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N and P Recovery Pathways in HTC of Solid Digestate from Winery Supply Chain

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The solid fraction of digestate, a major by-product of anaerobic digestion, represents a potential source of nutrients and energy. In Europe, digestate solid fraction production is projected to rise from 31 Mt (2022) to 177 Mt in 2050, highlighting the urgency for sustainable valorization strategies. This study explores Hydrothermal Carbonization (HTC) of digestate solid fraction derived from winery supply chain, to recover phosphorus (P) and nitrogen (N) in the liquid fraction while improving the energy content of the solid hydrochar. A systematic investigation was conducted on key HTC parameters: temperature (180-250 °C), reaction time (10-60 min), solid/liquid ratio (1/10-1/20), and acetic acid concentration (0-0.5 M), to assess their impact on nutrient recovery and hydrochar quality. Obtained results showed that P recovery was favored at lower temperatures, shorter times, higher acetic acid concentrations, and lower S/L ratios, while N recovery increased with higher temperature and longer reaction time. Explored HTC process condition allowed the tuning of P/N recovery ratios (0.2-1.4) in the liquid fraction, which could be suitable as a biomass-derived fertilizer. Solid hydrochar was obtained with carbon content and heating value (~16 MJ/kg) higher than those of the starting digestate. This study also demonstrates the use of acetic acid solutions as an HTC media; this confers circularity to HTC, since acetic acid is naturally present in anaerobic digestion and in winery supply chain. Overall, HTC emerged as a possible candidate to offer a dual benefit: generation of a nutrient-rich fertilizer and a sanitized, energy-dense solid, supporting circularity and sustainable management of agro-industrial residues.

1. Introduction

Anaerobic Digestion (AD) is a biological treatment that converts putrescible organic matter into a gas phase mainly composed by CO_2 and CH_4 named biogas and a humid solid residue called digestate (Ward et al., 2008). Biogas is acknowledged as a clean, renewable energy source with considerable potential to mitigate greenhouse gases emissions (IEA, 2024) Solid Fraction Digestate (SFD) is a substantial by-product of AD; in EU, SFD in 2022 was 31 Mt/year (dry matter), expected to increase due to AD development in EU (75 and 177 Mt/year in 2030 and 2050, respectively) (Exploring Digestate's Contribution to Healthy Soils, 2024). SFD contains valuable nutrients such as phosphorus (P) and nitrogen (N). In 2022, the overall P and N in SFD in Europe amounted to 0.3Mt and 1.7Mt, respectively; in 2050, respective forecasted projections are 1.7Mt and 9.7Mt (Exploring Digestate's Contribution to Healthy Soils, 2024). AD of lignocellulosic biomasses transforms a portion of the organic matter into biogas, while the complex residual organic matter (such as lignin) and the inorganic fraction (including N and P) remain in the digestate. Specifically, P is mainly present in the particulate fraction. In fact, even the P released in the soluble fraction in the form of phosphate is largely precipitated during the AD process due to the reaction with soluble cations (e.g., calcium, magnesium, iron, etc.). The digestate can therefore represent a veritable "mine" to obtain fertilizers within a circular economy framework; however, this virtuous system is hampered by legislative constraints, and in many cases the regulatory framework does not encourage this possibility (Bolzonella et al., 2018; Möller & Müller, 2012; Vaneeckhaute et al., 2013). Indeed, several studies (Bolzonella et al., 2018; Khalaf et al., 2023) investigate the recovery of nutrients from the digestate. In view of European sustainability policies, recovering P and N is pivotal for circularity; the

