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Assessment of energy crops alternative to maize for biogas production in the Greater Region

Frédéric Mayer^{a,b}, Patrick A. Gerin^b, Anaïs Noo^a, Sébastien Lemaigre^a, Didier Stilmant^c, Thomas Schmit^c, Nathael Leclech^d, Luc Ruelle^e, Jerome Gennen^f, Herbert von Francken-Welz^g, Guy Foucart^h, Jos Flammangⁱ, Marc Weylandⁱ, Philippe Delfosse^{a,*}

^a Centre de Recherche Public – Gabriel Lippmann, Department "Environment and Agro-biotechnologies", 41, rue du Brill, L-4422 Belvaux, Luxembourg

^b Université catholique de Louvain, Earth & Life Institute, Bioengineering, Croix du Sud 2, box L7.05.19, B-1348 Louvain-la-Neuve, Belgium

^c Centre wallon de Recherches agronomiques, Agriculture and Natural Environment Department – Farming Systems, Territory and Information Technologies Unit, Rue du Serpont 100, B-6800 Libramont, Belgium

- ^f Centre de recherche et de formations agricole pour l'Est de la Belgique Agra-Ost, Klosterstrasse 38, B-4780 Saint-Vith, Belgium
- ^g Dienstleistungszentrum Ländlicher Raum Eifel, Brodenheckstraße 3, 54634 Bitburg, Germany
- ^h Centre Indépendant de Promotion Fourragère, Croix du Sud 2, box L7.05.11, B-1348 Louvain-la-Neuve, Belgium
- ¹Administration des Services Techniques de l'Agriculture, 16 route d'Esch, L-1019 Luxembourg, Luxembourg

HIGHLIGHTS

• Biomethane yield per hectare of various energy crops was assessed.

• Miscanthus harvested in autumn is a promising alternative to maize for biomethanation.

• The biomass yield of energy crops can predict the biomethane yield.

• The volatile solids content of biomass can predict the biomethane chemical potential.

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ABSTRACT

The biomethane yield of various energy crops, selected among potential alternatives to maize in the Greater Region, was assessed. The biomass yield, the volatile solids (VS) content and the biochemical methane potential (BMP) were measured to calculate the biomethane yield per hectare of all plant species. For all species, the dry matter biomass yield and the VS content were the main factors that influence, respectively, the biomethane yield and the BMP. Both values were predicted with good accuracy by linear regressions using the biomass yield and the VS as independent variable. The perennial crop miscanthus appeared to be the most promising alternative to maize when harvested as green matter in autumn and ensiled. Miscanthus reached a biomethane yield of $5.5 \pm 1 \times 10^3$ m³ ha⁻¹ during the second year after the establishment, as compared to $5.3 \pm 1 \times 10^3$ m³ ha⁻¹ for maize under similar crop conditions.

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1. Introduction

Along with the world population growth, the response to the increasing energy demand is a major challenge for humanity. The anaerobic digestion process appears to have a high potential to contribute to sustainable energy production. This bioprocess is one of the most advanced option to convert fermentable biomass, including the organic fraction of municipal solid waste, kitchen wastes, green wastes, aquatic biomass and dedicated energy crops (Nallathambi Gunaseelan, 1997), into a multipurpose fuel (CH_4) and fertilizers readily available to plant production systems (Möller and Stinner, 2010), while reducing greenhouse gas emissions, as compared to fossil fuels (Uusitalo et al., 2014).

Among the broad variety of substrates suitable for anaerobic digestion (Raposo et al., 2012), energy crops were extensively investigated, especially for their use in co-digestion agricultural biogas plants, together with animal effluents (Weiland, 2009).





^d Chambre Régionale d'Agriculture de Lorraine, 9, rue de la Vologne – Building i, 54520 Laxou, France

^e Centre Provincial Liégeois des productions Végétales et Maraîchères, Rue de Huy, 123, B-4300 Waremme, Belgium

^{*} Corresponding author. Tel.: +352 47 02 61 442; fax: +352 47 02 64. *E-mail address:* delfosse@lippmann.lu (P. Delfosse).

Whereas using only agricultural by- and co-products may limit the feeding of an anaerobic digester over the year, using arable land to produce biomass for an energy purpose is considered as an environmentally-friendly strategy if sustainability criteria are reached (Hanegraaf et al., 1998).

Various energy crops have been tested for anaerobic digestion (Bauer et al., 2009). Ideally, energy crops should offer a high dry biomass yield at a low cost, a composition with the least contaminants such as soil and should require low nutrient and energy inputs (McKendry, 2002). It should also offer a low sensitivity to pest and a good soil cover, while not decreasing the biodiversity. In practice, maize is currently the most used energy crop for biomethanation because of its high biomass yield, good conversion rate into methane and easy storage as silage. Thus, the biomethane vield of maize silages has been widely assessed (Herrmann and Rath. 2012: Mayer et al., 2014). Its energy and CO₂ balances are quite favourable (Gerin et al., 2008). However, maize cropping is associated with environmental issues such as soil erosion, soil compaction, low biodiversity, nutrient leakages into surface and groundwater, and pesticide pollution of soil and water (European Environment Agency, 2006).

The main objective of the present study is to measure and assess the biomethane yield of other plant species, including hemp, immature rye, miscanthus, sorghum, spelt, sunflower, switchgrass and tall fescue, that can potentially address some of the environmental issues and could advantageously displace maize as a major substrate for biomethane production. The energy potential of these plant species was assessed for the Greater Region (the area including Saarland and Rhineland-Palatinate in Germany, Lorraine in France, the Luxembourg territory and Wallonia in Belgium). Additionally, factors such as the harvest time, the biomass yield, the volatile solids (VS) content and the anaerobic digestibility were analysed to identify their influence on the biomethane yield of these various plant species.

