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An overview of waste gasification and syngas upgrading processes

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The increasing attention towards climate change and greenhouse gas emissions makes the exploitation of renewable energy sources one of the key pathways for sustainable power generation or chemicals production.

The valorisation and disposal of municipal and industrial wastes is one of the challenges of the next generation and must have a key role in the energy transition, in order to reduce the carbon footprint of the human being activities. Landfilling is the most traditional and easiest way for waste disposal, but it is also characterized by significant impacts from both environmental and socio-economic viewpoints, hence landfilling should be avoided and replaced with waste reutilization techniques.

The use of waste or residual material as raw material for chemical production can be considered a smart solution for waste disposal, managing to give a new life to a carbon source. Thermochemical treatment is seen as an emerging technology that can help reducing the volume of waste by recovering energy and/or matter by obtaining products with high added value during the final treatment of municipal solid waste (MSW). The thermochemical conversion of waste aimed at the synthesis of new chemical products represents a valid solution and is one of the pillars of the circular economy philosophy.

Gasification transforms low-value materials, converting them into gaseous products with usable calorific value and/or marketable products. Syngas, also called synthesis gas, is mainly composed of carbon monoxide (CO) and hydrogen (H₂), besides CO₂. After proper cleaning and upgrading processes, the syngas can be used as an alternative fuel in turbogas to generate heat and electricity, or as a raw material for a large number of products in the petrochemical industry and in refinery, such as methanol, plastic monomers, oxo alcohols, ammonia, synthetic gasolines, etc.

This high gasification flexibility, both in terms of raw material type and power generation or chemicals production options, is what drives the expansion of research and implementation opportunities for biomass and waste gasification.

Although these technologies are commercially available, research work on optimizing and exploring its further potential is still ongoing. In particular, in recent years, new pyrolysis and gasification technologies have emerged, with the aim of increasing the possible feedstocks improving energy recovery and reducing the environmental impact.

A number of theoretical studies on these kinds of processes are currently available in the scientific literature, mainly focused on the development of thermodynamic models or on computational fluid dynamics (CFD) process simulation, in some cases with the experimental model validation in pilot units. Several studies are available on pilot-scale experimental development of the process for waste gasification.

In this editorial, an essential scenario of several aspects regarding the waste gasification and syngas upgrading will be reported with reference to selected papers published

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in the journal *Energies* during the last two years, thus providing an updated vision of what is being currently studied in the field.

The topics covered are numerous, and although the contributions include leading innovative elements in the field of waste gasification, the most important aspects have been reported following a common guideline among the studies analyzed. The selected papers are strongly interrelated among each other in several points, as quite different problems converge in the area of advanced waste to syngas plant challenge. Therefore, selecting the proper keywords that, according to the authors, characterize the research, allows to build the correlation matrix reported in Table 1, which helps the reader to have a global view of the arguments of the considered advanced research papers. Moreover, a short summary of all the papers is reported. The order of the discussed papers has been accurately chosen as follow.

Table 1: Correlation matrix of the selected keywords.

	[1]	[2]	[3]	[4]	[5]	[6]	[7]	[8]	[9]
Gasification	X	X	X	X	X	X	X	X	X
Hydrogen	X	X	X	X	X	X	X	X	X
CO ₂	X		X			X	X	X	X
Decarbonization	X					X	X	X	X
Syngas	X	X	X	X	X	X	X	X	X
Thermochemical Conversion	X	X	X	X	X	X	X	X	X
MSW & Plastic Waste				X			X		X
Upgrading Processes	X				X	X			X

Gasification technologies for small- and medium-scale combined heat and power (CHP) generation from waste biomass have been significantly developed in the last decades. Most of the attention is focused on fixed-bed downdraft processes, but few studies also consider bubbling or circulating fluidised-bed gasification processes, sometimes promoted with specific catalysts or integrated with hydrothermal carbonisation to treat high-moisture biomass or waste. With respect to these technologies, fixed-bed updraft gasification allows a better conversion efficiency (thanks to the countercurrent heat exchanges) and it is typically characterised by simple construction, easy operation, fuel flexibility in terms of type (biomass, coal, wastes, etc.), particle size (5 to 100 mm) and moisture content (up to 60%), but also involves a relatively high production of pyrolysis liquids (i.e., oils and tar).

