Thermodynamic Analysis of Digestate Pyrolysis Coupled with CO_2 Sorption

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Abstract. To date the management of digestate is a crucial task for anaerobic digestion process. In the present work a strategy for digestate management is thermodynamically analyzed by a commercial software for process simulation called CHEMCAD®. Pyrolysis of digestate is simulated by a minimization of the free Gibbs energy. The sequestration of the carbon dioxide (CO_2) released by the pyrolysis is investigated by the addition of calcium oxide, in order to reduce CO_2 emissions. The effect of the pyrolysis temperature between 400–900 °C and of the CaO/digestate mass ratio between 0–0.5 was discussed, as well. The CHEMCAD application allowed to investigate the chemisorption behaviour by focusing on the temperature-dependent CO_2 sorption trends in relation to different values of the CaO mass ratio. Temperature below 650 °C should be considered for CO_2 sorption by CaO. CO_2 molar fraction below 10% was obtained for temperature below 450 °C and CaO/digestate mass ratio higher than 0.4.

Keywords: Pyrolysis · Digestate · CO_2 Sorption · Gas

1 Introduction

Anaerobic digestion (AD) consists of a sequence of processes through which microorganisms break down the biodegradable compounds in anaerobic environment through the following four key steps, such as hydrolysis, acidification, acetogenesis, and the final conversion of acetic and hydrogen gas into methane (CH_4) and carbon dioxide (CO_2) [1, 2]. This process is used for industrial or domestic purposes to manage waste or to produce biogas for heat and power production. Digestate is the solid by-product remaining after the anaerobic digestion of a biodegradable feedstock. Digestate comprises of the solid fibrous material fraction emanating from the AD bio-reactor, and the liquid portion. It usually contains macro-elements such as nitrogen (N), phosphorous (P), potassium (K), calcium (Ca), sulphur (S), magnesium (Mg); recalcitrant organic molecules such as lignin, cutin, humic acids, complex proteins which allow to consider it as valuable

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substitute, with lower environmental impact, of synthetic fertilizers. Digestate is often widespread in agricultural fields near the site where it is produced, unfortunately this is not always the optimal strategy as it could cause soil and water pollution, namely eutrophication, under specific condition. Therefore, planning how to manage the digestate is a crucial task when a biogas plant needs to be realized [3].

Since the present paper focuses on a pyrolysis digestate, it is relevant to shortly deal with how this process works. As reported by Stauffer et al. [4], pyrolysis is a thermal degradation process, an endothermic one, aimed at reducing a solid (or a liquid) into smaller volatile molecules, without interacting with oxygen or any other oxidants. It is a necessary process for the combustion of most solid fuels. Such process can produce a very complicated pattern of products depending on the substance being pyrolyzed as well as the environment (temperature, pressure, presence of extra reactants, etc.) in which it takes place [5].

Also, as argued by Al-Haj Ibrahim [6], the pyrolysis process is a proven and energetically efficient chemical technology that is used in the chemical industry. Moreover, pyrolysis may be used in biorefineries for making a wide range of products and materials aimed at making society more sustainable across time, including many forms of carbon, fuels and other potentially valuable chemicals and chemical feedstocks. In terms of air emissions, comparing this process with other treatment processes, such as gasification, pyrolysis produces, in general, fewer air emissions, lower emission of nitrogen and sulphur oxides, less CO_2 generation, less dust emission and no emission of dioxin inside the pyrolyzer due to the pyrolysis with deoxidized hydrocarbon gas [6]. Thermochemical treatment processes are generally classified according to their equivalence ratio (ER), which is defined as the amount of air added relative to the amount of air required for stoichiometric combustion. The equivalence ratio for pyrolysis is 0 ($ER = 0$). In terms of reactions, they typically occur at temperatures between 400 and 800 °C. The distribution of the products may be changed as a function of temperature, with lower pyrolysis temperatures often producing more liquid and solid products and higher temperatures capable of generating more gases as a result of more potent thermal cracking events. The characteristics of the pyrolysis products are significantly impacted by the pyrolysis temperature as well. Solid residual coproducts and ash, non-condensable gases, and condensable liquids, also referred to as pyrolysis oil, pyrolytic oil, bio-oil, or tar, are the end products of pyrolysis [6]. The type of material treated largely determines the type and yields of the pyrolysis products. By regulating pyrolysis variables like temperature, heating rate, residence duration, pressure, input particle size, and reactor type, the end products of pyrolysis may also be controlled. Specifically, the pyrolysis products can be classified into three typologies, such as biochar, syngas and bio-oil [7].