2. Methods

2.1. Plant material

Annual and perennial plants studied for their biomethane yield are presented in Table 1. Hemp (*Cannabis sativa* L.), rye (*Secale cereal* L.), maize (*Zea mays* L.), miscanthus (*Miscanthus* \times giganteus J.M. Greef & Deuter ex Hodk. & Renvoize), sorghum (*Sorghum bicolor* (L.) Moench), spelt (*Triticum aestivum* L. ssp. Spelta (L.) Thell.), sunflower (*Helianthus annuus* L.), switchgrass (*Panicum virgatum* L.) and tall fescue (*Festuca arundinacea* Schreb.), were produced in 2009, 2010 and 2011 at Gerbéviller (France), Mötsch (Germany), Libramont, Gembloux, and Tinlot (Belgium). The

Table 1

Plant material, cropping details, number of samples analysed, total solids (TS) and volatile solids (VS) contents.

energy crops were thus grown under various agro-climatic conditions, including various fertilisation schemes, in order to induce variability within the sample set and assess the various crop potentials in a way that is representative for the Greater Region. All plant species were harvested once a year, except tall fescue that was harvested three times per year. The crops were grown in 9–24 m² plots. The total aerial biomass was harvested and chopped at 10 cm above ground with a Haldrup M-65 harvester. In case of lodging, the biomass was harvested manually. Maize (additional 379 samples) that was previously assessed (Mayer et al., 2014) was included as a reference energy crop.

Since three ways of conversion of the biomass into energy (bioethanol, biomethanation and combustion) were envisaged in the ENERBIOM research project (ENERBIOM, 2012), some species were cropped or harvested in specific ways. Indeed, grains (targeted for food) were separated from straw (biomass for energy) at the harvest of spelt. Rye was harvested as an immature cereal for silage production. Some maize and sorghum (18 and 9 samples, respectively) were harvested at the end of the winter in March, in order to produce biomass with low moisture content suitable for combustion. In addition, a specific field trial that aimed at comparing maize, sorghum and miscanthus was conducted at Tinlot (Belgium) during the 2009–2011 cropping seasons.

The wet weight biomass yield (biomass_{WW} yield in t ha⁻¹) of each sample was measured at harvest before carrying a sample to the laboratory. Each sample was then packed in plastic bags under vacuum to allow a silaging process and storage. In case of gas production due to the silaging process, bags were opened and resealed under vacuum (Mayer et al., 2014). If no gas was produced (no silaging process was observed for spelt) or after the silaging process period (2–3 weeks at room temperature to reach stable and preserved silage), all samples were stored at room temperature in vacuum sealed bags until laboratory analysis.

Total solids content in the wet silages (TS) were measured after a drying step in an oven at 105 °C for 24 h, and volatile solids content (VS) in the wet silage was quantified subsequently after combustion in a furnace at 550 °C for 6 h.

2.2. Biochemical methane potential measurement

The biomethane produced by the silages was measured according to the VDI 4630 standard, with the method described previously (Mayer et al., 2014). The main parameters that characterise the BMP assays are summarised in Table 2, as recommended by Raposo et al. (2012). Briefly, the 2 L total capacity batch anaerobic digesters were filled with the crop samples to be analysed individually and an inoculum collected from the anaerobic digester of a wastewater treatment plant. The inoculum was collected from a

Plant species	Culture	Sowing or planting period	Harvest period	Samples	TS (%WW)	VS (%WW)
Hemp	Annual	Spring	Late autumn	4	44.8 ± 2.9	40.3 ± 3.2
Immature rye	Annual	Autumn	Early spring	28	18.1 ± 1.6	16.5 ± 1.6
Maize	Annual	Spring	Late autumn	491	32.4 ± 9.7	30.0 ± 6.4
Maize (post winter)	Annual	Spring	Late winter	18	69.8 ± 4.8	67.1 ± 8.0
Miscanthus	Perennial	Early spring	Late autumn	30	41.9 ± 3.5	40.2 ± 3.6
Sorghum	Annual	Spring	Late autumn	65	21.1 ± 4.5	19.4 ± 4.6
Sorghum (post-winter)	Annual	Spring	Late winter	9	30.3 ± 2.6	27.5 ± 2.8
Spelt (grain and straw)	Annual	Autumn	Summer	37	87.4 ± 4.3	82.8 ± 3.5
Sunflower	Annual	Spring	Late autumn	12	22.0 ± 3.0	19.0 ± 2.6
Switchgrass	Perennial	Mid-spring	Late autumn	27	62.8 ± 12.2	58.3 ± 11.4
Tall fescue	Perennial	Early spring or end summer	Mid spring	426	26.3 ± 6.2	23.0 ± 5.5
			Mid-summer			
			Mid-autumn			

Mean ± standard deviation of TS and VS are expressed as percentage of wet weight (WW).

Table 2

Conditions used to perform the biochemical methane potential (BMP) assays.

Parameters	Value
Inoculum	
Origin	MWTP (Schifflange, Luxembourg),
	mesophilic anaerobic digester
Number of batch campaigns	38
Total solids	$2.6 \pm 0.7\%$ WW
Volatile solids	$1.4 \pm 0.4\%$ WW
Activity	Checked with microcrystalline
	cellulose
Degassing period prior to assays	4 days at 37 °C
Control substrate	
Туре	Microcrystalline cellulose
Total solids	96.2%WW
Volatile solids	96.2%WW
Amount and concentration at	10 gWW and 6 gVS.kg Inoculum ⁻¹
start-up of the experiment	
BIMP	367 ± 15 mL.gvS
Substrates	
Туре	Energy crop silages and post-winter
	harvests
State	Wet
lotal solids (%WW)	33.8 ± 17.7
Volatile solids (%VVVV)	31.4±17.1
Experimental conditions	
Replicates	1 or 3 for maize
Measurement system	Volumetric, drum-type gas metre
Type of gas analysed	Biogas
Biogas composition	Methane and carbon dioxide by
	specific infrared sensors
Operational conditions	
Reactor capacity	Total volume: 2 L, working volume:
	1.6 L
Temperature	Mesophilic (37 °C), thermostatic water
	bath
Stirring	Manual, daily
Duration	No pre-incubation, 42–56 days
Headspace gas	No flushing at start-up
pH/alkalinity adjustment	No adjustment
Mineral medium	No mineral medium added
ISR	2.55 ± 1.04