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development of biomass- and waste-based production pathways (following the concept of biorefinery) should be integrated with other unit operations to establish beneficial cascading systems aligned with circular economy principles (Macarthur, 2017). Hydrothermal Carbonization (HTC) represents a promising process to valorize by-products such as digestate since it meets key requirements including low environmental impact, high energy efficiency and strong flexibility for process optimization. These features have contributed to the steadily increasing body of literature on the subject. Additionally, HTC offers several advantages, such as the treatment of heterogeneous mixtures of non-pre-dried biomass at relatively mild temperature of reaction which reduce energy consumption of the process. Therefore, HTC is suitable to treat very moist biomass such as digestate, allowing the recovery of valuable chemicals in the liquid phase (e.g., P and N) and the simultaneous valorization and sanitation of the solid phase (Taglieri et al., 2024). This study investigates the valorization of SFD by HTC, aiming to evaluate nutrient recovery and energetic content of the produced solid phase. The influence of key HTC process parameters (temperature, reaction time, and solid/liquid ratio) was studied concerning P and N recovery, and properties of solid product (Taglieri & Gallifuoco, 2025). Furthermore, the circular usage in HTC of acetic acid (a compound naturally present in AD and winery value chain) was introduced, in contrast to the usage of mineral acids (e.g., HCl and H_2SO_4) (Marin-Batista et al., 2020). A sensitivity analysis was conducted by varying HTC temperature (*T*= 180-250 °C), reaction time (*t*= 10-60 min), solid-to-liquid ratio (*S/L*= 1/10-1/20), and acetic acid concentration (*Ac*= 0-0.5 M): measured responses included P and N content in liquid phase, CHNS composition and ash content of residual solid obtained by HTC (hydrochar), hydrochar HHV.

2. Materials and methods

2.1 Biomass pre-treatment and HTC tests

The pellets from the SFD were produced by BARTEN Distillery (Italy) with a digestate produced by the AD of waste products from their production chain. These pellets were ground through a cutting mill (MF 10 basic IKA WERKE fine grinder) until obtaining a fine particle size <500 µm, to decrease the influence of intraparticle mass transfer phenomena. The liquid medium consisted of distilled water (*Ac* = 0) or an acetic acid solution (*Ac* = 0.5 M) prepared with glacial acetic acid 100% anhydrous (Supelco) and distilled water. The liquid phase and the solid biomass were loaded into the HTC reactor, considering the chosen solid/liquid ratio (*S/L* = 1/10-1/20).
HTC tests were conducted in a bench-scale batch reactor made of AISI 316 stainless steel (operating volume: 15 mL). The reactor was internally lined with a removable PTFE chamber to prevent corrosion phenomena and to avoid metal contamination of the reacting slurry under acidic hydrothermal conditions. Based on the configuration previously adopted (Taglieri et al., 2024; Taglieri & Gallifuoco, 2025), the reactor was housed inside an electrically heated oven equipped with band heaters (1250 W each) and controlled through a PID temperature regulation system. The internal temperature was continuously monitored by a K-type (Chromel/Alumel) mineral-insulated thermocouple (Inconel 600 sheath) and connected to a dedicated HTC controller, ensuring a temperature precision of ±2%. The heating rate was approximately 15 °C/min. The reaction time (*t* = 10–60 min) was counted once the set temperature (*T* = 180–250 °C) was reached.
During the isothermal holding time, to enhance heat and mass transfer and to minimize temperature gradients within the reactor, the temperature of the heating bands was constrained to remain within 90 °C above the reactor set point to avoid local overheating at the reactor wall.
At the end of each experiment, the reactor was quenched in a water bath to stop the reaction.
After HTC tests, the reaction products (solid and liquid phases) were recovered and separated by centrifugation (NEYA8 bench top centrifuge) at 3000 rpm for 10 min, to separate and get complete stratification of the solid phase and the liquid supernatant. After the solid-liquid separation, the solid phase was dried following the UNI EN 18134 standard, and the *Solid Yield* was evaluated (Equation (1)).

$$Solid\ Yield\ (wt\%) = \frac{mass\ of\ hydrochar\ dried\ (g)}{initial\ mass\ of\ SFD\ (g)} \cdot 100 \quad (1)$$

2.2 Solid and liquid phase characterizations

As-received biomass (i.e, SFD), and residual liquid and solid phases after HTC were characterized.
The ash content of SFD and hydrochar (i.e., HTC solid residue) were quantified according to UNI EN ISO 18122. The ultimate analysis of SFD and hydrochar was performed through CHNS Perkin Elmer Series II 2400 in order to quantify elemental carbon, hydrogen, nitrogen and sulphur, according to ISO 16948. The P content of SFD was determined by X-ray fluorescence (XRF, Spectro Xepos). HHV (MJ/kg) of SFD and hydrochar was calculated by Equation (2) (Channiwala & Parikh, 2002)), where *C*,*H*, *N*, S,*O*, and *Ash* respectively represent the mass percentage on dry basis of carbon, hydrogen, nitrogen, sulfur, oxygen, and ashes of the material.