The generated biogas can be used as a renewable fuel for a variety of operations, such as the direct combustion generation of heat and/or power. When properly stored and applied to avoid nitrate leaching, the digestate produced can be utilized as a fertilizer [8]. Since the anaerobic digestion industry's sustainability is inextricably linked to proper digestate management and disposal, the aim of the present research work consisting of studying an alternative strategy able to efficiently and effectively manage digestate.

Particularly, the digestate pyrolysis is proposed coupled with the CO_2 sorption by calcium oxide (CaO). Calcium oxide (CaO, well-known as quicklime) is one of the

most suitable heterogeneous base catalysts due to their comparatively high basic sites, nontoxic, low solubility in methanol and can be manufactured from cheap materials like lime stone and calcium hydroxide [9].

As reported by Zhang [10], CaO is industrially produced by calcining $CaCO_3$ at temperatures ranging from 810 °C to 1100 °C, according to the following solid-gas phase heterogeneous reaction:

$$CaCO_3 \rightarrow CaO + CO_2$$

The use of CaO-based adsorbents is characterized by a great potential for capturing CO_2 in a variety of systems due to their high reactivity for CO_2 high capacity and low cost of naturally occurring CaO. Such carbon dioxide removal is based on a reversible reaction between CaO and CO_2 [11]. The use of high-temperature adsorbents, including CaO, has a high potential to capture CO_2 from various systems [12], both in pre-combustion and post-combustion capture [13].

As demonstrated by Chen et al. [14], from the thermodynamic equilibrium point of pyrolysis process, if the CO_2 formed during pyrolysis can be absorbed, then it may promote the decarboxylation of carboxyl compounds, ultimately promoting the deoxygenation of bio-oil in the form of CO_2. Based on the specific observations and the favou-rable CO_2 adsorption performance of CaO in biomass gasification [15–19], it was proposed that CaO could represent a superior additive for deoxygenation in the fast pyrolysis process.

Wiśniewski et al. [20] pyrolyzed dried digestate in an electrically heated batch reactor. At pyrolysis temperature of 500 °C the composition of pyrolysis gas was checked (24 vol% CO_2, 10 vol % CO, 8 vol% CH_4, and 2 vol% H_2, and the calorific value was assessed (3.7 MJ/Nm^3). Doukeh et al. [21] pyrolyzed conditioned digestate over WO3/γ-Al_2O_3 catalyst in a continuous laboratory system using a quartz tubular reactor at atmospheric pressure, temperature 425 °C and feeding rate of 0.33 mL/min. They analyzed by GC–MS the bio-oil and they detected that it is composed by a large number of linear and branched aliphatic hydrocarbon components, alcohols, phenols and alkyl aromatic hydrocarbons with two or three methyl-type substituents. The major components present in the cracking gas are methane (CH_4) and carbon oxide (CO). Petrovic et al. [22] carried out a kinetic and thermodynamic study about digestate pyrolysis by thermogravimetric analysis data recorded up to 800 °C. Bio char was characterized, as well. Kinetic and thermodynamic parameters revealed a complex degradation mechanism of digestates, as they showed higher activation energies than undigested materials. Liu et al. [23] evaluated the digestate generated in AD of food wastes as a potential feedstock for the preparation of biochars by pyrolysis. They executed thermogravimetric analyses with different heating rates, and they calculated apparent activation energy. The TG–FTIR–MS gas analysis showed that dehydration and CO_2 emission were the main reasons for mass loss, and light hydro-carbons were released in step II of the pyrolysis.

The pyrolysis temperature significantly influenced the physicochemical properties and surface properties of the biochars.

From this literature review it can be argued that there is a recent and crescent interest of the scientific community towards the investigation of the pyrolysis as method to manage the digestate from biogas plants.

At the best of our knowledge and bibliographic search, all the works were carried out at laboratory scale and with the help of theoretical model. Therefore, in this strategic and interesting field, the authors of the present work paid their efforts to an unexplored topic that is the pyrolysis of digestate with negative CO_2 emissions by the addition to the thermal process of calcium oxide.

2 Materials and Methods

In the present work a thermodynamic approach was set. Thermodynamic equilibrium model is a smart tool to calculate the output streams of a pyrolyser. As already observed by Freda et al. in a previous research work, it is relevant to highlight that the model calculation is independent of reactor design. It is also described as zero-dimensional and unaffected by residence periods of the reactants and their hydrodynamics. Thence, it is extremely helpful for studying the influence of the process parameters, such as temperature, pressure, moisture of feedstock, secondary reaction with sorbents [24].

In relation to reaction with sorbents and related chemical adsorption processes, it is relevant to highlight that, in this case, two species have been considered, such as CaO as adsorbent and CO_2 as adsorbate. A chemical adsorption process is a chemical reaction and the development of a covalent bond between the molecule and one or more surface atoms are both necessary components of such adsorption process known as chemisorption.

