Influence of pretreatment with Fenton’s reagent on biogas production and methane yield from lignocellulosic biomass

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ABSTRACT

Biomass from Miscanthus giganteus, Sida hermaphrodita and Sorghum Moensch was treated with Fenton’s reagent for 2 hours under optimal conditions (pH = 3, mass ratio of [Fe²⁺]:[H₂O₂] equals 1:25 for Miscanthus and Sorghum and 1:15 for Sida). The degrees of delignification were 30.3%, 62.3% and 48.1% for the three plant species, respectively. The volatile fatty acids concentration after chemical pretreatment was high enough for production of biogas with a high methane content. Combined chemical oxidation and enzymatic hydrolysis with cellulase and cellobiase led to glucose contents of above 4 g/L. Among the tested plants, the highest biogas production (25.2 Ndm³/kg TS fed) with a 75% methane content was obtained with Sorghum Moensch. The results of the three-step process of biomass degradation show the necessity of applying a chemical pretreatment such as oxidation with Fenton’s reagent. Moreover, the coagulation of residual Fe³⁺ ions is not required for high biogas production.

1. Introduction

Due to its chemical structure and relatively high energy value, green biomass can be utilized for liquid and gas fuel production (bioethanol, biogas), and for heat generation and electricity (da Costa Sousa et al., 2009; Wyman et al., 2005). The biomass is employed in anaerobic digestion, gasification, composting or combustion for energy production, and plantations with selected, high-energy plants have been established in many areas to satisfy local energy needs (Amon et al., 2007; Kacprzak et al., 2009).

The process of anaerobic degradation of green biomass in its classical version is currently the technology most commonly used (Amon et al., 2007). Low adverse environmental effects, high efficiency of biogas production and wide feasibility and selection of raw materials make this method very attractive (Kacprzak et al., 2009); however, the time required for the entire process, especially biological hydrolysis, makes it necessary to find pretreatments that shorten the time required for fermentation (Appels et al., 2008; Mosier et al., 2005). Hence, chemical decomposition of biomaterials which leads to the transformation of high-molecular, polymeric structures of lignocellulosic materials into products easily biodegradable under anaerobic conditions are being investigated (Hendriks and Zeeman, 2009; Wyman et al., 2005).

Thermo-chemical pretreatments with diluted acids (Cara et al., 2008; Lenihan et al., 2010) or alkali (McIntosh and Vancov, 2010; Wang et al., 2010), biomass oxidation by hydrogen peroxide (Chen et al., 2008; Rabelo et al., 2008) or ozonation (Carballa et al., 2007; Weemaes et al., 2000) have already been studied. Each of these treatments leads to more or less degradation of hemi- and cellulosic structures and to the considerable delignification of the plant material. The intermediate products formed during such transformations are easily available for methanogenic microorganisms, and the disintegration of polymeric structures allows for more effective enzymatic hydrolysis.

Although the classic Fenton’s reaction has been applied in the treatment of highly loaded industrial wastewater (De Heredia et al., 2001), utilization of landfill leachate (Kochany and
The Fenton reaction is a process of non-selective degradation of organic compounds (Mert et al., 2010). The high efficiency of this method results from the formation and release of hydroxyl radicals \( \text{HO}^+ \) (Dogruel et al., 2009; El-Gohary et al., 2009) generated during hydrogen peroxide decomposition in the presence of \( \text{Fe}^{2+} \) ions, in accordance with Eq. (1). The \( \text{Fe}^{3+} \) can be reduced again to \( \text{Fe}^{2+} \) (2). Due to the high oxidative potential, these radicals may react with almost all known chemical compounds.

\[
\begin{align*}
\text{H}_2\text{O}_2 + \text{Fe}^{2+} & \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{HO}^+ \quad (1) \\
\text{Fe}^{3+} + \text{H}_2\text{O}_2 & \rightarrow \text{Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad (2)
\end{align*}
\]

The effectiveness of this reaction does not increase with the amount of ferrous salt and hydrogen peroxide used in the process. The presence of these reagents in excess leads to secondary reactions (3) and (4), and the reagents become typical radical scavengers instead of generating new quantities of radicals (Lucas and Peres, 2009):

\[
\begin{align*}
\text{Fe}^{2+} + \text{HO}^- & \rightarrow \text{Fe}^{3+} + \text{OH}^- \quad (3) \\
\text{H}_2\text{O}_2 + \text{HO}^- & \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \quad (4)
\end{align*}
\]

The advantage of Fenton’s reaction is its simplicity, availability and low cost (Deng, 2007; Torrades et al., 2008).

