CHEMICAL ENGINEERING TRANSACTIONS
VOL. 124, 2026
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Marco Bravi, Antonio Marzocchella, Giuseppe Caputo

ISBN 979-12-81206-25-0; **ISSN** 2283-9216
DOI: 10.3303/CET26124011

A Novel Energetically Self-Sufficient Process for the Hydrogen Production from Waste Biomasses

Alessandro Cosenza, Giulia Raccampo, Serena Lima, Francesca Scargiali, Franco Grisafi, Giuseppe Caputo*

Department of Engineering, University of Palermo, Viale delle Scienze Ed. 6, 90128, Palermo, Italy
giuseppe.caputo01@unipa.it

A conceptual design with Aspen Plus simulations of an integrated Supercritical Water Gasification and Oxidation (SCWG-coOx) is presented in this work. Global municipal solid waste already exceeds 2 billion tonnes per year and could reach about 3.4 billion tonnes by 2050, underscoring the need for advanced waste-to-energy routes. Supercritical water gasification (SCWG) converts wet organic residues into a hydrogen- and methane-rich gas at conditions above the critical point of water, but its strong energy demand hampers standalone deployment. Supercritical water oxidation (SCWO) is an exothermic aqueous oxidation process that avoids energy-intensive drying and can achieve near-complete mineralization of organics with very low emissions of NO_x, SO_x and particulates. Coupling SCWG and SCWO into an integrated SCWG-coOx system allows energetic self-sufficiency while treating aqueous waste streams that are poorly suited to conventional thermal or biological processes. In this study, the oxidation step is modelled as a Gibbs reactor and the gasification step as a plug-flow reactor with reaction-specific kinetics, with thermal integration assessed for different feed splits and organic loadings. For an 8 t/h sludge feed split equally between SCWG and SCWO, the process is predicted to be energy self-sufficient and to deliver more than 3 MW of fuel-gas thermal power, highlighting SCWG-coOx as a promising low-impact route for sewage-sludge valorization.

1. Introduction

Rapid global population growth, urbanization and industrialization have sharply increased both resource consumption and waste generation. Recent assessments indicate that worldwide municipal solid waste (MSW) generation already exceeds 2 billion tonnes per year and, under a business-as-usual scenario, is expected to rise to about 3.4 billion tonnes annually by 2050 (Kaza et al., 2018). In this context, waste management and valorization have become critical environmental and economic priorities, as prevailing production and consumption patterns remain predominantly linear and still fall short of circular economy principles. Municipal wastewater treatment plants (WWTPs) play a central role in this urban metabolism, typically employing a treatment train that includes preliminary screening and grit removal, primary settling, biological treatment via conventional activated sludge (Maddela et al., 2021) or related processes, secondary clarification, and, increasingly, tertiary disinfection using ultraviolet irradiation, ozonation or chlorination to meet stringent discharge standards (B. Cosenza et al., 2025; Schneider et al., 2026). Despite different strategies were proposed to minimize the sludge production and for the use of the treated water (Collivignarelli et al., 2019; Di Salvo et al., 2017), inevitably large quantities of waste sludge are generated. Because raw sludge contains more than 90% water, the first essential step in its management is mechanical dewatering (often by gravity thickening and centrifugation), frequently followed by thermal drying to reduce volume and improve handling properties; however, these operations are both energy-intensive and cost-intensive. On a dry basis, municipal wastewater sludge typically contains on the order of 30-40 wt% carbon (Król et al., 2019), highlighting its potential as a carbon-rich feedstock for energy recovery. Supercritical water gasification (SCWG) is a thermo-chemical conversion process that operates at temperatures above the critical point of water (typically 400-700 °C) and pressures above about 22 MPa. In these conditions, mass-transfer limitations are minimized, and reaction rates are high, making SCWG particularly suitable for liquid and slurry wastes that contain water (Brunner, 2009).