Usually, thermodynamic equilibrium models are stoichiometric or non-stoichiometric. The stoichiometric model requires a definition of chemical species and of the equilibrium constants of pyrolysis reactions [25]. In the non-stoichiometric model, Gibbs free energy of the system is minimized without specifying any chemical reaction [26]. The two models (stoichiometric and non-stoichiometric) are essentially equivalent, when in the stoichiometric approach all possible chemical reactions are consi-dered. In this work the non-stoichiometric approach was applied. The Gibbs free energy of the chemical species involved in the process is minimized.

In order to find the equilibrium composition for a given feed to the pyrolyser at fixed temperature and pressure, the phases chemical reaction equilibrium criterion can be applied that is expressed as follows:

$$\left(\mathrm{dG_{gasifier}}\right)_{\mathrm{T,P}} = 0 \tag{1}$$

The Gibbs free energy is:

$$nG = \sum n_i \Delta \mathrm{G}_{\mathrm{fi}}^{0} + RT \ln P \sum n_i + RT \sum n_i \ln y_i + RT \sum n_i \ln \phi_i \tag{2}$$

where:

$\mathrm{n_i}$ is number of moles of $\mathrm{i^{th}}$ species in the system;
$\Delta \mathrm{G^0_{fi}}$ is standard Gibbs free energy of formation of compound *i*;
y_i is the molar fraction of the compound i;
ϕ_i is the fugacity coefficient;
P is the pressure;
T is temperature;

R is universal gas constant.

As reported by Freda et al. [27], the minimization of this function occurs under restraints imposed by the atomic mass balances of each elements of the system and by the method of Lagrangian undetermined multipliers. A system of n-linear equation is obtained in as many unknown (chemical species involved in gasification).

An iterative solution method provided by the commercial freeware software CHEMCAD® gives the composition corresponding to the minimum Gibbs free energy [28]. The chemical species considered for the chemical equilibrium calculation were: $C_6H_{10}O_4$ (ethylidene diacetate), H_2O (water), C (carbon), H_2 (hydrogen), CO (carbon monoxide), CO_2 (carbon dioxide), CH_4 (methane), C_2H_6O (ethanol). Digestate was simulated by ethylidene diacetate, because its elemental composition and heating value (LHV, low heating value) are remarkably close to digestate, as Table 1 clearly shows [29].

Table 1. Elemental composition and low heating value (LHV) of digestate and $C_6H_{10}O_4$.

	Digestate dry ash free	$C_6H_{10}O_4$
C, wt %	51	49
H, wt %	6	7
O, wt %	43	44
LHV, MJ/kg	19.5	19.6

Char was simulated by pure carbon. In the sensitivity analyses, CaO was co-fed with the biomass in mass ratio variable from 0 to 0.5. More in detail, CaO/digestate mass ratio was set at 0, 0.2, 0.4 and 0.5. Pyrolysis temperature was varied from 400 up to 900 °C, in eleven temperature steps. The dependent variables detected were dry gas yield ($m^3/kg_{\ biomass}$) and gas volumetric composition (H_2, CO, CO_2, CH_4). Therefore, for each dependent variable a total of 44 output values were calculated.

The calculation of the simulated process was performed by the abovementioned software, CHEMCAD®.

In Fig. 1 a layout of process simulation is shown. The stream 1 is composed of the biomass (digestate) and the adsorbent CaO. The unit 1 is a Gibbs reactor, where the minimization of Gibbs free energy occurs. The stream 2 gives the thermodynamic equilibrium composition of the mixture at the set temperature. The unit 2 is a phase separator, where the solids are removed.

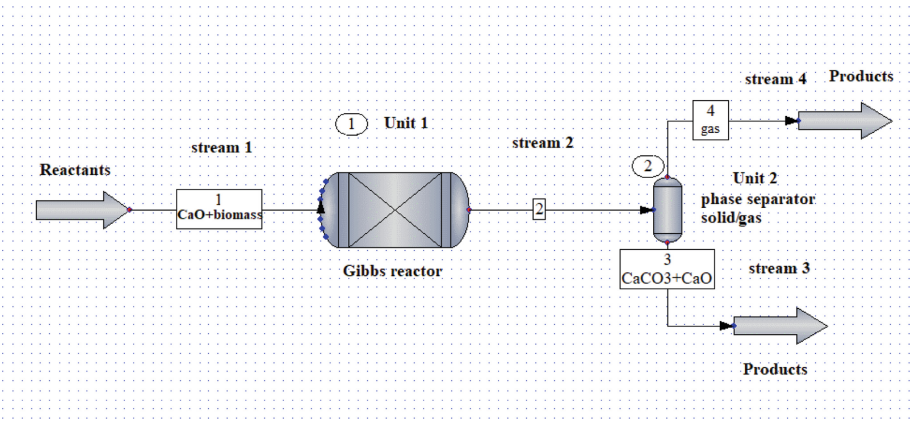


Fig. 1. CHEMCAD software application: pyrolysis process scheme in relation to the streams and reactors set.

