HTC both at 0.82 MPa. This was expected since thermal pretreatment is known to disrupt chemical bonds in cell wall thereby solubilising the organic matter (Chandra et al., 2014). However there were losses of carbon (reduction of tCOD) for all treatment tested, which were in a narrow range: between 20 and 33%. There was a trend for HTC to have slightly more tCOD loss than WetOx (30-33% versus 20-32%), which was unanticipated, since HTC conditions were non-oxidative and significantly less CO₂ was produced with HTC than WetOx (e.g. 6 mL/bottle for HTC at 0.82 MPa instead of 36-61 for WetOx). It is possible that this carbon loss was associated with a higher release of volatiles in HTC at high temperature.

Table 1. Comparative performance of WetOx and HTC on the digestate solids degradation and solubilization, as a function of the treatment pressure.

Parameter	Untreated digestate	Treated digestate					
		WetOx	WetOx *	WetOx	WetOx *	HTC	HTC
Pressure (MPa)		0.10	0.10	0.82	0.82	0.10	0.82
TS (g/kg)	12.5 ±0.05	9.11 ±1.64	11.59 ±0.17	9.38 ±1.17	10.75 ±0.42	11.10 ±0.59	10.77 ±0.01
VS (g/kg)	12.1 ±0.03	8.68 ±1.62	10.87 ±0.46	8.91 ±1.17	10.02 ±0.30	10.67 ±0.56	10.51 ±0.29
SS (g/kg)	12.3 ±0.16	6.20 ±0.34	7.62 ±0.23	2.12 ±0.34	5.19 ±0.52	7.07 ±0.43	6.58 ±0.46
VSS (g/kg)	12.0 ±0.14	6.06 ±0.30	7.43 ±0.17	2.06 ±0.34	4.33 ±0.18	6.91 ±0.39	6.35 ±0.49
tCOD (mg/L)	22,816 ±1,782	15,462 ±1,969	17,029 ±2,616	18,222 ±4,084	16,929 ±715	15,329 ±462	16,082 ±1,126
sCOD (mg/L)	129 ±14	10,469 ±590	6,185 ±356	10,905 ±570	10,161 ±245	7,007 ±496	9,000 ±232
VSS conversion (%)		50	38	83	64	42	47
tCOD loss (%)		32	25	20	26	33	30

* Re-testing

Conditions for all tests: temperature 200°C; holding time 0 min.

The methane yields obtained during the BMP assays were all significantly higher than the CH₄ produced from the raw digestate (Table 2). These BMP results are consistent with the higher soluble content, as reported from the overall increase in sCOD and overall decrease in VSS (Table 1). At the pressure conditions of 0.82 MPa (for N₂ or O₂), where more soluble materials were produced, the methane yields of digestate treated by WetOx and HTC at 200°C were similar and at the highest level (268±1 and 270±8 mL_{STP} CH₄/g VS added, respectively). These yields, as measured after a long incubation (42 days), can be considered as ultimate. Hence considering a theoretical CH₄ yield of 500 mL_{STP} CH₄/g VS degraded, it can be inferred

that the hydrothermal treatments improved the digestate biodegradability to 54%, as compared to the residual long-term biodegradability of 14% for the raw digestate, i.e. a 4-fold improvement. When the CH₄ production is reported to the VS content of the digestate before the hydrothermal treatment, the CH₄ yields decrease to 195±3 and 207±6 mL_{STP} CH₄/g initial VS. This implies there is a methane potential loss of 27 and 23 %, with the WetOx and HTC treatments, respectively, both at 200°C and 0.82 MPa (Table 2). It is noteworthy that, while the CH₄ potential improvement by WetOx and HTC were similar, the maximum methanisation rate after HTC was 40 and 25% higher than after WetOx, at 0.1 and 0.82 MPa, respectively.

Table 2. Ultimate methane yield and maximum methane production rate (MMPR) of the algal digestate before and after hydrothermal treatment.

<i>Treatment</i>	<i>Initial pressure MPa</i>	<i>CH₄ yield mL_{STP}/g VS post-treated (liquid+solid)</i>	<i>Biodegradability %</i>	<i>CH₄ yield as reported to the solids before treatment mL_{STP}/g VS</i>	<i>Methane potential loss with treatment %</i>	<i>Methane potential increase factor</i>	<i>Specific MMPR mL_{STP} CH₄/g VS_{added}.d</i>
<i>Untreated</i>		66 ±1	13	66 ±1	-	1	6 ±0.1
<i>WetOx</i>	<i>0.1</i>	193 ±14	39	156 ±11	19	2.4	24.2 ±1.4
<i>WetOx</i>	<i>0.82</i>	268 ±4	54	195 ±3	27	3.0	33.8 ±0.1
<i>HTC</i>	<i>0.1</i>	204 ±9	41	159 ±7	22	2.4	40.6 ±0.7
<i>HTC</i>	<i>0.82</i>	270 ±8	54	207 ±6	23	3.1	45.6 ±0.1

Conditions for all hydrothermal treatments: temperature 200°C; holding time 0 min.

Incubation duration of the BMP tests: 42 days.

4. CONCLUSIONS

Wet oxidation significantly improved the degradation of the digestate solids and their conversion into soluble products, with some carbon loss. Amongst the conditions tested, a pressure of 0.82 MPa, a temperature of 200°C and no holding time after the process had reached the temperature setpoint, were maximizing the solid conversion efficiency while minimizing the carbon loss. It is under those conditions that hydrothermal carbonization was compared to WetOx and using the same algal digestate. Both treatments achieved VSS conversion at a significant efficiency (from 47% for HTC up to 83 with WetOx), resulting in the generation of high soluble products concentrations (from 6.2 to 10.9 g sCOD/L) while the tCOD loss ranged between 20 and 33%.

These hydrothermal treatments allowed for a 4-fold improvement of the digestate anaerobic biodegradability. This resulted into a methane potential of about 200 L_{STP} CH₄/kg VS when based on the organic content of the untreated digestate.

Assuming a 50% efficiency of crude microalgal biomass degradation by AD without pretreatment, one may expect a production of methane of 250 Nm³/dry ton, with 0.5 dry ton of

remaining digestate. Applying hydrothermal treatment to that digestate and recycling the hydrothermal product to the primary AD would produce another 100 Nm³, i.e. an overall methane yield improved by 40%, based on this study. The solid mass being halved by AD as primary treatment, this gain would logically be obtained at an extra cost by half lower than it would have been by using WetOx or HTC as a pre-treatment applied to the crude biomass before AD.

ACKNOWLEDGEMENTS

This research was supported by the Algal Carbon Conversion (ACC) program of the National Research Council of Canada. The authors also wish to thank Fred Ngoundjo for assistance with the pressure vessel reactor, Alain Corriveau and Fanny Monteil-Rivera for analytical assistance, and Patrick McGinn and Crystal G. Lalonde for growing and supplying the microalgae. One author (S.N.) was supported by the Royal Golden Jubilee Ph.D. Program of Thailand (grant PHD/0311/2551). This publication is recorded as NRC-EME- 55778.

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