Exploitation of rapeseed and sunflower residues for methane generation through anaerobic digestion: the effect of pretreatment

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The present study aimed at assessing the anaerobic digestion process efficiency on rapeseed and sunflower residues. Batch mesophilic biochemical methane potential (BMP) tests were carried out and the methane potential as well as the biodegradability of all feedstocks, were determined. The experimental studies indicated that the biological methane potential of rapeseed and sunflower meal were 0.450 m^3 / kg and 0.481 m^3 / kg, respectively. Moreover, the biological methane potential of rapeseed straws was 0.264 m^3 / kg, while the respective value from sunflower straws was 0.260 m^3 / kg. For both rapeseed and sunflower residues, the methane potential of meal residues is much higher than the respective for straws residues. A possible reason for this could be the different composition of the feedstocks in terms of lignin. Various pretreatment methods, such as thermal, chemical (through alkali or acid addition) or combination of the above methods were also tested in the effort to enhance the methane productivity and yield. The experiments showed that the pretreatment methods tested did not enhance the methane potential of the rapeseed and sunflower residues. This could be attributed to the inhibitory compounds which were possibly released during the pretreatment.

1. Introduction

Agricultural wastes, if not properly handled, can be a serious environmental concern. Anaerobic digestion is one of the most environmentally friendly and suitable treatment methods for this type of wastes. In this process, the complex organic matter is converted into methane through a series of successive and/or parallel reactions, which are performed by anaerobic microorganisms. The anaerobic digestion process has been applied to agricultural solid wastes and has received increased attention during the last few years since it is well known that methane can be produced from a wide range of lignocellulosic types of biomass (Antoni et al. 2007; Levin et al. 2007).

Among other energy crops, rapeseed and sunflower represent important crops in the EU, where they occupy a notable proportion of arable land. However, while they are mainly harvested for their oil, the remainder of the plant, such as the straw, remains to a large extent unutilized. In order to maintain a competitive advantage in the world market and ensure a sustained economic return in the production of oil crops, the potential of these residues in added value applications such as bioenergy, should be explored and exploited. In addition, rapeseed and sunflower processing industries produce enormous amounts of residues. In 2006 in the EU alone, 9 million tons of rape meal residue were generated from rape oil production. Moreover, large quantities of waste from the sunflower oil industry are generated after the sunflower oil extraction processes.

In this work, the biochemical methane potential of the residues of rapeseed and sunflower harvesting (rapeseed and sunflower straws) as well as of the solid wastes derived from rapeseed and sunflower oil extraction process (rapeseed and sunflower meal) was determined. In addition, various pretreatment methods, such as thermal, chemical (through alkali or acid addition) or combination of the above methods were also tested, in order to evaluate the effect of the pretreatment on the methane productivity and yield.

2. Materials and methods

2.1 Analytical methods

The measurements of total chemical oxygen demand (T. COD), dissolved chemical oxygen demand (d.COD), total solids (TS) and volatile solids (VS) were carried out according to Standard Methods (APHA, 1975).

2.2 Inoculum

Anaerobic sludge from the anaerobic digester of the Patras wastewater treatment plant, treating municipal sewage sludge and operating at steady state at an HRT of 15 d, was used as inoculum. The main characteristics of the sludge were: pH = 7.1, total chemical oxygen demand (T.COD) = 40g/L, dissolved chemical oxygen demand (d.COD) = 0.52 g/L, total suspended solids (TSS) = 34.62 g/L and volatile suspended solids (VSS) = 12.53 g/L.

2.3 Feedstocks

For rapeseed (RM) and sunflower meal (SM), as well as for rapeseed (RS) and sunflower (SS) straws, a physicochemical characterization was carried out and the main measured characteristics are presented in table 1. Prior to use, samples were grinded to desirable particle size by a small laboratory scale mill and sieved to powder of < 1mm diameter.

Table 1: The main characteristics of all feedstocks

Characteristic	RM	SM	RS	SS
Dry matter (wt%)	91.2	92.1	91.0	87.0
Moisture (wt%)	8.8	7.9	9.0	13.0
Volatile Solids (wt% dry basis)	86.8	89.2	91.0	90.0
Ash (wt% dry basis)	13.20	10.82	9.40	10.00
Chemical Oxygen demand (g O_2 /g dry basis)	1.44	1.38	1.07	1.04

2.4 Pretreatment

For all pretreatment methods tested the mass ratio of solid (g) to liquid (mL) was 5:100 (organic load 5% w/v). Thermal pretreatment method was conducted at 121^0C for 60 min in a pressure cooker. Acid or alkali pretreatment of the feedstocks was conducted by the addition of 2% w/v H_2SO4 or NaOH, respectively, for 60min at a temperature of 25^0C or at 121^0C for 60 min in a pressure cooker (thermal acid or thermal alkali pretreatment).