3 Results and Discussion

In Fig. 2 the equilibrium composition of a mixture equimolar of CaO (1 mol/h) and CO_2 (1 mol/h) that gets at 20 °C and 1 bar into a thermodynamic Gibbs unit is plotted as function of the reactor temperature. At temperature below the 500 °C the formation of $CaCO_3$ is clearly favoured with heat loss; on the contrary, at temperatures above 800 °C, the $CaCO_3$ decomposition with formation of CaO and CO_2 occurs with heat duty (Fig. 2).

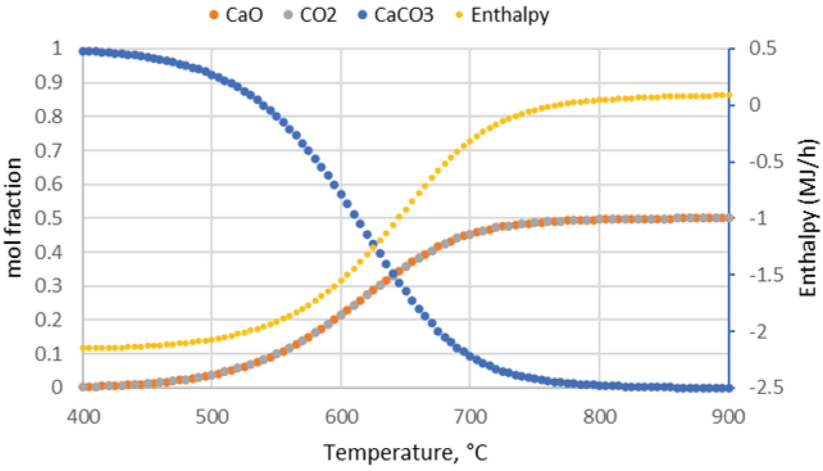


Fig. 2. CHEMCAD software application: carbonatation of the carbon dioxide as a function of the temperature.

Focusing on the results of sensitivity analyses, chemisorption mechanisms were observed and evaluated through CHEMCAD® process simulation software. Specifically,

the CO_2 sorption *vs* temperature trends related to the CaO mass ratio values ranging from 0 to 0.5 were evaluated. It is relevant to observe that the most significant temperature-dependent CO_2 sorption capacity is registered into a temperatures ranging from 400 °C to 650 °C, with a strongly decreasing behaviour of CO_2 adsorption at higher temperatures, as shown in Fig. 2. Thus, CO_2 capture capacity is increased with the CaO content strictly related to the abovementioned temperature range (Fig. 3).

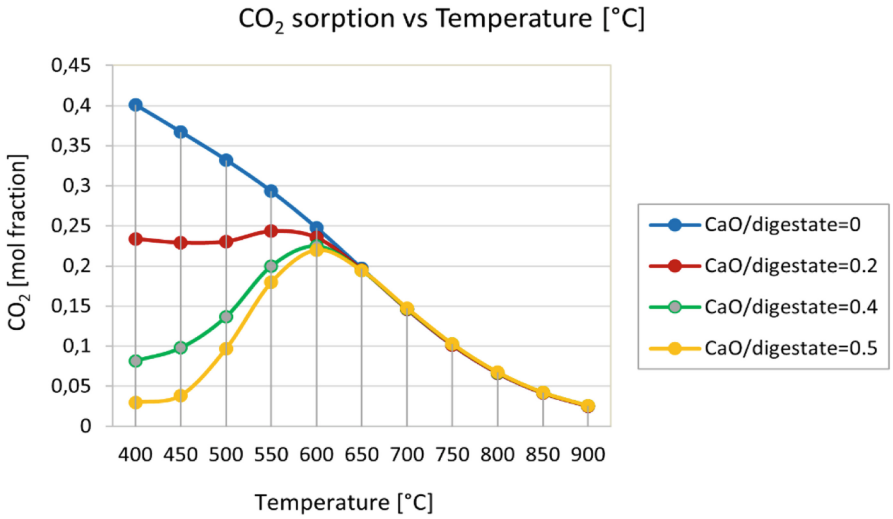


Fig. 3. CO_2 sorption vs Temperature [°C] trend in relation to an increasing CaO/digestate mass ratio.