Cali G. et al. [1] present the experimental development at demonstration scale of an integrated gasification system fed with wood chips. This paper aims to establish the baseline performance of a 5 MWth demonstration-scale updraft gasifier, operating since 2014 at the Sotacarbo Research Centre in Sardinia, Italy, and tested for some 1500 h with different kinds of coal and biomass. In particular, the experimental results here reported are focused on the gasification of two kinds of local waste biomass, with the aim to assess operating conditions, syngas composition and properties and the whole

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plant performance. In addition, the syngas cleaning and wastewater treatment process performance is also evaluated, on the basis of a novel configuration of a tar management system optimised to minimise water consumption and sludge disposal and recirculate part of the separated tar and exhaust activated carbon to the gasification unit (thus improving the efficiency of the whole project).

The gasification unit is characterized by a high cold gas efficiency (about 79–80%) and an operation stability during each test. Particular attention has been paid to the optimization of an integrated double stage wastewater management system—which includes an oil skimmer and an activated carbon adsorption filter—designed to minimize both liquid residues and water make-up. Syngas has a very stable composition during the whole run, with a mean lower heating value in the order of 4.3–4.6 MJ/kg (syngas being composed of 52–53% by nitrogen from the gasification air). Moreover, the optimal process parameters for the operation of the syngas cleaning section have been identified and the configuration has been modified, with the result of a 60% reduction of wastewater disposal.

To meet the global demand for energy and to reduce the use of fossil fuels, alternative system such as the production of syngas from renewable biomass gasification have been investigated by Muhammad et al. [2]. To design such gasification systems, model equations can be formulated and solved to predict the quantity and quality of the syngas produced with different operating conditions (temperature, the flow rate of gasifying agent, etc.) and with different types of biomasses (wood, grass, seeds, food waste, etc.).

The modelling of biomass gasification generally involves the formulation and solving of sets of equations, including mass and energy balances, in addition to either rate-based or equilibrium-based expressions to determine the effect of the reactions occurring. To simplify this approach, various assumptions can be made, and correlations can be utilized relating to experimentally measured properties (e.g., feed composition and operating conditions). The more complex approaches include the use of computational fluid dynamics (CFD) models and kinetic rate expression models, which require knowledge of the reaction and diffusion parameters and potentially require relatively longer computational times than the simpler modelling methods available. Several models can be obtained using different correction factors, model parameters, and assumptions, and these models are compared and validated against experimental data and modelling studies from the literature.

In this study, several different stoichiometric thermodynamic models are compared to determine which are the most suitable and reliable. The analysis has been carried out for the prediction performance to predict the syngas composition. To correct some of the errors associated with thermodynamic models, correction factors are utilized to modify the equilibrium constants of the methanation and water gas shift reactions, using the data from 27 experimental values published in the literature, which allows them to better predict the real output composition of the gasification reactors. The models are formulated and optimized in MATLAB. These models also have the ability to estimate the performance of biomass gasification for different operating conditions, such as temperature and moisture contents. In this study we show that similar results and model accuracies can be achieved with a simpler model where the correction factors are fixed parameters.

Thermodynamic equilibrium models are based on the assumption that the system of chemical reactions involved in the process reaches a state of thermochemical equilibrium inside the gasifier reactor. Equilibrium models are able to predict the producer gas composition, the maximum yield and the optimal conditions of energy efficiency and syngas heating value for the operation of each specific reactor according to biomass feedstock properties.