The aim of the present study was to determine the efficiency of the oxidation with Fenton’s reagent as pretreatment step in anaerobic digestion of biomass. An additional purpose was the selection of the species of green biomass which was most susceptible to methane fermentation. Three of the most popular plants envisioning was biomass production and that differ in biopolymer contents and culture conditions were selected: Miscanthus, Sida and Sorghum.

2. Methods

2.1. Preparation of the raw plant material

Dried biomass from Miscanthus giganteus, Sorghum Moensch and Sida hermaphrodita was ground in a mill to obtain particles with dimensions of 0.1–1 mm. In order to remove chlorophyll which interferes with spectrophotometric measurements, the milled material was placed in a Soxhlet’s apparatus and subjected to extraction with 96% ethanol according to Polish Standard Method PN-92/P-50092. Extracted biomass was rinsed with distilled water until the pH of the rinsate was neutral. The material was dried in an oven at 45 °C and used for oxidation and enzymatic processes.

2.2. Hydrolysis by Fenton’s reagent

A 5-g biomass sample prepared as described in Section 2.1 was suspended in 100 mL of distilled water and thoroughly mixed. The pH of the mixture was adjusted to three using diluted sulfuric acid. The sample was stirred with a mechanical agitator for 5 min at 550 rpm. The desired amount of FeSO\(_4\)/H\(_2\)O was added and stirred for another 5 min, until dissolved. The desired dose of 30% H\(_2\)O\(_2\) was added and the mixture was stirred at 200 rpm for 2 h. In order to complete the reaction and precipitate iron (III) hydroxide, the pH was raised to 11 using 20% NaOH. The sample with sludge formed during coagulation of residual Fe\(^{3+}\) ions was placed in a water bath at 50 °C for 30 min in order to decompose residual H\(_2\)O\(_2\). The sample was removed from the waterbath, allowed to settle for 30 min and centrifuged at 6939g for 5 min. The pellet was rinsed by vacuum filtration with distilled water until the pH of the filtrate was neutral. The material was dried in an oven at 45 °C.

The same process was conducted with pure crystalline cellulose (Sigma–Aldrich), glucose (CHEMPUR) and xylose (Carl Roth GmbH + Co.KG). The \([\text{Fe}^{2+}]:[\text{H}_2\text{O}_2]\) ratio was equal to 1:25 and was in accordance with the optimum dose determined for two of the three tested plants (see Section 2.3). A 5-g sample of substrates was used.

2.3. Optimization of oxidant and ferrous salt doses

Raw, ethanol-extracted plant material was treated with Fenton’s reagent at different doses of hydrogen peroxide and ferrous sulfate. Initially, a constant amount of 2 g/L of Fe\(^{2+}\), and different doses of 30% H\(_2\)O\(_2\) ranging from 5 to 40 g/L, were added to the suspension of plant samples. The second step took place at a constant dose of H\(_2\)O\(_2\) (15 g/L), with different amounts of Fe\(^{2+}\) ranging from 1 to 15 g/L. In the third step of optimization, in order to minimize the dosage of iron salt used for the oxidation, 1 g/L of Fe\(^{2+}\) and 25 g/L of H\(_2\)O\(_2\) were added to the suspension of plant sample to perform Fenton’s oxidation.

2.4. Enzymatic hydrolysis

A 5-g sample of plant biomass pretreated with Fentons reagent was suspended in 100 mL of 50 mM citrate buffer solution pH = 4.8. Cellulase (Celluclast 1.5 L) and cellobiose (Novozyme 188) were added to the sample. The cellulase had an initial activity of 800 endoglucanase units (EGU)/g (Sigma–Aldrich) and the loading was 160 EGU/g of solids. The cellobiose had an initial activity of 280 cellobiose units (CBU)/g (Sigma–Aldrich) and the loading was 17.2 CBU/g of solids. The flask with the sample was placed in a shaker at 50 °C for 24 h. The hydrolysate was used as feedstock in the process of methane fermentation carried out in shaken cultures.

The same process was conducted with untreated and Fenton’s reagent-treated crystalline, pure cellulose.

