THE EFFECT OF BIOWASTE DEGRADATION ON BIOETHANOL AND BIOGAS YIELDS

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SUMMARY: Anaerobic digestion is a common and sustainable way for the treatment of easily degradable biomass to produce biogas energy and nutrient rich digestate. Another option to produce biofuel from biowaste is bioethanol fermentation, and its integration with biogas production. Thus, biowaste can be recognized as a valuable commodity, at least as a valuable source of energy and nutrients. However, during collection and storage, even in room temperatures, biowaste cause unpleasant side effects, such as odour and leachates, which are challenges for the utilization chain – including source separation, storing, collection, transportation and processing.

Besides odour and other disadvantages of deterioration, also the energy as a carbon is lost. Organic compounds convert into volatiles due to microbial activity, and a part of the carbon is used for the growth of mould. In addition, liquefaction of biowaste results in the formation of leachates containing solubilized carbon. What are the effects of different storage conditions of biowaste on its bioethanol and biogas yields were studied in this work. The biowaste contains a large amount of different carbohydrates resulting in the formation of water soluble sugars due to microbial activity during storage. Further, these soluble sugars may be used by acidifying bacteria to form organic acids or by moulds during storage, thus decreasing the ethanol yield in the subsequent fermentation. Clear differences were found in the loss of the soluble sugars in different storing conditions tested in this study. The storage in anaerobic conditions and the preservation of biowaste with formic acid were beneficial to ethanol production compared to the storage in open air, aerobically. The biogas yield, however, was not affected by the loss of sugars – the biogas can be produced also from the reaction products, like organic acids and microbial mass, like moulds. However, the mass loss into air as gases in open storage conditions decreased the biogas yield by ca. 30% compared to the fresh biowaste.

1. INTRODUCTION

Biowaste, including left over food, kitchen waste, grocery waste and industrial food waste, should be increasingly recycled due to the target to stop the landfilling of biodegradable waste. The landfill directive in the EU obliges member states to reduce significantly the amount of biodegradable municipal waste ending up on landfills by 2016 (Council Directive 1999/31/EC 1999). The directive creates the pressure and the possibility to search for more sustainable ways for handling organic wastes. Thus, biowaste should be recognized as a valuable commodity, at least as a valuable source of energy and nutrients. Biowaste is, however, easily degradable causing...
exquisitely unpleasant side effects during storage, such as odour and formation of leachates. Biowaste is also a favourable environment for various bacteria, moulds and yeasts, causing a possible severe hygienic risk for anyone being in contact with biowaste. The quality of biowaste varies and is difficult to control. Thus, the biowaste management, from its sources to final users, is a challenging task for the operators.

Besides the above mentioned challenges, the loss of energy by the deterioration of organic matter and the formation of volatiles and leachates during storing and the transportation of biowaste is a matter of concern. The conversion of sugars to other compounds, such as acids or even moulds, is more critical when utilizing biowaste to ethanol than to biogas - biogas production is more versatile in terms of substrates. However, the variations in biowaste quality are always a challenge in the subsequent processing, and there is a need to improve the stability of biowaste for both processing and hygienic reasons. In animal feeding, ensiling of the fresh crops is a necessary and common procedure to provide nutrient-rich fodder for animals throughout the year. Ensiling has also been successfully used to preserve energy crops and residues targeted for the production of energy, mainly biogas (Pakarinen et al. 2011). Besides crops, ensiling has been promoted to store waste from the fish industry. Ensiled fish waste is rich in protein and has been used as a protein source for e.g. fish farming or sheep feed (Samuels et al., 1991; Vidotti et al. 2003). Ensiling is normally carried out in anaerobic conditions in which organic acids, especially lactic and acetic acids produced by endogenous microflora, decrease the pH, preserve the substrate against the growth of fungi, bacteria or yeasts, and thus prevent carbohydrate losses (McDonald et al. 1991). Another widely used method to accomplish acidic conditions in silage is the addition of organic acids, mainly formic acid, into the material.

