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## **Evolution of the methane potential of agricultural wastes in different storage conditions: catch crops and cattle manure**

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#### **Abstract**

In order to enable a continuous supply of biogas plants throughout the year, seasonal feedstocks need to be preserved and in most cases for extended periods. However, several doubts still persist about the good management practices for part of the organic residues used for anaerobic digestion, since this subject has received limited attention so far. This work brings together a compilation of long-term storage assays at laboratory scale for two different types of catch crops and cattle manure. Comparison between the impact of ensiling and open-air storage techniques on organic matter and energy preservation was performed. Effects of co-ensiling of cattle manure with several additives on silage quality were assessed as well. Aerobic storage led to methane potential losses of more than 80% after 3 months of storage for catch crop assays and around 74% for cattle manure after 4 months. Higher energy recovery rates were obtained after ensiling, strongly depending on the nature of the organic residue used. For both catch crops, at least 96% of methane potential was preserved after 3 months. On the opposite, cattle manure lost 46-65% of its methane potential after ensiling. Conservation of cattle manure was successfully enhanced through co-ensiling with fermentation stimulants or inhibitors. The best storage performance was obtained while combining cattle manure with glucose at high concentration (10% of total weight), for which methane potential increased by 9% after 4 months of co-ensiling. These results highlight a major advantage in using ensiling rather than open-air storage for these agricultural wastes. Moreover, the use of precursors of organic acids as additives/co-substrates may improve silage quality of non-adapted biomass for ensiling, such as cattle manure. These outcomes may contribute to enhance economics of downstream anaerobic digestion plants.

#### Keywords

Cattle manure; catch crop; storage; ensiling; anaerobic digestion; methane potential

#### INTRODUCTION

In recent past, biomass storage before anaerobic digestion (AD) has become an issue of great interest, mainly due to storage requirements of seasonal raw materials and their degradation rates during conservation. However, storage research is still in its infancy, so that existent literature does not cover all its important issues. Ensiling is being used and pointed out as the logical choice to store wet biomass. Nevertheless, to the best of our knowledge, currently does not exist any comparison between open-air storage and ensiling regarding the conservation of energy potential of raw materials. Moreover, ensiling is neither been applied nor studied by researchers for some organic residues such as manure (Teixeira Franco *et al.*, 2016). This important feedstock for AD is mainly open-air stored, which will lead to important energy losses.

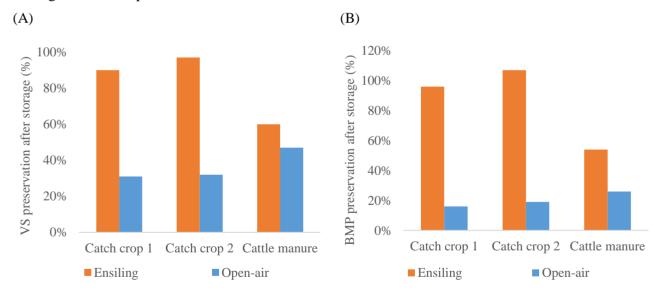
This work evidences the best management practices for two types of catch crops and cattle manure before biogas production. First of all, a comparison between open-air storage and ensiling was established during at least 3 months at laboratory scale. In addition, long-term assays of co-ensiling of cattle manure with several additives were performed. Finally, this work contributes to the optimization of organic residues preservation before AD, which will definitively have an impact on the energy recovered downstream.

#### MATERIAL AND METHODS

Two different types of catch crop and fresh cattle manure, which were collected on an agricultural site in the AURA region of France (Gaec Béreyziat, Les Teppes, 01340 Béréziat, France), were used as raw materials. Catch crop 1 (or "winter" catch crop) was a mixture of triticale, peas, vicia and fodder radish. It was chopped at 4cm maximum length at harvesting. Catch crop 2 (or "summer" catch crop) was a mixture of sunflower, sorghum, peas, vicia and trifolium alexandrinum, and it was chopped at 3cm maximum length before use. For co-ensiling trials, cattle manure was mixed with the following additives: formic acid 2%w/w; glucose 4%w/w and; glucose 10%w/w. Laboratory trials were conducted for all raw materials in 3.5 airtight round plastic storage drums. Silo sealing was different depending on the storage method tested. For ensiling assays, proper plastic lid and rubber ring were used and its airtightness was reinforced with silicone sealant. For aerobic storage purposes no cover was used and the silo was left air-open. Once sealed, the silos were weighed and placed in a temperate room at 25±2°C. After storage, silos were opened, weighed and samples were taken for total solids (TS), volatile solids (VS) and bio-chemical methane potential (BMP) analysis. TS was measured by oven drying at 105°C during 24h and VS was subsequently calcinated for 2h at 550°C. TS/VS values were corrected for loss of volatile compounds during procedure. BMP tests followed the recommendation provided by Holliger et al. (2016).

