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# COMBINED STORAGE AND PRETREATMENT PROCESS OF SUNFLOWER CATCH CROP UNDER ALKALINE CONDITIONS PRIOR TO ANAEROBIC DIGESTION

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Application to the following topics:

**2.6** *Anaerobic digestion for biogas and biomethane production*

**1.3** *Biomass crops and energy grasses*

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## Aim and approach used

With the objective to reduce the use of fossil fuels, the demand in sustainable energies such as biomethane is increasing constantly. More feedstocks have to be mobilized for anaerobic digestion (AD) in order to enable a consistent growth in biomethane production, coming from sustainable sources. The use of catch crops (CC) in agricultural biogas production is an interesting option for that extent. CC allow an important intake of high methane potential biomass for on-farm biogas plants without competing for arable land with food crops and provide many agro-ecological advantages [1]. However, while digesters have to be fed continuously, CC harvests only take place once or twice a year, making the efficient storage of the biomass before AD mandatory, which is usually done by ensiling. In addition, the cell walls of crops such as sunflower are made of a complex lignocellulosic matrix whose methane potential can be greatly increased by pretreatments aiming to increase the bacteria access to the highly fermentable carbohydrates of holocelluloses [2]. Among the different pretreatment technologies, alkaline pretreatments with reagents like NaOH or CaO have shown an interesting efficiency for that purpose [3,4]. The pretreatments using CaO are particularly interesting since this product is much less expensive than NaOH and compatible with the use of the digestate as a fertilizer. Lime pretreatments are efficient with relatively mild conditions at low temperature, but a long reaction time may be needed [4,5]. Considering these two problematics about storage and pretreatment of catch crops, this work aims to study the long term alkaline pretreatment as a storage process.

For the experiments, a sample of sunflower cultivated as a summer catch crop and harvested at the end of the ripening stage (BBCH 88, 43%DM) on an agricultural site in France (Biométharn, Aiguefonde, France) was used. The crop was hand harvested and chopped into approx. 1-2 cm particle size, similarly as usually done for ensiling. Laboratory-scale storage experiments were conducted in 2 L glass jars equipped with a rubber septum that allows gas analysis and pressure release. Six replicates were prepared for each storing condition to be sacrificed after 2, 7, 21, 60, 180 and 365 d of storage. CaO was added as a dry powder at the dose of  $100\text{g}_{\text{CaO}} \text{kg}_{\text{DM}}^{-1}$  and homogenized manually. After preparation, the samples were packed into the jars and then flushed with  $\text{N}_2$ , sealed and stored in a dark place at  $22^\circ\text{C}$ . A second set of samples was also prepared without CaO addition, as a control for final comparison with the ensiling process. For each studied time, a jar was opened and its content was further shredded and homogenized before characterization. Dry and organic matters (TS and VS) were measured on fresh and stored samples immediately after opening and corrected as described in [6]. Soluble compounds were extracted by maceration in distilled water as described in [6]. After extraction, the pH was measured and the liquid phase was collected and frozen for further analyses of Volatile Fatty Acids (VFA), Water Soluble Carbohydrates (WSC) and metabolites. Solid samples were freeze-dried for further analysis of fiber distribution according to the modified Van Soest procedure [7] after lipid extraction with heptane:ethanol (2:1, vol%:vol%) at  $40^\circ\text{C}$ . Gas production was analyzed periodically and weight loss was measured after gas release. Biochemical Methane Potential (BMP) tests were conducted in batch as described in [3] and using an automatic batch system (AMPTS II, Bioprocess Control, Sweden) for methane volume measurement.

## Scientific innovation and relevance

If a large number of scientific works have studied alkaline pretreatments and their use on lignocellulosic biomass prior to anaerobic digestion, the problematic of their applicability on agricultural sites is still a major concern. High pressure or temperature pretreatment steps may require some important investments that may be incompatible with small scale agricultural plants. Because the pretreatment

process presented in this work requires few modifications from the silage making that is currently made on farm, it may be easily implemented specifically depending on the crop characteristics.

