Catch crops for agricultural biogas production, case study for *Brassicaceae sp.*

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Abstract
Catch crops cultivated in autumn or over winter can be used as feedstock for agricultural biogas production. *Brassicaceae* crops are good candidates for this specific use due to their agronomic values in intercropping conditions. However their high content in glucosinolate may conduct to sulphur release in the digesters and induce anaerobic digestion troubles or biogas pollution with hydrogen sulphide. In this study, *Brassicaceae* crops were used as co-substrate with pig slurry in anaerobic digesters. Their anaerobic biodegradability was close to other lignocellulosic biomass with a large fraction of slowly biodegradable organic matter content. The sulphur and glucosinolates contents in plants did not inhibit the overall anaerobic process neither severely impacted hydrogen sulphide concentration in the biogas.

Keywords
Catch crops; anaerobic digestion; co-digestion; *Brassicacea*; sulphur; hydrogen sulphide

INTRODUCTION

To reduce pollution of surface water and groundwater by macro-nutrients, and recover a good quality of water resources, the European Union has set up the Nitrate Directive (Borja, 2005). This directive requires defining vulnerable areas and implementing good agricultural practices to limit transfer of agricultural nitrate sources to water resources. To facilitate the implementation of this Directive by farmers, different best practices have emerged like fertiliser plan and intermediate cropping. Intermediate crops have positive effects on soil fertility, eliminating erosion and limiting nutrient loss by fixing the remaining soil nutrients (especially mineral nitrogen) not used by the main crop. Nowadays, these cultures are occasionally used as co-substrates in some agricultural biogas plants in combination with liquid manure, they are thus considered as energetic catch crops. *Brassicaceae* (*Brass.*), formerly called "cruciferous", are interesting cover crops since they have particularly high growth yields in several intercropping conditions (Brant et al., 2011). However they are rich in sulphur (S), because of a high glucosinolate content that could inhibit anaerobic microorganisms during anaerobic digestion or conduct to pollute biogas with hydrogen sulphide (H_2S).
The goal of this study was to focus on the use of these intercrops as co-substrate in agricultural anaerobic digesters particularly by studying agronomic yields, anaerobic biodegradability and sulphur fate.

MATERIALS AND METHODS

Catch crops cultivation

Intercropping trials were conducted in Boigneville (France) at the experimental station of plant Institute Arvalis-Institut du végétal. Five species of *Brass*. crops were used in this experiment: Camelina (*Camelina sativa*), Radish fodder (*Raphanus sativus*), White mustard (*Sinapsis alba*), Brown mustard (*Brassica juncea*), Winter rapeseed fodder (*Brassica Napus*). The total area of plots was 120 m^2. Catch crops were sowed after wheat crop in August 20^{th} 2010 (T_0). Harvesting of catch crops were realised 53 and 77 days after seeding. Agronomic yields were measured for each harvesting day.

Anaerobic biodegradability

Anaerobic biodegradability of crops was measured by biochemical methanogenic potential (BMP) using the method developed by Vedrenne et al. (2008) and by anaerobic respirometry.
Anaerobic respirometry was done using mesophilic continuously mixed batch reactors (1 L) filled with an anaerobic inoculum. After one day, a pulse of substrate was injected into each reactor and their methane production rate was continuously monitored by pressure measurements for a period of 13 days. The amount of *Brass*. substrate added was calculated to obtain a pulse with a base weight ratio of 0.2:1 (chemical oxygen demand of *Brass*. versus inoculum volatile solids). Biogas composition of each reactor (methane-CH_4 and carbon dioxide-CO_2 contents) was analysed by gas chromatography. The methane producing rate curves obtained were numerised using a specific numerical model developed by Girault et al. (2012). Fractionation of the substrate was obtained by optimising the numerical representation of each experimental methane producing rate curve.

Anaerobic reactors procedure

For this study, six continuously stirred anaerobic reactors were designed with a working volume of 3.5 L ± 0.05 L. The reactors were completely stirred and operated in mesophilic conditions (38 °C ± 1° C) with a hydraulic retention time close to 30 days. Feeding of the reactors was sequential and realised on the basis of one cycle of 2 or 3 days followed by one or two day(s) of feedless. For five reactors, a mixture of 250 g of pig slurry (PS) and *Brass*. (75% / 25% wet basis respectively) with a total organic load ranging between 2.1 and 2.3 g O_2/L/d was used. One reactor was fed with only PS (organic load: 1.3 g O_2/L/d). The six reactors were monitored during 90 days. At the steady state the performance of each reactor was measured individually, including CH_4 production measured by wet tip gas meters coupled with an online chromatograph (µGC, 4900 Varian USA) twice a day. At the end of experiment, during last 14 days, influents (n=6) and effluents (n=6) from each reactor were sampled and physically and chemically characterised.

Physical-chemical characterisation

Chemical oxygen demand (COD), total solids (TS), volatile solids (VS), total Kjeldahl nitrogen (TKN) and total ammoniacal nitrogen (TAN) were determined using standard methods (APHA, 1998). Elementary analysis of S was performed using specific analysers according to the manufacturer's instructions (LECO SC-144DR). Sulphate was quantified by ionic chromatography and *Brass*. glucosinolate (GS) content was determined on frozen plant by high performance liquid chromatography according to standard methods (AFNOR, 1995). Total dissolved sulphide (TDS) was determined following the procedure describe by Ubuka et al. (2001).

RESULTS AND DISCUSSION

Catch crop yields

Measured yields for crops varied between a maximum productivity for mustards of about 5 tons TS/ha and a minimum for camelina and rapeseed around 2 tTS/ha (Table 1). These measured productivities for year 2010 are significantly high compared to previous years. Measured values for same catch crops on years 2001, 2004 and 2005 reached only 1.5 tTS/ha. The results for year 2010 are related to the exceptional weather conditions for this year.