#### RESULTS AND DISCUSSION

The main results obtained for the first long-term storage assays are summarized in Figure 1. Ensiling led to better biomass preservation than aerobic storage, especially for catch crop tests. These raw materials are normally rich in water-soluble carbohydrates, which are consumed during ensiling by lactic acid bacteria for organic acid production. During this period of fermentation silage is acidified, stabilizing the raw material. This hypothesis is corroborated by low organic losses observed for ensiling of catch crops.

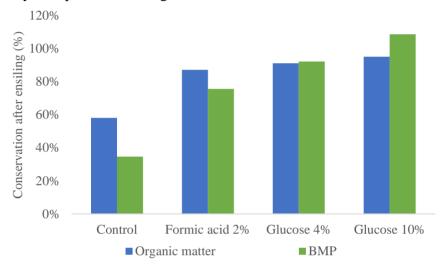


**Figure 1**. Organic matter (A) and BMP (B) losses after 3 months of storage for Catch crop 1 / Catch crop 2 and 4 months for Cattle manure. BMP losses are related to the differences between values on a VS<sub>original</sub> basis, therefore taking into account storage losses

Indeed, use of ensiling instead of open-air storage reduced organic matter losses from around 70% to less than 10% for catch crops. High biomass stability led to little effect of ensiling on BMP after 3 months of storage. Contrary to the more than 80% BMP losses after aerobic storage, ensiling conserved 96% of the BMP of catch crop 1 and increased 7% of the BMP of catch crop 2. This latter value suggests that gains in biochemical accessibility during ensiling of catch crop 2 overcame organic matter losses. For cattle manure, benefits in using confined storage were less obvious, since

ensiling was inefficient: after 4 months, organic matter losses only decreased from 53% to 40% and BMP losses from 74% to 46% in ensiling rather than outdoor storage. The main reason for this is that manure does not have the necessary chemical characteristics (low water-soluble carbohydrates content; high buffer capacity, etc.) for an efficient self-acidification during ensiling.

In order to optimize conservation of cattle manure during storage, the effect of additives were tested during 4 months of co-ensiling. Since ensiling is an acidification-based process, direct and indirect sources of acidity were used as additives. Formic acid was added at 2% w/w so as to act as fermentation inhibitor by lowering the pH value to around 4. Glucose at high concentrations (4% w/w and 10% w/w) was used as fermentation stimulant, *i.e.*, as precursor of lactic acid production. Results of co-ensiling assays are presented in Figure 2.



**Figure 2.** BMP and organic matter preservation of co-ensiled cattle manure after 4 months. Control represents cattle manure ensiled without additives. Formic acid 2% stands for cattle manure co-ensiled with 2% w/w of formic acid. Glucose 4% and Glucose 10% stand for cattle manure co-ensiled with 4% w/w and 10% w/w of glucose, respectively. BMP balance takes into account storage losses.

Results showed that co-ensiling improved silage quality for biogas production. On one hand, single-handedly cattle manure (control) lost 42% and 65% of original organic matter and BMP after 4 months of ensiling, respectively. On the other hand, for instance, formic acid 2% w/w enhanced biomass conservation to 87% and 75% of initial VS and BMP. Nevertheless, as while using fermentation inhibitors biomass degradation should be minimal, this indicates that partial loss of acidity occurred during ensiling with formic acid. Regarding glucose addition, remarkable results were found. On glucose 4% w/w assay, losses of organic matter and methane potential were limited to less than 10% after 4 months. For glucose 10% w/w addition 95% of VS was conserved and an increase of 9% of original BMP was found after co-ensiling. This suggest that optimal conservation of energy content of cattle manure during storage may be achieved through co-ensiling with an organic residue containing high concentration of available carbohydrates.

#### **CONCLUSIONS**

Energy losses during storage of these organic wastes can be limited through ensiling. Even though, during prolonged storage, ensiling of cattle manure leads to important biomass degradation. In this case, the use of additives is an efficient way to avoid it, or even increase methane potential. Coensiling with a substrate containing high concentration of available water-soluble carbohydrates appears to be the most resourceful method to optimize cattle manure storage before biogas production. These outcomes may contribute to enhance economics of downstream anaerobic digestion plants.

#### **ACKNOWLEDGEMENTS**

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