NRC Publications Archive
Archives des publications du CNRC

Enhancing solubilisation and methane production kinetic of switchgrass by microwave pretreatment

Jackowiak, D.; Frigon, J.C.; Ribeiro, T.; Pauss, A.; Guiot, S.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.
For the publisher's version, please access the DOI link below./ Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:
https://doi.org/10.1016/j.biortech.2010.11.069
Bioresource Technology, 102, 3, pp. 3535-3540, 2011-02-01

NRC Publications Record / Notice d'Archives des publications de CNRC:
https://nrc-publications.canada.ca/eng/view/object/?id=60e3a60b-e386-4c54-9104-9cd7c5080b3(
https://publications-cnrc.canada.ca/fra/voir/objet/?id=60e3a60b-e386-4c54-9104-9cd7c5080b30

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at
https://nrc-publications.canada.ca/eng/copyright
READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site
https://publications-cnrc.canada.ca/fra/droits
LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at
PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

National Research Council Canada | Conseil national de recherches Canada

Bioresource Technology 102 (2011) 3535–3540

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Enhancing solubilisation and methane production kinetic of switchgrass by microwave pretreatment

D. Jackowiak [a,b], J.C. Frigon [c], T. Ribeiro [a], A. Pauss [b,*], S. Guiot [c]

[a] Institut Polytechnique LaSalle Beauvais, 19 rue Pierre Waguet, 60026 Beauvais, France
[b] Université Technologique de Compiègne, rue Personne de Roberval, 60319 Compiègne, France
[c] National Research Council Canada, 6100 Royalmount, Montreal, Canada H4P 2R2

A R T I C L E I N F O

Article history:
Received 18 August 2010
Received in revised form 14 November 2010
Accepted 16 November 2010
Available online 26 November 2010

Keywords:
Pretreatment
Lignocellulose
Digestibility
Microwave
Anaerobic digestion

A B S T R A C T

This study investigated the effects of microwave pretreatment of switchgrass in order to enhance its anaerobic digestibility. Response surface analysis was applied to screen the effects of temperature and time of microwave pretreatment on matter solubilisation. The composite design showed that only temperature had a significant effect on solubilisation level. Then the effects of the microwave pretreatment were correlated to the pretreatment temperature. The sCOD/tCOD ratio was equal to 9.4% at 90 °C and increased until 13.8% at 180 °C. The BMP assays of 42 days showed that microwave pretreatment induced no change on the ultimate volume of methane but had an interesting effect on the reaction kinetic. Indeed, the time required to reach 80% of ultimate volume CH_4 is reduced by 4.5 days at 150 °C using the microwave pretreatment.

© 2010 Elsevier Ltd. All rights reserved.

1. Introduction

Anaerobic digestion is an efficient process both for the treatment of waste and the energy recovery. Most of the biogas plants are using substrates such as sludges, industrial wastes or manures. However, the use of energy crops grows up (Bruni et al., 2010). For the past 20 years, US and Europe have a increased interest in the use of perennial grasses. In 1990s the US Department of Energy focused on switchgrass (*Panicum vergatum*) as the crop model in the Bioenergy Feedstock Development Program (Lewandowski et al., 2003). This choice was motivated by different factors such as the high yielding of switchgrass (13–18 tons per hectare per year in Southeastern United States). Switchgrass is a warm-season perennial grass, has a tolerance to heat and cold, has a low water and nutritional requirement, can grow to more than 2.75 m in height, has extensive root system which allows it to tolerate poor soils, and finally has a high resistance to naturally occurring pest and diseases. As a perennial grass, switchgrass need only be planted once every 10 years or more, but can be harvested annually using conventional hay equipment. In Europe, research on perennial grasses as a crop for bioenergy was focused on *Miscanthus* but showed some limitations such as its high price for establishment (Casler et al., 2007; Jensen et al., 2007; Keshwani and Cheng, 2009, 2010).

The structure and composition of lignocellulosic biomass, which include switchgrass, is one of the critical points to use this material in anaerobic digestion to produce methane. Indeed, lignocellulosic material is constituted by three polymers closely linked which are cellulose, hemicellulose and lignin (Hendriks and Zeeman, 2009). The presence of lignin in this structure forms a physical barrier and induces a non-productive adsorption of enzyme (Zhu and Pan, 2010). Therefore, a pretreatment is needed to disrupt the lignocellulosic biomass structure in order to increase the accessibility to cellulose and thus its biodegradability. A large spectrum of methods was studied in literature. These pretreatment can be physical (mechanical, thermal, *etc.*), chemical (ozonolysis, acid hydrolysis, alkaline hydrolysis, *etc.*), biological (fungi, enzymatic hydrolysis, *etc.*) or combination of them (Adel et al., 2010; Fernandes et al., 2009; Mosier et al., 2005; Sun and Cheng, 2002). The efficiency of a pretreatment can be evaluated by the induced matter solubilisation, the increase of anaerobic biodegradability and its cost.