2.5. Anaerobic digestion

The chemically and enzymatically pretreated plant biomass with the 300 mL of hydrolysate obtained after enzymatic pretreatment was mixed with 200 mL of sludge received from the Group Wastewater Treatment Plant in Lodz, Poland. The pH of mixture was adjusted to 7 using NaHCO\(_3\) and the flask was placed at 37 °C and shaken at 80 rpm. Volumes of biogas and methane produced were measured on alternate days by the liquid displacement method with the use of 33% NaCl and 3% NaOH solutions, respectively. The installation diagram is given in Fig. 1.

2.6. Analytical methods

The following parameters were determined: hemicellulose content (according to the Polish Standard Method PN-92/P-50092), cellulose content (Kürschner and Hoffer, 1931), lignin content (Polish Standard Method PN-92/P-50092), Total Solids (TS, drying at constant temperature of 105 °C), Volatile Solids (VS, mineralization in an oven at constant temperature of 550 °C), ash (subtraction TS–VS), Chemical Oxygen Demand (COD, Polish Standard Method PN-74/C-0457), elemental content (C, H, N, S; Elemental Analyzer NA 2500, CE Instruments, UK), ammonium nitrogen (N–NH\(_4^+\)), distillation in BÜCHI apparatus B–324, Germany), volatile fatty acids (VFA, distillation with steam in BÜCHI apparatus B–324, Germany), Chemical Oxygen Demand (COD, mineralization in HACH-LANGE...
LT 200 apparatus, spectrophotometric analysis in DR 5000 apparatus, HACH-LANGE, Germany), total organic carbon (TOC Analyzer, HACH-LANGE, Germany), general nitrogen (TOC Analyzer, HACH-LANGE, Germany), Total Phenolic Content (TPC, Folin Ciocalteu’s Method; (Singleton and Rossi, 1965); UV-VIS T80 + PG Instruments Limited spectrophotometer, England \( \lambda = 765 \) nm), glucose and xylose concentration upon HPLC analysis (Waters 600 equipped with a Bio-rad Aminex HPX-87H column, Waters 410 RI Detector and Waters 717 + sampler; column temperature 60°C, mobile phase 0.01 N sulfuric acid at a flow rate of 0.6 ml/min, USA).

3. Results and discussion

3.1. Optimization of oxidant and ferrous salt doses

The physicochemical characteristics of the three plant species subjected to chemical hydrolysis are shown in Table 1. Elemental content of biomass is given in Table 2.

The concentrations of basic indicators (COD, VFA, TOC, N, N–NH\(_4^+\), TPC, glucose and xylose) were determined in supernatants of all pretreated plant species obtained after the reaction. As a leading indicator for biomass degradation, the concentration of released phenolic compounds was chosen (TPC). Fig. 2 shows the dependence of the concentration of released phenolic compounds on the Fe\(^{2+}\) and H\(_2\)O\(_2\) doses for the three plant species. Fig. 3 shows the values of the key parameters (TPC, COD and VFA concentrations) of the hydrolysates after Fenton’s reaction under optimal conditions described below for the three tested plant species. Table 3 lists the parameters for the oxidation with Fenton’s reagent under optimal conditions. They all show a strong dependence on the ratio of reactants to their concentration in the obtained hydrolysates after oxidation. The higher the TPC, the higher COD and VFA, and vice versa. The analysis of TPC (Fig. 2) showed that the optimum mass ratio of Fe\(^{2+}\):H\(_2\)O\(_2\) was equal to 1:25 for Miscanthus and Sorghum (optimum doses, 100:2500 mg), and 1:15 for Sida (optimum doses, 100:1500 mg). S. hermaphrodita contains much more organic matter than Miscanthus and Sorghum; moreover, it is less susceptible to mechanical destruction. The concentration of VFA during hydrolysis of Sida was almost two- and three-fold higher compared to that of Miscanthus and Sorghum; moreover, it is less susceptible to mechanical destruction. The concentration of VFA during hydrolysis of Sida was almost two- and three-fold higher compared to that of Miscanthus and Sorghum, respectively (see Tables 1 and 3, Fig. 3).