MWTP: municipal wastewater treatment plant, TS: total solids, VS: volatile solids, WW: wet weight, ISR: inoculum to substrate ratio. Results are expressed as mean ± standard deviation for the inoculum, the substrates tested and the inoculum to substrate ratio (ISR).

mesophilic anaerobic digester of the municipal wastewater treatment plant of Schifflange (SIVEC, Luxembourg). As recommended by Angelidaki et al. (2009), the inoculum was incubated at 37 °C for four days to decrease the endogenous biogas production.

An inoculum to substrate ratio of 2 (VS basis) was targeted at the start-up of the anaerobic digestion. The digesters were kept in water baths at constant mesophilic temperature (37 °C) during batch assays. The produced biogas was cooled down in the exit tubing to condense water vapour (6 °C). The biogas was collected into 10 L gas bags and regularly measured on a daily basis during the first week, then once a week for the rest of the anaerobic digestion period. Biogas measurements consisted in volume quantification with a wet drum-type gas metre (TG05 wet-type, Ritter) and in composition analysis for methane and carbon dioxide, with specific infrared sensors (Dynament, UK). The biomethane volumes were normalised (273 K, 1013 hPa) according to the temperature and pressure conditions for each measurement. The measurements were then cumulated to quantify the BMP of the silage samples on a wet weight basis (BMP_{WW}). The endogenous biomethane production of the inoculum was measured in batch assays (triplicates) involving the inoculum alone. Microcrystalline cellulose was used as a control substrate in each series to check the inoculum activity. The BMP result of each experiment was validated when the BMP of microcrystalline cellulose digested simultaneously was in agreement with its expected biogas potential.

For each silage sample (a total of 693 silages without maize samples), a single digestion test was carried out, except for maize which was analysed in triplicates, whereas all the field replicates were analysed individually (3–16 replicates).

2.3. Data processing and analysis

The biomass yield and the BMP on a VS basis (biomass_{VS} yield and BMP_{VS}) were calculated using (*i*) the measured biomass_{WW} yield of the wet sample in the field, (*ii*) the measured BMP_{WW} of the wet silage, and (*iii*) the measured VS of the wet silage. The biomethane yield per hectare was calculated from the biomass_{WW} yield and the BMP_{WW} (Mayer et al., 2014).

For spelt treated as two separated harvests (grain and straw), the whole plant VS, BMP, biomass yields and biomethane yield were calculated by adding the contribution of grains to the one of straw.

For tall fescue, the biomass yields (both $biomass_{WW}$ yield and $biomass_{VS}$ yield) and the biomethane yield of the three harvest dates were cumulated to obtain the annual yields.

Comparison of the means was carried out with SPSS, version 19 (SPSS Inc., 2010). The general linear model (GLM) procedure was used after assessing the normality of the distributions (Shapiro–Wilk's test) and the homoscedasticity (Levene's test). The Tukey or the T3-Dunnet post hoc tests were carried out to compare means, depending of the homogeneity of the variances. An α -risk of 0.05 was used as the significant probability level for all statistical tests.

First-order linear regressions and non-linear regressions were also carried out with SPSS, version 19 (SPSS Inc., 2010) to determine the slope, the offset, the coefficient of determination (R^2) and the standard error of estimates (SEE). The same software was used to model the BMP_{VS} as a function of the VS content [BMP_{VS} = a + (b/VS)].

Non-linear curve fitting of points representing biomethane production over the digestion period were carried out for crops (maize, miscanthus, hemp, spelt straw, and switchgrass) showing incomplete digestion, using a 3-parameters logistic function (Groot et al., 1996) with SigmaPlot 12.5 (Systat Software, 2011), to define the asymptotic value of biomethane production.

3. Results and discussion

3.1. Energy crops alternatives to maize

The measured biomass yields and BMP of the various energy crops are presented in Fig. 1, together with the calculated biomethane yields per hectare. For most crops, the TS and VS contents in the wet biomass showed similar values. It was the case for maize (32 and 30%WW), post-winter sorghum (30 and 28%WW), immature rye (18 and 17%WW), miscanthus (42 and 40%WW), sorghum (21 and 19%WW), sunflower (22 and 19%WW), post-winter maize (70 and 67%WW), and tall fescue (26 and 23%WW) (Table 1). Thus, these biomasses showed a low content in ash. The TS and VS contents were less alike for hemp (45 and 40%WW), switchgrass (63 and 58%WW), spelt grains (86 and 81%WW) and spelt straw (91 and 85%WW), these crops showing a content in ash of about 5%WW. The biomass production and the BMP were highly variable between the various plant species, but also between field replicates of each plant species. The variability of both parameters, biomass yield and BMP, resulted in a wide range of biomethane yield for each plant species. When converting crops into energy, the choice of the plant species influences the produced biomethane yield.



Fig. 1. Influence of crop species on biomass yields and volatile solids (VS) content (top), biochemical methane potentials (BMPs) (middle) and biomethane yield per hectare (bottom). The VS content is indicated by black dots. Biomass and biomethane yields are annual yields per cropped area, except for "Tall fescue (single)", which represent a single, and not cumulated, harvest. White bars represent biomass yields and BMP relative to the wet weight (WW) and grey bars represent biomass yields and BMP relative to the volatile solids. White bars and grey bars are overlaid and not cumulated bars. Error intervals represent the standard deviations of all field replicates tested for each crop.

