

# Biogas production from sunflower residues: effect of pretreatment

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#### **Abstract**

Sunflower residues are a prominent substrate of renewable source for biogas production during anaerobic digestion (AD). However, due to its recalcitrant structure, pretreatment is necessary to increase its biodegradability. The objective of the present work was to evaluate the effect of the NaOH pretreatment on the methane production from sunflower residues. The residues were separated into stalks and heads after seed removal. It was observed that pretreatment caused an increase in the biochemical methane potential (BMP) during batch tests, but a decrease was recorded during continuous experiments.

**Keywords:** anaerobic digestion; lignocellulosic biomass;; NaOH pretreatment;

# 1. Introduction

Agricultural wastes are considered important feedstocks for the production of second-generation biofuels (e.g. H<sub>2</sub>, CH<sub>4</sub>). Agricultural areas produce large quantities of crop residues which could be a potential source of feedstock for biogas plants developing in Greece during the recent decade. The case study considered in this work was the sunflower residues, abundant in the area of East Macedonia and Thrace. An area of 77000 hectares for sunflower seeds cultivation in Greece was recorded by FAOSTAT, with a yield of 4818 kg/ha (FAOSTAT, Greece). If the ratio of residue to product is taken into account (1.77), the quantities of this residual biomass type are significantly large and could be exploited

Sunflower residues are a typical lignocellulosic renewable source for bioenergy production (e.g. biogas) via anaerobic digestion (AD). However, the recalcitrant structure of this lignocellulosic substrate requires the use of physicochemical pretreatment, to make hollocelluloses (hemicelluloses and cellulose) more accessible to bacteria during AD. The main drawback of applying pretreatment on plant biomass, besides the cost added to a biogas plant project, is that lignin derived compounds are released which may be inhibitory to AD (Monlau et al., 2012). Therefore, the inhibitory factors should be always taken under consideration during AD process. This is why Monlau et al (2012), applied a mild NaOH pretreatment at 55° C and noticed an increase of 26% during continuous experiments. However, it was not clear how the different parts of the residues (i.e. stalks and heads) could respond to this pretreatment scheme. Therefore, these two different parts of the residues were studied separately and their methane yield in batch and continuous experiments was assessed.

# 2. Materials and Methods

#### 2.1. Substrate characterization

Sunflower stalks and heads were harvested from a field located in the area of Xanthi city (Northern Greece) and were immediately dried at 40°C. Afterwards, the dried residues were milled separately into a particle size range of 0.15-1 mm using a cutting mill (Retsch SM 100) and stored. Analysis of total solids (TS), volatile solids (VS), chemical oxygen demand (COD), lipids and total Kjeldahl nitrogen (TKN) was done according to Standard Methods (APHA et al., 1999). Data are the means of triplicates along with their standard deviations.

### 2.2. Alkaline pretreatment process

During the alkaline pre-treatment, the stalk or head was disposed to sodium hydroxide at a ratio of 0.04 gNaOH/gDryMatter at 55°C for 24h after Monlau et al (2015), while mixing. After treatment the mixture was adjusted to pH=7 by adding hydrogen chloride (6N) and was filtered through 2.5 $\mu$ m cellulose filter to separate the liquid from the solid fraction.

# 2.3. Biochemical methane potential

For the evaluation of the BMP, liquid and solid fractions after the alkaline process, were separately digested in batch anaerobic serum bottles (110 mL). Each bottle was inoculated with 85 mL of anaerobic sludge (25.66±0.28 gVS/L), taken from a full-scale anaerobic digester treating various wastes. A volume of ca. 12.5 mL of each liquid fraction or  $1067\pm2$ mg dry matter (DM) with 12.5 ml of tap water were loaded. Each BMP test was conducted in triplicate at  $37^{\circ}$ C. For control tests, only tap water (12.5ml) was added into the vials. The vials were finally sparged with  $N_2/CO_2$  mixture (80/20) for 1 min sealed with butyl rubber septum-type stoppers. The headspace of each bottle was connected with a NaOH (6N) trap. Methane volume was expressed at STP conditions.

# 2.4. Continuous experiments using sunflower head residues

Two mesiphilic continous stirred tank reactors (CSTRs) were set up and operated in parallel. The volume of each CSTR was 2.5 L Both CSTRs were fed with sunflower head residues; however one was after alkaline pretreatment, while the other one was without any pretreatment (used as control). The HRT was 25 d, but the OLR varied based on the COD concentration of the feeding medium which was prepared after adding 5 g of sunflower head residues into 100 mL of tap water. Both CSTRs were previously operated using the water extract as the feeding medium. Biogas volume is expressed at STP conditions.

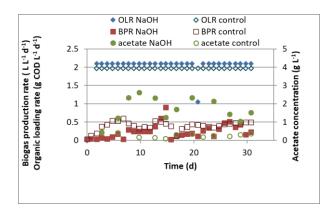
#### 3. Results and Discussion

The characteristics of the sunflower residues are presented in Table 1. The head contains less VS (resulting in less COD), while the TKN is more than double compared to the stalk characteristics. However, the methane yields of stalk and head residues were  $112.2 \pm 8.2$  and  $183.0 \pm 7.3$  ml CH4 gTS-1. After pretreatment, the methane yields were  $150.7\pm12.4$  and  $196.4\pm10.9$  ml CH<sub>4</sub> gTS<sup>-1</sup>. Alkaline pretreatment as assessed from the BMP tests resulted in an increase in the methane yield of 34.3% and 7.3% for the stalk and head residues respectively.

Table 1. Characteristics of sunflower residues' parts.

Parameter	Stalk	Head
TS (%WM)	$91.9 \pm 0.3$	$90.5 \pm 0.4$
VS (% TS)	$87.7 \pm 0.1$	$79.9 \pm 0.4$
COD (g kg <sup>-1</sup> DM)	1074±34	890±26
TKN (g kg <sup>-1</sup> DM)	$6.25 \pm 0.02$	$13.3 \pm 0.3$
Lipids (g kg <sup>-1</sup> DM)	$0.989 \pm 0.056$	2.541±0.1

Following the BMP tests, continuous experiments were performed to evaluate the effect of pretreatment on the biogas production from sunflower head residues. The head residues were chosen since the increase in the BMP was little. The response of the CSTRs is shown in Figure 1. The CSTR fed on the pretreated sunflower heads was rather unstable, the acetic acid concentration was high  $(1.53 \pm 0.45~{\rm g~L^{-1}})$  and the methane yield was low  $(90.9\pm38.2~{\rm ml~CH4~gCOD\text{-}1})$  compared to the CSTR which was fed on untreated material ( $0.26 \pm 0.07~{\rm g~L^{-1}}$  and  $131.3\pm14.8~{\rm ml~CH4~gCOD\text{-}1}$  respectively). This means that there was a decrease in the methane yield (-31%), in contrast to the increase of the methane yield (7.3%)observed in th BMP test.



**Figure 1.** Biogas production rate compared to organic loading rate and acetate concentration in two CSTRs fed on alkaline pretreated sunflower heads (solid symbols) and sunflower heads with no pretreatment - control (open symbols)

#### 4. Conclusions

The experiments showed that the sunflower head residues after alkaline preteatment had a negative effect on the biogas production, although the BMP tests indicated the opposite. It is obvious that alkaline ptretreatment produces inhibitory compounds, the effect of which is not active in short term (e.g. in batch tests) but in long term (e.g. in continuously operated reactors where biomass is continuously exposed to positive or adverse conditions. This indicates, that BMP tests cannot always reveal the true response of a digester.

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