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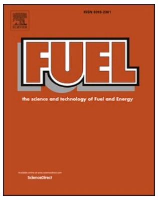

Review article

A review of cleaning technologies for biomass-derived syngas

J.R.C. Rey [a], A. Longo [a], B. Rijo [a], C.M. Pedrero [a], L.A.C. Tarelho [b], P.S.D. Brito [a], C. Nobre [a,*]

[a] *VALORIZA – Research Centre for Endogenous Resource Valorization, Polytechnic University of Portalegre, Campus Politécnico 10, 7300-555 Portalegre, Portugal*
[b] *Department of Environment and Planning - Centre for Environmental and Marine Studies (CESAM), University of Aveiro, Campus Universitário de Santiago, 3810-193 Aveiro, Portugal*

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ABSTRACT

Biomass gasification is a promising thermochemical conversion technology with substantial potential for sustainable global energy development. It can replace various fuels and chemicals derived from fossil fuels, producing a gas composed of CO, H_2, and CH_4 as targeted compounds and CO_2, H_2O, and N_2 as adulterating compounds. However, the gas also contains impurities like tars, particulate matter, nitrogen and sulfur compounds, hydrogen halides, and trace metals, posing challenges for its use. Efficient gas purification is essential before application in internal combustion engines, gas turbines, or chemical processes.

This paper provides a comprehensive survey of gas purification technologies arising from biomass gasification. Two main categories are explored: wet purification systems, notably using wet scrubbers, and dry purification systems, which are more appealing due to avoiding gas cooling and associated energy losses. Traditional particulate removal devices and modern catalysts for tar, acid gases, and trace metal elimination are examined in the dry purification category. Furthermore, this work describes alternative gasification concepts such as integrated gasification, supercritical-water gasification, and, chemical loop gasification, also addressing carbon capture technologies for syngas conversion. Finally, advances in syngas cleaning methods are revised and commercially available purification systems are presented and discussed, offering insights into current outcomes in this field.

1. Introduction

Amidst the swift expansion of the global population and the evolution of modern society, the rapid escalation in worldwide energy demand becomes evident. Notably, approximately 82 % of the total energy produced globally in 2022 stems from non-renewable origin, primarily fossil fuels [1]. This increase leads to an urgent need to further develop and implement alternative energy generation pathways with enhanced environmental compatibility and enduring economic viability. Though various technologies aimed at harnessing energy from renewable sources show promising advancements, they are not yet matching the global demand for energy predominantly supplied by fossil fuels. While some countries are making strides towards parity with fossil fuel and nuclear energy, this is not yet a widespread reality [2]. In the current energy landscape, biomass has emerged as a viable alternative for providing relatively clean and economically feasible primary energy. While it holds potential to replace fossil fuels in certain applications, it is crucial to acknowledge that its scalability and impact vary across regions. Biomass, although promising, is not a universal solution and comes with its own set of limitations and environmental considerations [3,4].

Carbon dioxide emissions mitigation and increased fuel security are the inherent benefits of biomass energy and biofuels. Biochemical and thermochemical processes are the main types of biomass conversion technologies. Overall, thermochemical routes offer higher efficiencies and productivity than their biochemical counterparts. Among the thermochemical methods, gasification stands out as one of the most pertinent strategies for transforming biomass and waste materials into energy.

By definition, gasification is a thermochemical conversion process wherein solid or liquid carbon-based substances (referred to as feedstock) are converted into a gaseous fuel through partial oxidation, using air, oxygen, steam, carbon dioxide or their combinations, as gasifying agents [5–7]. Traditional biomass gasification is an endothermic process, so heat is required to run the process. Depending on how heat is supplied, gasification is either autothermal or allothermal. In autothermal biomass gasification, heat is generated *in situ* by the partial oxidation of biomass in the gasifier [8,9]. On the other hand, in autothermal gasification an oxidizing agent (typically air or oxygen) in sub-

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* Corresponding author.
E-mail address: catarina.nobre@ipportalegre.pt (C. Nobre).

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stoichiometric conditions, is fed to the gasifier where drying, pyrolysis, oxidation and reduction, take place simultaneously. However, in allothermal gasification the heat that is needed is provided by an external source, which is often associated with problems of heat transfer into the high temperature gasification region [10–12].

