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Experimental and economical evaluation of bioconversion of forest residues to biogas using organosolv pretreatment

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HIGHLIGHTS

- Organosolv-pretreatment of forest residues for enhanced CH_4 yield was performed.
- The pretreatment increased the CH_4 yield by 50%.
- Acetic acid and ethanol pretreatments led to the highest methane yields.
- Techno-economical evaluation suggest, methanol pretreatment was more efficient.

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ABSTRACT

The methane potential of forest residues was compared after applying organic solvent, *i.e.*, acetic acid, ethanol, and methanol pretreatments using batch anaerobic digestion (AD). The pretreatments were performed at 190 °C with 50% (V/V) organic solvent for 60 min. The accumulated methane yields after 40 days of AD from pretreated forest residues were between 0.23 and 0.34 m^3 CH_4/kg VS, which shows a significant improvement compared to 0.05 m^3 CH_4/kg VS, from untreated forest residues. These improvements count up to 50% increase in the methane yields from the pretreated substrates based on expected theoretical yield from carbohydrates. Among the organic solvents, pretreatments with acetic acid and ethanol led to highest methane yields, *i.e.*, over 0.30 m^3 CH_4/kg VS. However, techno-economical evaluation showed, pretreatment with methanol was more viable financially. The capital investments of the plant operating 20,000 tons of forest residues varied between 56 and 60 million USD, which could be recovered in less than 8 years of operation.

1. Introduction

According to European Commission Energy, 2010, EU members aim to reach a 20% share of final energy consumption from renewable sources, with a binding target of 10% renewable energy in the transport sector by 2020. A development of renewable energy sources for production of heat and electricity is spread across the energy sectors; however, the production of renewable fuels for the transport sector is less established and requires a substantial progress to promote the contribution of biofuels for transportation (European Commission, 2011).

Among the renewable fuels, biogas is becoming an important part of the biomass-to-energy chain. Biogas is a renewable energy source, which is commercially produced from various organic waste materials such as wastewater sludge, municipal solid waste, and energy crops. Moreover, biogas has several advantages, since the overall energy efficiency is much higher in biogas production compared to that for bioethanol production (Murphy and Power, 2009) Furthermore since most of the industrial yeast species cannot assimilate pentoses, the utilization of pentoses remains one of the challenges in a lignocellulose to ethanol process (Karimi and Zamani, 2013). An alternative solution can be to produce biogas as only product from lignocellulosic biomass. Many industrial, municipal, agricultural, and forestry waste streams contain high portions of lignocelluloses, representing a great potential for biogas production. However, these energy-rich fractions are not commonly used yet for biogas production (Deublein and Steinhauser, 2008).

Due to the recalcitrant structure of the lignocelluloses, the crystallinity of the cellulose, and the presence of lignin, there is a limitation in the first step of the anaerobic degradation, *i.e.*, the hydrolysis step. Therefore, an appropriate pretreatment is essential, aiming to disrupt the cell wall barriers, to remove the lignin and to decrease the cellulose crystallinity, so that hydrolytic enzymes produced by facultative anaerobes acting during the

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anaerobic digestion process can easily access the biomass macrostructure (Fan et al., 1981; Zhao et al., 2009). Additionally, another limitation can occur even in the methanogenic step, where the methane is produced (Noike et al., 1985), since methanogenic bacteria have a low growth rate and are sensitive to the inhibitory products that might form during some specific pretreatment conditions. The application of the pretreatment methods, such as dilute acid pretreatment, steam explosion, and ammonia fiber explosion can lead to the formation of furans and phenolic compounds that negatively affect the balance of the anaerobic digestion process (Chundawat et al., 2007; Taherzadeh and Karimi, 2008). Therefore, applying a suitable pretreatment method that avoids these problems is of vital importance.

Among all the pretreatment methods, organosolv-pretreatment has been considered as one of the promising methods for pretreating lignocellulosic biomass and now being developed as part of a commercial lignocellulose biorefinery (Alvira et al., 2010; Pan et al., 2005). Pretreatment with an organic solvent partially hydrolyzes the lignin fraction and the bonds between the lignin and carbohydrates, aiming to remove the major barrier for an enzymatic attack (Hu et al., 2011; McMillan, 1994). Moreover, using organic solvents, like low molecular weight alcohols and organic acids for pretreatment of lignocelluloses, are not inhibitory for the methane producing microorganisms, since these easily-degradable compounds can be utilized by the microorganisms in the anaerobic digestion system.

So far, most of the studies carried out on investigating organosolv-pretreatment of lignocellulosic materials were focused on either the fractionation of biomass or the improvement of the enzymatic hydrolysis for bioethanol production. Pan et al. (2006) applied hot aqueous ethanol pretreatment on the hybrid poplar, which successfully improved the recovery of glucose by 85% after enzymatic hydrolysis. In another study, a combined treatment using sulfuric acid and ethanol on lodgepole pine (softwood) resulted in up to 97% conversion of cellulose to glucose (Pan et al., 2007). Nevertheless, no previous research has been reported for organosolv-pretreatment on lignocellulosic biomass aiming to improve biogas production.