Despite the CaO/digestate mass ratio increases, at temperatures higher than 650 °C, the CO_2 behaviour is not affected by the CaO content. In fact, as emerged from the plot results coming from the CHEMCAD® software application, CO_2 sorption by CaO should be performed at the temperature below of about 646 °C. Such thermal conditions would allow to reach a greater adsorption process efficiency. At temperature above 750 °C the molar fraction of CO_2 is below 10%, but in this case the low content is reached by other chemical reactions such as Boudouard reaction and dry reforming of methane, as follows:

$$C + CO_2 = 2CO \quad \text{(Boudouard reaction)}$$

$$CH_4 + CO_2 = 2CO + 2H_2 \quad \text{(Methane dry reforing)}$$

In Fig. 4 the molar fration of H_2 of the dry gas is plotted versus temperature at fixed parametric values of CaO/digestate mass ratio. Figure 4 shows that at temperatures higher than 650 °C the concentration of H_2 is independent of CaO/digestate. This indirectly means that the chemisorption of CO_2 by CaO is inefficient at temperatures above 650 °C.

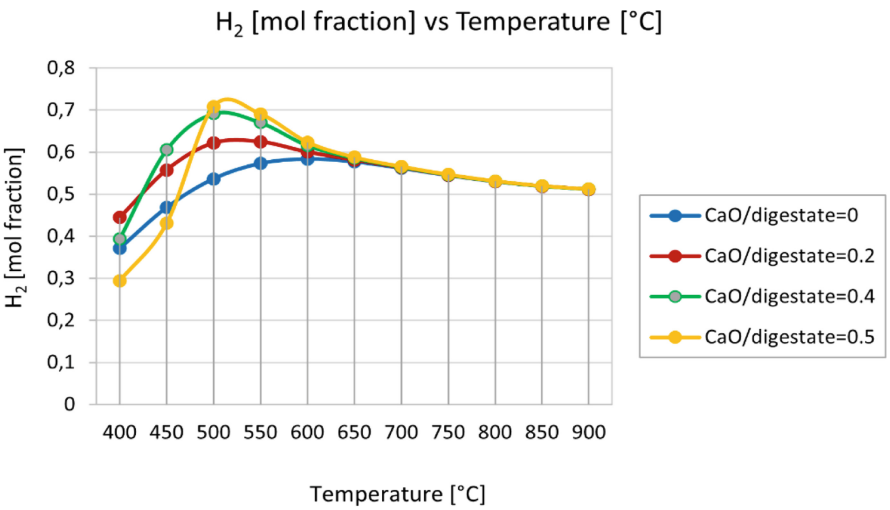


Fig. 4. H_2 [mol fraction] vs Temperature [°C] trends in relation to an increasing CaO/digestate mass ratio.

Above 650 °C the H_2 molar fraction in the dry gas has a slight decreasing trend that can be probably justified by the exothermicity of the following water gas shift reaction:

$$H_2O + CO = CO_2 + H_2$$

Below 650 °C the hydrogen molar fraction ranges from 0.3 to 0.7. The highest variability is observed at the highest CaO/digestate mass ratio (0.5), that gives the maximum CO_2 chemisorption with the higher fluctuations of the relative composition of the other permament gas.

Regarding the behaviour of CO [mol fraction] in relation to the temperature (ranging from 400 °C to 900 °C), as shown in Fig. 5, it is possible to observe that at temperatures ranging from 400 °C to 550 °C the CO trend decreases in relation to the CaO/digestate content (ratio) in a range from 0.008 to 0.06 mol fraction, highlighting that CO reaches the minimum value of 0.0008 with the higher CaO/digestate content (0.5) at temperature of 400 °C. A faster and more evident growth is observed at temperatures higher than 550 °C with a more evident growing trend up to 900 °C, where it reaches 0.46 ($\approx$ 0.5) mol fraction.

Figure 6 shows that CH_4 [mol fraction] trend is affected by the CaO/digestate content, since its behaviour describes a systematic and directly proportional growth from 0 to 0.5 Ca/digestate ratio at temperature of 400 °C. At temperature of 450 °C, an evident growth of CH_4 trend is observed in relation to the maximum content of CaO/digestate (0.5). Such an evident growing trend is observed from 400 °C to 550 °C. It is probably linked to the higher CO_2 adsorption at the lower temperature and higher CaO/digestate and to the less advancement of the dry reforming of methane. At temperatures higher than 600 °C it is possible to notice that the CH_4 trends tend to reach a plateau, reporting values ranging from 0.01 to 0.0006 mol fraction.