The main product of biomass gasification is a mixture of combustible constituents such as carbon monoxide (CO), hydrogen (H_2), methane (CH_4), nitrogen (N_2), other lighter hydrocarbons, and trace quantities of heavier hydrocarbons (tar). This resulting mixture of gases is referred to as producer gas, and its composition and calorific value depends, among other factors, on the gasifying agent. For instance, a producer gas with high contents of N_2 and low calorific value (4–7 MJ/Nm^3) is obtained when the gasification medium is air, but the use of steam results in a gas with higher amounts of H_2 and a higher calorific value (10–18 MJ/Nm^3) [13,14]. After undergoing a comprehensive purification and refining process to remove or to reduce impurities to very low levels depending on its further use, syngas is obtained, which consists mainly of CO and H_2. Syngas can be employed as a fuel in internal combustion engines (ICE) or gas turbines (GT) for power and heat generation [15,16]. Additionally, it serves as a foundation for the synthesis of diverse chemical compounds and biofuels [17–19].

Biomass gasification's main advantage regarding other thermochemical conversion technologies stems from the significantly higher temperatures that are used, which result in superior quality and cleaner syngas due to the sharp elimination of unwanted impurities [9]. Moreover, biomass gasification offers higher efficiencies in contrast to alternative technologies. The work by Moura et al. [20] examines several technologies using waste biomass for the production of energy and advanced biofuels based on various performance evaluation criteria, including efficiency. According to these authors, in terms of efficiency, gasification behaves similarly to combustion and outperforms most of the studied biomass conversion technologies, including, anaerobic digestion, fermentation, dark fermentation, and pyrolysis. The production of hydrogen through dark fermentation also shows lower efficiency than steam gasification [21]. Similar findings are reported by Wu et al. [22] in the case of biomethane (also designated as synthetic natural gas, SNG) production from anaerobic digestion (energy efficiency 25–35 %) and gasification (energy efficiency up to 94 %). Interestingly, the efficiency of gasification to generate SNG strongly depends on the technology used. For instance, efficiencies of around 62 % are achieved when using sorption enhanced reforming reactors, where solid sorbents capture carbon dioxide promoting the water gas shift (WGS) reaction [23]. Supercritical gasification to produce SNG exhibits much higher energy efficiencies, namely total efficiencies up to 77 % were obtained in the production of SNG by supercritical water gasification of woody biomass, but optimal energy efficiencies as high as 94 % can be achieved when SNG production is carried out under isothermal conditions [23,24].

Furthermore, the escalating environmental restrictions imposed by governmental bodies and international organizations underscore the significance of gasification [25,26]. This technology enables the use of a large range of feedstocks, including but not limited to, lignocellulosic materials, plastics and other wastes with different moisture contents, depending on the type of gasification technology. Therefore, gasification processes are flexible regarding the feedstocks and do not involve land use changes, unlike other biomass conversion technologies which use bioenergy crops, like the production of bioethanol through fermentation. It is the only technology enabling the direct conversion of biomass into several gaseous biofuels, namely, syngas, SNG, and hydrogen which could be used for power generation, heating, and transport fuels with lower carbon footprint [27]. In addition, the potential utilization of the biochar derived from the process could be used for soil amendment to improve soil health, mitigate soil degradation, and control soil and water pollution [28]. This high versatility of gasification in comparison to other biomass conversion technologies, makes it a powerful tool to promote energy green transition while reducing its environmental burden.

Nevertheless, biomass gasification has limitations such as challenging logistics, due to the small bulk density of biomass when compared to fossil fuels. Moreover, biomass gasification often leads to a syngas with a broad composition of gaseous components and non-desired impurities, which requires demanding cleaning and purification steps resulting in increased process complexity and costs. Tar formation is likely one of the major concerns of biomass gasification, since tars can block equipment, lowers process efficiency and syngas quality while increasing operational costs. Tar release into the atmosphere also represents human and environmental risks because most of these compounds are carcinogenic [26]. Improved gasifier configurations and using proper operating conditions are some of the strategies applied to minimize tar formation. Tar content in entrained flow and circulating fluidized bed gasifiers is much lower (0–10 g/Nm^3) than in updraft fixed bed configurations (140 g/Nm^3) [26]. Working at higher temperatures or in the presence of catalysts are also ways to reduce tar formation [29,30]. Recent advances towards overcoming this barrier include the use of microwave-based technologies [31,32]. Thus, the significant amount of impurities found in biomass-derived syngas is in fact a critical problem that holds back the extensive-scale advancement and implementation of gasification. These impurities include diverse tar compounds, particulate matter, nitrogen compounds (such as ammonia (NH_3) and hydrogen cyanide (HCN)), sulfur-laden inorganic compounds (including hydrogen sulfide (H_2S), carbonyl sulfide (COS), and carbon disulfide (CS_2)), hydrogen halides and halogens (like hydrogen chloride (HCl) and chlorine (Cl)), along with alkaline metals (like sodium (Na) and potassium (K)). These contaminants arise during the thermochemical transformation of biomass and are found at varying levels of concentration in the produced syngas [33–35]. The existence of these contaminants causes several technical and operational difficulties, such as equipment corrosion due to hydrogen sulfide (H_2S), fouling attributed to tar or catalyst deactivation caused by tar, H_2S, NH_3, HCl, and trace metals [33,34,36,37].