Paper Received: 22 December 2025; Revised: 10 February 2026; Accepted: 20 March 2026
Please cite this article as: Cosenza A., Raccampo G., Lima S., Scargiali F., Grisafi F., Caputo G., 2026, A Novel Energetically Self-Sufficient Process for the Hydrogen Production from Waste Biomasses, Chemical Engineering Transactions, 124, 61-66 DOI:10.3303/CET26124011

Organic feedstocks can be directly converted without prior drying into a combustible gas mixture mainly composed of hydrogen, methane, carbon dioxide, carbon monoxide and light hydrocarbons. In addition to energy recovery, the severe hydrothermal conditions promote the breakdown of complex organic pollutants, making SCWG attractive for simultaneous waste sanitization and resource recovery (Picone et al., 2025). Similarly, Supercritical Water Oxidation (SCWO) is a wet oxidation process that treats organic wastes in water at conditions above the critical point of water, typically 400-650 °C and 22-25 MPa (Brunner, 2014). In the context of sewage sludge, SCWO achieves high removal of organic carbon and pathogens (H. Chen et al., 2016). SCWO units are often energetically self-sustaining once at temperature, since oxidation is strongly exothermic and only start-up energy and oxygen pressurization are required (Svanström et al., 2004). Different feedstocks for treatment in supercritical water were proposed and successfully tested, such as the olive oil mill wastewater and agro-food residues (Nanda et al., 2016), the organic fraction of municipal solid waste (A. Cosenza et al., 2026; Sathish et al., 2024), swine wastewaters (Qi et al., 2024), micro- and macroalgal biomass (A. Cosenza et al., 2025; Heeley et al., 2024). As is easy to understand, the process of gasification is highly energy-intensive, and this represent the main bottleneck for an industrial-scale application. Many efforts were made to find alternative heat sources in order to reduce the operative costs of the process. Gutiérrez Ortiz and López-Guirao through Aspen simulations proposed a train of heat exchangers, in order to pre-heat the feedstock constituted by orange peel for its gasification exploiting the heat coming from another process (Gutiérrez Ortiz & López-Guirao, 2024). Chen et al. carried out a life cycle assessment (LCA) of a novel solar energy-driven plant of gasification of biomass for hydrogen production (J. Chen et al., 2019). In the same way, Caputo et al. proposed a design for a novel plant concept for the gasification of wastes using Fresnel solar collectors (Caputo et al., 2025). This study focuses on the SCWG of sewage sludge since it represents one of the most common wastes produced globally. In this context, an Aspen simulation is proposed to describe a new process of gasification energetically supported by oxidation in supercritical water of activated sludges from an urban wastewater treatment plant.

2. Materials and methods

A pilot-scale plant treating 8-ton h^{-1} of feedstock, consisting of activated sludge in water with a concentration between 10 and 20% w/w, was simulated using Aspen Plus software. The total mass flow was equally divided between the SCWG and SCWO processes in order to recover heat from the oxidation section and supply the endothermic gasification reactor, thereby achieving thermal self-sufficiency. The oxidation section was modelled using an ideal equilibrium reactor (RGIBBS), which minimizes the total Gibbs free energy and calculates the equilibrium product composition. This approach effectively simulates an exothermic oxidation reaction, as thermodynamic equilibrium is assumed to be reached. The reactor was modelled as adiabatic, with no heat exchange, in order to evaluate the maximum achievable temperature. Two different configurations were investigated and compared for the gasification section. In the first case, the reactor was modeled as an RGIBBS unit, in which CO, CO_2, H_2O, N_2, and O_2 were specified as outlet products to satisfy the atomic balance. In the second case, the gasification reactor was modeled as a plug flow reactor (PFR) to obtain a more rigorous representation, based on the kinetic parameters of the different macro-components as reported by Yakaboylu et al. (Yakaboylu et al., 2015). Regarding the feedstock, a representative biomass composition was implemented in Aspen Plus to mimic the actual composition of activated sludge. The selected composition, proposed by Ochieng and Sarker (Ochieng & Sarker, 2025), is based on the classification of major macro-components, including proteins, lipids, cellulose, hemicellulose, and lignin. Each component was approximated as a key representative compound to reduce computational complexity (Table 1). Inert compounds and ashes were neglected, as they do not participate in the reactions and were assumed not to significantly affect the process kinetics.

