

Original Research Article

Determination of the Chemical Oxygen Demand (COD) of Hydrothermal Pretreated Hay Samples

ABSTRACT

Energy production is one of the significant challenges our world will face in the future. The utilization of fuels originating from plants as an alternative energy source will impact fossil fuel utilization and energy production. This research focuses on the hydrothermal treatment of hay biomass by analyzing the chemical oxygen demand (COD), which is a commonly used testing method to determine the amount of organic pollutants found in drinking or wastewater. The test indicates the mass of oxygen consumed per liter of solution, expressed in milligrams per liter (mg/L), also referred to as ppm. In this paper, COD tests were used to indirectly determine whether the yield of biogas in a biogas plant could be increased by pretreating the biomass (hay) with heat and/or decreasing the particle size. It was assumed that the potential space-time-yield of biogas in biomass is directly linked to the amount of its accessible organic compounds. Hence the COD of filtrates of different hydrothermal pretreated hay samples was measured in order to determine if there is a relation to temperature and particle size.

Keywords: Biomass; biogas, pre-preparation; chemical oxygen demand, hydrothermal treatment; grinding

Nomenclature

°C Degree Celsius;
kg Kilogram
m³ Cubic meter
mg l⁻¹ Milligram per liter
min Minute
ml Milliliter

mm Millimeter
MPa Mega pascal
nm Nanometer
l Liter
rpm Revolutions per minute

Chemical Abbreviation

CH₄ Methane
CO₂ Carbon dioxide
Cr³⁺ Chromic ion
Cr₂O₇²⁻ Dichromate ion

Acronyms

COD Chemical oxygen demand
OH Ohio State
USA United States of America

1. INTRODUCTION

The most significant challenge facing our world in the future pertains to energy. Fossil fuels, the primary source of energy on earth, are finite and have adverse effects on greenhouse gas emissions and the environment [1]. Declining petroleum reserves and concerns about future energy security require finding new alternative energy systems that utilize technologies to minimize the impacts of fossil fuel utilization [2]. Therefore, there is an interest in the production and use of fuels originating from plants or organic wastes [3]. Agricultural residues such as straw, hay and forest waste products, hardwood and softwood biomass are ~~also~~ ^{additional} sources of energy. They are widely available, burn cleaner than fossil fuels and do not add CO₂ to the atmosphere [4]. Anaerobic digestion, a common technology that converts biomass to green energy, has been a common treatment for lignocellulosic biomasses and municipal waste in recent years [5], [6]. However; the hydrolysis of lignocellulose is limited by several factors, such as crystallinity of cellulose, degree of polymerization, moisture content, available surface area and lignin content [7]. In order to maximize the biogas yield, different pretreatment methods have been developed. In this paper we investigated the effect of a combination of hydrothermal and mechanical pretreatment on hay. Both methods have cost-savings potential, as they need no catalysts or special reactor design [8]. Mechanical treatment of biomass reduces size, enlarges the available specific surface area of the biomass particles and can improve anaerobic digester operation, digestion time as well as biogas production [9]. The objective of the hydrothermal pretreatment is to solubilize the hemicellulose and lignin to make the cellulose more accessible. Combined with high pressure, this method can lead to a 2- to 5-fold increase in enzymatic hydrolysis of the substrate experienced in experiments by Weil et al. (2003) [10]. In our experiments, chemical oxygen demand (COD) was used to indirectly measure whether the yield of biogas (Methane, CH₄) in a biogas plant could be increased by pretreating the hay biomass with grinding and hydrothermal heat treatment. COD tests are commonly used to indirectly measure the organic content in watery solutions, like wastewater, and are one of the most important indicators for water quality [11], [12]. It was assumed that the potential biomass biogas yield is directly linked to the amount of its oxidizable organic compounds. According to D. W. Hamilton (2012) each removed kilogram COD equals 0.40 kg CH₄ produced with anaerobic fermentation [13]. Depending on the retention time and experimental method, COD removals rates have been reported for different biomasses between 7% for food processing and domestic wastewater, and 83% for biological and industrial wastewater [14]; [15].

2. METHODOLOGY

2.1 Materials and Methods

Alfalfa (*Medicago sativa*) hay material, sometimes also called “lucerne hay” was obtained from a farm in New York State.