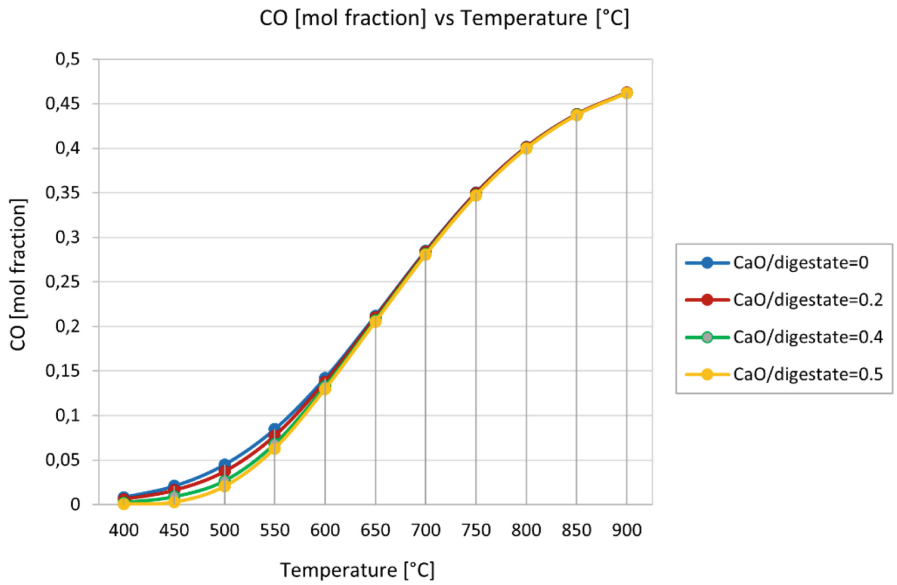


Fig. 5. CO [mol fraction] vs Temperature [°C] trends in relation to an increasing CaO/digestate mass ratio.

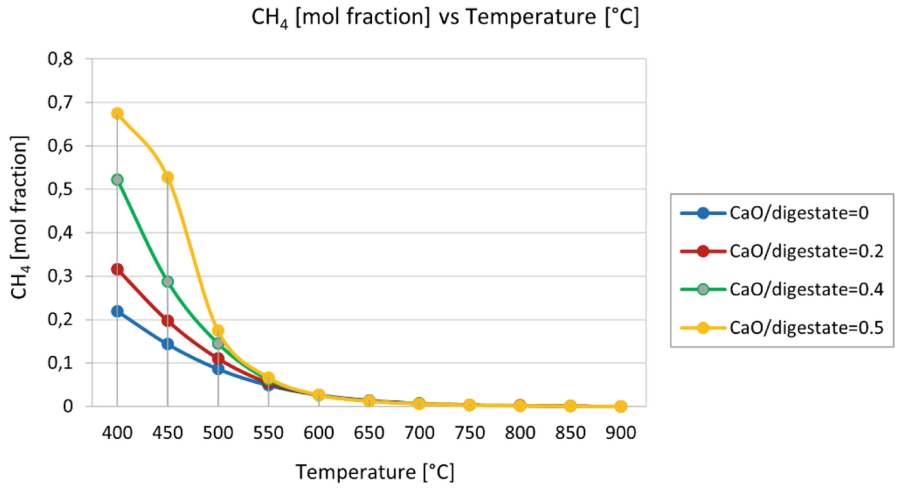


Fig. 6. CH_4 [mol fraction] vs Temperature [°C] trends in relation to an increasing CaO / digestate mass ratio.

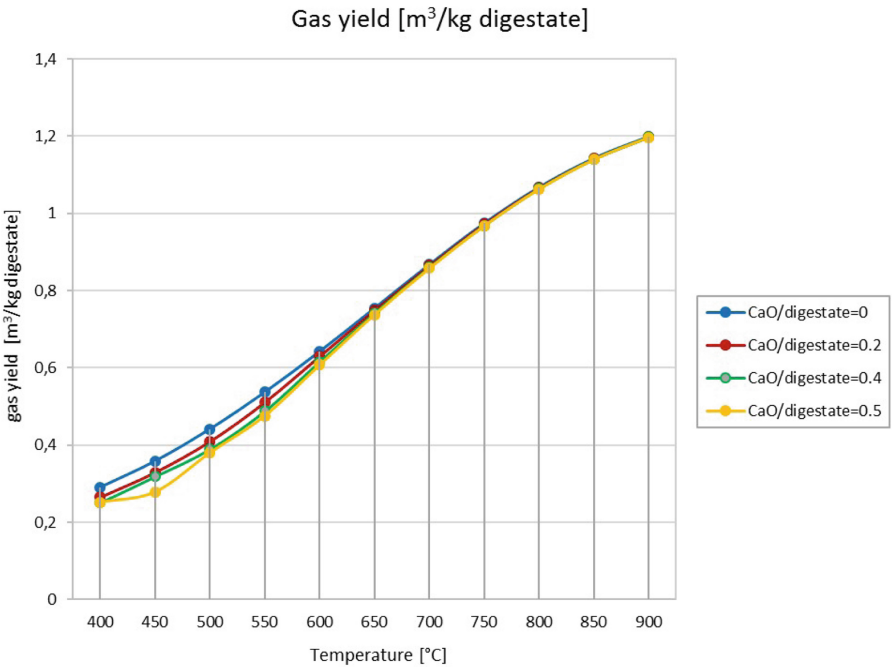


Fig. 7. Gas yield vs Temperature [°C] trends in relation to an increasing CaO/digestate mass ratio.