This paper deals with one of the thermal pretreatment: microwave. In microwave processing, energy is supplied by an electromagnetic field directly to the material. This results in rapid heating throughout the material thickness with reduced thermal gradients. Volumetric heating can also reduce processing times and save energy. The microwave field and the dielectric response of a material govern its ability to heat with microwave energy (Thostenson and Chou, 1999).

Microwave is thus an alternative method for conventional heating and can give better results than classical thermal pretreatment.

* Corresponding author. Tel.: +33 3 44 23 44 57; fax: +33 3 44 23 52 16.
E-mail address: andre.pauss@utc.fr (A. Pauss).

0960-8524/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.biortech.2010.11.069

NRCC 53341

However, microwave pretreatment has thermal effects on matter. So it is important to take care to the production of inhibitors induced by heating, such as phenolic compounds and furfural. Indeed, a biomass treatment by high temperature liquid water induces hydrolysis of hemicellulose in monomers including xylose which decomposes into furfural which is inhibitor for anaerobic digestion (Qi and Xiuyang, 2007). Ximenes et al. have studied the effects on cellulases activity of phenols released during lignocellulosic biomass pretreatment and observed an inhibition induced by phenolic compounds (Ximenes et al., 2010).

It is important to keep in mind that compound toxicity depends on many parameters including toxicant concentration, biomass concentration, toxicant exposition time and acclimation of bacteria (Chen et al., 2008).

Based on the existing knowledges about pretreatments, including knowledge about pretreatment of lignocellulosic biomass and sludge, the aim of this study is to determine the efficiency of microwave pretreatment on switchgrass by evaluating its impact on matter solubilisation and anaerobic biodegradability.

2. Methods

2.1. Raw materials and sample preparation

The switchgrass, a Kanlow variety, was obtained from a 12 years old field yielding 10–12 tons per hectare per year. It was harvested during September 2009 while it was mature and still fully green, cut in pieces of approximately 10 cm and compressed in 10 L pails which were then flushed with N_2. It contained around 69% humidity. Characterization of switchgrass is shown in Table 1.

Before microwave pretreatment, switchgrass was either cut in pieces of 1 cm or grinded during 30 s with a knives mill Grindomix model GM200 (Retsche, Newton, PA), with blades spinning at 5000 rpm.

2.2. Microwave pretreatment

Samples for microwave pretreatment consisted in 5 g of cut or grinded switchgrass and 40 mL of distilled water. Samples were irradiated in a closed-vessel microwave accelerated reaction system (MARS-5, CEM, US) which run at 2450 MHz, the power range was between 400 and 1600 W, the maximum temperature and pressure were 260 °C and 33 bars. It was equipped with a turning carousel with a maximum of 12 vessels (XP-1500) of 100 ml each, with pressure and temperature probes. After target temperature was reached, the temperature was hold during a specify time, then cooled down until 90 °C. The liquid and solid fractions of samples were separated by centrifuging at 10,000g for 10 min in a J2-21M centrifuge (Beckmann, Canada) and then stored at 4 °C.

2.3. Experimental design

The first step of this study was to screen the effects of temperature and exposition time of microwave pretreatment by the use of a composite design. Response surface analysis was used to represent the linkage between the responses (pH, sCOD/tCOD, glucose and phenolic acids) and experimental variables (temperature and the exposition time at temperature targeted). This relationship can be written as function of variables,

$$Y = a_0 + a_1 \cdot X_1 + a_2 \cdot X_2 + a_{12} \cdot X_1 \cdot X_2 + a_{11} \cdot X_1^2 + a_{22} \cdot X_2^2 \qquad (1)$$

where Y is the response (pH, sCOD/tCOD, glucose or phenolic acids), X_1 and X_2, respectively temperature and exposition time, a_0, a_1, a_2, a_{12}, a_{11}, a_{22} are coefficients. The method of least squares was used to estimate the coefficients. The coded and real values used in the experimental design are given in Table 2.

