Hydrogen production through Dark Fermentation process of Agricultural Residues

D. Bertasini, D. Bolzonella, N. Frison, F. Battista.

Department of Biotechnology, University of Verona, Via Strada Le Grazie 15, Verona, Veneto, 37134, Italy

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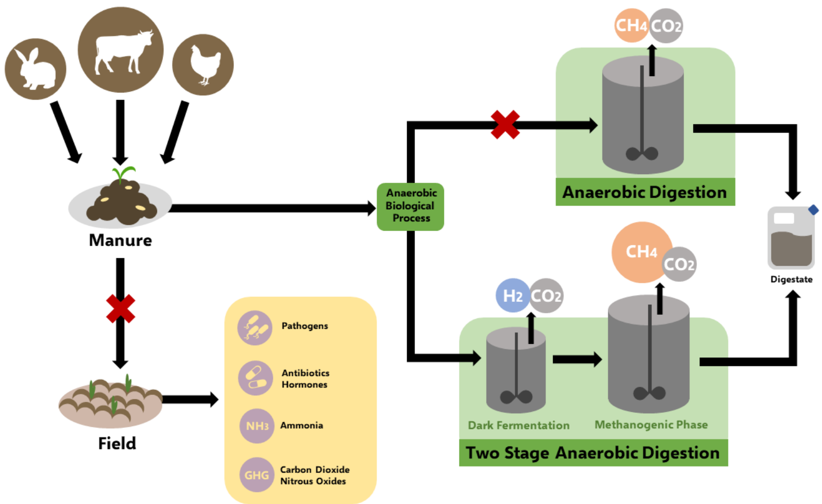
Presenting author email: davide.bertasini@univr.it

Graphical abstract



Abstract

The anaerobic digestion technology is already well known as a virtuous solution for managing agricultural residues. The double stage alternative, the so called two phase AD process, is getting more and more attention in the scientific community due to the peculiarity of combining the hydrogen at the methane production in the same plant. Hydrogen mixed in 10%-30% v/v with biomethane is called biohythane, a gaseous blend usable in the current gas grid that allows for a better energy yield and a lower carbon impact compared to the common natural gas (Bolzonella et al., 2018). The application of the two stage process to the agricultural residues is now under study, given the necessity of identifying the optimal operative parameters to optimize the fermentation phase. After the straw, animal manure is the most abundant agricultural residue (1.2 Gt/y) in the European Union (Li et al., 2021), with the 75% derived from cattle husbandry. This agrowaste is often used as soil conditioner of agricultural soils, but this procedure is responsible for undesirable effects, as the emission of greenhouse gases emission (nitrous oxide, carbon dioxide and methane), about 380 Mt per year (Eurostat, 2024), as well as ammonia and odors. The ammonia is an air pollutant that can be the cause of the deposition of atmospheric nitrogen, source of acidification and eutrophication for ecosystems, more over it is dangerous for human health, due to its nature of precursor of the PM 2.5 formation. The employment of unstabilized manure as soil conditioner is also a source of pathogens and consequent zoonoses (Burch et al., 2018), antibodies that can exacerbate the stigma of antibiotic resistance, hormones, nitrates and phosphorus that can percolate and eutrophicate groundwaters. Adoption of the anaerobic digestion process as a solution to the manure disposal, alleviates its impact in the ecosystem, also leading an energetic payback and the digestate production, a more stable soil conditioner. The difficulty that can arise from the use of this residue in the digestion process is correlated to its low C:N ratio, determined from the important ammonia content, element that over the 1.7-5.0 gN/L inhibits the acidogenic and methanogenic activity (Nielsen et al., 2007; Yenigün & Demirel, 2013). The codigestion of manure with feedstock with high carbon content can be a solution to this problem, for example mixing corn residues, triticale residues, prunings or straw. However, the high percentage in recalcitrant material, as lignin and hemicellulose, it is another challenge to the traditional digestion process, which manages to convert no more of the 50% of the volatile solids of these feedstocks (Usman Khan & Kiaer Ahring, 2021). In this regard, some studies on double phase process suggest that the application of a specific fermentation phase is beneficial to the subsequent methanogenesis. In fact, the fermentation acts as a pretreatment of the biomass, increasing its biodegradability and causing a higher yield in biomethane, adding to the hydrogen production (Bertasini et al., 2024). In literature, are reported lab-scale studies on double stage that

reached a hydrogen yield of about 106 mLH_2/gVS (Yilmazel & Duran, 2021). Therefore, the perspectives on the use of manure in a two stage anaerobic digestion process appear promising.

This study proposes the optimization of the fermentation process of agricultural residues, as: i) manure, ii) vegetal by-products and residues and iii) their codigestion. Specifically, the influence of the hydraulic retention time (HRT) on hydrogen production are investigated. In addition, the fermented output follows biomethanation potential tests (BMPs) to track as the first stage affect the biomethane yield at different HRT values. Specifically, the study employs 1 L and 2 L continuous stirred tank reactors (CSTRs), maintained at 38 °C and pH 5.5-6.5, working with a feedstock with 5% content in total solids, for a period equivalent to 3 times the HRT value. The HRT values analysed are from 1.5 days to 10 days. During the fermentation tests the pH value, total solid content, total volatile solids content, chemical oxygen demand content, ammonia content and volatile fatty acid content are analysed, in order to monitor the status of the process. Gaseous samples are recovered for the qualitative analysis with gas chromatography and quantitative analysis with the water displacement method. Each output from the fermentation is used as feedstock for the BMP tests. In particular, through glass sealed bottles, maintained at 38 °C, completely mixed and refilled with fresh inoculum. The results are then compared with the biomethanation potential of the fresh (not fermented) substrate. The aim of these tests is to verify the pretreatment effect of the first phase.

In the table below are reported some preliminary results, i.e. the characterization of agricultural residues used as feed.

Table 1. Characterization of Agricultural residues

Agricultural residue	**TS**	**TVS**	**VS/TS**	**COD**	**Ammonia**
	%	%	%	g/kgTS	gN/KgTS
Cattle manure	17.4	15.3	87.9	874.8±6.5	3.38±0.1
Poultry manure	30.5	20.7	68.0	781.1±99.3	15.08±0.7
Rabbit manure	26.1	22.1	84.7	807.2±147.9	3.58±0.3
Silage corn	33.7	31.7	94.0	940.5±35.9	0.81±0.1

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