The highest concentrations of phenolic compounds released after Fenton’s reaction at optimal conditions was achieved for Miscanthus (633.1 mg/L). For Sorghum and Sida the values were 549.7 and 235.2 mg/L, respectively. Compared to other methods of chemical treatment like alkali or H\(_2\)O\(_2\) oxidation, these concentrations indicate a low level of biomass delignification and, consequently, poor degradation (Kumar et al., 2009; Mosier et al., 2005). In order to determine the influence of Fenton’s reagent on delignification of the treated biomass, acid-soluble and insoluble lignin in

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**Table 1** Characteristics of the raw materials.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Miscanthus</th>
<th>Sida</th>
<th>Sorghum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemicellulose content (%)</td>
<td>21.3</td>
<td>26.8</td>
<td>17.9</td>
</tr>
<tr>
<td>Cellulose content (%)</td>
<td>48.3</td>
<td>52.2</td>
<td>53.1</td>
</tr>
<tr>
<td>Lignin content (%)</td>
<td>28.8</td>
<td>19.1</td>
<td>27.9</td>
</tr>
<tr>
<td>Total solids (%)</td>
<td>94.1</td>
<td>95.6</td>
<td>95.7</td>
</tr>
<tr>
<td>Volatile solids (%)</td>
<td>89.8</td>
<td>92.0</td>
<td>86.3</td>
</tr>
<tr>
<td>Ash (%)</td>
<td>4.3</td>
<td>3.6</td>
<td>9.4</td>
</tr>
<tr>
<td>COD (mgO(_2)/g)</td>
<td>52632</td>
<td>57843</td>
<td>50971</td>
</tr>
</tbody>
</table>

**Table 2** Chemical composition of biomass before and after chemical pretreatment.

<table>
<thead>
<tr>
<th>Chemical composition (%)</th>
<th>Miscanthus Raw</th>
<th>Treated</th>
<th>Sida Raw</th>
<th>Treated</th>
<th>Sorghum Raw</th>
<th>Treated</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>46.5</td>
<td>46.7</td>
<td>45.9</td>
<td>47.7</td>
<td>44.9</td>
<td>45.4</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>6.0</td>
<td>6.2</td>
<td>6.1</td>
<td>6.3</td>
<td>5.8</td>
<td>6.1</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.5</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
<td>0.7</td>
<td>0.7</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>21.3</td>
<td>23.3</td>
<td>26.8</td>
<td>37.0</td>
<td>17.9</td>
<td>20.8</td>
</tr>
<tr>
<td>Cellulose</td>
<td>48.3</td>
<td>52.1</td>
<td>52.2</td>
<td>58.9</td>
<td>53.1</td>
<td>60.2</td>
</tr>
<tr>
<td>Acid-soluble lignin</td>
<td>2.1</td>
<td>1.8</td>
<td>2.0</td>
<td>1.9</td>
<td>2.3</td>
<td>1.4</td>
</tr>
<tr>
<td>Insoluble lignin</td>
<td>26.7</td>
<td>20.8</td>
<td>17.1</td>
<td>6.8</td>
<td>25.6</td>
<td>16.0</td>
</tr>
<tr>
<td>Total lignin</td>
<td>28.8</td>
<td>22.6</td>
<td>19.1</td>
<td>8.7</td>
<td>27.9</td>
<td>17.4</td>
</tr>
</tbody>
</table>

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![Fig. 1. Scheme of installation used in biogas and methane measurements.](image-url)
the samples after Fenton’s oxidation under optimal conditions were analyzed (Table 2). Compared to the lignin content in the raw plant materials (Table 1), Fenton’s oxidation led to a decrease in both acid-soluble and insoluble lignin contents by 30–60%. The delignification yield of Fenton’s oxidation of all plant sources is given in Table 4.

The values of COD covered a wide range and depended on the tested material. The maximum values were 10180, 7240 and 6880 mgO₂/L for Miscanthus, Sorghum and Sida, respectively. Similarly, the VFA concentrations were equal to 1710, 1128 and 3060 mg CH₃COOH per liter, for Miscanthus, Sorghum and Sida, respectively. Compared to the other methods of chemical pretreatment, i.e. dilute acid pretreatment and alkali pretreatment, the yield of hemicellulose degradation measured as VFA concentration, especially for Sida, was high (Hsu et al., 2010; Park et al., 2005). The yields for hemicellulose and cellulose degradation after Fenton’s oxidation is given in Table 4.

TOC, N and N–NH₄⁺ showed similar trends, depending on the dose of an oxidant and ferrous salt (data not shown). Glucose and xylose were not observed in the hydrolysates of pretreated biomass plants. This may indicate that poor delignification of plant material took place and degradation of other structures was low and directed into VFA or more complex products of decomposition. Another reason may be degradation of monosaccharides during Fenton’s reaction. To confirm the latter hypothesis additional experiments were conducted.