The hay was milled into two different fractions using a Wiley Knife Mill. Fraction one had a particle size smaller than 2 mm. Fraction two had a particle size smaller than 0.5 mm. A 2.4% hay-water suspension was prepared from each of the hay fractions using distilled water. The hay water suspension was heated for 45 min in a 500 ml beaker, on a heating plate with stirring function, to temperatures of 20°C, 37.5°C, 55°C, 70°C, 90°C 100°C, and 120°C. To achieve temperatures over 100°C a pressure cooker operating at 0.2 MPa was used. After cooling the samples down to room temperature, the samples were filtered twice using a 150 mm Büchner Funnel and white, rapid draining filter paper with a 1000ml suction

flask. After filtering, the liquid samples were centrifuged for 60 min. at 4100 rpm in a Thermo Scientific Sorvall T1 Centrifuge to remove particulate matter. After centrifugation 0.2 ml of the samples was pipetted into a high range YSI COD Vial containing potassium dichromate (oxidant) and silver sulfate catalyst in sulfuric acid. The vial was then heated in an YSI CR 2200 thermo-reactor block for 2 hours at 150°C. With this method almost all organic compounds except pyrimidine rings and some nitro bonds are oxidized [16], by reducing the dichromate ions ($\text{Cr}_2\text{O}_7^{2-}$) to green chromic ions (Cr^{3+}). After the samples had been cooled overnight, the amount of Cr^{3+} was measured with an YSI 910 COD colorimeter at 430 nm and 610 nm. The results are displayed in the amount in oxygen consumed in milligrams per liter (mg/l), also referred to as ppm [17].

3. RESULTS AND DISCUSSION

3.1 Pre-Testing

Before actual measurements were taken, an adequate method for the test procedure had to be found to improve practicability and reproducibility of the results.

The first pre-evaluation determined the ratio of water and hay in the suspension by preparing different suspensions at 2.4%, 5%, 8% and 12% using fraction one with a particle size smaller than 2 mm. Table 1 shows that a suspension with hay concentrations of 8% and 12% had COD values higher than $15,000 \text{ mgL}^{-1}$, exceeding the measurement range of the YSI colorimeter. The 5% hay suspensions resulted in a COD value of $11.88 \cdot 10^3 \text{ mgL}^{-1}$ which was still too close to the limit of the colorimeter. Therefore, the 2.4% hay suspension with a COD value of $6.32 \text{ mgL}^{-1} \cdot 10^3$ was chosen for further usage in the experiments.

Table 1: Determination of adequate mass-percentage of hay in suspension

Mass-% hay	12%	8%	5%	2.4%
Temperature [°C]	72	72	72	72
COD [$\text{mgL}^{-1} \cdot 10^3$]	>15	> 15	11.88	6.32

In the next step, the treatment time for the hydrothermal pretreatment needed to be defined. Therefore, the suspensions with a percentage of 2.4% hay and a particle size smaller than 2 mm was treated for 15; 30; 45 and 60 minutes in order to determine which treatment time would did not change the COD value. Results from this experiment showed that the COD-value did not increase any further after 45 minutes of hydrothermal treatment.

After the pre-evaluation, the experiments were conducted. Figure 1 shows the average COD based on the two experiments. The COD increases with increasing temperatures in a linear relation. Also, the smaller particle size seems to have an increasing effect on the COD value. In general the plotted results show a linear relation of COD of the hydrothermal treatment to temperatures between 25°C and 120°C.

The results of the experiments indicate that hydrothermal pretreatment in combination with physical treatment improves the COD and could consequently improve the methane yield in a biogas power plant. In the experiments the COD increased by up to 10.7% for the fraction one with a particle size smaller then 2 mm and up to 15.2% for fraction two with a particle size smaller than 0.5 mm if the hay suspension is pretreated from 38°C to 120°C.

This would result in an additional methane gas yield for a biogas plant from hydrolyzed biomass per m^3 suspension. At 2.4% hay-water suspension, 244 liter of methane could be

achieved for the fraction with a particle size smaller than 2 mm and 344 liter for the fraction with a particle size smaller than 0.5 mm as shown in Figure 2.