2.5 BMP assays

BMP experiments for all substrates were carried out in duplicate at 35ºC according to Owen and Chynoweth (1993). Serum bottles of 160 mL were seeded with 20 mL of mixed anaerobic culture, 76 mL water and the pretreated feedstocks composed of 4 mL of H_2SO4 or NaOH or water, thermally or not treated (depending on the experiment) and 0.2194 g RM, 0.2171 g SM, 0.2194 g RS and 0.2300 g SS, to a final concentration of the organic content in the bottles of 2g TS /L. The microbial culture was supplemented with 10 mL/L of a solution of $(NH_4)_2HPO_4$ (0.721 g/L) and 10 mL/L of a solution with trace metals (Skiadas and Lyberatos, 1998). The acid or alkali treated feedstocks were neutralized with concentrated NaOH or H_2SO4 respectively, to a final pH of 7. Blank experiments were also carried out in order to determine the background gas productivity of the inoculum. The content of the vials was gassed with a gas mixture of N_2/CO_2 (80/20) in order to secure anaerobic conditions. The vials were sealed with butyl rubber stoppers and aluminum crimps and methane production was monitored versus time according to Owen and Chynoweth (Owens and Chynoweth, 1993).

3. Results and discussion

3.1 Methane production from rapeseed and sunflower meal

The production of methane from rapeseed and sunflower meals, in the gas phase are presented in figure 1.

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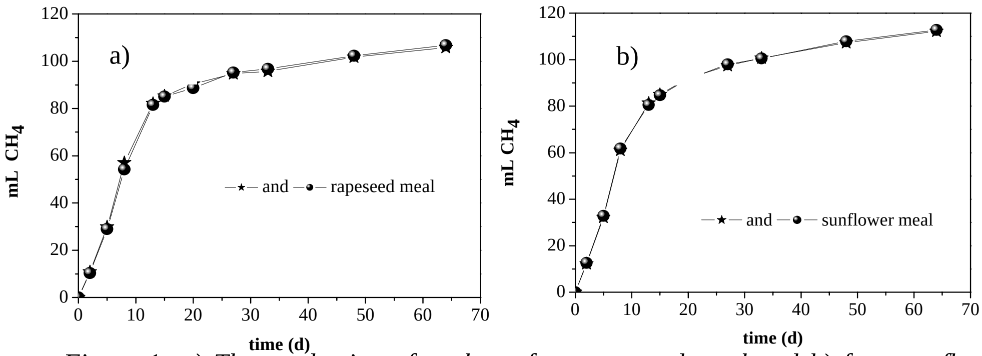

Figure 1: a) The production of methane from rapeseed meal and b) from sunflower meal, during BMP experiments

The calculated methane production of rapeseed meals, after subtraction of the methane produced from blank experiments was 98.3 mL of CH_4. From figure 1a, it is obvious that a significant portion of the methane produced totally (85%) evolved within the first 20 days, while the experiment lasted more than 2 months. These values indicated that the biological methane potential of rapeseed meal was 450 L CH_4/ kg rapeseed meal or 643 L biogas / kg of feedstock. In figure 1b, the methane produced from the sunflower meal is presented. The cumulative methane production (after subtracting the methane produced from blank experiment) was 104.5 mL. Similarly to the experiment with the rapeseed meal, a significant part of the total methane produced was released within the first 15 days, while the experiment lasted more than 2 months. The methane potential of the sunflower meal was determined to be 481 L CH_4/ kg sunflower meal and the biogas production efficiency was 693 L biogas / kg feedstock

3.2 Methane production from rapeseed and sunflower straws

The production of methane from rapeseed and sunflower straws is presented in figure 2. The biological methane potential was 263.8 L CH_4/ kg rapeseed straws or 405.5 L biogas/kg of feedstock, respectively and 260 L CH_4/ kg sunflower straws or 393.4 L biogas / kg feedstock.