The results obtained after oxidation of pure glucose and xylose by Fenton’s reagent showed that this method of pretreatment leads to the degradation of desired products (data not shown). Experiments with crystalline cellulose showed that Fenton’s reagent caused a weight loss of 20% (data not shown). In addition, no glucose was observed in the achieved supernatant.

When the oxidation was carried out with the same mass ratio but with twice the amounts of reactants a significant decrease, and thus reduction in efficiency of the reaction was observed (Fig. 4 a).

When the Fenton reaction was carried out for 3 h (Fig. 4 b), the efficiency of the degradation of Miscanthus was affected negatively, while in the case of Sorghum and Sida a longer reaction time...
increased effectiveness, although for *Sida* only the level of delignification increased.

### 3.2. Enzymatic hydrolysis

Plant material oxidized under optimal conditions was subjected to enzymatic hydrolysis using cellulase and cellobiase and to determine the influence of the pretreatment step, enzymatic hydrolysis of raw plant material was also carried out. The results are presented in Table 5. Without a chemical pretreatment step, no monosaccharides were present in the hydrolysates. This fact indicates that, when cellulose is not hydrolysed by enzymes, biogas production is impossible.

For plant material oxidized with Fenton’s reagent, the concentrations of sugars in the hydrolysates were too low for an efficient methane fermentation, likely due to unsatisfactory delignification.

When treated and untreated crystalline cellulose were hydrolyzed, the concentration of glucose was 27.4 and 26.9 g/L, respectively. When these concentrations are compared with glucose concentrations after enzymatic treatment of plant materials preceded by Fenton’s reaction (Table 5), the values achieved after the two-step process were lower than those obtained for the pretreated cellulose. The yield of enzymatic hydrolysis calculated for all three plant sources based on the released glucose concentration were much lower (17.1% for *Miscanthus*, 19.6% for *Sida* and 22.3% for *Sorghum*) than for cellulose (48%).

The overall yield of the two-step process of biomass pretreatment is shown in Table 4. The total yield was calculated using two methods. In the first method the yield was achieved on the basis of glucose and xylose concentration in the obtained supernatants in relation to the chemical composition of raw plant material and theoretical efficiency of polysaccharides degradation. In the second method the degradation yield from each step was summed. The yield calculated by means of the first method was lower because of the losses of monosaccharides during the oxidation step. The highest degradation yield was achieved for *Sorghum*, and the lowest for *Miscanthus* (Table 4).

### 3.3. Anaerobic digestion

In this study, not only the effectiveness of biogas and methane production was compared, but also the influence of the final coagulation step in the Fenton’s process on the composition and volume of biogas were checked (Fig. 5). In case of raw plant material, biogas production was not observed. For the pretreated samples, the volumes of biogas differed depending on the plant material used. The highest production was observed for *Sorghum* (25.2 Ndm³/kg TS fed) and *Sida* (26.1 Ndm³/kg TS fed).

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**Table 4**

Degradation yields for the oxidation process, enzymatic process and overall two-step process for various plant sources and polysaccharides.

<table>
<thead>
<tr>
<th>Type of process</th>
<th><em>Miscanthus</em></th>
<th><em>Sida</em></th>
<th><em>Sorghum</em></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Y_H$ (%)</td>
<td>$Y_C$ (%)</td>
<td>$Y_L$ (%)</td>
</tr>
<tr>
<td>Oxidation step</td>
<td>2.8</td>
<td>4.2</td>
<td>30.3</td>
</tr>
<tr>
<td>Enzymatic step</td>
<td>10.2</td>
<td>17.1</td>
<td>13.2</td>
</tr>
<tr>
<td>Overall two-step process</td>
<td>a$^b$</td>
<td>9.9</td>
<td>16.4</td>
</tr>
<tr>
<td></td>
<td>b$^b$</td>
<td>13.0</td>
<td>21.3</td>
</tr>
</tbody>
</table>

$^a$ $Y_H$ – yield of hemicellulose degradation; $Y_C$ – yield of cellulose degradation; $Y_L$ – yield of delignification.

$^b$ a – yield based on monosaccharides concentration, b – yield calculated as a sume of yield of individual steps.

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**Table 5**

Effects of enzymatic hydrolysis on degradation of hemicellulose and cellulose after Fenton’s oxidation pretreatment for different plant sources.