$$HHV(MJ \cdot kg^{-1}) = 0.3491 \cdot C + 1.1783 \cdot H + 0.1005 \cdot S - 0.1034 \cdot O - 0.0151 \cdot N - 0.0211 \cdot Ash \quad (2)$$

As to the post-test liquid phase, the pH was determined using the equipment METTER TOLEDO SevenCompact pH/ion, the P content according to the APAT CNR-IRSA 4060 Man 29/2003 methods, the N content according to the APAT CNR-IRSA 4030 A2 – Man 29/2003method. Equation (3) calculates the recovery of the components *i* transferred from the solid phase into the liquid phase at the end of each HTC test: *i(%)* is *P(%)* or *N(%)* percentage recovery; $C_{i,l}$ is the concentration of *i* (P or N) determined in the liquid phase (expressed in wt%); L_{tot} is the total mass of liquid expressed in g (it takes into account the separated liquid and the amount of liquid present in the wet solid post-test); $C_{i,s}$ is the content of *i* (P or N) in the as received SFD (expressed in wt%); and w_s is the mass of SFD loaded into the HTC reactor.

$$i\ (\%) = \frac{C_{i,l} \cdot L_{tot}}{C_{i,s} \cdot w_s} \cdot 100 \quad (3)$$

Equation (4) calculates the *P/N* ratio, i.e., the relative recovery of P referred to N one.

$$P/N = \frac{P(\%)}{N(\%)} \quad (4)$$

3. Results

Table 1 reports CHNS analysis, ash and P content, and HHV of SFD feedstock for HTC experiments. SFD pellets had a relatively high ash content on a dry basis (32.55 wt%), if compared to lignocellulosic biomasses (typically with ash content on a dry basis below 15 wt% (Mu et al., 2024)). This ash content significantly affected the HHV of SFD, which shows a value of 13.8 MJ/kg. It is also important to note that the HHV of SFD was slightly lower than that of the raw sludge studied by (Volpe et al., 2020), which shows an HHV of approximately 16 MJ/kg, but is still comparable to that of a lignocellulosic biomass (Volpe et al., 2016). The high ash must be duly considered for energy applications, due to the high risk of slag and encrustation formation during combustion (Reza et al., 2013; Reza et al., 2014). On the other hand, the absence of potentially hazardous metals in the SFD ashes (Mammarella et al., 2025) enhance the possibility of dual valorization of both the solid and liquid phases obtainable by HTC.

Table 1: Characterizations of as-received SFD (values reported on dry basis)

C (wt%)	H (wt%)	N (wt%)	S (wt%)	Ash (wt%)	P (wt%)	HHV (MJ/kg)
33.53	4.44	4.74	1.05	32.55	1.3	13.8

Figure 1 shows properties of HTC liquid product (*P(%)* and *N(%)* recoveries, pH, and *P/N* recovery ratio) as functions of *T*, *t*, *S/L*, and *Ac*. Figure 2 shows and properties of the HTC hydrochar (*C* and *ash* contents, with related HHV, all on a dry basis) as functions of *T*, *t*, *S/L*, and *Ac*.