In [3], Moretti and co-authors present an overview of biomass gasification modeling approaches in order to evaluate their effectiveness as a tool for the design and

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136 optimization of poly generation plants based on biomass gasification. The authors devel-
137 oped two equilibrium models using both a commercial software and a simulation tool
138 implemented in a non-commercial script. In this paper, the reliability of equilibrium gas-
139 ification models currently available in the scientific literature was investigated to establish
140 whether they can be employed to build new control and optimization schemes and oper-
141 ating maps of biomass gasification systems integrated into polygeneration plants coupled
142 with energy networks. The developed thermodynamic equilibrium models were ap-
143 plied to different case studies on downdraft gasifiers available in the literature in order to
144 evaluate the accuracy of the simulation results on varying the biomass type and composi-
145 tion and the operating conditions of the gasification process, evidencing the advantages
146 and disadvantages of both models.

147 The obtained results highlighted strengths and limitations of using equilibrium mod-
148 els as a function of biomass type and composition. They showed that the analytical model
149 predicted syngas composition with better accuracy for biomass types characterized by a
150 low ash content, whereas the Aspen model appeared to fairly predict the syngas compo-
151 sition; however, its accuracy might be reduced if the properties of the treated biomass
152 changed. The proposed overview of thermodynamic equilibrium models has significant
153 industrial implications, allowing for selection of the most suitable and reliable model as a
154 function of biomass properties and industrial operating conditions. Therefore, industries
155 will benefit from this work by having a clearer view of the most reliable models for the
156 gasification process.

157 Stasiak J. et al. [4] present an advanced thermal conversion system involving high-
158 temperature gasification of biomass and municipal waste into biofuel, syngas or hydro-
159 gen-rich gas. The decomposition of solid biomass and waste by gasification was experi-
160 mented with a modern and innovative updraft continuous regenerator and gasifier. A
161 ceramic high-cycle regenerator provided extra energy for the thermal conversion of bio-
162 mass or any other solids waste. Highly preheated air and steam gas (heated up to 1600
163 °C) was used as gasifying agent (feed gas). The preheated feed gas also improved the
164 thermal decomposition of solid feedstock for fuel gas. However, the main objective of this
165 work was to promote new and advanced technologies for the thermochemical conversion
166 of biomass for the production of alternative energy. Finally, this novel and unique tech-
167 nology could ensure significant energy savings of more than 30%, downsizing of equip-
168 ment, very low NO_x emissions (around 50%) and harmful pollutants reduction (about
169 25%). This technology has tremendous potential for many applications, primarily energy-
170 saving and fulfills all new regulations on waste incineration proposed by the European
171 Commission. The presented results concerning HiTAG/HiTSG technology
172 proved to be very useful for gas fuel, hydrogen or syngas generation. The high
173 temperature of the process generated in the preheater eliminates harmful substances such
174 as tars, dioxins and furans which can be produced in low-temperature conversion pro-
175 cesses. The fuel gas can be later used to produce heat and electricity, or even hydrogen by
176 means of the separation process.

177 In order to reach much higher efficiency, coupling systems of biomass gasification
178 with advanced power generation have been developed: the gas turbine, internal combus-
179 tion engine (ICE), and solid oxide fuel cell (SOFC) are the most common types of coupling.
180 These combined heat and power (CHP) units on a small scale, based on gasification, can
181 use an ICE or micro and small gas turbine with electrical efficiencies up to 25% of the
182 biomass lower heating value (LHV). Biomass gasification coupled with SOFC gives elec-
183 trical efficiencies up to 60%. The SOFC has become a very important energy technology,
184 due to its clean, greener, and efficient operation. Fuel cells allow conversion of the energy
185 with high efficiency; in fact, they convert the chemical energy contained in a fuel gas di-
186 rectly to electrical energy by electrochemical reactions.
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volte il passato, decidete il tempo verbale e usate
solo quello

In the last years, many works were carried out to study the optimal operating conditions, the overall system performance, and the limitations and the potentials of a variety of SOFC power plants integrated with biomass gasification systems. However, the current commercial process simulation software packages do not include built-in models for SOFC. In the literature, the most common SOFC system modelling approach is to integrate process simulators with a stack model in a programming language.