<table>
<thead>
<tr>
<th>Sugars concentration (g/L)</th>
<th><em>Miscanthus</em></th>
<th><em>Sida</em></th>
<th><em>Sorghum</em></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw</td>
<td>Treated</td>
<td>Raw</td>
</tr>
<tr>
<td>Xylose</td>
<td>0.0</td>
<td>1.2</td>
<td>0.0</td>
</tr>
<tr>
<td>Glucose</td>
<td>0.0</td>
<td>4.4</td>
<td>0.0</td>
</tr>
</tbody>
</table>

---

**Fig. 4.** Comparison of values of main parameters determined in supernatants obtained after Fenton’s oxidation of plant samples under different conditions with respect to, (A) dose of reactants; (B) reaction time (SD – single doses; DD – doubled doses; 2 h – two hours; 3 h – three hours).
and the lowest for Miscanthus (13.6 Ndm³/kg TS fed). The amount of nitrogen and carbon in the biomass influenced biogas production to a large extent. In the case of Sorghum, the quantity of nitrogen released in the chemical pretreatment was very high, but the C/N ratio in the raw material was the lowest. As a consequence there was only a low probability to inhibit further anaerobic digestion by ammonium. In the case of Miscanthus, these values (C/N ratio, N) were the opposite; despite a high nitrogen content in raw biomass in relation to the carbon content, only a small amount of nitrogen was released into the supernatant after Fenton’s oxidation. Methanogenic microorganisms might have been inhibited by ammonium formed from nitrogen during anaerobic digestion process. The C/N ratio is not the only parameter on which the efficiency of biogas production depends. The data obtained after the enzymatic hydrolysis compared to the chemical content of the raw plant materials (Tables 1 and 5) show that the highest degradation level of lignocellulosic components was achieved for Sida and Sorghum. Although the concentration of phenolic compounds in the supernatants after the chemical pretreatment was the lowest for Sida (Table 3), it should be mentioned that the delignification yield was rather high (Table 4). As a consequence, a significant part of hemicellulose and cellulose might have been affected during the enzymatic and chemical operations, leading to a high biogas yield in the anaerobic digestion process. In the case of Sorghum, the delignification yield was not as high after Fenton’s reaction (10% lower than in case of Sida) but the enzymatic hydrolysis yield was the highest. The degradation of Miscanthus was not strong enough for effective biogas production. The yield of enzymatic hydrolysis of Miscanthus was the lowest, therefore biogas production was the lowest among of all the plants treated with Fenton’s reagent. The methane content in the biogas was highest for Sorghum and Miscanthus (ca. 75%), while that obtained for Sida (65%) was the lowest.

When the quantities and the composition of obtained biogas for different plant materials after Fenton’s process with coagulation (c) and without (wc) were compared, significant and repeatable differences were observed. While biogas production with and without the iron (III) hydroxide precipitation was more or less the same, the methane content was significantly higher in the case of Fenton’s reaction without classical precipitation of Fe³⁺ (for Miscanthus and Sorghum: 75% (wc) and 70% (c); for Sida: 65% (wc) and 45% (c)), than for chemical pretreatment with coagulation step. It is possible that ferric ions entered biomass pores during rinsing under vacuum conditions, and were transferred into the fermentation chamber with the pretreated plant material. The increased redox potential lowered the activity of methanogenic bacteria and inhibited methane formation by changing the direction of the electrons flux between particular molecules.

4. Conclusions

Fenton’s reagent has only a low ability for chemical degradation of lignocellulosic structures. Incomplete delignification of biomass led to low concentrations of sugars released after enzymatic hydrolysis; however, the concentration of VFA after chemical hydrolysis was very high and biogas with a significant methane content was produced. Among the tested plant materials the best results were obtained for Sorghum Moensch. Moreover, the study showed that the produced biogas is characterized by higher energy value in case of Fenton’s process without a classical coagulation step. Despite of the low delignification level due to chemical pretreatment, both hemicellulose and cellulose structures were disrupted by enzymes. Fenton oxidation can therefore be useful as a pretreatment step for anaerobic digestion. The advantage of this pretreatment method is its low ability to degrade cellulose resulting in a correspondingly low glucose loss.

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References


Fig. 5. Biogas production and methane content after chemical and enzymatic hydrolysis of different plant materials; (a) Miscanthus, (b) Sida, (c) Sorghum; (c) – with coagulation; (wc) – without coagulation.