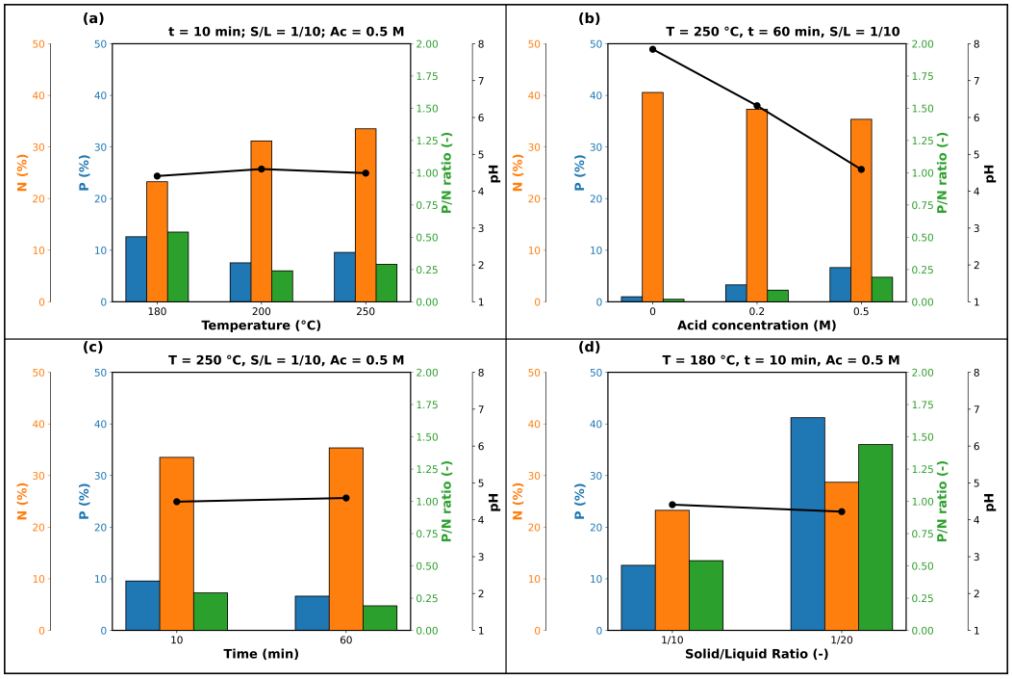

Figure 1: Nutrients recovery (P(%), N(%)), P/N ratio, and pH of HTC liquid phase as a function of: (a) temperature (10min; 1/10; 0.5M), (b) acid concentration (250°C, 60min, 1/10); (c) time (250°C, 1/10, 0.5M); (d) solid/liquid ratio (180°C, 10min, 0.5M).

P recovery from SFD to HTC liquid (*P(%)*, Figure 1) was increased at lower *T*, shorter *t*, higher *Ac* and lower *S/L*. These trends agreed with those of (Ekpo et al., 2016a), who observe that the extent of P extraction decreases with the severity of the reaction, and that increasing the acid concentration leads to a decrease in the pH of the liquid phase which in turn favors the recovery of P in the reaction medium (Ekpo et al., 2016a). Conversely, N recovery (*N(%)*, Figure 1) increased at higher *T* and longer *t*, due to ammonium release from decomposition of organic matter in SFD. These results were confirmed by observation from (Ekpo et al., 2016a), who found that ammoniacal nitrogen in the liquid reaction medium increases with increasing process temperature, as well as by findings in (Ekpo et al., 2016b) who report that the amount of NH_4^+-nitrogen increases significantly with increasing process severity.