As expected, Fig. 7 shows that the gas yield is temperature-dependent: it tends to increase. At temperature lower than 600 °C, it is possible to observe an inversely proportional behaviour between the gas yield value and the CaO/digestate mass ratio. Such behaviour is consistent with the sorption of CO_2 by the CaO.

4 Conclusions and Final Remarks

The resulting framework of the present modelling application has allowed to highlight that CO_2 chemisorption capacity of CaO is a temperature-dependent process and CaO/biomass ratio-dependent up to about 646 °C, along with the gases (H_2, CO, CH_4) behaviour temperature- and CaO/digestate-related, included in the simulated process.

Since it has been widely demonstrated that anaerobic digestion can lead several environmental benefits, such as reduction in greenhouse gas emission, reduction in organic waste and production of methane gas [30], carrying out thermodynamic analyses of digestate can synergically contribute to give qualitative and quantitative responses on the ever-increasing energy requirements as well as environmental pollution management.

As a long-term response in sustainability scope, anaerobic digestion is a process able to act as a full circular economy technology in bioproduction, since it plays a key role in residual waste valorization and energy production, and can be incorporated into the biorefinery context [31]. Such specific aspect derives from the utilization of biomass for generating *value-added* products as chemicals or energy, in order to ever-extend and

improve the development of biorefineries [2]. For this purpose, it is relevant to remind that, as mentioned by Sathyan et al., recent advancements in anaerobic digestion highlighted that this process needs significant improvement in its yield and efficiency [32]. In terms of sustainability, the integration of anaerobic digestion and pyrolysis is a well-defined type of cascade biomass valorization scheme aimed at solving the challenge of digestate management by producing a higher amount of biofuels (pyro-gas and bio-oil) [33].

References

1. Hussain, C.M., Paulraj, M.S., Nuzhat, S.: Source reduction, waste minimization, and cleaner technologies. In: Chapter 2: Source Reduction and Waste Minimization, pp. 23–59 (2022)
2. González, R., González, J., Rosas, J.G., Smith, R., Gómez, X.: Biochar and energy production: Valorizing swine manure through coupling co-digestion and pyrolysis. Carbon **6**(2), 43 (2020)
3. Freda, C., Nanna, F., Villone, A., Barisano, D., Brandani, S., Cornacchia, G.: Air gasification of digestate and its co-gasification with residual biomass in a pilot scale rotary kiln. Int. J. Energy Environ. Eng. **10**(3), 335–346 (2019). https://doi.org/10.1007/s40095-019-0310-3
4. Stauffer, E., Dolan, J.A., Newman, R.: Fire debris analysis. Academic Press (2007)
5. Irwin, W.J.: Chromatographic Science Series. In: Analytical Pyrolysis - A Comprehensive Guide, vol. 22. Marcel Dekker, New York (1982)
6. Ibrahim, H.A.H.: Introductory chapter: pyrolysis. Recent Advances in Pyrolysis, 1. BoD – Book on Demand (2020)
7. Zaman, C.Z., et al.: Pyrolysis: a sustainable way to generate energy from waste. vol. 1, p. 316806. Rijeka, Croatia: IntechOpen (2017)
8. Roddy, D.J., Manson-Whitton, C.: Biomass gasification and pyrolysis. Comprehensive Renewable Energy-Biomass & Biofuels (2013)
9. Lam, M.K., Lee, K.T.: Production of biodiesel using Palm oil. Biofuels: alternative feedstocks and conversation process, pp. 353–374 (2011)
10. Zhang, D.: Ash fouling, deposition and slagging in ultra-supercritical coal power plants. In: Ultra-Supercritical Coal Power Plants, pp. 133–183 (2013)
11. Konopacka-Łyskawa, D., Czaplicka, N., Szefer, A.: CaO-based high temperature CO2 sorbents–Literature review. In: Chemical and Process Engineering-Inżynieria Chemiczna i Procesowa 42, pp. 411–438 (2021)
12. Sreenivasulu, B., Sreedhar, I., Suresh, P., Raghavan, K.V.: Development trends in porous adsorbents for carbon capture. Environ. Sci. Technol. **49**(21), 12641–12661 (2015)
13. Perejon, A., Romeo, L.M., Lara, Y., Lisbona, P., Martinez, A., Valverde, J.M.: The Calcium-Looping technology for CO2 capture: On the important roles of energy integration and sorbent behavior. Appl. Energy **162**, 787–807 (2016)
14. Chen, D., Cen, K., Cao, X., Li, Y., Zhang, Y., Ma, H.: Restudy on torrefaction of corn stalk from the point of view of deoxygenation and decarbonization. J. Anal. Appl. Pyrol. **135**, 85–93 (2018)
15. Acharya, B., Dutta, A., Basu, P.: Chemical-looping gasification of biomass for hydrogen-enriched gas production with in-process carbon dioxide capture. Energy Fuels **23**(10), 5077–5083 (2009)
16. Acharya, B., Dutta, A., Basu, P.: An investigation into steam gasification of biomass for hydrogen enriched gas production in presence of CaO. Int. J. Hydrogen Energy **35**(4), 1582–1589 (2010)
17. Guoxin, H., Hao, H.: Hydrogen rich fuel gas production by gasification of wet biomass using a CO2 sorbent. Biomass Bioenerg. **33**(5), 899–906 (2009)

