ULTRASONIC PRETREATMENT OF DDGS FOR ANAEROBIC DIGESTION

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EXTENDED ABSTRACT

In the last years the need to face both climate change and energy supply requirements has promoted the interest towards biofuels. Among the most promising ones there is bioethanol, whose production relies for approximately 80% on biomass fermentation. The main obstacle in spreading the production of bioethanol is related to its productive process competitiveness. In order to improve ethanol plant energy balance, anaerobic digestion has been suggested for the treatment of DDGS (Distilled Dried Grains with Solubles), which is one of the main process by-products. This study aims to evaluate anaerobic digestion yields of DDGS and its variation after ultrasonic pretreatment. Sonolysis is a promising disruptive technique, whose effects are generated by the collapse of cavitation bubbles. It has been proved that low frequency ultrasound can promote mainly physical effects. In this study, the basic unit of a low frequency commercial ultrasonic device was used. Its effects were expected to result in carbon and nitrogen solubilisation improvement and, consequently, in the enhancement of anaerobic digestion yields of sonicated substrates. Main results were provided in order to highlight both chemical-physical and biological effects of sonolysis on DDGS. Their analysis highlighted the absence of a relation between solubilisation and anaerobic digestion yields in terms of biogas production. This evidence highlighted the tight relation between sonolysis effects and investigated substrate composition, which can result in relevant variation in anaerobic digestion yields of sonicated substrates to be treated by means of anaerobic digestion.

Keywords: bioethanol, DDGS, anaerobic digestion, sonolysis, ultrasound.

1. INTRODUCTION

Since in Europe the transport sector accounts for around 30% of the total energy consumption, great attention has been raised towards biofuels. According to European Commission estimation, biofuel production is expected to grow from the actual 2% of the total amount of used fuels to the target of 25% in 2030 (European Commission, 2006). One of the most promising biofuels in replacing conventional fuels is bioethanol: in the world, approximately 80% of ethanol production is obtained from fermentation of biomass; the remainder comes largely by synthesis of the petroleum product, ethylene (Lin and Tanaka, 2006). Ethanol fermentation is a biological process, developing in four steps: liquefaction, fermentation, distillation and purification. During the process, organic material is
converted by microorganisms to simpler compounds, such as sugars, which are then fermented by microorganisms to produce ethanol and CO$_2$. Typically, the distillation stage, which requires 46% of the thermal parasitic demand, determines the production of the stillage, a residue containing about a quarter of the grain feedstock dry solids. Although it is a suitable feedstock for livestock, in order to lengthen its shelf life and reduce transport costs, it is dried from 88% to 9% water. The drying process that transform stillage in DDGS (Distillers Dried Grains with Solubles), is very energy intensive and can account for up to 35% of the total parasitic thermal demand of the ethanol process (Murphy and Power, 2008).

In order to improve ethanol process energy balance, thus making it economically competitive with petroleum fuel production, adequate measure should be developed. One of the most valuable options is DDGS anaerobic digestion. In 2010, ethanol biorefineries produced approximately 32.5 million metric tons of DDGS. Almost all of the DDGS produced is currently utilized as low-value animal feed; estimated consumption by animal species in 2010 was beef 41%, dairy, 39%, swine 10%, poultry, 9%, and others 1% (RFA, 2011). However, DDGS inclusion in animal feeds is generally limited due to the fiber content, so that this material could be valuably used in different ways.

Anaerobic digestion can convert a significant portion (>50%) of the COD to biogas, which may be used as an in-plant fuel (Wilkie et al 2000). Blonskaya et al (2003) studied the anaerobic digestion of distillery waste in a mesophilic two-stage system: the treatment efficiencies (COD removals) achieved were 54 and 93% in the first and second stage, respectively and biogas production in the second stage was significantly higher (6 l/day) than that in the first stage (1 l/day), due to the acidogenesis control in the first reactor. Even though stillage anaerobic digestion yield strongly depends on the technology and operating condition, several studies provide encouraging data of the methane production from different kind s of stillage (Godwin et al., 2001; Hutnan et al., 2003). This study aims to evaluate anaerobic digestion yields of DDGS and its variation after ultrasonic treatment.