2.4. Biochemical methane potential test

The methane potential assays with the switchgrass were prepared based on the biochemical methane potential (BMP) assay for wastewater from Cornacchio et al. (1986). A few modifications were done to adapt the test to solid samples. The inoculum which was composed by sewage sludges, was starved for 48 h prior to the start-up of the assays, by being incubated at 35 °C and 100 rpm agitation with no substrate. The bottles were prepared anaerobically in duplicates in 500 mL serum bottles and filled under a constant nitrogen flow. Each bottle received 20 g of inoculum, 6 mL of complemented medium, 4 mL of bicarbonate buffer and 0.5 mL of reducing agent. The amount of substrate added was 5 g of pretreated switchgrass with 40 mL of distilled water in microwave. The volume of the bottles was completed at 100 mL with distilled water. The bottles were incubated at 35 °C with an agitation of 100 rpm. Control bottles were prepared to allow the removal of endogenous methane production from the assays. The control bottles were identical to the test bottles, except that switchgrass suspension was replaced with the same volume of distilled water. The assays were conducted until the methane production became negligible (<3 mL CH_4/day) as performed by Lehtomaki et al. (2008).

2.5. Analyses

To evaluate the physico-chemical changes in samples, measurement of pH, total organic carbon (TOC), total nitrogen (Nt), phosphorus, iron, chemical oxygen demand (COD), volatile suspended solids (VSS), volatile dissolved solids (VDS) and total volatile solids (TVS) were determined according to standard methods (APHA, 2005).

The soluble COD (sCOD) of switchgrass sample dissolved in distilled water, was equal to zero before the microwave pretreatment. The sCOD was compared to the total COD (tCOD) to determine the solubilisation ratio of matter, by the following formula:

$$\text{COD solubilisation} = (\text{sCOD after microwave treatment}/\text{tCOD of raw matter}) \times 100. \qquad (2)$$

Glucose, cellobiose and xylose were monitored using an HPLC from Waters consisting of a pump model 600 and an autosampler model 717 Plus equipped with a refractive index detector from

Table 1
Characteristics of switchgrass.

Parameters	Values
Total solid (TS, % of raw material)	30.99 ± 1.74
Total volatile solid (TVS, % of raw material)	29.20 ± 1.01
Total organic carbon (TOC, mg/kg)	430,000 ± 6.9%
Total nitrogen Kjeldahl (Nt, mg/kg)	9900 ± 4%
Phosphorus (P, mg/kg)	2300 ± 2%
Iron (Fe, mg/kg)	58 ± 5%
Chemical oxygen demand (COD, mg/g)	350 ± 40

Table 2
Coded units used in the composite design.

Coded unit	True value	
	Temperature (°C)	Time (min)
−1.21	84	7′54
−1	90	10
0	120	20
1	150	30
1.21	156	32′06

Waters (model 2414). The column used for the separation is a Supelcogel Pb (300 × 7.8 mm OD). The mobile phase is distilled water at 0.5 mL/min. Analysis is carried out at 80 °C.

Measurement of phenolics was made on an Agilent HPLC consisting of a quaternary pump model G1311A and an autosampler model G1329A equipped with a DAD detector model G1315A. 10 μL was injected on a reverse phase HPLC column Gemini-NX C18 3 μm from Phenomenex of 4.6 × 150 mm maintained at 40 °C. A methanol gradient from 10% to 20% during 35 min then up to 60% for 25 min was performed at a flow rate of 0.5 ml/minutes. The other mobile phase was H_3PO_4 0.027 N. Phenolics were quantified at 280 nm. Neat compounds were obtained from Sigma–Aldrich: 4-hydroxybenzoic acid, 4-hydroxybenzaldehyde, vanillic acid, caffeic acid, vanillin, syringic acid, syringaldehyde, acetovanillone, p-coumaric acid, acetosyringone, ferulic acid, sinapic acid, trans-cinnamic acid. Prior to analysis standards and samples were acidified to pH 2 with HCl.

The biogas production was measured in the serum bottles with a water-displacement system. After equilibrium of the bottle headspace to 1 atm, a gas sample (0.3 mL) was taken with a model 1750 gas-tight syringe (Hamilton, Reno, USA) and analyzed for H_2, N_2, CH_4 and CO_2 by gas chromatography (GC). The GC was a Agilent 6890 (Agilent Technologies, Wilmington, USA) coupled to a thermal conductivity detector (TCD). The gas sample was injected on a 11 m × 2 mm I.D. Chromosorb 102 packed column (Supelco, Bellafonte, USA). The column was heated at 50 °C and argon was used as the carrier gas. The injector and detector were maintained at 125 and 150 °C, respectively.