In this study, fresh kitchen biowaste was stored in three different conditions from two to fourteen days, and the effects on biogas production and enzymatic sugar hydrolysis were tested. The major changes in chemical composition and the loss of material were analysed and measured, as well. The three different storing conditions in room temperature tested were a) open air – aerobic conditions, b) anaerobic conditions as such, and c) anaerobic conditions with addition of formic acid.

2. RESULTS AND DISCUSSION

2.1 Changes in chemical composition

A mixture of biowaste was collected from households and staff canteen, hence containing mainly food waste (cooked food, fruits, vegetables, and bread), cookery waste (peeling waste, coffee grounds) and napkins. No raw meat or garden waste was included. The original dry matter (DM) content of biowaste was 27.4 %.

Total nitrogen content (Kjeldahl N) of fresh biowaste was 9.8 mgN/g wet weight and 38.5 mgN/g DM. The amount of ammonium-N in fresh biowaste was 4.3 mgN/g DM (Table 1) and, thus, 11.1% of the total nitrogen. Subtracting the amount of ammonium-N from the total-N, and using the conversion factor of 6.25 for the rest of the nitrogen to protein, the protein content of fresh biowaste would be 21.4% of DM. Preserving biowaste in anaerobic conditions the protein amount increases up to 25.5 % of DM. Since the mass loss, was rather low for the preserved biowaste, the protein seems to be remained in the biowaste. Part of the proteins, however, may have been cleaved into shorter peptides or even aminoacids during the storage (McDonald, 1991).
Prior to acid hydrolysis, the biowaste was extracted (washed) with water and ethanol. The amount of extractives, including water soluble sugars (WSC) and proteins, acids and fats, was rather high, 37.5% of DM, from which the share of WSC was nearly 40% (Table 1). The amount of WSC decreased in seven days of storing both in aerobic and anaerobic conditions, but slightly more in aerobic conditions (Table 1). This indicates better preservation of biowaste in anaerobic conditions. Presumably, in anaerobic conditions sugars were utilized by lactic acid bacteria forming lactic acid, whereas in aerobic conditions sugars were used mainly for the growth of undesirable micro-organisms such as moulds. In aerobic conditions, the liquefaction of biowaste, i.e. formation of leachate was also more visible than in anaerobic conditions.

Total carbohydrates from extractive free material after acid hydrolysis were almost 50% of DM (Table 1). Slight decrease was observed in the material preserved in aerobic and anaerobic conditions. However, when the mass loss is considered the amount of total carbohydrates was the equal.

Solid residue from acid hydrolysis, containing acid insoluble lignin, protein and ash was 12.5% of DM (Table 1). The solid residue after acid hydrolysis in Klason lignin determination contains, however, not only acid insoluble lignin but also ash and insoluble protein compounds (Sluiter et al. 2011). Therefore, the residue cannot be all identified lignin in the case of protein rich biowaste. The amount or the residue was clearly less in the material stored in the aerobic conditions compared with fresh or material stored in anaerobic conditions. It may suggest that solubilisation of protein is reduced or prevented in anaerobic conditions.

Composition between biowaste batches vary greatly, however, the share of different compounds is similar to previous results (Rättö et al. 2009).

Table 1. Chemical composition of fresh and stored biowaste, either in aerobic or anaerobic conditions for seven days in room temperature.