Among the energy crops assessed in the present paper, maize harvested before the winter had the highest mean biomethane yield $(6934 \pm 1850 \text{ m}^3 \text{ ha}^{-1})$, followed by miscanthus harvested before the winter $(4468 \pm 1265 \text{ m}^3 \text{ ha}^{-1})$ and sorghum harvested before the winter $(4332 \pm 1175 \text{ m}^3 \text{ ha}^{-1})$. Based on this large assessment in the Greater Region, these two plant species were the best alternatives to maize, among the assessed biomasses, to maximise the biomethane yield per hectare of cropped area.

3.1.1. Comparison between miscanthus, sorghum and maize

The biomass yield, BMPs and biomethane yield of the specific trial where miscanthus, maize and sorghum were cropped in the same field over a two to three years period (maize and sorghum in 2009–2010, miscanthus in 2009–2011) are shown in Fig. 2. This is the first report on the biomethane yield per unit of cropped area of green miscanthus harvested in autumn and processed as silage.



Fig. 2. Influence of the harvest years (2009, 2010 and 2011) on biomass yields and volatile solids (VS) (top), biochemical methane potentials (BMPs) (middle) and biomethane yield per hectare (bottom) of miscanthus, maize and sorghum. The VS content is indicated by black dots. White bars represent biomass yields and BMPs relative to the wet weight (WW) and grey bars represent biomass yield and BMP relative to the VS. White bars and grey bars are overlaid and not cumulated bars. Error intervals represent the standard deviations of all field replicates tested for each condition. Bars holding different letters for a single parameter differ significantly (p < 0.05).

The biomass_{ww} yield of miscanthus increased over the three consecutive years after plantation of rhizomes. After the first establishment year, its biomassvs yield was higher than those of maize and sorghum, owing to its high VS content at harvest. However the BMP_{VS} of miscanthus were significantly lower than those of maize and sorghum and did not show a clear tendency to increase or decrease with the age of the crop. Excluding miscanthus plantation year (2009), the biomethane yields of the three plant species were not significantly different. However in 2010, the second year after establishment for miscanthus, this plant tend to show the highest biomethane yield on average $(5.5 \pm 1 \times 10^3 \text{ m}^3 \text{ ha}^{-1})$, as compared to maize $(5.3 \pm 1 \times 10^3 \, m^3 \, ha^{-1})$ and sorghum $(4.1 \pm 0.4 \times 10^3 \text{ m}^3 \text{ ha}^{-1})$. According to this specific field trial, miscanthus harvested in autumn is the most promising alternative to maize for anaerobic digestion, because of its higher biomassys yield, nevertheless counterweighted by a lower BMP_{VS}.

Miscanthus is usually harvested at the end of winter and is mainly recommended for combustion due to its low moisture content (Lewandowski and Heinz, 2010) and not for biomethanation (RMT Biomasse, 2009). However, low moisture content is not important for anaerobic digestion and an extended harvest window is thus available for miscanthus (Hayes, 2013). The biomass_{VS} yield is higher before the winter due to the presence of the leaves, which are mainly lost during this period (Lewandowski and Heinz, 2010). An early harvest is then advised to reach high biomass yield and improve biorefinery yields (Hayes, 2013).

While miscanthus offers high biomass yields over its lifespan when harvested at the end of winter (Gauder et al., 2012; Caslin et al., 2011), the sustainability of an autumn harvest has yet to be assessed over a long period (15–20 years). Indeed, Godin et al. (2013b) pointed out that miscanthus harvested too early in autumn might not be able to translocate its nutrients to its rhizomes and a higher fertilisation level would be needed. The detrimental effect of an early harvest in August was pointed out elsewhere (Bayern Biogas Forum, 2010). Such problems for harvest in October, when plant metabolites and nutrients are potentially translocated to the rhizomes, were neither observed nor reported so far.

Different methane production kinetics were observed between maize and miscanthus (Fig. 3). Over the digestion period in batch assays, the biomethane production was faster for maize than for miscanthus. An asymptotic plateau was reached for maize samples at the end of the digestion (42 days), whereas the tilted profile of the biomethane production curve of miscanthus indicated that the conversion of biomass to biomethane was still on-going at this time. A curve-fitting of the time points according to a 3-parameters sigmoidal model (Groot et al., 1996) showed that for maize the calculated asymptotic BMP value ($115 \pm 7 \text{ mL gWW}^{-1}$) was similar to the measured value ($115 \pm 8 \text{ mL gWW}^{-1}$), whereas for miscanthus, the calculated asymptotic BMP value ($166 \pm 20 \text{ mL gWW}^{-1}$) was higher than the measured BMP ($110 \pm 10 \text{ mL gWW}^{-1}$).

The chemical composition of miscanthus, maize and sorghum samples of the present study was characterised in a previous paper (Godin et al., 2013b). Miscanthus presents higher contents of structural compounds compared to maize and sorghum. The slow methane production kinetic of miscanthus, as compared to maize, can be explained by the lignocellulosic composition of the biomass. Cellulose fibres are tightly linked to other polymers, such as hemicellulose and lignin and are difficult to degrade (Tsavkelova and Netrusov, 2012). Consequently, it is highly probable that the BMP and biomethane yield per cropped area of miscanthus would be higher if this substrate was exposed to long digestion time. Such long digestion times (longer than 100 days) are commonly

observed in agricultural anaerobic digestion plants (Linke et al., 2013).

Some authors (Triolo et al., 2011; Buffiere et al., 2006) reported that the lignocellulosic fraction of biomass is negatively correlated with the BMP_{VS} and that lignin is the principal substance that limit the conversion of VS to methane. The high amount of lignocellulosic components within the biochemical composition of the biomass induces a slow methane production kinetic than can explain the lower BMP_{VS} measured after 42 days of digestion for miscanthus, as compared to maize and sorghum.