3. Results and discussion

3.1. Effects of temperature and exposition time on matter solubilisation

The aim of the first step was to define the effects of microwave irradiation on matter solubilisation and to study the efficiency of temperature and exposition time. The effects of microwave pretreatment on matter solubilisation were investigated with a composite experimental design (Goupy, 2000).

Temperature and time profiles are shown in Table 3 with the associated responses which are pH of the supernatant, sCOD/tCOD ratio, and also glucose and phenolic acids in supernatant. Results were correlated as function of temperature and time (Eq. (1), Table 4) and represented with response surfaces (Fig. 1A).

The correlation coefficient (R^2) for pH, sCOD/tCOD ratio, glucose and phenolic acids was 0.99, 0.96, 0.98 and 0.91, respectively. Table 4 gives the relative importance between temperature and time. The weighting of time represents 4%, 7%, 18% and 3% of temperature weighting for pH, sCOD/tCOD, glucose and phenolic acids, respectively. Moreover, with the study of the *p*-value at a 5% threshold, it appeared that only the temperature gave significant responses. The small significance of time parameter could be explained by the fact that this parameter was the exposition time at desired temperature, but did not include the time of ramp temperature and time of cooling down to reach 90 °C.

To conclude, this experimental design showed that time had non-significant importance against temperature and then results could be represented as function of temperature only (Fig. 1B). This conclusion was also found in others works. According to Hu and Wen, the pretreatment time on enzymatic digestibility of switchgrass after a microwave-assisted alkali pretreatment has almost no effect. The yields of xylose, glucose and total sugars remained at almost constant level at a temperature of 190 °C for different durations between 5 and 40 min (Hu and Wen, 2008). In studies done on other matters especially on waste active sludge, the main parameter for classical thermal treatment is temperature also. It is reporting that exposition time has less influence (Bougrier et al., 2007).

Microwave treatment on switchgrass led to changes of the physico–chemical characteristics of switchgrass immersed in distilled water. A decrease of 1 pH unit was observed between the 90 °C treatment and the 150 °C treatment. This can be explained by the formation of acid compounds induced by the thermo-lysis effect of microwave treatment and transferred from suspended solids to supernatant (Bougrier et al., 2006). To confirm this transfer of matter, sCOD was measured after each assay. The matter solubilisation was calculated with sCOD/tCOD ratio. Soluble COD represented 9% at 90 °C, 10.5% at 120 °C and 12.5% at 150 °C of total COD. As expected, these results indicated that more the matter was

Table 3
Temperatures and times used in the composite design and responses associated.

Run	Variables		Responses			
	Temperature (°C)	Time (min)	pH of supernate (−)	sCOD/tCOD (%)	Glucose (mg/L)	Phenolic Acids (mg/L)
1	90	10	5.65	8.8	382	35.26
2	90	30	5.69	9.4	482	48.97
3	120	20	5.30	11.1	729	39.81
4	150	10	4.86	12.9	799	86.05
5	150	30	4.77	12.0	898	65.88
6	84	20	5.66	8.5	405	47.34
7	156	20	4.64	12.8	1054	78.96
8	120	7.9	5.34	9.6	517	61.42
9	120	32.1	5.28	10.6	597	63.71

Table 4
Coefficients values of equations representing the response surfaces of pH, sCOD/tCOD ratio, glucose and phenolic acids as function of temperature and time.

Variables		Values of coefficients			
Coded unit	Name	pH	sCOD/tCOD	Glucose	Phenolic acids
a_0	Constant	5.28	10.80	716.29	45.08
a_1	Temperature	−0.42	1.74	233.73	15.29
a_2	Time	−0.02	0.13	42.61	−0.53
a_{12}	Temperature × time	−0.03	−0.36	−0.23	−8.47
a_{11}	Temperature^2	−0.08	0.08	16.80	8.98
a_{22}	Time^2	0.03	−0.29	−101.16	8.58

