

Integrated Treatment of Agro-industrial Waste

Subjects: Others

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This document reports a synthetic description of a research work in which a new integrated treatment was defined for the production of biofuel and the recovery of phosphorus compounds from agro-industrial residues. As the first step of the proposed process, anaerobic co-digestion was carried out to produce biogas by exploiting raw waste mixtures. Afterwards, the residual digestates were converted to syngas using supercritical wet gasification (SCWG). Finally, the liquid phases from SCWG were treated to recover the phosphorus content as $\text{MgKPO}_4 \times 6\text{H}_2\text{O}$ crystals. This integrated treatment could be a suitable approach to exploit agro-wastes because it can produce biofuel and valuable chemicals and generates a residual effluent with a very low polluting load.

Keywords: Anaerobic digestion ; biogas ; biomass ; magnesium potassium phosphate ; supercritical water gasification

1. Introduction

The identification of novel and suitable approaches for the exploitation of agro-industrial residues is an important environmental and economic issue^{[1][2][3]}. In fact, these wastes are generally not properly disposed of, which causes severe damage to soils and aquatic systems^{[4][5][6][7]}. Therefore, they often constitute a substantial source of pollution. On the other hand, many byproducts of agricultural activities have an enormous potential for energy production and for the recovery of valuable compounds^{[8][9][10][11]}. Anaerobic digestion (AD) is a sustainable, environmentally friendly technology for organic residue exploitation. In anaerobic processes, the organic substrates are metabolized according to a series of sequential steps carried out by different microorganisms species that operate in the absence of dissolved oxygen at two typical temperature ranges, mesophilic (35–40 °C) or thermophilic (55–60 °C)^[11]. As a consequence of these biological reactions, a valuable biogas is produced. AD is suitable to efficiently treat seasonal wastes and it can be applied in large facilities and small agricultural companies^[12]. Indeed, many batch and continuous digesters with suspended and attached biomass, such as the completely-stirred tank reactor (CSTR), up-flow anaerobic sludge blanket (UASB), up-flow anaerobic filter, etc., have been used^[11]. The processes efficiency, in addition to typical operating parameters (OLR: organic load rate, HRT: hydraulic retention time, etc.), is mainly affected by the characteristics of feedstock^[11]. The co-digestion of various types of residues is an advantageous method to improve the performance of treatments^{[11][12][13]}. In fact, by properly mixing different matrixes it is possible to obtain a mixture with adequate characteristics in terms of pH, COD/N/P ratio, alkalinity, etc.^{[13][14][15][16]}. Therefore, it is very important to accurately select the type and the amount of waste to be mixed.

Besides biogas, anaerobic processes produce a wet residue (digestate) with a remarkable pollutant load. Digestates are often used as organic fertilizers; however, this practice can cause soil deterioration due to their properties such as the high salinity and the potential presence of pathogenic microorganisms [17]. Moreover, spreading wet AD residues leads to the accumulation of nutrients in aquatic systems, and, thus, the eutrophication of water bodies^[17]. Therefore, there is a need to develop appropriate technologies for the post-treatment of wet residues generated in anaerobic processes. In this regard, the supercritical wet gasification (SCWG) and the recovery of nutrients as struvite type compounds (MAP: magnesium ammonium phosphate; MPP: magnesium potassium phosphate) can be profitable approaches. In particular, SCWG exploits the organic matter content of biomass for biofuel production^{[18][19][20]}. The process is performed at high temperature (300–600 °C) and pressure (210–400 bar) under supercritical water conditions^{[21][22][23]}. The SCWG process could be schematized in two main stages: an early stage where there is the breakdown of macromolecules to smaller molecules and a second stage, similar to hydrocarbon steam reforming, composed of a water gas shift reaction and methanation reaction^{[24][25]}. In SCWG, water becomes a real reagent for gasification reaction and it is also able to solubilize complex organic compounds. Therefore, this technology is particularly suitable for the treatment of wet residues such as digestates, which are characterized by remarkable levels of organic matter^{[26][27][28][29]}. SCWG has significant advantages over traditional methods for the production of biofuels^{[30][31]}, such as higher energy, greater separation efficiency, and the possibility to eliminate the need to pre-dry the matrices^{[32][33]}. Indeed, as demonstrated by previous works, the SCWG process, compared to the conventional technologies, has a great potential because it is a cost-effective

process for the treatment of humid wastes and it is highly recommended for energy production from digestates [32][33]. Another advantage is that the liquid resulting from hydrothermal processes has a low amount of organic matter and it is completely sterilized, avoiding, in the case of digestates, the presence of pathogenic organisms such as bacteria and viruses [26,27]. After the SCWG stage, dimensioning ad hoc the CO₂ removal section, it is possible to obtain a syngas containing only the molecules necessary for the synthesis of biofuels and/or chemicals such as synthetic natural gas (SNG), pure hydrogen, methanol, dimethyl ether etc.[22]. The gas production could notably change in response to the concentration and type of organic matter, as well as the water content of feedstock[34].

The residual aqueous phase, depending on the waste type subjected to SCWG, could be characterized by a high level of nutrient compounds. In particular, the amount of phosphate could be much more remarkable than that of nitrogen compounds. Indeed, during the gasification reaction, depending on samples' pH, the ammonium nitrogen could be converted into gaseous ammonia and recovered by means of neutralization in acid solutions. Instead, the phosphorus content remains both in the solid and liquid phase. Some works investigated the possibility of recovering the phosphorus amount from solid residue[35][36]. However, there is a lack of studies focused on the removal and recovery of P dissolved into the liquid phase of SCWG. In this regard, the precipitation of magnesium potassium phosphate hexahydrate (MPP, MgKPO₄×6H₂O)[37][38] can be considered a suitable and advantageous option. In fact, this process allows the P recovery in the form of one of the struvite-type compounds that are considered potential fertilizers[39][40][41][42][43][44]. MPP precipitation occurs when Mg²⁺, K⁺, and PO₄³⁻ concentration overcomes the solubility product in an alkaline environment[37][38]. Generally, to promote the MPP formation, the pH correction and the addition of potassium and magnesium reactants is required[37][38], which increases the process costs. Therefore, the reduction of chemical consumption is a significant issue for practical applications[45][46][47][48].

In order to define a suitable method to efficiently exploit the agro-industrial residues, an integrated treatment based on AD, SCWG, and MPP precipitation has been developed (Fig.1). This treatment represents a new approach combining all the above techniques. Through an experimental investigation, the factors affecting the production of biogas, from co-digestion of agro-wastes, and of syngas, from gasification of digestate, were identified. Moreover, the application modality of MPP precipitation for the treatment of the liquid phase of SCWG was determined. In particular, this process, in comparison to conventional applications, guarantees a reduction of chemicals consumption.

The developed integrated treatment is advantageous because, in addition to biofuel production and recovery of a valuable phosphorus compound, it can obtain a residual effluent characterized by a very low amount of organic matter and nutrient compounds.

Figure 1. Integrated treatment

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