Miscanthus, a perennial plant which can thrive up to 15–20 years, looks like a promising alternative to the annual cropping of maize for biomethane production, if harvested before the winter.

3.1.2. Influence of wintering on biomethane yield of maize and sorghum

The effect of a longer cropping period on the biomethane yield was assessed for some maize and sorghum plots that were left in the field over the winter period (Fig. 1). Biomethane yields of these plots (maize: 3441 ± 1341 m³ ha⁻¹, sorghum: 1287 ± 330 m³ ha⁻¹) were significantly (p < 0.05) lower than those obtained for the plots harvested in autumn. Maize and sorghum harvested after the winter have a higher VS content but a lower biomass_{VS} yield than those harvested in autumn. The anaerobic digestibility of the post-winter sorghum was significantly lower (p < 0.05) than that of autumn green mater. In case of maize, the lower BMP_{VS} for the post-winter harvest was not significant (p = 0.21). The biomass composition at the end of the winter showed higher structural compounds (hemicellulose, cellulose and lignin) and less soluble sugars and proteins (Godin et al., 2013a). A higher proportion of starch was found in maize after winter. Leaves were lost during the winter for both plant species. The solubilisation and the leaching of the nonstructural components during the winter (Cadoux et al., 2009) can also explain the loss of digestible material. The stalks with cobs and some leaves were harvested in the case of maize whereas sorghum stalks suffered from lodging and were found on the ground. The physiological changes and the different biochemical composition of biomass before and after the winter can explain the difference of biomass yield and BMP.

Miscanthus was not harvested after the winter in the present study. However, the BMP_{VS} of miscanthus harvested after the winter was described as low (84 mL gVS⁻¹) and the use of steam-explosion was suggested to improve the biomethane production of miscanthus (Menardo et al., 2012). The BMP_{VS} of miscanthus



Fig. 3. Comparison of CH_4 production kinetics during biochemical methane potential (BMP) assays between maize and miscanthus silages. A 3-parameter logistic regression (Groot et al., 1996) was used to fit a curve on the cumulated biomethane production over time and determine the asymptotic BMP value relative to the wet weight (WW). The results are expressed as average ± standard deviation. The number of samples is indicated in brackets.



Fig. 4. Influence of the volatile solids (VS) content of silage on the biochemical methane potential relative to the wet weight (BMP_{WW}, top) and relative to the volatile solids content (BMP_{VS}, bottom). Miscanthus samples (oblique crosses) were grouped and differentiated according to the harvest year (2009: open, 2010: grey, 2011: black). BMP: biochemical methane potential, WW: wet weight.

harvested before the winter and measured in the present study (higher than 200 mL gVS⁻¹, Fig. 2) was higher than that reported by Menardo for post-winter harvest. As for maize and sorghum, an increase in the fibre fraction (cellulose, hemicellulose and lignin), balanced with a decrease in total soluble sugars and proteins, impacted negatively the miscanthus digestibility from October to April (Godin et al., 2013b). It can be hypothesised that an earlier harvest of miscanthus than what was performed in the present trials could provide miscanthus with better digestibility.

3.1.3. Switchgrass

Similarly to miscanthus, switchgrass is usually harvested after the winter to be valorised through combustion. In the present study, switchgrass was harvested early, in autumn. As illustrated in Fig. 1, switchgrass provided low biomass yields and the lowest BMP among the plant species assessed, resulting in very low biomethane yields.

The BMP_{VS} were similar to the ones reported by Massé et al. (2010). Godin et al. (2013b) observed that switchgrass samples harvested in autumn have no soluble sugars and a similar fibre part as compared to miscanthus harvested in autumn. The low BMP_{VS} of

switchgrass can be explained by the high proportion of poorly digestible lignocellulosic fibres.

The biomass_{VS} yields of switchgrass observed in the present trial were lower than in other trials (Massé et al., 2010). Switchgrass was sown in 2009 and showed a low germination potential of 33% compensated by an adjusted sowing rate (ENERBIOM, 2012). Moreover, herbicide application at the beginning of the trial to control weeds was not as efficient as in other crop. The establishment and biomass production of switchgrass was then poor. Therefore, the biomass yield of switchgrass presented here is not representative of the full potential of this plant for its use as an energy crop. Massé et al. (2010) reported a maximum annual dry biomass yield of 12 t ha⁻¹. However the biomass yield of switchgrass, which could result from such a biomass yield and from its digestibility measured here, is not competitive as compared to the measured biomethane yield of maize silages.

3.2. Anaerobic digestibility of plant materials

The influence of the VS content of various ensiled plant materials on the measured BMP is presented in Fig. 4 and in Table 3.

Table 3

Parameters of the regressions between the volatile solids content (VS) and (A, linear) the biochemical methane potential relative to the wet weight (BMP_{WW}) or (B, non-linear) relative to the volatile solids content (BMP_{VS}) .