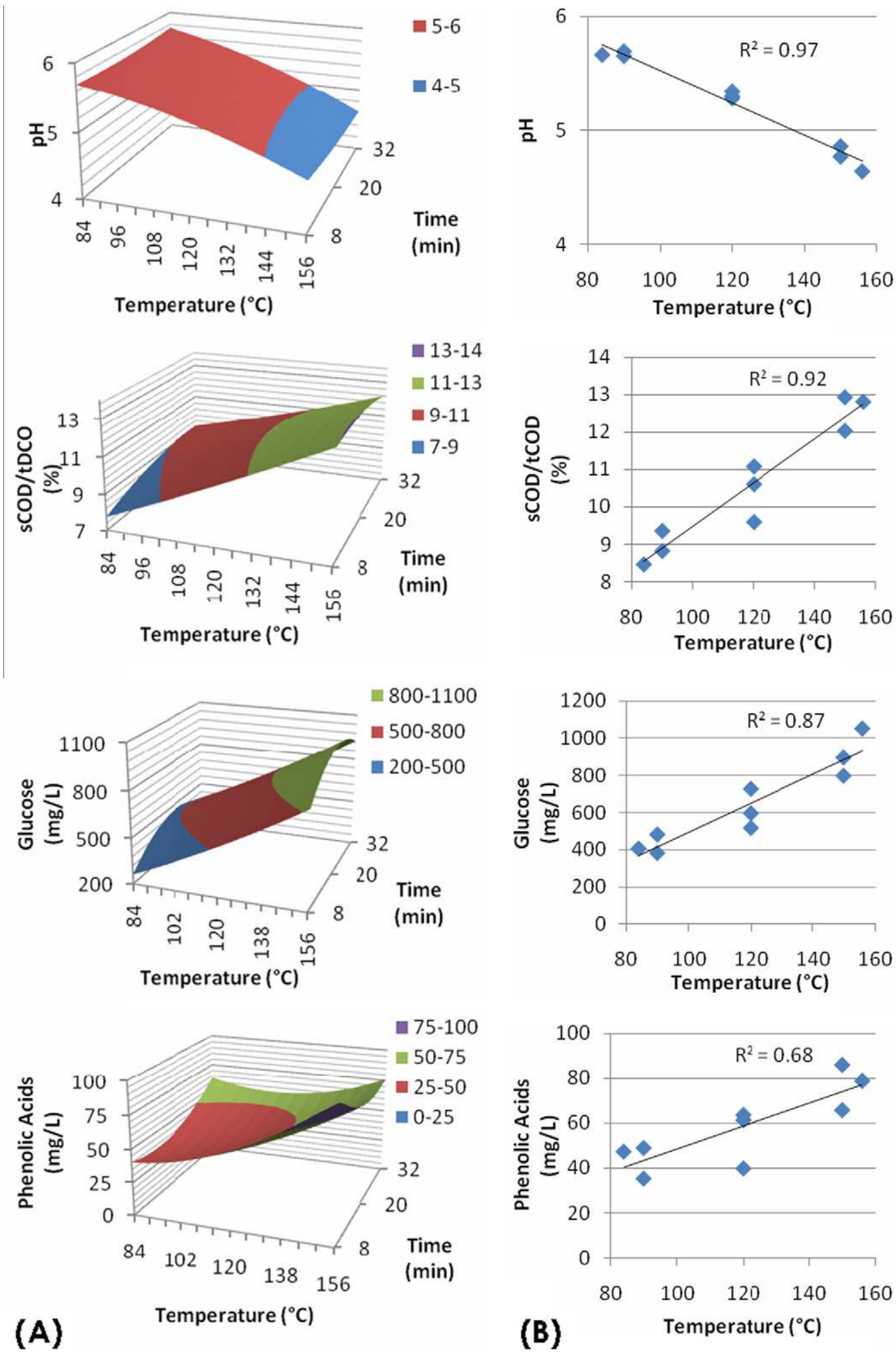

Fig. 1. (A) The response surfaces of pH, sCOD/tCOD ratio, glucose and phenolic acids as function of temperature and time. (B) pH, sCOD/tCOD ratio, glucose and phenolic acids as function of temperature.

heated, more the solubilisation was high. In their review, Hendriks and Zeeman reported that temperature above 160 °C led to formation of compounds which are often phenolic compounds and have in many cases an inhibitory or toxic effect on microorganisms (Hendriks and Zeeman, 2009).In order to follow the degradation of switchgrass, two compounds were focused: glucose and phenol acids (Hu and Wen, 2008).

The microwave pretreatment allowed an augmentation of glucose in supernatant, from a concentration of 400 mg/L at 90 °C until almost 1 g/L at 150 °C. Respectively, these two concentrations corresponded to the dissolution of 3.2 and 8 mg of glucose per gram of raw switchgrass treated by microwave. It could be noticed that amount of cellobiose (dimer of glucose) arose until 120 °C then reduced. The amount of xylose remained at zero and furfural

Table 5
Values of VSS, VDS, TVS, sCOD and solubilisation ratio of samples treated by microwave at 90, 105, 120, 135, 150 and 180 °C (tCOD = 1750 mg).