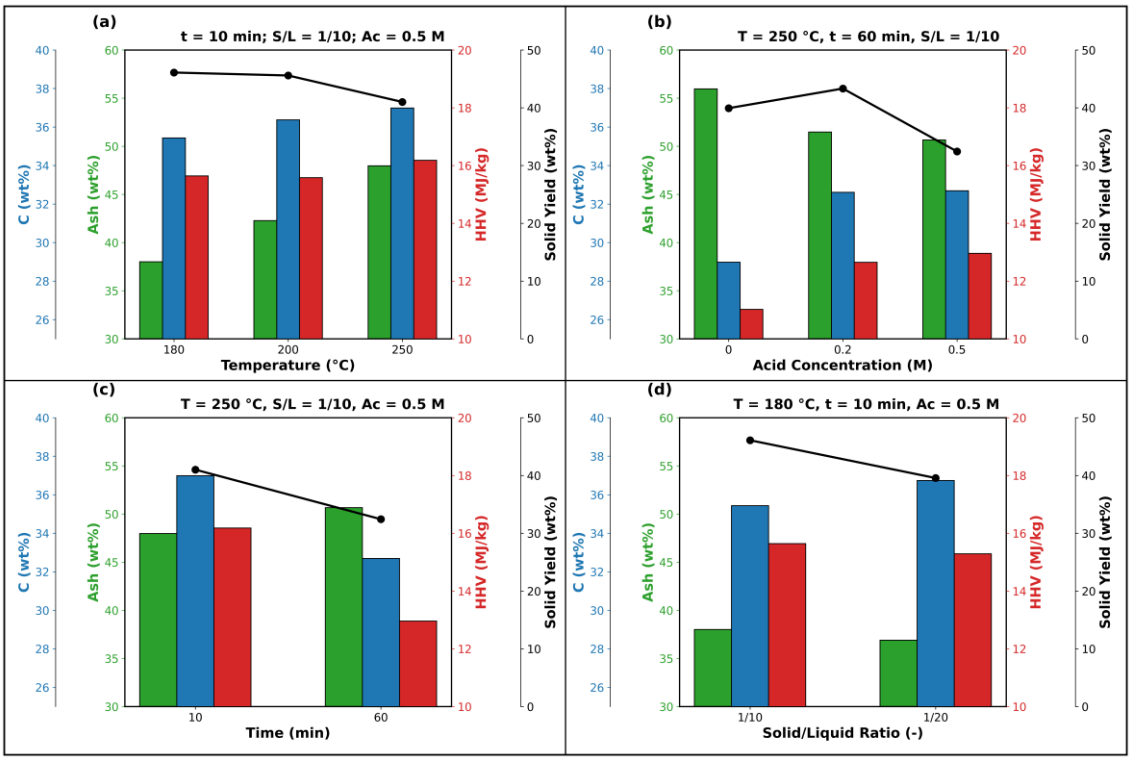

Figure 2: Characteristics of the HTC solid phase (hydrochar) as a function of: (a) temperature (10min; 1/10; 0.5M), (b) acid concentration (250°C, 60min, 1/10); (c) time (250°C, 1/10, 0.5M); (d) solid/liquid ratio (180°C, 10min, 0.5M).

S/L of 1/20 enhanced the solubilization of P and N until reaching a *P(%)* and *N(%)* recovery of approximately 45% and 33%, respectively (Figure 1 (d)). The resulting *P/N* recovery ratios provides key insight into the process conditions under which P recovery and N recovery are favored. Specifically, lower *T* and *S/L*, shorter *t*, and higher *Ac*, favored enhanced P recovery while still maintaining an N recovery approximately of 30% (*P/N* recovery about of 1.4, Figure 1) . Overall, the improved recoveries obtained are lower than those obtained using strong acids such as HCl and H_2SO_4, which reach 52-96% of recovered P (Khalaf et al., 2023). However, the use of a less hazardous, more easily manageable, and less expensive acid such as dilute acetic acid, along with the possibility of maximizing P and N recovery by optimizing process parameters, offers interesting prospects for future circular developments. Furthermore, the possibility of obtaining a P and N recovery that can be modulated according to process conditions allows the tuning of P and N contents in the liquid phase with which may be suitable for obtaining struvite, a renewable fertilizer that can be effectively used to reduce dependence on non-renewable fertilizers (Becker et al., 2019; Huang et al., 2011; Yan et al., 2023). Alternatively, the direct application of the HTC liquid phase as a biomass-derived liquid organic fertilizer can be considered, as investigated by (Gao et al., 2021). The quality of hydrochar obtained by HTC was significantly increased with reaction severity, higher *Ac*, and lower *S/L* (Figure 2). Increasing temperatures from 180 to 250 °C increased carbon content from approximately 35 to 37 wt%, which was reflected in the growth of HHV, as also observed by (Nakason et al., 2018). This indicated that carbonization was enhanced at higher temperatures; however, an increase in ash content was observed as the severity of the process increased, reaching up to approximately 48 wt% (Figure 1(a)). This may be due to both the dissolution of other elements in the liquid phase and the fact

that some inorganic components may have been resorbed onto the hydrochar surface (Nakason et al., 2018). Meanwhile, Figure 2(b) shows how increasing the acetic acid concentration, compared to the HTC test performed only with water, led to a slight decrease in hydrochar ash content (from ~56 wt% to ~51 wt%) due to mineral leaching, and a consequent increase in C content and HHV. The lower *S/L* improved the quality of the hydrochar (Figure 2), since the ash content decreased, and the carbon content and HHV increased from ~13 to ~16 MJ/kg; a further advantage came from the overall decrease of solid waste mass, as indicated by the solid yield ranging from ~32 to ~46% (Figure 2).