Plant species	Ν	Sl	ope l	ntercept	R^2	SEE
(A) BMPWW = Slope * VS + Intercept						
All	972	2 2.	7	36	0.80	21
Hemp	3	3 14	4.1	-499	0.81	17
Immature rye	28	3 2.	3	45	0.25	7
Maize	459	3.	3	25	0.76	12
Maize (post-winter)	8	3 2.	7	64	0.51	13
Miscanthus	26	6 0.	8	67	0.05	14
Sorghum	50) 2.	7	28	0.71	8
Sorghum (post-winter)	8	3 2.	5	27	0.86	3
Spelt (grain)	23	B 0.	8	233	0.10	7
Spelt (straw)	25	5 —	3.0	514	0.02	28
Spelt (whole plant)	23	3 –	0.2	298	0.01	14
Sunflower	12	2 2.	8	22	0.82	4
Switchgrass	23	31.	7	13	0.68	14
Tall fescue (single)	307	7 2.	5	37	0.72	9
Plant species	Ν	а	b	a + (b/100)	R^2	SEE
Plant species (B) $BMP_{VS} = a + (b/VS)$	Ν	а	b	a + (b/100)	<i>R</i> ²	SEE
Plant species (B) $BMP_{VS} = a + (b/VS)$ All	N 995	a 291	b 2915	a + (b/100) 320	R ²	SEE 56
Plant species (B) $BMP_{VS} = a + (b/VS)$ All Hemp	N 995 3	a 291 1439	b 2915 51,078	a + (b/100) 320 1949	R ² 0.35 0.77	SEE 56 39
Plant species (B) $BMP_{VS} = a + (b/VS)$ All Hemp Immature rye	N 995 3 28	a 291 1439 250	b 2915 51,078 4204	a + (b/100) 320 1949 292	R ² 0.35 0.77 0.30	SEE 56 39 42
Plant species $(B) BMP_{VS} = a + (b/VS)$ AllHempImmature ryeMaize	N 995 3 28 459	a 291 1439 250 348	b 2915 51,078 4204 1950	a + (b/100) 320 1949 292 367	R ² 0.35 0.77 0.30 0.12	SEE 56 39 42 41
Plant species $(B) BMP_{VS} = a + (b/VS)$ AllHempImmature ryeMaizeMaize (post-winter)	N 995 3 28 459 8	a 291 1439 250 348 285	b 2915 51,078 4204 1950 5030	a + (b/100) 320 1949 292 367 335	R ² 0.35 0.77 0.30 0.12 0.09	SEE 56 39 42 41 19
Plant species (B) BMP _{VS} = a + (b/VS) All Hemp Immature rye Maize Maize (post-winter) Miscanthus	N 995 3 28 459 8 26	a 291 1439 250 348 285 106	<i>b</i> 2915 51,078 4204 1950 5030 5786	a + (b/100) 320 1949 292 367 335 164	R ² 0.35 0.77 0.30 0.12 0.09 0.12	SEE 56 39 42 41 19 37
Plant species (B) BMP _{VS} = a + (b/VS) All Hemp Immature rye Maize Maize (post-winter) Miscanthus Sorghum	N 995 3 28 459 8 26 50	a 291 1439 250 348 285 106 299	<i>b</i> 2915 51,078 4204 1950 5030 5786 2170	a + (b/100) 320 1949 292 367 335 164 321	R ² 0.35 0.77 0.30 0.12 0.09 0.12 0.28	SEE 56 39 42 41 19 37 41
Plant species (B) BMP _{VS} = a + (b/VS) All Hemp Immature rye Maize Maize (post-winter) Miscanthus Sorghum Sorghum (post-winter)	N 995 3 28 459 8 26 50 8	a 291 1439 250 348 285 106 299 302	<i>b</i> 2915 51,078 4204 1950 5030 5786 2170 1233	a + (b/100) 320 1949 292 367 335 164 321 314	R ² 0.35 0.77 0.30 0.12 0.09 0.12 0.28 0.05	SEE 56 39 42 41 19 37 41 18
Plant species (B) BMP _{VS} = a + (b/VS) All Hemp Immature rye Maize Maize (post-winter) Miscanthus Sorghum Sorghum (post-winter) Spelt (grain)	N 995 3 28 459 8 26 50 8 23	a 291 1439 250 348 285 106 299 302 80	<i>b</i> 2915 51,078 4204 1950 5030 5786 2170 1233 23,549	a + (b/100) 320 1949 292 367 335 164 321 314 315	R ² 0.35 0.77 0.30 0.12 0.09 0.12 0.28 0.05 0.55	SEE 56 39 42 41 19 37 41 18 8
Plant species (B) BMP _{VS} = a + (b/VS) All Hemp Immature rye Maize Maize (post-winter) Miscanthus Sorghum Sorghum (post-winter) Spelt (grain) Spelt (straw)	N 995 3 28 459 8 26 50 8 23 25	a 291 1439 250 348 285 106 299 302 80 -258	<i>b</i> 2915 51,078 4204 1950 5030 5786 2170 1233 23,549 48,170	a + (b/100) 320 1949 292 367 335 164 321 314 315 224	R ² 0.35 0.77 0.30 0.12 0.09 0.12 0.28 0.05 0.55 0.08	SEE 56 39 42 41 19 37 41 18 8 33
Plant species (B) BMP _{VS} = a + (b/VS) All Hemp Immature rye Maize Maize (post-winter) Miscanthus Sorghum Sorghum (post-winter) Spelt (grain) Spelt (straw) Spelt (whole plant)	N 995 3 28 459 8 26 50 8 23 25 23	a 291 1439 250 348 285 106 299 302 80 -258 -19	b 2915 51,078 4204 1950 5030 5786 2170 1233 23,549 48,170 29,905	a + (b/100) 320 1949 292 367 335 164 321 314 315 224 280	R ² 0.35 0.77 0.30 0.12 0.09 0.12 0.28 0.05 0.55 0.08 0.19	SEE 56 39 42 41 19 37 41 18 8 33 16
Plant species (B) BMP _{VS} = a + (b/VS) All Hemp Immature rye Maize Maize (post-winter) Miscanthus Sorghum Sorghum (post-winter) Spelt (grain) Spelt (straw) Spelt (whole plant) Sunflower	N 995 3 28 459 8 26 50 8 23 25 23 12	a 291 1439 250 348 285 106 299 302 80 -258 -19 279	b 2915 51,078 4204 1950 5030 5786 2170 1233 23,549 48,170 29,905 2196	a + (b/100) 320 1949 292 367 335 164 321 314 315 224 280 301	R ² 0.35 0.77 0.30 0.12 0.09 0.12 0.28 0.05 0.55 0.08 0.19 0.51	SEE 56 39 42 41 19 37 41 18 8 33 16 18
Plant species (B) BMP _{VS} = a + (b/VS) All Hemp Immature rye Maize Maize (post-winter) Miscanthus Sorghum Sorghum (post-winter) Spelt (grain) Spelt (straw) Spelt (whole plant) Sunflower Switchgrass	N 995 3 28 459 8 26 50 8 23 25 23 12 23	a 291 1439 250 348 285 106 299 302 80 -258 -19 279 166	b 2915 51,078 4204 1950 5030 5786 2170 1233 23,549 48,170 29,905 2196 1815	a + (b/100) 320 1949 292 367 335 164 321 314 315 224 280 301 184	R ² 0.35 0.77 0.30 0.12 0.09 0.12 0.28 0.55 0.55 0.58 0.19 0.51 0.09	SEE 56 39 42 41 19 37 41 18 8 33 16 18 23 23