Marcantonio et al. [5] coupled Solid Oxide Fuel Cells (SOFCs) to gasification technology. A steady-state model of a biomass-SOFC was developed using process simulation software, ASPEN Plus. The present paper showed a whole plant composed by a gasification part, a gas cleaning unit, and SOFC system. This is one of the few works available in the literature that includes all the parts. The goal of this work was to develop a biomass-SOFC system capable of predicting performance in function of operating conditions. The results show that there must be a trade-off between voltage, electrical efficiency, and power with respect to current density and it is preferable to stay at a low steam-to-biomass ratio. The electrical efficiency achieved under the operating conditions is 57%, a high value, making these systems very attractive.

According to the study from Di Giuliano et al. [6] the chemical looping gasification of residual biomasses, operated in fluidized beds composed of oxygen-carriers, may allow the production of biofuels from syngas. The chemical looping gasification for sustainable production of biofuels (CLARA) research project, funded by the EU Horizon 2020 framework program, aims to contribute to this sense. This project deals with chemical looping gasification (CLG) of biogenic residues, with the obtained syngas used in the Fischer-Tropsch synthesis to produce liquid fuels, as also obtained by the hydrocracking of waxes resulting from Fischer-Tropsch. The main goal of CLARA is the realization of a full biomass-to-fuel chain up to 1 MWth scale, in an industrially relevant environment (targets: cold gas efficiency of 82%, carbon conversion of 98%, tar in outlet syngas lower than 1 mg Sm^{-3}).

Devolatilization is a key step of the gasification process, and strongly influences both quantity and quality of obtained syngas. At the temperatures of gasification (typically up to 900 °C), vapours and tars—developed by primary devolatilization reactions, undergo secondary reactions, which contribute to both gaseous products (cracking and reforming) and solid products (polymerization).

This work aims to provide useful experimental data about the devolatilization of residual biomasses. The study investigates wheat-straw-pellets (WSP) and raw-pine-forest-residue (RPR) pellets as feedstocks for chemical looping gasification presenting experimental results from devolatilizations of WSP and RPR, in bubbling beds made of three different oxygen-carriers or sand (inert reference), at 700, 800 and 900 °C. Tests were performed at laboratory-scale, by a quartz reactor, using nitrogen as fluidizing agent. For each test gas yield (η_{av}), carbon conversion (χ_{avC}), H₂/CO ratio (λ_{av}) and syngas composition are determined. Temperature is the dominating parameter: at 900 °C, the highest quality and quantity of syngas was obtained (WSP: $\eta_{\text{av}} = 0.035\text{--}0.042 \text{ mol gas/g biomass}^{-1}$, $\chi_{\text{avC}} = 73\text{--}83\%$, $\lambda_{\text{av}} = 0.8\text{--}1.0$); RPR: $\eta_{\text{av}} = 0.036\text{--}0.041 \text{ mol gas/g biomass}^{-1}$, $\chi_{\text{avC}} = 67\text{--}71\%$, $\lambda_{\text{av}} = 0.9\text{--}1.0$), and oxygen-carriers generally performed better than sand. The kinetic analysis suggested that the fastest conversion of C and H atoms into gases, at tested conditions is ensured by the oxygen-carrier ilmenite.

Collected results have an important novelty value for both experimental and modeling studies, since they deal with: (i) residual biomasses with a great availability potential, nowadays unexploited; (ii) devolatilization, a single step of the more complex gasification process, tricky to be experimentally isolated especially at higher scales; (iii) formulation of kinetic expressions of devolatilization/pyrolysis, a crucial point, often lacking, for a full-predictive modeling approach; (iv) chemical looping gasification by means of OCs, a thermochemical process which has not been developed yet at industrial scale.

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The next study [7] provides a comprehensive review of the micro-scale thermal treatment technologies for non-sewered practiced up to date in commercial/pilot and small scales for various types of solid fuels. Furthermore, the challenges observed with the non-inated (pyrolysis) technology are discussed in detail and addressed. This study suggests rapid energy recovery from by-products primarily made up of the highest yield of syngas with a desirable calorific value. The optimum operating ranges are discussed to ensure a reliable thermal conversion of sludge materials considering the application constraints and technology drawbacks due to the energy demand for drying. A pyrolysis temperature of 400–600 °C and the heating rates pursued at low ranks could result in a sustainable thermal conversion range for moist waste materials.