From figures 2a and 2b, it is obvious that contrary to sunflower and rapeseed meals (figures 1a and 1b), in the case of straws, more than half of the produced methane was released after the first 15 days, implying that the hydrolysis is carried out at a lower rate. This observation could be possibly attributed to the different lignocellulosic content of the feedstocks. The fact that both rapeseed and sunflower straws exhibited smaller methane potentials and biogas yields than the respective values of rapeseed and sunflower meals corroborates the fact that the lignin content is higher in the case of straws.

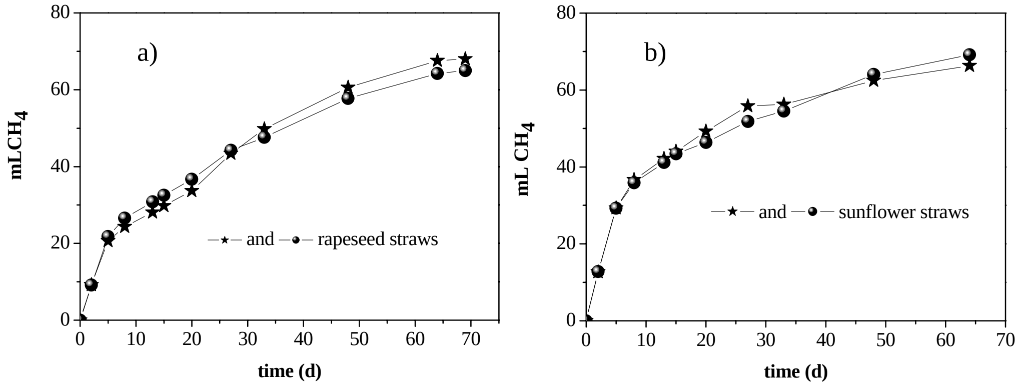

Figure 2: a) The production of methane from rapeseed straws and b) from sunflower straws, during BMP experiments

3.3 Effect of pretreatment

In table 2, the effect of thermal or acid or alkali pretreatment, or combination of the above methods (thermal acid or thermal alkali) in methane potential of rapeseed (RM) and sunflower meals (SM) and rapeseed (RS) and sunflower straws (SS), are presented.

Table 2: The effect of pretreatment methods in the methane potential of all feedstocks

	Methane yield (L methane / kg feedstock)					
	No thermal treatment			Thermal treatment		
		Acid	Alkali		Acid	Alkali
RM	450	320	357	452	298	339
SM	481	303	371	475	371	332
RS	264	122	191	285	178	217
SS	260	136	181	240	167	190

It is obvious that the pretreatment methods tested did not enhance methane yields neither of meals nor of straws. In general, thermal treatment had no effect in methane potential since the yields of all feedstocks which were thermally treated were approximately the same with the respective yields which were obtained without thermal treatment. Except for the case of rapeseed straws, where the methane potential increased with thermal treatment from 264 to 285 LCH_4/kg feedstock. This corresponds to an increase of 7.5%. But, the application of a thermal treatment method demands high temperatures and pressures which would have a significant contribution to the total cost of the process. Since in order to decide for the appropriate pretreatment method of a feedstock, both technical based on yields and economical aspects need to be taken into account, a thermal pretreatment is probably nonfeasible.

On the other hand, the alkali and acid pretreatment methods tested, had a negative effect on the methane potential of all feedstocks. Especially acid pretreatment caused a significant decrease of the total biogas and of the methane which was produced. This could be attributed to the compounds which were probably released during the pretreatment conditions tested, causing methanogenic bacteria inhibition (Fox et al. 2003). It is well known that during dilute acid pretreatment, the hemicellulose is hydrolyzed and simultaneously some toxic, for bacteria, substances such as furfural and hydroxymethylfurfural may be generated (Larsson et al. 1999). So, the addition of H_2SO4 or NaOH 2%w/v did not enhance the methane potentials, but the latter could be higher using more diluted acid or alkali solutions.

4. Conclusions

In this study the biochemical methane potential of the residues of rapeseed and sunflower harvesting and oil processing, was determined. The methane potential of rapeseed and sunflower meal were 0.450 m^3 / kg and 0.481 m^3 / kg while the respective value for rapeseed and sunflower straws were 0.264 m^3 / kg and 0.260 m^3 / kg. The methane potential of rapeseed and sunflower meal is much higher than the respective value for rapeseed and sunflower straws which could be attributed to the different composition of the feedstocks in terms of lignin. The experiments showed that the pretreatment methods which were tested did not enhance methane potential of all feedstocks. A possible reason could be the inhibitory effect to the methanogenic bacteria of the toxic compounds which were possibly released during pretreatment process, decreasing the methane yields.

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