Sonolysis is an emerging and promising mechanical disruption technique, whose effects are generated by the collapse of cavitation bubbles (Mason and Peters, 2002). In particular, low frequency ultrasound mainly promotes physical effects, that facilitate particle solubilisation, thus ensuring the availability of larger quantities of readily digestible organic matter in the liquid phase (Thiem et al., 1997). It has been widely applied on sewage sludge to be treated anaerobically at both research (Thiem et al., 2001; El-Hadj et al., 2007; Naddeo et al., 2009) and industrial level (Hogan et al., 2004; Neis et al., 2012). However, the enhancement of methane production after ultrasonic pretreatment is highly variable, according to the different parameters affecting the combined process and still uncertainties exist in judging the efficiency (Pilli et al., 2011).

In this study a commercial ultrasonic device was used. It was designed in order to promote mainly ultrasonic physical effects, such as high pressure gradients, an increase in temperature, mechanical shear forces (Thiem et al., 1997). These physical actions were expected to affect the presence of carbon and nitrogen in DDGS soluble phase, thus varying anaerobic digestion yields of sonicated substrates. Main results are provided in order to highlight both chemical-physical and biological effects of sonolysis on the substrate and to find any correlation between these effects and biogas production from anaerobic digestion of pretreated substrates.

2. MATERIALS AND METHODS

The overall aim of this research was the assessment of anaerobic digestion yields of DDGS and its variation after the application of a proper ultrasonic treatment.

To this end, the experimental activity was structured in two steps:
- the first one was focused on sonolysis effects on DDGS soluble fraction;
the second one dealt with batch anaerobic digestion tests, in order to evaluate biogas production from untreated and sonicated substrates. All tests were performed in triplicate, so that average values were considered for discussion.

2.1. Substrate and inoculum composition

The DDGS used for the experimental tests was Protigrain®, a dried and pelletized stillage, with an average total solids content of 93.0%, produced from the Südzucker bioethanol plant in Zeitz (Saxony-Anhalt). It is a certified animal feed for cattle, pigs and poultry and a valuable protein and energy source, whose nutritional composition is reported in Table 1.

Table 1. Nutritional composition of Protigrain®

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Value [%DM]</th>
</tr>
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<tbody>
<tr>
<td>Fat</td>
<td>9.1</td>
</tr>
<tr>
<td>Protein</td>
<td>31.4</td>
</tr>
<tr>
<td>Starch and sugar</td>
<td>7.8</td>
</tr>
<tr>
<td>Fibre</td>
<td>7.5</td>
</tr>
<tr>
<td>Ash</td>
<td>6.0</td>
</tr>
</tbody>
</table>

In order to provide ultrasonic treatment, this material was milled and used to prepare a 5% total solid (TS) solution. Thickened digested sludge, was used as inoculum for biological tests. The sludge, which had an average TS content of 3% (± 0.23) and a volatile solid (VS) content of 62% TS (± 6.60), was sampled at the wastewater treatment plant in Hamburg (Germany) and incubated at 35°C for 5 days, in order to reduce sufficiently sludge own gas production by means of a hunger phase.

2.2. Experimental set up

Ultrasonic pretreatment was carried out by low frequency Ultrawaves GmbH sonication unit. It consists of a sonotrode, with a 50 mm diameter tip. The nominal given power to the sonotrode is 1 kW; the power released to the sample was displayed on an energy counter attached to the power source and it was recorder every 15 seconds, in order to calculate energy input. The solution to be treated was put in a cylindrical beaker with the US sonotrode placed in the centre and immersed up to 2 cm. During sonolysis application, the solution was continuously stirred in order to avoid precipitation of solids to the bottom of the beaker. The specific energy supplied was calculated as the ratio between the energy supplied (kJ) and the initial TS content of the mixture. In this investigation, instrument amplitude was set to 100%, according to company recommendation. Ultrasound test conditions are reported in Table 2.

Table 2. Ultrasound test conditions

<table>
<thead>
<tr>
<th>Specific energy [kJ/kgTS]</th>
<th>Sonication time [Wh/L]</th>
<th>Sonication time [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.835 ± 63</td>
<td>31</td>
<td>5</td>
</tr>
<tr>
<td>5.630 ± 122</td>
<td>62</td>
<td>10</td>
</tr>
<tr>
<td>8.493 ± 252</td>
<td>93</td>
<td>15</td>
</tr>
</tbody>
</table>
Biological tests were performed through the Eudiometer system. It is made of 500 mL reactors, connected to Eudiometer tubes, filled with a block solution. Biogas produced in each reactor flows in the tube, thus allowing the measure of its volume through the displacement of the solution. Rubber septa allowed the sampling of biogas, whose methane (CH₄) content was detected through a gas chromatograph with thermocconductivity detector (GC-TCD), model HP 6890 (Hewlett Packard, Waldbronn, Germany).