N, number of samples; R^2 , coefficient of determination; SEE, standard error of estimates.

Samples of miscanthus, switchgrass, hemp and spelt straw have lower BMP_{WW} than other samples included in the main linear scatterplot (Fig. 4). Since the VS content is responsible for the methane production, the BMP_{WW} was modelled from the VS content according to a linear function crossing the axis origins. When excluding miscanthus, switchgrass, hemp, spelt straw and spelt whole plant samples, the BMP_{WW} increases linearly with VS content according to a mean slope of $395 \pm 2 \text{ mL}_{CH_4} \text{ gVS}^{-1}$ (R^2 of 0.89) (Fig. 4, top). For most of the tested biomasses, the organic matter conversion yield seems quite constant.

Miscanthus, switchgrass, hemp and spelt straw have lower digestibilities than other plant species (Fig. 4). Moreover, the biomethane production curves over the digestion period of those plant species (not shown) were very similar to that of miscanthus (Fig. 3) while the other samples were similar to maize. Hemp, spelt straw and switch grass have measured BMP_{WW} of 90 ± 27, 258 ± 28 and $117 \pm 24 \text{ mL gWW}^{-1}$ respectively, whereas those biomasses have higher asymptotic BMP_{WW} of 100 ± 25 , 332 ± 56 and $153 \pm 21 \text{ mL gWW}^{-1}$ respectively, calculated from the curve fittings. Those biomasses have high levels of structural compounds (lignocellulosic fibres) within their biochemical composition, as compared to tall fescue, immature rye and maize, which were characterised by higher amount of total soluble sugars, proteins and starch (Godin et al., 2013b). The conversion of the VS into methane was thus affected by the VS composition and its ability to be digested. For such plant species with high fibrous content, the digestion of the VS content was slow and not fully completed after 42 days of anaerobic digestion. Longer digestion period should be recommended to assess the BMP of biomass characterised by high fibre fractions.

The BMP_{VS} tend to decrease when the VS content increases (Fig. 4 and Table 3, bottom). Anaerobic biodegradation of the organic material is more advanced for plant with a low VS content than for plant species with a high VS content. The VS content increased over the cropping period and can be related to the maturity of the plant for tall fescue (data not shown) and maize (Mayer et al., 2014). It has been shown that the structural compounds of most plant species increase with maturity (Godin et al., 2013a). The VS content is thus correlated with the biochemical composition of the plant, especially the less digestible fraction (fibres). For most biomasses, the digestibility decrease can be related with increasing maturity and the corresponding increase of structural components in the biomass.

Grains of spelt are characterised by a high amount of starch in the endosperm, which is surrounded by outer layers showing a composition similar to straw (Shewry et al., 2013). Such a composition explains the higher digestibility of grains compared to straw, at a high VS content.

3.3. Prediction of the biomethane yield and the BMP

3.3.1. Bmp

Linear regressions between the VS content and the BMP were determined for all and each plant species (Table 3 and Fig. 4). Owing to the good correlation and low SEE observed for all plant species tested together ($R^2 = 0.80$, SEE = 21 mL gWW⁻¹), the VS content of a biomass can be used to predict its BMP_{WW}. However, this result is mostly valid for maize and tall fescue since it is highly influenced by their large number of samples (maize: N = 459, and tall fescue: N = 307), as compared to other plant species. The samples were also mostly distributed in a range where the VS content is less than 45%WW. Such a distribution gives better prediction results for plant species having VS in this range. Nevertheless, the prediction of BMP_{WW} using the VS content showed good results for most plant species assessed individually, as shown by the SEE values. The low coefficient of determination for miscanthus, spelt and immature rye indicates that the BMP_{WW} was less influenced by their VS content than for the other biomasses. Such results can be explained by a low variability of the digestibility between the biomasses as seen above. Relationships specific to a plant can also be used, paying attention to the regression coefficient, sample number and the SEE, that are variable according to the plant species (Table 3).

Since the BMP_{WW} can be modelled with a first-order linear regression using the VS content as predictor (BMP_{WW} = a * VS + b) and considering that the BMP_{VS} is the ratio between the BMP_{WW} and the VS content (BMP_{VS} = BMP_{WW}/VS), the BMP_{VS} can be modelled as BMP_{VS} = a + (b/VS) using the VS content as the only predictor. With such a model, the asymptotic value equal to a + (b/100) corresponds to the minimum digestibility of the plant species.

However, the VS content alone was not a good predictor to measure the BMP_{VS}, according to low R^2 values (Table 3 and Fig. 4). Moreover, regressions for hemp or spelt are not realistic due to the low number of samples or to the data distribution that does not fit to such model.