Various methods exist for enhancing the quality of syngas by reducing the concentration of contaminants, encompassing primary and secondary processes [38]. Primary processes entail the on-the-spot reduction of contaminant concentrations (e.g., tar) during the gasification process and within the gasification reactor. Conversely, secondary processes involve the post-gasification treatment of the syngas [39]. *In-situ* processes involve proficient control of operational variables and the utilization of additives or catalysts during operation to curtail the generation of contaminants (e.g., tar) within the gasifier. On the other hand, post-gasification processes do not interfere with the gasification reaction within the reactor. Instead, they expel contaminants downstream through physical and chemical processes [34]. In practical implementation, achieving a high level of efficiency in removing all contaminants from syngas using only one method proves challenging. Frequently, a blend of *in-situ* and post-gasification procedures offers a more effective alternative [34,40].

This study focuses on analyzing post-gasification methods for cleaning up syngas. The goal is to build up on past research by covering recent studies on syngas purification techniques, highlighting the main challenges in this area, and offering an overview of current research on gasification technologies for a cleaner syngas and advancements on specific techniques for syngas cleaning.

2. Syngas production technology

2.1. Biomass

According to the United Nations Framework Convention on Climate Change (UNFCCC) [41], the term "biomass" refers to non-fossilized and biodegradable organic materials derived from plants, animals, and microorganisms. This includes by-products, residues, and waste from agriculture, forestry, and related industries, as well as non-fossilized and biodegradable organic fractions of industrial and municipal waste. Biomass also encompasses gases and liquids obtained from the decomposition of non-fossilized and biodegradable organic matter. Table 1 illustrates instances of gasifiable biomass primarily constituted by cellulose, hemicellulose, lignin, and proteins. Cellulose and hemicellulose consist of saccharides that polymerize to create extended chains, forming the fibers within the biomass. Lignin, functioning as a phenolic polymer, serves as an adhesive for the fibers, thereby exerting a pivotal influence on the maintenance of structural rigidity in proteins. The latter are predominantly found in herbaceous species [42–44].

2.2. *Gasification technology*

Gasification is the conversion of solid or liquid feedstock into useful and convenient gaseous fuel or chemical feedstock that can be burned to release energy or used for production of value-added chemicals. The gasifier serves as a primary component in a gasification plant, where biomass and a gasifying agent (e.g., air, steam, or CO_2) are mixed at very high temperatures, frequently in the presence of primary catalysts and/or additives, resulting in the production of syngas (a mixture of CO, H_2, CO_2, CH_4, and other trace gases). Furthermore, syngas presents a higher H/C ratio when compared to the original biomass, thus improving its combustion characteristics [45–47].

The design of a gasifier is contingent upon factors such as fuel availability, shape, size, moisture content, and ash content of the feedstock, and the intended applications of the syngas [26]. Various types of gasifiers have been devised to address these considerations, including fixed bed reactors (updraft, downdraft, and cross-draft), fluidized bed reactors (bubbling, circulating, dual, and multistage), entrained flow reactors (top-fed and side-fed), and plasma reactors. Globally, in commercial applications, approximately 75 % of gasifiers are of the downdraft type, followed by 20 % using fluidized bed technology, with the remaining 5 % attributed to other designs [43,48–51]. Fig. 1 shows schematic representations of the different types of gasifiers.

2.3. *Syngas*

Syngas, the primary output of the biomass gasification process, is a fuel gas that predominantly consists of H_2, CO, CH_4, CO_2, H_2O, other hydrocarbons, inert gases, and contaminants. Acknowledged for its considerable potential in electricity generation, Fischer-Tropsch (FT) liquid fuel synthesis, or chemical manufacturing, syngas emerges as a versatile fuel source [33,54].