Table 1: Category and key component chosen to describe the activated sludge composition used for Aspen simulations.

Category	Component	wt%
Hemicellulose	Xylose	18.7
Lignin	Guaiacol	23.9
Lipids	Glycerol	16.2
Cellulose, Glucose	Sucrose	6.7
Proteins	Aspartic Acid	34.5

All reagents, products and intermediates that took part in the chosen reaction were defined in the Properties section along with the selected thermodynamic models. The Peng-Robinson equation of state was chosen as the primary method, as it is widely used for hydrocarbon systems and provides a reliable representation of non-

ideal phase behavior. The ELECNRTL model was applied for electrolyte systems, particularly suitable for aqueous solutions. Additionally, the PSRK method was considered for lighter gas systems where its predictive capabilities are advantageous. Figure 1 shows a close up of the reactor section of the Aspen Plus simulation flow diagram, where the dotted streams represent heat flows.

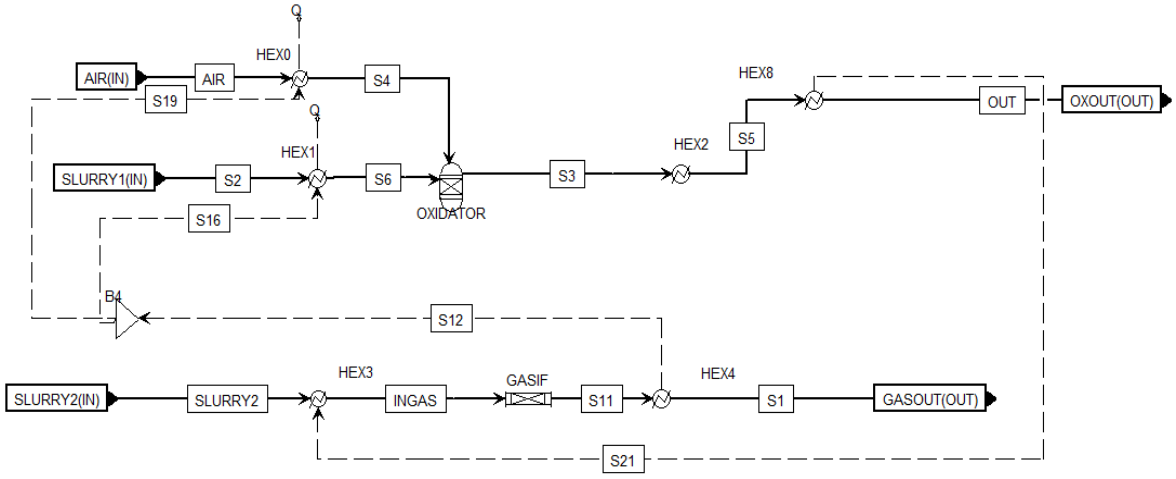

Figure 1: Combined reactor scheme

Water and sewage sludge, initially at 25 °C and 1 bar, are mixed and pumped to 250 bar before entering the oxidation reactor together with air. The AIR stream consists of 79% N_2 and 21% O_2, and its flow rate was set to ensure complete oxidation of the reactants. The AIR and SLURRY1 streams are first sent to heat exchangers HEX0 and HEX1, respectively, where they are preheated prior to entering the oxidation reactor. Inside the reactor, the temperature reaches approximately 750 °C at a pressure of 250 bar, ensuring supercritical conditions. The outlet stream from the oxidation reactor is directed to HEX8, which simulates the heat exchange between the oxidation and gasification sections via HEX3, thereby supplying heat to the gasifier. The SLURRY2 stream is first sent to HEX3 for preheating and then fed into the gasifier. HEX2 acts as an auxiliary heat exchanger to control the reactor temperature if it exceeds the realistic range for oxidation reactions. The gasifier outlet stream is subsequently cooled in HEX4 to room temperature (25 °C) in order to calculate the theoretical heat available for preheating SLURRY1 and AIR in HEX0 and HEX1. S12 represents the thermal energy associated with the gas exiting the gasification process. This stream is directed to a splitter (B4), which was configured to allocate 70% of the heat to preheat SLURRY1 and the remaining 30% to preheat AIR. These fractions were selected to achieve an oxidation reactor outlet temperature of approximately 750 °C. If the heat duties of these exchangers are positive, the excess heat is considered surplus energy not required by the system. Conversely, negative heat duties indicate that additional heat input is needed, meaning the reactor section does not operate under autothermal conditions. In this study, different scenarios were analyzed, including a comparison between an ideal equilibrium reactor (RGIBBS) and a plug flow reactor (PFR) for the gasification section, fed with slurry mixtures containing different biomass weight fractions (10%, 15%, and 20% w/w). The reactor yields were calculated with respect to the dry biomass mass, according to the following expression:

$$Y_{global} = \frac{kg\ of\ dry\ syngas}{kg\ of\ dry\ biomass} \quad (1)$$

Where dry syngas indicates the gas mixture excluding water (CO_2, H_2, CH_4, CO). It should be noted that this yield definition can give values higher than 1, because it explicitly accounts for the fraction of hydrogen originating from water (reaction medium) via reactions such as the water-gas shift, in addition to the hydrogen contained in the biomass itself (Fiori et al., 2012). A hydrogen yield was defined to provide information about the amount of H_2 produced per unit of biomass treated, taking into account its content in the inlet slurry:

$$Y_{H_2} = \frac{kg\ of\ H_2}{kg\ of\ dry\ biomass} \quad (2)$$

3. Results

Figure 2, shows the molar gas composition of outlet gas coming from the gasification reactor, once simulated as an ideal reactor, then as a PFR with reaction kinetics and equilibrium of products. The syngas composition

predicted by the Gibbs reactor is consistent with results reported in the literature for sewage sludge gasification (Hantoko et al., 2019).

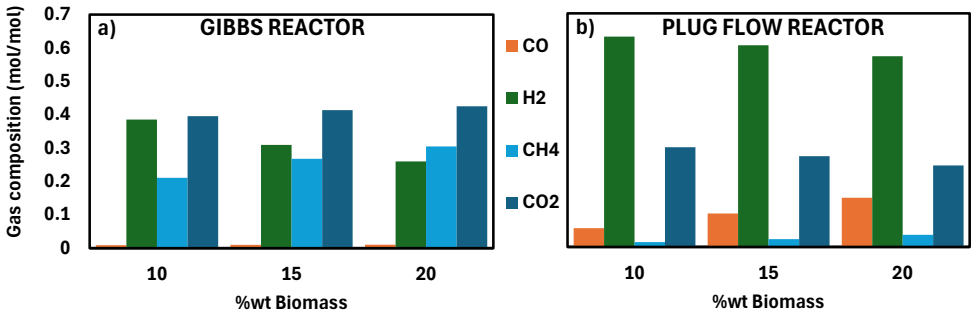

Figure 2: a) Molar fraction gas composition as a function of different % of biomass (10%, 15%, 20%), in a GIBBS reactor and b) in a PFR.