Table 1: Dry matter production of different *Brass*. catch crops after seeding (T_0).

Catch crop	Agronomic yield T_0+53d	Agronomic yield T_0+77d

	tTS/ha	tTS/ha
Camelina	2.1	2.6
Radish fodder	3.7	3.7
White mustard	3.2	3.9
Brown mustard	3.5	5.0
Winter rapeseed fodder	2.1	2.3

Catch crops characterisations

Sulphur content

Catch crops total S contents are presented in Table 2, they range between 2.4 and 4 gS/kgTS. Speciation of the total S content in the whole plant come from many forms such as sulphur amino acids (SAA), sulphates (SO_4^{2-}), and specific S forms recovered in *Brass*. such as GS. Thus, the GS-S content of mustard and radish represents nearly 30% of the total S content of the plant.

Table 2: Total S and glucosinolate-S content (GS-S) of Brass. catch crops.

Catch crop	Total S	GS-S	GS-S/ Total S
	gS/kgTS	gS/kgTS	%
Camelina	4.0	0.0	1.0
Radish fodder	2.9	0.9	30.3
White mustard	3.3	0.4	11.0
Brown mustard	3.7	1.2	32.1
Winter rapeseed fodder	2.4	0.2	9.0

Anaerobic biodegradability

BMP for catch crops harvested at T_0+77d were on average close to 250 Nm^3CH_4/tVS with a maximum for rapeseed and a minimum for mustard (305 and 222 Nm^3CH_4/tVS, respectively). Values recovered in this study on whole plant are similar to those found in the literature. These figures are quite characteristic of rich carbohydrate substrates like cellulose.

Anaerobic respirometry analyses were realised with each *Brass*. crop (data not shown), and biogas production simulations were then compared with BMP results. With these analyses, we observed that: (1) the rapidly biodegradable organic matter fraction of catch crops was comprised between 25 and 42% of the total COD for mustards and rapeseed respectively, (2) the organic matter fraction requiring a hydrolysis step was between 17 and 56% respectively of the total COD for rapeseed and radish, and (3) the part of refractory organic matter was between 20 and 40% of the total COD of radish and rapeseed respectively. Average anaerobic biodegradability of organic matter of *Brass*. crops was estimated to be 69%. Furthermore, these characterisations highlights that biodegradability levels calculated with the model used for anaerobic respirometry were either equivalent to those found through BMP tests or significantly increased with a maximum value of 18%.

Performance of reactors and sulphur fate

The methane yields measured in our reactor experiments were compared with those measured during BMP tests and 79 to 104% of the BMP yield was recovered in reactors. These results suggest that there was no co-digestion synergy between *Brass*. crops and manure. Our second conclusion is that no strong inhibition of anaerobic digestion occurred despite the presence of glucosinolate in the feed of reactors.

Total S load coming into reactors ranged between 8.2 and 12.1 mg/L/d (table 3). This S charge is slightly higher for reactors that are feed with crucifers (27% on average). Sulphur load is mainly brought into reactors by PS since more than 50% of the total S comes from manure. Sulphates were also measured for all influents and cruciferous sulphates represent a significant part of the total S introduced (25% on average) with a little contribution of PS. After digestion part of the total S is transferred into the biogas phase as H_2S, however, all H_2S productions are limited because the concentrations found into the biogas are very acceptable for combined heat and power installations after biological desulphurisation (<1% volume/volume). Total dissolved sulphides were limited in the reactors effluents (<0.1 gS/L/d).

Table 3: S fate of influents and effluents per liter of reactor after 90 of running days.

		Total S	GS-S	SO_4^{2-}-S	SAA[c]	TDS	H_2S
		mgS/L/d	mgS/L/d	mgS/L/d	mgS/L/d	mgS/L/d	mgS/L/d (ppm)
Camelina+PS	Influent	11.2 (2.7)[a]	0.1	2.9	4.5	Nd	-
	Effluent	10.5 (0.6)	Nd[b]	0.0	2.4	0.0	1.7 (1900)[d]
Radish fodder+PS	Influent	12.1 (1.7)	1.1	2.3	3.7	Nd	-
	Effluent	13.0 (0.7)	Nd	0.0	2.8	0.0	0.1 (200)
White mustard+PS	Influent	11.7 (0.2)	0.6	3.2	4.2	Nd	-
	Effluent	11.1 (0.5)	Nd	0.0	2.7	0.1	3.1 (3100)
Brown mustard+PS	Influent	10.9 (0.6)	1.6	4.4	4.0	Nd	-
	Effluent	11.0 (1.1)	Nd	0.0	2.5	0.1	3.4 (3900)
Rapeseed +PS	Influent	11.1 (0.3)	0.4	2.0	4.2	Nd	-
	Effluent	11.9 (2.3)	Nd	0.0	2.6	0.0	0.1 (185)
PS	Influent	8.2 (0.5)	Nd	0.4	3.5	Nd	-
	Effluent	8.6 (1.5)	Nd	0.0	2.5	0.1	0.1 (880)

[a]Standard deviation; [b]Nd: not determined; [c]Estimated values with bibliographic data (S-SAA = 0.013*(TKN-TAN)*6.25); [d]Average H_2S concentration into the biogas

CONCLUSION

The use of biomass from catch crops for biogas production is a great challenge to feed agricultural anaerobic digester with new feedstock. The use of *Brass*. catch crops as co-substrates seems to be technically feasible without interfering with anaerobic process and acceptable for biogas H_2S content. However, the basic problem is the excessive variation of agronomic yields, which depends on climatic conditions, residual minerals in the soil, soil conditions etc. to crops.

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