Valorisation of Agricultural residues to produce H_2 through Two Stage Anaerobic Digestion process

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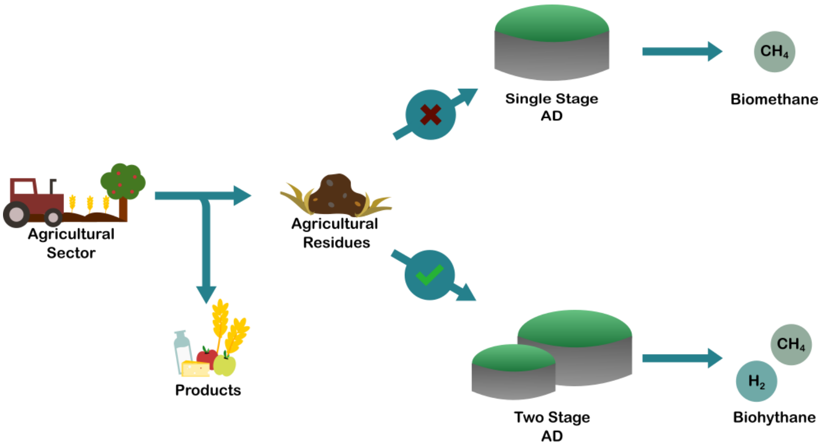
Graphical abstract



Abstract

In the European Union (EU) there are about 20,000 anaerobic digestion (AD) plants that produce biogas; over the 70% of them adopts agricultural residues as feedstocks. The recent policies of the European Commission (i.e. "The European Green Deal", "the REPowerEU") encourage the upgrading of these plants to two stage AD process to address the needs to produce more sustainable fuels and to counteract the rising natural gas price (Bertasini et al., 2023). In this regard, in fact, in 2020 the global GHG emissions reached the 54 $GtCO_2$ equivalent ($GtCO_2e$) and it is estimated that following the current trend will reach the 58 $GtCO_2e$ in 2030 (UN environment programme, 2022). In addition to that, due also to the crisis for war in Ukrainian territory, the price of natural gas has risen of about 135% for households, compared to the 2021 cost (from 0.0638 €/kWh to 0.0861 €/kWh) (Eurostat, n.d.-b). This growth in price heavily impacts economically because the natural gas constitutes up to the 24% of World's primary energy source (Erias & Iglesias, 2022). Consequently, two stage anaerobic digestion (TSAD) would seem a senseless choice from an economic point of view, due to the higher cost of setup; but actually, it is favourable by ensuring not only higher methane production, but also that of hydrogen, cornerstone fuel of most recent energy strategies for sustainable development. Based on the foregoing, the two stage could represent an opportunity both to favour the transition toward a circular economy and to reduce the energetic dependency of the European continent by the exploitation of agricultural residues as secondary raw materials. In addition, it could alleviate the cost of disposal for the 9.1 million of European agricultural companies, that produce annually tons of residues, as straw, leaves and manure (Eurostat, n.d.-a). The conventional final destiny of these wastes is often the uncontrolled soil disposal, the landfill, the incineration or, in the best cases, the composting. All these practises are not virtuous and represent a cost for the primary sector. Technologically, the TSAD operates the acidogenic and the methanogenic phases in physically separated reactors, which permits the selection of specific microbial community and the setting up of different operational parameters (Bolzonella et al., 2020). Consequently, TSAD allows to optimize the production of hydrogen and volatile fatty acids in the first phase, and methane in the second. Additionally, the process developed in two stage increases the efficiency of organic matter removal and the methane production than the single stage. These gases are the main constituents of biohythane, a gaseous blend which accounts for the 80-90% methane and for the 10-20% hydrogen (Bolzonella et al., 2018). Biohythane has better performances than biomethane. In particular, the hydrogen presence reduces the carbon impact and improves the energetic yield during the combustion. Whereas, the methane, enables an easier storaging of the fuel and the direct injection in the current gas network (Quarton & Samsatli, 2020).

The present research work is focused on the biohythane production on agricultural byproducts both from vegetable (corn, triticale, wheat for mushroom cultivation) and animal (poultry manure, cattle manure) origins. Before the

TSAD tests the substrates have been characterized in terms of total solids (TS), total volatile solids (TVS), chemical oxygen demand (COD) and ammonia. These parameters have been summarized in the following table.

Table 1. Characterization of Agricultural residues

Agricultural residue	**TS%**	**TVS%**	**VS/TS%**	**COD**	**Ammonia**
	%	%	%	g/kgTS	g/kgTS
Corn	29%	28%	95%	940.5±35.9	97.9±2.5
Triticale	27%	26%	94%	960.6±68.7	42.1±0.5
Wheat for mushroom cultivation	19%	17%	88%	866.6±22.3	60.2±9.5
Poultry manure	32%	22%	67%	696.0±132.3	154.8±9.0
Cattle manure (semi-solid)	20%	15%	72%	796.5±70.4	89.5±8.7

In the following months, semi-continuous TSAD tests will be performed on the different substrates evaluating the effect of the hydraulic retention time (HRT), organic loading rate (OLR), temperature and pH on hydrogen and methane production. In addition, for the more recalcitrant lignocellulosic substrates different pretreatments (acidic, alkaline, thermal, enzymatic) will be tested to favour the substrates' hydrolysis and the consequently the increasing of hydrogen and methane's yields.

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