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Enhanced biogas production from sunflower stalks using hydrothermal and organosolv pretreatment

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ABSTRACT

Biomethane production through anaerobic digestion of sunflower stalks was improved by the hydrothermal and isopropanol-based organosolv pretreatments. The pretreatments were conducted at different temperatures (140, 160, 180, and 200 °C) for 30 and 60 min with/without addition of 1% sulfuric acid. The pretreatment of stalks with 50% (v/v) aqueous isopropanol containing 1% w/w (based on dry stalks) sulfuric acid at 160 °C resulted in the highest lignin removal. Methane production yield of the pretreated substrate was improved by 45–124% compare to 124 mL CH_4/g VS obtained from the digestion of untreated stalks. In the best case, hydrothermal pretreatment at 180 °C for 60 min and organosolv pretreatment at 160 °C for 30 min with 1% H_2SO_4 followed by 45 days anaerobic digestion resulted in 234 and 278 mL CH_4/g VS, respectively. Structural analyses of the stalks indicated that lignin removal, crystallinity reduction, and structural modifications by the pretreatments were the main reasons for the improved biogas production.

1. Introduction

Biomethane, a renewable source of energy, is currently considered as a respectable alternative to replace fossil fuels for heating, electricity production, transportation fuel and production of value-added chemicals (Teghammar et al., 2012; Weiland, 2010). All types of raw materials containing carbohydrates, fats, proteins, cellulose, and hemicelluloses as the major components can be employed as substrates for biomethane production (Weiland, 2010). In particular, lignocellulosic materials such as agricultural residues have been widely considered as the most suitable raw materials for biomethane production due to relatively low costs, high availability, and no direct competition with food and feed production (Shafiei et al., 2013; Taherzadeh and Karimi, 2008). Sunflower residues, especially sunflower stalks which are lignocellulosic biomass, are globally produced 78–182 million tons per year (reported by FAO in 2013) and typically disposed as a waste or burned in the fields causing environmental pollution (Ruiz et al., 2013). In contrast, high cellulose and hemicellulose contents of sunflower stalk makes it a potential feedstock for biomethane production (Ziebell et al., 2013). However, the highly crystalline cellulose is well packed by a matrix of lignin and hemicellulose in the natural structure, and it is the main drawback of using lignocellulosic materials limiting the production of methane (Frigon and Guiot, 2010; Taherzadeh and Karimi, 2008). Lignin, as a main factor of integrity and structural rigidity, is responsible for the recalcitrance of lignocellulosic substrate to bacterial degradation by limiting cellulose accessibility (Gupta et al., 2011; Shafiei et al., 2013). Therefore, an effective pretreatment step is required to enhance the digestibility of lignocellulose (Bateni et al., 2014; Hendriks and Zeeman, 2009). Alkaline and oxidative pretreatments have been evaluated for biomethane production from sunflower stalks (Monlau et al., 2012). Although these processes are often performed at a low temperature, they are associated with a high energy consumption and high wastewater production.

Hydrothermal pretreatment by hot water has been applied for the pretreatment of lignocellulosic biomass over last few decades (Taherzadeh and Karimi, 2008). In this process, water penetration into the biomass structure increases the accessible and susceptible surface area of cellulose by removing hemicellulose and a part of lignin (Chandra et al., 2012). Organosolv pretreatment is about the same as hydrothermal pretreatment; however, the lignin and hemicellulose removals are conducted using organic liquid solvents such as alcohols, ketones, glycols, phenols, and ethers. This organic mixture partially hydrolyzes internal lignin and hemicellulose bonds, and consequently removes a considerable portion of lignin

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from the biomass. This phenomenon leads to an increase in the pore volume and surface area which can facilitate enzyme accessibility (Zhao et al., 2009). The recovery of relatively pure lignin as a value-added byproduct is a major advantage of organosolv pretreatment compared to other chemical pretreatments (Huijgen et al., 2012; Zhao et al., 2009). Lignin removal in a separate phase can also decline the economic and environmental problems associated with wastewater treatment of typical chemical pretreatment methods (Amiri et al., 2014). Furthermore, a strong inorganic catalyst, e.g., sulfuric acid, may be used to decrease the operating temperature or improve the delignification process (Zhao et al., 2009). These advantages along with the solvent recovery with minimal energy consumption have made organosolv process as one of the most promising methods to improve the conversion yield of different lignocellulosic materials for biofuel production (Amiri et al., 2014; Mesa et al., 2011; Wildschut et al., 2013; Zhao et al., 2009).

Alcohols, especially the low boiling point alcohols such as methanol and ethanol, appear to be the most frequent organic solvents used in alcohol-based organosolv pretreatment, due to their low cost and easy recovery (Zhao et al., 2009). However, methanol is a toxic chemical and forms flammable vapors at relatively low temperatures making the pretreatment process more complicated (Zhao et al., 2009). On the other hand, even though ethanol is less toxic than methanol, very high pressure is needed due to low boiling point of ethanol resulting in high equipment costs with accompanying safety concerns and maintenance difficulties (Zhao et al., 2009). Isopropanol is the other low boiling point alcohol which is similar to methanol and ethanol in solvent properties and evaporation rate. Unlike methanol and ethanol, isopropanol can be separated from aqueous solutions either through an evaporation step followed by condensation or by addition of a salt such as sodium chloride, sodium sulfate, or other inorganic salts (Othmer, 1999). Therefore, isopropanol can be employed for organosolv pretreatment of lignocellulosic biomass. However, based on our knowledge, there is no report in the literature on the utilization of isopropanol as a lignin solvent in the organosolv pretreatment of lignocellulosic materials for biofuel production.