In this study, forest residues were selected among the lignocellulosic wastes for the investigations, since they represent an abundant waste stream in Sweden. The tree tops and branches obtained from the Swedish forests counted up to about 1.6 M tons total solids in 2008. This amount is expected to increase to 3.5 M tons total solids/year by the year of 2018 (Teghammar et al., 2014), corresponding to a biomethane potential of 154 M m^3 CH_4/year.

One of the main problems faced in the biogas industry is its profitability as well as the supply chain of the raw materials (Rajendran et al., 2014). Given the fact that the volume of forest residues is estimated to grow in Sweden, the important question that arises is the profitability. In a previous study, process design and cost-estimation had been performed for co-digestion of the pretreated forest residues, using a cellulosic solvent, *i.e.*, *N*-Methylmorpholine-*N*-oxide (NMMO), with municipal solid waste (MSW) (Teghammar et al., 2014). The results showed that the cost of the solvent reflected the main part of the material costs; therefore, effective recovery of the NMMO was crucial for the feasibility of the industrial scale process. Whereas, when using low molecular weight organic solvents for the pretreatment they can be recovered and re-used easily, leading to a better economics of the process (Amiri et al., 2014; Zhao et al., 2009).

The aim of this study was to increase the digestibility of the forest residues using ethanol, methanol, and acetic acid pretreatments prior to biogas production. Specifically, to determine the biomethane potential of the pretreated forest residues using the above mentioned solvents in the presence and absence of catalysts such as sulfuric acid, hydrochloric acid, and acetic acid. The mass balances as well as the solvent recovery were accurately studied. Based on the experimental data, a process design was performed to estimate the overall energy needs and economics of the process.

2. Methods

2.1. Materials

Native forest residues (mixture of spruce, pine, bark, etc.) were obtained from the forests outside Borås in Sweden. These residues were dried at room temperature for a couple of days, followed by cutting, milling, and screening to achieve 2 mm particle size.

2.2. Organosolv pretreatment

Three different organic solvents including: ethanol, methanol, and acid acetic were used for the pretreatments. The pretreatments were carried out based on the process description by Pan et al. (2006). First, eight grams (dry weight) of the forest residues were mixed with 80 g (solid-to-liquid ratio of 1:10) of 50% (V/V) aqueous organic solvents. In the case of the ethanol and methanol pretreatments, the addition of 1% (W/W) (based on the forest residues dry mass) of two different acids (each separately), as catalysts were also investigated (*i.e.*, ethanol + sulfuric acid, ethanol + acetic acid, methanol + sulfuric acid, methanol + acetic acid). Moreover, the effect of the addition of two other catalysts, including sulfuric acid or hydrochloric acid (each added separately) was investigated in the case of the acetic acid pretreatment. The organosolv-pretreatments were carried out in sealed 150 ml stainless steel tubular reactors (Swagelok, U.S.A.), heated in an oil bath at 190 °C for 60 min. After the pretreatment, the reactors were taken out from the oil bath and placed in an ice chamber to cool below room temperature. The pretreated-forest residues were washed with 80 g aqueous organosolv (50% V/V) solution and then washed with 80 g of water. The washed biomass (*i.e.*, solid fraction) samples were allowed to dry prior to the composition analyses regarding carbohydrates and lignin. Finally, the materials were stored at 5 °C until use.

2.3. Anaerobic batch digestion assays

Anaerobic batch digestion assays at thermophilic conditions (55 °C) were performed in triplicates to investigate the effects of the different pretreatment conditions on the methane potential. The digesters used were serum glass bottles, each with a total volume of 118 ml, and closed with butyl rubber seals and aluminum caps (Hansen et al., 2004). The inoculum was obtained from an industrial 3000-m^3 municipal solid waste digester operating at thermophilic (55 °C) conditions (Borås Energi och Miljö AB, Borås, Sweden). Each flask contained 20 ml inoculum and 0.15 g VS (Volatile Solids) of untreated or treated substrate, and the final working volume was then adjusted to 25 ml with the addition of deionized water. Furthermore, a mixture of deionized water and inoculum was also prepared and used as a control to determine the gas production from the inoculum.

Finally, the headspace of each bottle was flushed with nitrogen to obtain anaerobic conditions. Gas samples were withdrawn regularly from the headspace of each bottle, and the accumulated methane production was determined using gas chromatography.

2.4. Analytical methods

The Total Solids (TS) and Volatile Solids (VS) were determined by oven drying the samples first at 105 °C until a constant weight was achieved and then by ignition at 575 °C in a furnace,

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