Syngas produced by high-temperature gasifiers, typically operating in the range of 1100 to 1300 °C, primarily consists of H_2 and CO, with a limited presence of hydrocarbons, such as CH_4. On the other hand, syngas generated by moderate-temperature gasifiers, typically in the range of 800 to 900 °C, may contain up to 10 % hydrocarbons, predominantly CH_4, C_2H_4, and C_6H_6. When air serves as the gasifying agent during the oxidation stage, inert N_2 becomes a component of the gas phase. Additionally, the process yields various minor compounds, including tars, nitrogen- and sulfur-based compounds, hydrogen halides, and alkali metals [42]. The quantities of these minor components are contingent upon the specific composition of the biomass. Syngas yield can vary between 1 and 3 Nm^3/kg db, exhibiting a LHV ranging between 4–18 MJ/Nm^3. These values are markedly influenced by the chosen gasification technology and operational variables. Special attention must be paid to the condensable phase, particularly the tar, which comprises various organic compounds, which will be examined in the next sections. Table 2 presents some typical syngas compositions using different gasifying agents and reactor configurations.

Table 1
Composition of hardwood, softwood, and straw (wt.% db) [42].

Biomass type	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Ash (%)	LHV (MJ/kg)
Hardwood	42–48	27–38	16–25	< 2	12.5–19
Softwood	40–45	24–29	26–33	5–10	10–18
Straws	36–40	21–45	15–20	> 8	8.5–16

3. Syngas main contaminants

The untreated syngas resulting from biomass gasification (producer gas) typically includes tar, NH_3, HCN, H_2S, COS, CS_2, HCl, particulate matter, and trace amounts of metals like Na and K. Furthermore, CO_2 is often considered a contaminant requiring removal from the syngas, particularly when considering the subsequent utilization of the gas in diverse applications. Depending on the end-use, syngas may need to be conditioned to adjust the H_2-to-CO ratio to meet downstream process requirements. For instance, SNG production through the Sabatier process requires a H_2-to-CO ratio of 1:3 or higher [56]. However, H_2-to-CO ratios of 1 and 2 are preferred to produce dimethyl ether and methanol from catalytic CO hydrogenation [57,58].

The concentration of impurities in the untreated syngas depends on various factors, with the predominant factors regulating gas quality being the type of reactor and the operational conditions. For many downstream applications, stringent technical specifications must be met by the syngas (Table 3).

These contaminants pose substantial challenges that have restrained the progression of gasification systems and the ultimate utilization of syngas [49,60]. The subsequent sections delve into the evaluation of the impact and the upper permissible thresholds of the principal contaminants for varied applications of syngas.

3.1. *Particulate matter and alkali compounds*

Biomass comprises certain inorganic compounds that are integrated into its structure. The most prevalent among these compounds are alkali metals (e.g., Na and K), alkaline-earth metals (e.g., Ca and Mg), various other metals (Fe, Al), non-metals (e.g., Si), as well as trace amounts of several other chemical elements (e.g., As, Se, Sb, Zn, Cr, Pb). Alongside these, there are also minor quantities of unconverted solid carbon (char). The char yield from gasification can be as high as 10 % of the input biomass. The characteristics of the char obtained by gasification vary in both ash and carbon content, i.e. 4 – 100 % and 1–92 %, respectively [61]. Collectively, these components constitute most of the particulate matter present in the syngas. The syngas can also encompass residual bed materials and traces of catalysts [49]. The particle sizes within the biomass-derived syngas range from particles smaller than 1 μm to larger than 100 μm. Due to this wide variability in particle dimensions, effectively separating the particles from the gaseous stream using conventional devices like the cyclone separator (which is typically integrated at the gasifier outlet) proves to be highly challenging. Consequently, a substantial quantity of particles consistently remains in the syngas stream. The proportion of particulate material within the syngas is significantly influenced by the gasification technology used. For instance, fluidized bed gasifiers tend to exhibit a higher particle concentration in the syngas compared to fixed bed gasifiers [36,49].