Figure 1: COD of hay with different particle sizes and temperatures

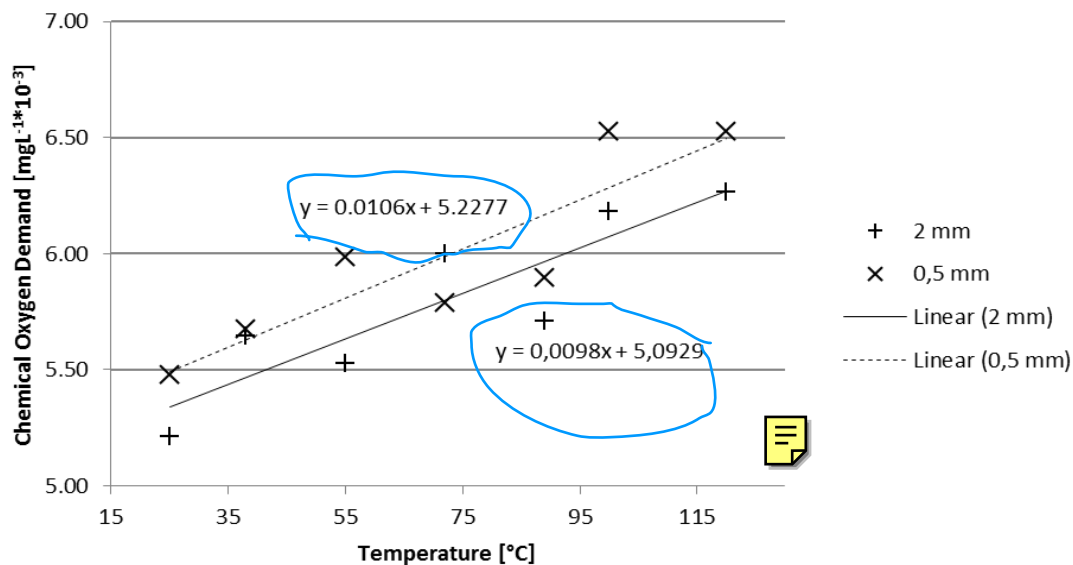
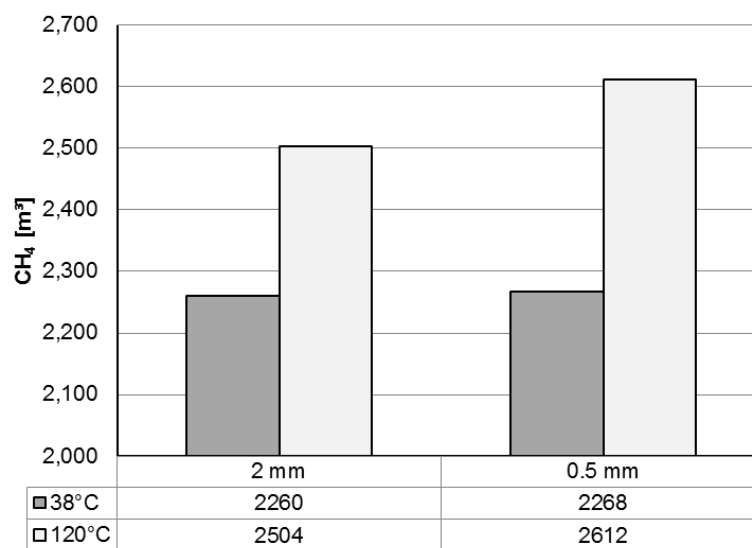


Figure 2: COD of hay with different particle sizes and temperatures



4. CONCLUSION

The results of the experiments indicate that hydrothermal pretreatment in combination with physical treatment improves the COD and could consequently improve the methane yield in a biogas power plant. Results from this experiment showed that a 2.4% hay suspension works best for the chosen experimental set up. The COD-value did not increase any further after 45 minutes of hydrothermal treatment. However, large scale processes might work better and are more economic valuable at higher concentrations above 2.4%. Based on the above results it is likely that biogas plants would benefit from the pretreatment of lignocellulosic biomasses and or increased operation temperatures, e.g. termophilic operation above 50°C. However; COD measurements cannot differentiate between biodegradable and inert organic matter or between readily and slowly biodegradable fractions [18].

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