Some rare examples of alkaline storage are found in the literature. Pakarinen *et al.* [8] studied the use of urea as an additive for hemp storage, but the low pH which was reached (around 9) possibly limited the pretreatment effects. Digman *et al.* [9] applied very similar conditions on switchgrass and reed canarygrass for ethanol production and obtained some interesting results, increasing the cell wall glucose conversion into ethanol by up to 55% but to our best knowledge, no such experiment has been conducted for biogas production from crops.

### Preliminary results

The results presented here focus on the 180d storage time but all storage times will be shown during the conference. The general characteristics of the raw harvest and the two storage conditions after six months are described in Table 1. The fresh crop was characterized by a high level of TS (42.5%), which causes the alkaline pretreatment to be applied in much drier conditions than met in the literature where global TS is usually set at less than or equal to 10% [3–5,10]. Both processes allowed a high preservation of the organic matter, since very low VS losses were observed. Ensiled samples underwent a classic silage fermentation with a high production of Lactic Acid (LA) associated with a drop in pH. Few metabolites were released in alkaline samples, excepted Acetic Acid (AA). No undesirable reactions took place since neither butyric acid nor hydrogen were measured in significant amounts in none of the cases.

Table 1: Total and volatile solids, composition of solid and liquid phase, weight loss, and biomethane potential before and after storage

	Freshly harvested	Ensiling 180d	Alkaline storage 180d
TS <sup>a</sup>	42.5 ± 0.5	43.6 ± 0.2	48.6 ± 0.1
VS <sup>a</sup>	40.1 ± 0.2	41.1 ± 0.1	39.5 ± 0.1
pH	6.1 ± 0	4.3 ± 0.0	11.7 ± 0.1
AA <sup>c</sup>	0	1.6 ± 0	2.9 ± 0
LA <sup>c</sup>	0	5.7 ± 0	0.5 ± 0
Other VFA <sup>c</sup>	0	0.5 ± 0	0.2 ± 0
Lipids <sup>c</sup>	5.6	8.8	6.5
W-SOLU <sup>c</sup>	22,9 ± 5,9	22,5 ± 0,5	25,4 ± 0,5
SOLU <sup>c</sup>	13,9 ± 4,9	12,7 ± 0,4	21,8 ± 1,3
HEMI <sup>c</sup>	16,7 ± 0,2	14,6 ± 1,5	12,2 ± 0,4
CELL <sup>c</sup>	29,7 ± 1,8	32,4 ± 1,1	27,4 ± 0,1
LIG <sup>c</sup>	17,7 ± 3,1	16,5 ± 0,7	14,5 ± 0,8
BMP <sup>b</sup>	264 ± 32	271 ± 28	319 ± 11
Weight losses <sup>b</sup>	0	1.9 ± 0.1	0.3 ± 0.0

Results presented as <sup>a</sup> % of total sample weight ; <sup>b</sup> %VS<sub>init</sub> ; <sup>c</sup> %VS<sub>added</sub> ; W-SOLU : water soluble ; SOLU : neutral detergent soluble ; HEMI : hemicellulose ; CELL : cellulose ; LIG : lignine

The effect of the different storage conditions on fiber distribution is presented in Table 1. While ensiling had few effect on the share between the different fractions, the alkaline process increased by 28% the most accessible fractions (W-SOLU + SOLU) when compared with the fresh crop. The effect of the alkaline conditions also reduced the hemicellulose (-27%) and lignin (-18%). As lignin is known to have a detrimental effect on the crops degradation into biogas, this result may explain the increase in BMP observed after alkaline storage (+21%) [2].

## Conclusions

These primary results show that alkaline storage can constitute an interesting alternative to ensiling for both storage and pretreatment of catch crops. This process may find an interesting application with crops like sunflower that include highly fibrous stalks whose conversion in biomethane can be greatly increased by the application of pretreatments.

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