<table>
<thead>
<tr>
<th>Biowaste</th>
<th>Fresh</th>
<th>7 days in aerobic</th>
<th>7 days in anaerobic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extractives</td>
<td>37.5</td>
<td>43.6</td>
<td>38.3</td>
</tr>
<tr>
<td>WSC</td>
<td>14.1 (0.2)</td>
<td>5.4 (0.3)</td>
<td>9.0 (0.1)</td>
</tr>
<tr>
<td>Total carbohydrates (extractive free)</td>
<td>49.8 (1.4)</td>
<td>48.8 (1.0)</td>
<td>44.6 (0.7)</td>
</tr>
<tr>
<td>Total carbohydrates (as received)</td>
<td>31.1 (0.9)</td>
<td>27.5 (0.6)</td>
<td>27.5 (0.4)</td>
</tr>
<tr>
<td>Residue from acid hydrolysis</td>
<td>12.5 (0.5)</td>
<td>5.1 (0.1)</td>
<td>15.2 (1.2)</td>
</tr>
<tr>
<td>Protein</td>
<td>21.4 (2.4)</td>
<td>n.d.</td>
<td>25.5 (2.2)</td>
</tr>
<tr>
<td>Ammonium nitrogen</td>
<td>4.3</td>
<td>4.9</td>
<td>4.8</td>
</tr>
</tbody>
</table>

* WSC = water soluble carbohydrates ; n.d. not determined
2.2 Enzymatic hydrolysability

Fresh and stored biowastes were hydrolysed to determine the enzymatic hydrolysis of carbohydrates to sugars, thus indicating the bioethanol production potential. The hydrolysis yields are given in Figure 1.

The addition of formic acid (FA) to fresh biowaste clearly improved the preservation of sugars - the hydrolysable sugar content remained constant during 7 days of anaerobic storing with FA. The storing without formic acid resulted in a clear loss of utilizable sugars, presumably due to formation of lactic acid from easily degradable sugars. However, the most remarkable sugar loss was found in the material stored in open air, aerobically. The reason may be the use of sugars for the growth of moulds which was clearly visible. In addition, the prevention of the mass loss in anaerobic storing conditions is beneficial compared to open air conditions.

![Figure 1 Enzymatic hydrolysis yields of studied biowaste, expressed as kg sugars per dry tonne of biowaste. FA=formic acid.](image)

2.3 Methane production

Ensiling has been successfully used to preserve various lignocellulosic substrates, e.g. corn stover, prior to biogas production (Pakarinen et. al. 2011, joku muu). Several months prolonged ensiling time preserves carbohydrates well and contribute positively on further hydrolysis of lignocellulose resulting in an increased methane yields or less severe pre-treatment conditions prior to ethanol (Ambye-Jensen et al. 2013).

Storing times of biowaste in this study were rather short, from two to fourteen days. Although, the decrease in pH was found, indicating the start of preservation process by acidification, no strong hydrolysis of lignocellulose compounds were expected during this storing time. Methane yield of fresh biowaste was 423.7 dm$^3$ CH$_4$ g$^{-1}$ VS and the yield remained equal for the stored biowaste (Figure 2). Small increase, however, was observed, caused by additional FA, on samples supplemented with FA. Aerobic storing for two, seven or 14 days slightly decreased the methane yields, but most probably the mould grown on the deteriorated biowaste was also utilized as a
biogas substrate causing less decrease than expected.

However, if the mass loss during aerobic storage is considered the decrease of methane yield was considerable. The yield was found to decrease by 36%, calculated from the original mass, considering the mass loss during 14 days of aerobic storing.

![Figure 2](image)

Figure 2 Methane yields of the biowaste stored in different conditions. Yields are expressed as volume of methane per weight of volatile solids (VS).

5. CONCLUSIONS

Biowaste deterioration caused significant mass and energy loss during 14 days of storing in aerobic conditions. The amount of hydrolysable sugars decreased to a fourth of the original, due to acidification and moulds formation, whereas, the methane production lowered by ca. 30% due to mass loss into air during the aerobic storing. The addition of formic acid (FA) was an effective way to maintain the energy content of biowaste in anaerobic conditions - both the amount of hydrolysable sugars and the methane production remained at the original level during 7 days of storing. The storing in anaerobic conditions without acid (FA) supplementation resulted in the loss of sugars, combined with the decrease in pH indicating the acid formation. However, no effect on the methane production was found. The prevention of the mass loss in anaerobic storing conditions was found to be crucial for the energy content of biowaste.

ACKNOWLEDGEMENTS

The project called Bioliike funded by the ERDF programme for Southern Finland and several companies is acknowledged.

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