Temperature (°C)	TVS ± SD (g)	VSS ± SD (g)	VDS ± SD (g)	sCOD ± SD (mg)	sCOD/tCOD (%)
90	1.50 ± 0.06	1.43 ± 0.06	0.07 ± 0.01	164 ± 8	9.4 ± 0.5
105	1.49 ± 0. 05	1.41 ± 0.05	0.08 ± 0.01	163 ± 8	9.3 ± 0.5
120	1.44 ± 0.05	1.36 ± 0.05	0.08 ± 0.01	180 ± 7	10.3 ± 0.4
135	1.47 ± 0.06	1.37 ± 0.06	0.10 ± 0.01	189 ± 3	10.8 ± 0.1
150	1.43 ± 0.12	1.32 ± 0.12	0.10 ± 0.01	210 ± 5	12.0 ± 0.3
180	1.42 ± 0.06	1.31 ± 0.06	0.12 ± 0.01	241 ± 15	13.8 ± 0.8

and 5 hydroxymethyl furfural, which are thermal decomposition products of xylose (Qi and Xiuyang, 2007), appeared in these assays after 130 °C (data not shown).

Phenolic acids, which can be inhibitors at high concentration (Chen et al., 2008), were also found into supernatant. The microwave treatment released 0.32 mg of phenolic acids per gram of switchgrass at 90 °C and 0.64 mg per gram at 150 °C.

These results show that microwave pretreatment induces a matter solubilisation. Nevertheless, it was necessary to test these microwave treated samples with BMP assay in order to evaluate the effect of this matter solubilisation and to look at if inhibitors were released.

3.2. Effects of microwave pretreatment on anaerobic digestibility

In the previous part, switchgrass used was cut in pieces of 1 cm. In this present part, switchgrass was grinded to increase the homogeneity of the sample and allow a more precise comparison between the BMP assays. Matter solubilisation of grinded switchgrass was done at the temperatures of 90, 105, 120, 135, 150 and 180 °C. In order to verify if results were close of switchgrass cut in pieces of 1 cm, sCOD was measured after microwave treatment and compared to previous results.

Table 5 gives sCOD/tCOD ratio and matter distribution. In Tables 3 and 5, the three joint points of cut and grinded switchgrass were 90, 120 and 150 °C and had a difference of sCOD/tCOD ratio lower than 1% which was very close. Therefore, the impact of microwave pretreatment on matter solubilisation was similar regardless of the particle size of the switchgrass. The microwave pretreatment showed a solubilisation of 9.4% at 90 °C and increased until 13.8% at 180 °C. Pretreatment also led to a transfer of matter from suspended solid to supernatant. Indeed at 90 °C, 0.07 g of matter was released from the 5 g of raw material. This release increases with the temperature until 0.12 g at 180 °C. The volatile suspended solids (VSS) were equal to 96.7 (±0.5)% of total suspended solids (TSS), volatile dissolved solids (VDS) were equal 67.8 (±3.7)% of total dissolved solids (TDS) and total volatile solids (TVS) were equal to 94.0 (±0.4)% of total solids (TS). These results show that the volatile part is higher in suspended fraction and lower in dissolved fraction than the volatile part in the whole fraction. Thus, the microwave treatment induced a mineral solubilisation proportionately more important than organic solubilisation which was not influenced by the temperature of the pretreatment.

Fig. 2 presents methane production vs. time for treated and untreated switchgrass. With the standard deviation values, the maximum volumes of methane produced in 42 days were almost the same for untreated and treated samples. The exposition time was also tested in BMP assays and showed there was had no effect on methane production (data not shown) and confirmed the results seen previously which showed there was no effect on matter solubilisation.

Thus, the microwave pretreatment did not allow a significative improvement of methane production which was approximately equal to 290 ml per gram of TVS. According to the value of 1.199 $g_{(cod)}$ per gram of TVS, it could be determined that the

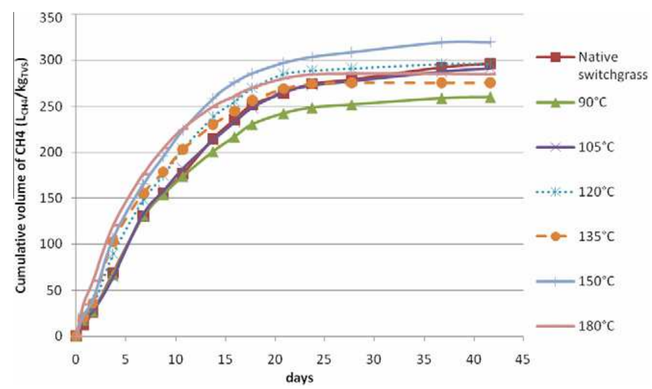

Fig. 2. Cumulative methane production from switchgrass untreated and treated by microwave.