4. Conclusions

This study demonstrates that hydrothermal carbonization is a promising approach for the integrated valorization of SFD within a circular economy framework. The raw SFD feedstock exhibited a low HHV (13.8 MJ/kg) due to its high ash content (~32 wt%), which limits its direct use as a solid fuel. HTC of SFD offers an efficient strategy for nutrient recovery and energy valorization of this waste biomass. Phosphorus recovery was favored under milder conditions, higher acetic acid concentration, and lower S/L ratios, while nitrogen recovery increased with reaction severity due to enhanced ammonium release. At an S/L ratio of 1/20, up to ~45% of P and ~33% of N were recovered. Although these recoveries were lower than those obtained using strong mineral acids, diluted acetic acid offers clear advantages in term of safety, cost and process sustainability. The tunability of P and N recovery in the liquid phase with HTC operative conditions enables the production of nutrient solutions suitable for struvite precipitation or a biomass-derived liquid fertilizer to direct use of HTC liquid phase. Simultaneously, HTC enhanced hydrochar quality, increasing carbon content and HHV up to ~16 MJ/kg. Higher reaction severity promoted carbonization but also led to ash enrichment, whereas acetic acid addition and lower S/L ratios reduced ash content through mineral leaching. The combined improvement in fuel properties and reduction in solid yield confirms HTC as an effective waste minimization strategy. Overall, HTC converts solid fraction digestate into valuable secondary sources, supporting nutrient recycling, renewable energy production, and reduced reliance on non-renewable fertilizers. Although the present investigation was carried out in a 15 mL batch reactor, the results provide robust screening of the effect of HTC operating variables on nutrient recovery and hydrochar upgrading. However, scale-up may alter the absolute process response because larger systems are typically characterized by different heat-transfer rates, temperature gradients. Accordingly, the optimal conditions identified here should be considered as a sound basis for further validation in larger laboratory and pilot-scale reactors, where reactor hydrodynamics, thermal inertia, and process integration requirements can be properly assessed.

References

Becker, G. C., Wüst, D., Köhler, H., Lautenbach, A., & Kruse, A. (2019). Novel approach of phosphate-reclamation as struvite from sewage sludge by utilising hydrothermal carbonization. Journal of Environmental Management, 238, 119–125.

Bolzonella, D., Fatone, F., Gottardo, M., & Frison, N. (2018). Nutrients recovery from anaerobic digestate of agro-waste: Techno-economic assessment of full scale applications. Journal of Environmental Management, 216, 111–119.

Channiwala, S. A., & Parikh, P. P. (2002). A unified correlation for estimating HHV of solid, liquid and gaseous fuels. Fuel, 81(8), 1051–1063.

Ekpo, U., Ross, A. B., Camargo-Valero, M. A., & Fletcher, L. A. (2016a). Influence of pH on hydrothermal treatment of swine manure: Impact on extraction of nitrogen and phosphorus in process water. Bioresource Technology, 214, 637–644.

Ekpo, U., Ross, A. B., Camargo-Valero, M. A., & Williams, P. T. (2016b). A comparison of product yields and inorganic content in process streams following thermal hydrolysis and hydrothermal processing of microalgae, manure and digestate. Bioresource Technology, 200, 951–960.

Exploring digestate's contribution to healthy soils. (2024). www.europeanbiogas.eu Accessed 15.01.2026

Gao, S., Lu, D., Qian, T., & Zhou, Y. (2021). Thermal hydrolyzed food waste liquor as liquid organic fertilizer. Science of The Total Environment, 775, 145786.

Huang, H., Xu, C., & Zhang, W. (2011). Removal of nutrients from piggery wastewater using struvite precipitation and pyrogenation technology. Bioresource Technology, 102(3), 2523–2528.

IEA. (2024). Renewables 2023, IEA, Paris https://www.iea.org/reports/renewables-2023, Licence: CC BY 4.0.