18. Han, L., Wang, Q., Yang, Y., Yu, C., Fang, M., Luo, Z.: Hydrogen production via CaO sorption enhanced anaerobic gasification of sawdust in a bubbling fluidized bed. Int. J. Hydrogen Energy **36**(8), 4820–4829 (2011)
19. Wei, L., Xu, S., Liu, J., Liu, C., Liu, S.: Hydrogen production in steam gasification of biomass with CaO as a CO2 absorbent. Energy Fuels **22**(3), 1997–2004 (2008)
20. Wisniewski, D., Gołaszewski, J., Białowiec, A.: The pyrolysis and gasification of digestate from agricultural biogas plant. Archives of Environmental Protection **41**(3), 70–75 (2015)
21. Doukeh, R., Bombos, M., Bombos, D., Vasilievici, G., Radu, E., Oprescu, E.-E.: Pyrolysis of digestate from anaerobic digestion on tungsten oxide catalyst. React. Kinet. Mech. Catal. **132**(2), 829–838 (2021). https://doi.org/10.1007/s11144-021-01952-7
22. Petrovič, A., et al.: Pyrolysis of solid digestate from sewage sludge and lignocellulosic biomass: Kinetic and thermodynamic analysis, characterization of biochar. Sustainability **13**(17), 9642 (2021)
23. Liu, J., Huang, S., Chen, K., Wang, T., Mei, M., Li, J.: Preparation of biochar from food waste digestate: pyrolysis behavior and product properties. Biores. Technol. **302**, 122841 (2020)
24. Freda, C., Tarquini, P., Sharma, V.K., Braccio, G.: Thermodynamic improvement of solar driven gasification compared to conventional one. Energy **261**, 124953 (2022)
25. Mendiburu, A.Z., Carvalho, J.A., Jr., Coronado, C.J.: Thermochemical equilibrium modeling of biomass downdraft gasifier: Stoichiometric models. Energy **66**, 189–201 (2014)
26. Mendiburu, A.Z., Carvalho, J.A., Jr., Zanzi, R., Coronado, C.R., Silveira, J.L.: Thermochemical equilibrium modeling of a biomass downdraft gasifier: Constrained and unconstrained non-stoichiometric models. Energy **71**, 624–637 (2014)
27. Freda, C., Della Vittoria, U., Fanelli, E., Cornacchia, G., Braccio, G.: Thermodynamic analysis of biomass gasification by different agents. Italian J. Eng. Sci. (2020)
28. Gartman, T.N., Sovetin, F.S., Novikova, D.K.: Experience in the application of the CHEMCAD program to the modeling of reactor processes. Theor. Found. Chem. Eng. **43**, 944–954 (2009)
29. ECN Phyllis Classification: Database for the physicochemical composition of (treated) lignocellulosic biomass, micro- and macroalgae, various feedstocks for biogas production and biochar, https://phyllis.nl/Browse/Standard/ECN-Phyllis#digestate, last accessed 07 May 2023
30. Čater, M., Fanedl, L., Malovrh, Š, Logar, R.M.: Biogas production from brewery spent grain enhanced by bioaugmentation with hydrolytic anaerobic bacteria. Biores. Technol. **186**, 261–269 (2015)
31. Szymanska, M., et al.: A bio-refinery concept for n and p recovery – a chance for biogas plant development. Energies **12**, 155 (2019)
32. Sathyan, A., Haq, I., Kalamdhad, A. S., Khwaraikpam, M.: Recent advancements in anaerobic digestion: A Novel approches for waste to energy. In: Advanced Organic Waste Management, pp. 233–246. Elsevier (2022)
33. Fabbri, D., Torri, C.: Linking pyrolysis and anaerobic digestion (Py-AD) for the conversion of lignocellulosic biomass. Curr. Opin. Biotechnol. **38**, 167–173 (2016)