The main difference between the RGIBBS and PFR models lies in the distribution of CO and CO_2. The equilibrium reactor (RGIBBS) predicts a higher CO_2 concentration, as CO_2 is thermodynamically more stable than CO and is therefore favoured under Gibbs free energy minimization. In contrast, the kinetically controlled PFR provides a more realistic representation of the reaction pathway. In the RGIBBS model, the CO concentration remains below 5%, whereas in the PFR reactor it can reach nearly 15% under the most favourable conditions. Hydrogen production increases as the biomass fraction in the slurry decreases. This is because a higher water content promotes H_2 formation, as water acts as a key reactant in hydrogen-producing reactions. Conversely, at higher biomass loadings (e.g., 20% w/w), the reduced water availability favours the formation of carbon-containing products. Although H_2 production follows the same qualitative trend in both the equilibrium and kinetic models, the predicted values differ significantly. In the RGIBBS case, hydrogen ranges approximately from 25% to 40%, whereas in the PFR model it ranges from about 57% to 62%. Another significant difference concerns methane production. In the RGIBBS model, methane was included as a product species and treated as an inert component, since allowing it to participate in the reaction set did not satisfy the imposed atomic balance constraints. In this way, the produced CH_4 was not involved in subsequent reactions. As a result, its predicted molar fraction is relatively high, ranging between 20% and 30%, and increases with higher biomass content in the slurry. In contrast, in the PFR model methane actively participates in the reaction network, leading to a more realistic predicted concentration of approximately 3%. Figure 3 shows the syngas yields at different biomass weight fractions. Both the RGIBBS and PFR models exhibit the same trend. However, since the PFR is based on reaction kinetics, it provides a more reliable prediction of product distribution and, consequently, of syngas yield.

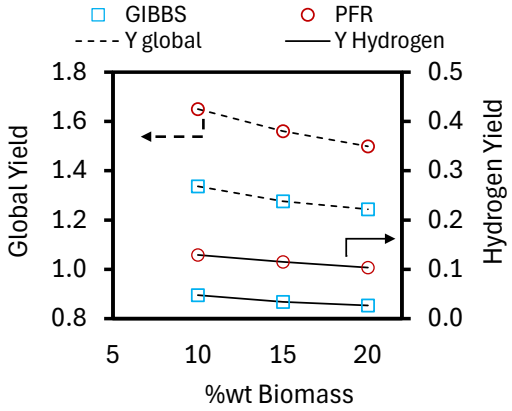

Figure 3: a) Syngas global yield and hydrogen yield at different %wt biomass, in a GIBBS simulated reactor and in a PFR simulated reactor.

One of the objectives of this reactor configuration is to ensure an energy surplus from the produced syngas, allowing the combined reactor system to operate under autothermal conditions without requiring auxiliary heat

from external sources. Table 2 summarizes the main evaluated properties. The results show that the energy surplus increases with increasing biomass fraction, in line with the higher syngas production. This behaviour can be explained by the fact that a greater sewage sludge content inherently provides a higher amount of chemical energy to the process.

Table 2: Summary of evaluated properties

	GIBBS	PFR
% Biomass	**Surplus heat [MW]**	
10%	0.98	0.97
15%	1.6	1.59
20%	2.18	2.17
	LHV [MW]	
10%	1.63	1.85
15%	2.3	2.67
20%	2.92	3.49

Analysis of the lower heating value (LHV) of the produced syngas indicates that increasing the biomass fraction leads to a higher overall syngas yield. Since hydrogen is the component with the highest specific calorific value among the main syngas constituents, its increased production contributes significantly to the rise in the overall LHV of the gas.

4. Conclusions

This work demonstrates the feasibility of an energetically self-sufficient supercritical water gasification and oxidation (SCWG-coOx) integrated system for sewage sludge valorization. Aspen Plus simulations of an 8 t/h pilot-scale plant with equal feed splitting between SCWG and SCWO reactors showed that thermal integration between the exothermic oxidation and endothermic gasification sections enables autothermal operation without external heat input. Comparison between equilibrium (RGIBBS) and PFR reactor models revealed that the PFR approach provides more realistic predictions of syngas composition. For all tested biomass concentrations (10–20 wt%), the system achieves energy self-sufficiency with a surplus heat ranging from 0.97 to 2.18 MW and delivers fuel gas with a LHV exceeding 3 MW at 20 wt% biomass loading. These results confirm that the SCWG-coOx process represents a promising low-impact, waste-to-energy route for sustainable sewage sludge treatment, addressing both the energy bottleneck of standalone SCWG and the urgent need for advanced valorization technologies for wet organic waste streams.

Acknowledgments

The present work was carried out within the framework of the "SUNGAS" project, Action 1.1.5 of the P.O. F.E.S.R. Sicily 2014-2020.

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