2.3. Analytical set up
TS and VS contents were estimated according to Standard Methods (DIVAPRA, 1998), while soluble COD (sCOD) was assessed by AWWA-APHA-WEF Standard Methods (1998). The soluble fraction of investigated samples, obtained after centrifugation (14000 rpm, 15 minutes) and filtration (< 0.45 µm) was also analyzed in terms of nitrogen content, determined by Kjeldahl Method and DOC, evaluated by Multi N/C 2000 (Analytikjena, Jena, Germany). Biological tests were carried out according to German guideline VDI 4630.

3. RESULTS AND DISCUSSION

3.1. Ultrasound effects on DDGS soluble fraction
Figure 1 plots both VS variation and soluble COD in investigated samples. The graph shows that the increase in ultrasonic energy input determined a slight reduction of soluble COD values. This result, however, was not related to the occurrence of mineralization phenomena, as the volatile solid content of treated samples remained almost constant, as displayed in Figure 1. Moreover, any variation in both organic carbon and nitrogen content of the soluble fraction of pretreated samples was observed after different sonolysis operating conditions, as shown in Figure 2. According to these results, sonolysis proved to be ineffective in increasing solubilisation of organic matter, both in terms of organic carbon and nitrogen. Similarly, any qualitative variation in terms of solubilisation could be underlined, as soluble COD values varied in a very narrow range for increasing ultrasonic specific energy provided.

![Figure 1](image-url)
3.2. Sonolysis effects on DDGS anaerobic biodegradability

According to the results of solubilisation tests, any increase in biogas production was expected. However, specific biogas volumes from anaerobic digestion of studied samples enhanced for increasing ultrasonic energy inputs. Figure 3 plots the cumulative biogas production from both untreated and sonicated samples and it highlights that the higher was the ultrasonic energy input, the greater was the specific biogas volumes produced from the anaerobic processing of investigated samples.

At the end of anaerobic digestion tests, the highest specific biogas volumes were obtained from the substrates pretreated with the maximum ultrasonic energy input considered, correspondent to 93 W h/L.

Figure 3. Biogas production from the anaerobic digestion both untreated and sonicated DDGS samples
Biogas methane content remained constant and this result was consistent with the absence of variation in DOC concentration. The absence of a relation between solubilisation and biogas production was observed, differently from literature results of studies dealing with sonolysis application to predominantly ligno-cellulosic materials, such as sludge (Chu et al., 2002) and organic waste (Cesaro et al., 2013).

This evidence can be related to the composition of DDGS, which is a protein-rich substrate. The ultrasonic-induced cavitation determines high-intensity shock waves, microjets, shear forces and turbulence, which can promote the alteration of the protein complex folded configuration, resulting in the so called denaturation. This phenomenon determines protein unfolding and, consequently, the loss of biological function and/or specific properties of the protein itself, such as the reduction of its solubility (Chandrapala et al., 2012) and the increase in digestibility (Ljøkjel et al., 2000; Sagum and Arcot, 2000), as found in this study. Since the evaluation of protein structure alteration involves a variation in protein structure itself, further core studies are necessary on this topic.

4. CONCLUSIONS

The experimental work carried out shows that ultrasound effects strongly depend on the dominant components of investigated substrates. Differently from predominantly ligno-cellulosic materials, a linear correlation between solubilisation and biogas production was not observed for the studied protein-rich substrate, suggesting the occurrence of the so called denaturation, a process largely investigated in food chemistry. This phenomenon, which consists in protein alteration and its consequent unfolding, can determine the loss of biological properties and/or specific function of the protein itself, such as the reduction of its solubility and the increase in digestibility. Although anaerobic biodegradability was positively affected by sonolysis, further studies are required in order to better define the nature of alteration that can be induced by different sonolysis treatment conditions as well as to address the evaluation of sonolysis feasibility as DDGS pretreatment for anaerobic digestion.

REFERENCES