Table 6
Values of maximum volume of methane produced and kinetic constant.

Temperature (°C)	Maximum volume of methane (L_{CH4}/kg_{TVS})	Kinetic constant (day^{-1})	80% of maximum volume of native sample (equal to 237 L_{CH4}/kg_{TVS})(day)
Native sample	296 ± 17	0.080 ± 0.001	16
90	260 ± 32	0.095 ± 0.022	19
105	291 ± 2	0.081 ± 0.010	16
120	296 ± 29	0.097 ± 0.003	13.5
135	275 ± 16	0.111 ± 0.001	14.5
150	320 ± 5	0.115 ± 0.001	11.5
180	284 ± 12	0.134 ± 0.013	12

biodegradability of untreated and treated switchgrass was 65% approximately. However, the microwave pretreatment led to a modification of the methane production kinetic.

In order to describe the effect of microwave pretreatment on methane production and to define a kinetic constant, the following first order model was used (Lei et al., 2010):

$$\mathrm{Vol}_{(t)} = \mathrm{Vol}_{(\infty)} \cdot (1 - e^{-kt}) \tag{3}$$

where $\mathrm{Vol}_{(t)}$ is the cumulative volume of methane as function of time t, $\mathrm{Vol}_{(\infty)}$ is maximum volume of methane and k is the kinetic constant.

The values of kinetic constants for the different temperatures of microwave pretreatment are shown in Table 6. At 90 and 105 °C no significant difference was observed. The enhancement of the kinetic constant appeared at 120 °C with an improvement of 21% compared to untreated switchgrass and continue to increase at 135, 150 and 180 °C with an improvement of 39%, 44% and 68%, respectively.

To evaluate the gain in days induced by the microwave pretreatment on the methane production, number of days to reach 80% of the methane volume obtained from untreated switchgrass was evaluated. Data shown in Table 6 reveal that a treatment at

90 °C induced a decrease of 19% and at 105 °C there was no time modification. Thus, a treatment below 105 °C decreases or does not change the biodegradability of switchgrass even if there was an improvement of matter solubilisation of 9%. At 150 °C the highest enhancement was observed with a gain in days of 28% which represent a reduction of 4.5 days compared to untreated samples and was almost equivalent at 180 °C. The difference between the treatment at 150 and 180 °C is too slight to conclude if 150 °C is the optimal temperature and if an higher temperature induce a decrease of effectiveness, or if temperatures above 150 °C induce better methane production. Jin et al. found in their study about microwave pretreatment on dairy manure, an optimal temperature for methane production at 147 °C (Jin et al., 2009).

The fact that the microwave pretreatment induced an enhancement of the kinetic constant value without gain of the ultimate volume of methane, could be explain by a breakdown of biomass matrix without transformation of weakly degradable material into easily degradable material. Indeed, if the structure of the lignocellulosic biomass is affected, the enzymes will access easily to their targets.

4. Conclusion

This study showed the effectiveness of microwave pretreatment to enhance solubilisation and anaerobic digestibility of switchgrass. Solubilisation increased with temperature; at 150 °C, 12.5% of initial COD was solubilised, among 8 mg of glucose and 0.64 mg of phenolic acids per gram of raw switchgrass. But subsequent BMP assays revealed that microwave pretreatment has no significant effect on the ultimate volume of methane produced from switchgrass. However, kinetics of methane production was increased; the time needed to reach the 80% value of ultimate volume of CH_4 was reduced by 4.5 days.

Acknowledgements

The authors would like to thank the Ministère de l'Education Nationale, de la recherche et de la Technologie for their financial support of the PhD of D. Jackowiak.

References

Adel, A.M., Abd El-Wahab, Z.H., Ibrahim, A.A., Al-Shemy, M.T., 2010. Characterization of microcrystalline cellulose prepared from lignocellulosic materials. Part I. Acid catalyzed hydrolysis. Bioresource Technology 101, 4446–4455.

APHA, 2005. Standard Methods for the Examination of Water and Wastewater, 21th ed. American Public Health Association, Washington, DC.

Bougrier, C., Albasi, C., Delgenes, J.P., Carrere, H., 2006. Effect of ultrasonic, thermal and ozone pre-treatments on waste activated sludge solubilisation and anaerobic biodegradability. Chemical Engineering and Processing 45, 711–718.