Khalaf, N., Leahy, J. J., & Kwapinski, W. (2023). Phosphorus recovery from hydrothermal carbonization of organic waste: a review. In Journal of Chemical Technology and Biotechnology (Vol. 98, Number 10, pp. 2365–2377). John Wiley and Sons Ltd.

Macarthur, E. (2017). What is a Circular Economy? | Ellen MacArthur Foundation. In Ellen Macarthur Foundation.

Mammarella, D., Di Giuliano, A., Nolfi, G. D. V., Nespeca, F., Gallucci, K., Passadoro, M., Daniele, V., Ferrante, F., Campitelli, P., & Rossi, L. (2025). Reuse of Ashes from Digestate Solid Fraction as a Catalytic Support for the Conversion of Vegetable Oils in Biofuels. Chemical Engineering Transactions , 119, 205–210.

Marin-Batista, J. D., Mohedano, A. F., Rodríguez, J. J., & de la Rubia, M. A. (2020). Energy and phosphorous recovery through hydrothermal carbonization of digested sewage sludge. Waste Management, 105, 566–574.

Möller, K., & Müller, T. (2012). Effects of anaerobic digestion on digestate nutrient availability and crop growth: A review. Engineering in Life Sciences, 12(3), 242–257.

Mu, Q., Aleem, R. D., Liu, C., Elendu, C. C., Cao, C., & Duan, P.-G. (2024). Oxygen blown steam gasification of different kinds of lignocellulosic biomass for the production of hydrogen-rich syngas. Renewable Energy, 232, 121132.

Nakason, K., Panyapinyopol, B., Kanokkantapong, V., Viriya-empikul, N., Kraithong, W., & Pavasant, P. (2018). Hydrothermal carbonization of unwanted biomass materials: Effect of process temperature and retention time on hydrochar and liquid fraction. Journal of the Energy Institute, 91(5), 786–796.

Reza, M. T., Emerson, R., Uddin, M. H., Gresham, G., & Coronella, C. J. (2014). Ash reduction of corn stover by mild hydrothermal preprocessing. Biomass Conversion and Biorefinery.

Reza, M. T., Lynam, J. G., Uddin, M. H., & Coronella, C. J. (2013). Hydrothermal carbonization: Fate of inorganics. Biomass and Bioenergy, 49, 86–94.

Taglieri, L., & Gallifuoco, A. (2025). Coupling biomass hydrothermal carbonization and green solvent extraction. Biomass and Bioenergy, 203, 108309.

Taglieri, L., Spera, A., & Gallifuoco, A. (2024). Green recovery of platform chemicals from hydrothermal carbonization process water. Bioresource Technology Reports, 26, 101815.

Vaneeckhaute, C., Meers, E., Michels, E., Buysse, J., & Tack, F. M. G. (2013). Ecological and economic benefits of the application of bio-based mineral fertilizers in modern agriculture. Biomass and Bioenergy, 49, 239–248.

Volpe, M., Fiori, L., Merzari, F., Messineo, A., & Andreottola, G. (2020). Hydrothermal carbonization as an efficient tool for sewage sludge valorization and phosphorous recovery. Chemical Engineering Transactions, 80, 199–204.

Volpe, M., Fiori, L., Volpe, R., & Messineo, A. (2016). Upgrading of olive tree trimmings residue as biofuel by hydrothermal carbonization and torrefaction: A comparative study. Chemical Engineering Transactions, 50, 13–18.

Ward, A. J., Hobbs, P. J., Holliman, P. J., & Jones, D. L. (2008). Optimisation of the anaerobic digestion of agricultural resources. Bioresource Technology, 99(17), 7928–7940.

Yan, Y., Kallikazarou, N. I., Tzenos, C., Kotsopoulos, T. A., Koutsokeras, L., Kokkinidou, DespoinaA., Michael, C., Constantinides, G., Anayiotos, A. S., Botsaris, G., Nisiforou, O., Antoniou, M. G., & Fotidis, I. A. (2023). Pilot-scale biogas and in-situ struvite production from pig slurry: A novel integrated approach. Journal of Cleaner Production, 431, 139656.