One objective of this critical review is to discuss the solid waste management/stabilisation technologies and their operational challenges. The state of the art of these thermal treatment technologies for on-site, non-sewered, sanitary applications in small scale is reviewed to clarify the specific operational challenges occurring through their implementation. The aim of this study overall is to outline the challenges for developing a suitable technology for on-site sanitary applications and to address optimum ranges of operating conditions for a reliable performance.

Various technologies have been employed to reduce, capture and utilise CO₂ from power generation. One such technique is integrated gasification combined cycle (IGCC) power generation with carbon capture and storage (CCS). CO₂ generated from gasification plants can be reused in the same cycle as a reactant, which helps cut costly oxygen-enriched air, oxygen and steam. Furthermore, the recycling of CO₂ offers a wide range of CO/H₂ production, which is the precursor for a wide range of chemicals. Numerous studies on coal and biomass gasification have been conducted using CO₂ as a reactant.

Shahabuddin et al. [8] evaluate the entrained-flow co-gasification characteristics of coal and biomass using thermodynamic equilibrium modeling. The effect of equivalence ratio, temperature, pressure and biomass to coal ratio have been investigated using CO₂ reactant. It has been understood that the lower heating value (LHV) and cold gas efficiency (CGE) increase with increasing temperature until the process reaches the steady state temperature of 1100 °C. Pressure affects syngas composition only at lower temperature (<1100 °C). The variation in syngas composition is minor up to the blending of 50% biomass (PB50). However, the PB50 shows a higher LHV and CGE than pure coal by 12% and 18%, respectively. Overall, biomass blending of up to 50% favours gasification performance with an LHV of 12 MJ/kg and a CGE of 78%. Results showed that the combination of steam and oxygen performs better compared to other reactants. The steam–oxygen reactant showed the highest H₂/CO ratio of 0.74, while the ratio was about 0.32 using steam–CO₂ and pure oxygen. The concentration of pollutants decreased consistently with increasing biomass ratio. Thus, co-gasification using CO₂ reactants can potentially increase gasification efficiency besides reducing pollutant emissions.

To achieve the goal of decreasing or even obtaining negative CO₂ emissions and producing clean energy, a proper model of biomass conversion needs to be developed. Because of the ultimate properties of biomass (low energy density and high moisture content), it is better to provide the thermochemical conversion of this material using processes such as pyrolysis or gasification than combustion.

The last analyzed work [9] is focused on biomass thermochemical conversion with integrated CO₂ capture, investigating the impact of pyrolysis temperature (500, 600 and 700 °C) and CaO sorbent addition on the chemical and physical properties of obtained char and syngas. In this study, a novel approach for syngas production from biomass with parallel biochar production and negative carbon emission was proposed. The conducted research allowed us to predict the most effective pyrolysis process conditions to obtain the highest yield of syngas and biochar.

The pyrolysis process temperature directly influences the syngas as well as biochar composition. The analysis of studied temperature range allowed us to conclude that a temperature increase leads to the production of biochar with a higher carbon content and lower VM, as the gaseous phase of biomass was processed and converted into syngas. With the increase of process temperature, higher hydrogen and methane concentrations are obtained. However, concentrations of higher hydrocarbons, such as C₂H₄, C₂H₆, C₃H₆ and C₃H₈, decrease.

The addition of a sorbent such as CaO for CO₂ capture improves the final gas composition. The presence of sorbent allows the capture of carbon dioxide from produced syngas. As the process temperature increases, the concentration of CO₂ in syngas decreases. The conducted tests and analysis prove the ability of capturing the CO₂ released during the pyrolysis process and transforming it into a carbonate phase by CaO. The processes of tar cracking are promoted by the presence of CaO with parallel removal of CO₂ and lead to an increase in H₂ production. In particular, the concentration of CO₂ in syngas decreased with increased temperature, and the highest decrease occurred in the presence of CaO from above 60% to below 30% at 600 °C.

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