Bougrier, C., Delgenes, J.P., Carrere, H., 2007. Impacts of thermal pre-treatments on the semi-continuous anaerobic digestion of waste activated sludge. Biochemical Engineering Journal 34, 20–27.

Bruni, E., Jensen, A.P., Pedersen, E.S., Angelidaki, I., 2010. Anaerobic digestion of maize focusing on variety, harvest time and pretreatment. Applied Energy 87, 2212–2217.

Casler, M.D., Vogel, K.P., Taliaferro, C.M., Ehlke, N.J., Berdahl, J.D., Brummer, E.C., Kallenbach, R.L., West, C.P., Mitchell, R.B., 2007. Latitudinal and longitudinal adaptation of switchgrass populations. Crop Science 47, 2249–2260.

Chen, Y., Cheng, J.J., Creamer, K.S., 2008. Inhibition of anaerobic digestion process: a review. Bioresource Technology 99, 4044–4064.

Cornacchio, L., Hall, E.R., Trevors, J.T., 1986. Modified serum bottle testing procedures for industrial wastewaters. In: Technology Transfer Workshop on Laboratory Scale Anaerobic Treatability Testing Technique. Wastewater Technology Center, Canada.

Fernandes, T.V., Klaasse Bos, G.J., Zeeman, G., Sanders, J.P.M., van Lier, J.B., 2009. Effects of thermo-chemical pre-treatment on anaerobic biodegradability and hydrolysis of lignocellulosic biomass. Bioresource Technology 100, 2575–2579.

Goupy, J., 2000. Modélisation par plans d'expériences, Techniques de l'ingénieur, Référence R275.

Hendriks, A.T.W.M., Zeeman, G., 2009. Pretreatments to enhance the digestibility of lignocellulosic biomass. Bioresource Technology 100, 10–18.

Hu, Z., Wen, Z., 2008. Enhancing enzymatic digestibility of switchgrass by microwave-assisted alkali pretreatment. Biochemical Engineering Journal 38, 369–378.

Jensen, K., Clark, C.D., Ellis, P., English, B., Menard, J., Walsh, M., e Ugarte, D., 2007. Farmer willingness to grow switchgrass for energy production. Biomass and Bioenergy 31, 773–781.

Jin, Y., Hu, Z., Wen, Z., 2009. Enhancing anaerobic digestibility and phosphorus recovery of dairy manure through microwave-based thermochemical pretreatment. Water Research 43, 3493–3502.

Keshwani, D.R., Cheng, J.J., 2009. Switchgrass for bioethanol and other value-added applications: a review. Bioresource Technology 100, 1515–1523.

Keshwani, D.R., Cheng, J.J., 2010. Modeling changes in biomass composition during microwave-based alkali pretreatment of switchgrass. Biotechnology and Bioengineering 105, 88–97.

Lehtomaki, A., Viinikainen, T.A., Rintal, J.A., 2008. Screening boreal energy crops and crop residues for methane biofuel production. Biomass and Bioenergy 32, 541–550.

Lei, Z., Chen, J., Zhang, Z., Sugiura, N., 2010. Methane production from rice straw with acclimated anaerobic sludge: effect of phosphate supplementation. Bioresource Technology 101, 4343–4348.

Lewandowski, I., Scurlock, J.M.O., Lindvall, E., Christou, M., 2003. The development and current status of perennial rhizomatous grasses as energy crops in the US and Europe. Biomass and Bioenergy 25, 335–361.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y.Y., Holtzapple, M., Ladisch, M., 2005. Features of promising technologies for pretreatment of lignocellulosic biomass. Bioresource Technology 96, 673–686.

Qi, J., Xiuyang, L., 2007. Kinetics of non-catalyzed decomposition of D-xylose in high temperature liquid water. Chinese Journal of Chemical Engineering 15, 666–669.

Sun, Y., Cheng, J., 2002. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresource Technology 83, 1–11.

Thostenson, E.T., Chou, T.W., 1999. Microwave processing: fundamentals and applications. Composites: Part A 30, 1055–1071.

Ximenes, E., Kim, Y., Mosier, N., Dien, B., Ladisch, M., 2010. Inhibition of cellulases by phenols. Enzyme and Microbial Technology 46, 170–176.

Zhu, J.Y., Pan, X.J., 2010. Woody biomass pretreatment for cellulosic ethanol production: technology and energy consumption evaluation. Bioresource Technology 101, 4992–5002.