The overall objective of this study is to evaluate the effect of hydrothermal and isopropanol organosolv pretreatment variables (pretreatment time and temperature) on the biomethane production from sunflower stalks. The effect of using sulfuric acid as a catalyst in both pretreatment processes on the lignin removal and biomethane production yields was also investigated. Moreover, the changes in the biomass structure and the reasons for the improvement were followed.

2. Materials and methods

2.1. Raw materials

Sunflower stalks were collected from a local field in the north of Isfahan (Isfahan, Iran) and dried in sunlight for 3 days. Stalks were milled and screened to achieve a size of less than 1 mm. The substrate was then dried at 105 °C in a convection oven to measure its dry weight content.

2.2. Organosolv and hydrothermal pretreatment procedures

Pretreatment experiments were carried out in a high pressure batch reactor with a working volume of 500 mL (Amiri et al., 2010). The reactor was loaded with 20 g (dry weight) of substrate and 200 mL of a 50% (V/V) isopropanol in water mixture (solid–liquid ratio of 1:10 (w/v)). In all pretreatment experiments, the ratio of biomass to organic solvent was kept constant the same as above and temperature and time of pretreatment were changed as below. The reactor was heated at a rate of 3 °C/min to a desired temperature (140, 160, 180, and 200 °C). The reactor was then kept for 30 or 60 min at the desired temperature to treat the biomass. Another set of pretreatments was conducted by adding 1% w/w sulfuric acid (based on dried weight of the stalk) as a catalyst. After the reaction time, the reactor was transferred to an ice bath. The solid phase was separated using filter, and then rinsed with 60 °C deionized water for several times until pH 7 and dried at room temperature. Finally, the pretreated samples were stored in resealable plastic bags at 4 °C until use.

Hydrothermal pretreatment was also performed under the same conditions as the organosolv pretreatment, except that the reactor was loaded with 200 mL water and 20 g substrate (dry weight) to obtain solid–liquid ratio of 1:10 (w/v).

2.3. Biogas production

The inoculum was obtained from a 7500 m^3 anaerobic digester (Isfahan municipal wastewater treatment plant, Isfahan, Iran) operating at 37 °C. Biogas production from the untreated and pretreated samples were performed in 118 mL serum glass bottles as anaerobic digesters at 37 °C (Hansen et al., 2004). Bottles were loaded with 20 mL inoculum and 0.25 g treated or untreated biomass (dry weight). By adding deionized water to each bottle, final volume was reached to 25 mL. Moreover, a sample containing 20 mL inoculum and 5 mL deionized water was used as a blank to be able to measure the gas production of inoculum alone. Bottles were capped by aluminum caps on butyl rubber stoppers. Then, to provide anaerobic conditions, bottles were purged using N_2 gas for about 2 min. The bottles were manually shaken every day and kept at 37 °C in an incubator. Gas samples were taken from the headspace of each bioreactor and analyzed using gas chromatography every three days during the first fifteen days and then every five days until the end of the experiment. All the experiments were carried out in duplicate. The biogas production results were analyzed using ANOVA toolbox of Microsoft Office Excel 2013. 2-factors ANOVA was used and the *p*-values less than 0.05 were considered as statistically significant.

2.4. Analytical methods

The composition of gas produced in the bottles (methane and carbon dioxide) was determined by a gas chromatograph (Sp-3420A, TCD detector, Beijing BeifenRuili Analytical Instrument CO.) equipped with a packed column (Porapack Q column, Chrompack). The carrier gas was nitrogen with flow rate of 45 mL/min. Temperatures of the injector, column, and detector were adjusted on 100, 40, and 150 °C, respectively. Carbohydrates, lignin contents, total solids, and volatile solids of treated and untreated sunflower stalks were analyzed according to the methods of Sluiter et al. (2008a,b). Sugars were analyzed by a high performance liquid chromatography equipped with RI and UV/vis detectors (Jasco International Co., Tokyo, Japan) and an Aminex HPX-87P column at 85 °C with deionized water as an eluent with a flow rate of 0.6 mL/min. Morphological changes in the treated and untreated sunflower stalks during the organosolv and hydrothermal pretreatments were observed by scanning electron microscopy (SEM). The dried samples were coated with a thin layer of gold and analyzed by a scanning electron microscope (KYKY-EM3200) at 26 kV.

The crystallinity and molecular structure of treated and untreated sunflower stalks were analyzed using a Fourier transform infrared (FTIR) spectrometer (Bruker Tensor 27 FTIR). The spectra were obtained with an average of 60 scans with 2 cm^{-1} resolution from 600 to 4000 cm^{-1}.