Other mathematical models using the VS as a predictor have been tested to predict the BMP_{VS} , but they did not improve the prediction results (data not shown). Other parameters than the VS content are thus required to predict adequately the BMP_{VS} of energy crops. Some authors succeeded to characterise BMP_{VS} as the result of linear relations between the different biochemical fractions for different biomass (Nallathambi Gunaseelan, 2007; Amon et al., 2007; Raju et al., 2011). Such models allow for the prediction of the BMP_{VS} from biochemical analysis, with some uncertainty. Analysis of the VS composition would thus be needed to predict accurately the BMP_{VS} of biomasses.



Fig. 5. Influence of the biomass yield relative to the wet weight (biomass_{WW} yield, top) and relative to the volatile solids content (biomass_{VS} yield, bottom) on the biomethane yield per hectare for the various crops studied. Miscanthus samples (oblique crosses) were grouped and differentiated according to the harvest year (2009: open, 2010: grey, 2011: black).

3.3.2. Biomethane yield

The influence of the biomass yields (both biomass_{WW} and biomass_{VS} yields) on the biomethane yield per hectare is presented in Fig. 5 and in Table 4. A relationship can be observed between the biomass_{WW} yields and the biomethane yield. The biomass_{WW} yield variability explains 87% of the variability of the biomethane yield. Since the moisture contained in the biomass does not contribute to the production of methane, the influence of the biomass_{VS} yield on the biomethane yield was also characterised. When considering all plant species together, the biomass_{VS} yield explains a larger part ($R^2 = 0.94$) of the variability of the biomethane yield, as compared to the biomass_{WW} yield.

Relationships between the biomass yield and the biomethane yield were further characterised specifically according to the plant species (Table 4). The lowest values of SEE for the local linear regressions showed that local assessments (plant species specific) describe better the influence of the biomass yield on the biomethane yield than the global linear regression (all plant species considered).

Linear regressions using only the biomass_{VS} yield as independent variable allow good predictions of the biomethane yield of the various biomasses. Miscanthus ($R^2 = 0.78$) and switchgrass ($R^2 = 0.40$) show coefficient of determination lower than 0.80 for the linear regression between the biomass_{VS} yield and the biomethane yield. The removal of only one outlier in each dataset increased the R^2 value to 0.89 and 0.73 for miscanthus and switchgrass respectively.

The amount of biomass, especially considered on a dry matter basis, produced in the field appears to be the main factor driving the biomethane yield. This conclusion has possibly to be adjusted

Table 4

Parameters of the linear regressions between the biomethane yield and (A) the produced biomass yield relative to the wet weight (biomass_{WW}) or (B) relative to the volatile solids content (biomass_{VS}).

Plant species	Ν	Slope	Intercept	R^2	SEE		
(A) Biomethane yield = Slope * biomass _{ww} yield + Intercept							
All	954	108	240	0.87	1099		
Hemp	3	124	-529	0.99	130		
Immature rye	28	72	67	0.98	50		
Maize	459	80	2309	0.61	1134		
Maize (post-winter)	5	291	-612	0.99	185		
Miscanthus	21	115	-434	0.91	382		
Sorghum	40	84	113	0.63	723		
Sorghum (post-winter)	8	99	-53	0.92	110		
Spelt (grain)	23	305	-15	0.99	30		
Spelt (straw)	25	241	54	0.92	99		
Spelt (whole plant)	23	269	105	0.95	115		
Sunflower	11	57	889	0.56	389		
Switchgrass	23	32	859	0.23	156		
Tall fescue (single)	267	74	150	0.94	190		
Tall fescue (annual)	18	84	107	0.98	237		
(B) Biomethane yield = Slope $*$ biomass _{VS} yield + Intercept							
All	912	410	-61	0.94	756		
Hemp	3	281	-416	0.99	191		
Immature rye	28	490	22	0.96	72		
Maize	458	433	-277	0.83	743		
Maize (post-winter)	5	371	-116	0.96	297		
Miscanthus	21	234	340	0.78	612		
Sorghum	40	357	496	0.86	440		
Sorghum (post-winter)	8	314	133	0.99	38		
Spelt (grain)	23	358	17	0.98	46		
Spelt (straw)	25	278	55	0.92	102		
Spelt (whole plant)	23	313	132	0.90	163		
Sunflower	11	320	666	0.92	172		
Switchgrass	23	112	520	0.40	138		
Tall fescue (single)	267	442	-27	0.92	213		
Tall fescue (annual)	18	473	-302	0.97	277		

N, number of samples; R^2 , coefficient of determination; SEE, standard error of estimate.

by considering that the net energy output from the biomethanation of an energy crop decreases with increasing water content because of higher energy investment in harvest and transportation of undesirable water (Berglund and Börjesson, 2006). In this perspective, miscanthus could have a comparative advantage to maize thanks to its higher VS content.

Whereas the BMP was extensively assessed for various biomasses (Bauer et al., 2009; Amon et al., 2007; Raposo et al., 2012), the present paper shows that the anaerobic digestibility influences the biomethane yield but does not appear to be of prior importance to reach high biomethane yield per cropped area. The choice of an energy crop dedicated to biomethane production should thus be driven by the main criterion of biomass_{VS} yield. However, the agricultural practices (annual vs perennial crops, planting vs sowing, single or multiple harvest per year, harvest and transport, water needs, pesticide use, etc.) which are specific to plant species must also be considered when assessing the energy and resource efficiency and the environmental benefit of a biomass-for-energy production system (Börjesson and Berglund, 2007).

4. Conclusion

Crops with high biomass yield should be preferred for biomethane production. The BMP is influenced by the biochemical composition of the biomass but has low influence on the biomethane yield ha⁻¹. Miscanthus silage harvested in autumn produces high and competitive biomethane yield, as compared to maize. A conversion yield of $395 \pm 2 \text{ mL gVS}^{-1}$ was observed for most plant biomasses, except for the most fibrous and poorly digestible ones. The VS content and the biomass_{VS} yield ha⁻¹ provide sufficient information to estimate the BMP and biomethane yield of known plant species.

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