The content of alkali and alkaline-earth metals in biomass exhibits considerable variability. For instance, woody biomass generally demonstrates a higher concentration of alkaline-earth metals, whereas herbaceous biomass contains greater concentrations of alkali metals [35]. Alkali metals pose more significant challenges for the final applications of syngas compared to alkaline-earth metals, largely due to their heightened reactivity [33,36]. The primary alkali metals found in biomass composition are K and Na. These metals can interact with other ash components within the biomass and form nonvolatile compounds that remain as ash at the lowermost section of the gasifier. However, certain alkaline compounds can undergo melting or even vaporization at temperatures surpassing 600 °C, consequently exiting the reactor in the form of aerosols and vapors [33,36]. These transported compounds

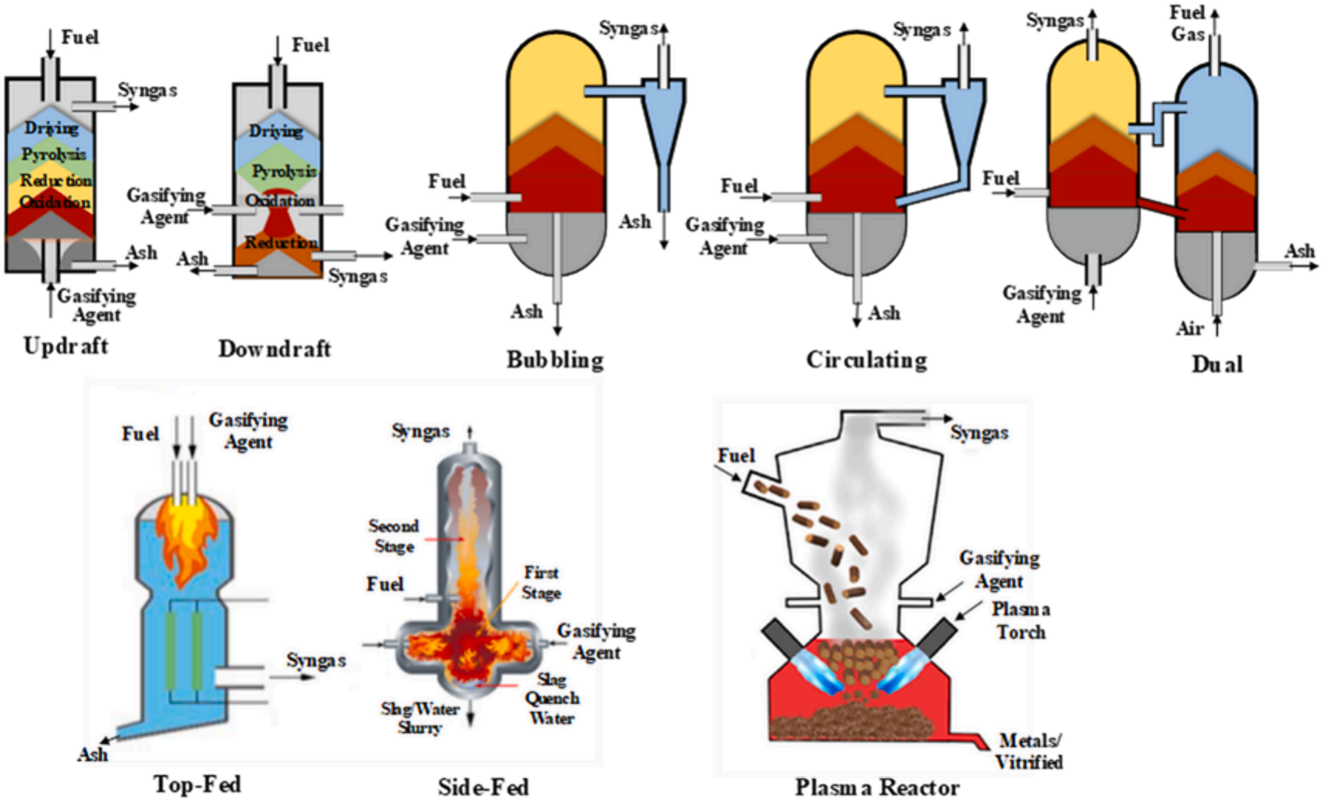

Fig. 1. Schematic illustration of different types of gasifiers: Fixed bed (left: updraft and right: downdraft); Fluidized bed (left: bubbling fluidized bed, center: circulating fluidized bed, and right: dual fluidized bed); Entrained flow (left: top-fed and right: side-fed); and Plasma gasification. (Reprinted from [49,52,53] with permission of Elsevier).

Table 2
Range of typical syngas compositions [43,54,55].

Compound	Air gasification Fixed bed	Oxygen gasification Entrained flow	Steam gasification Fluidized bed
Carbon monoxide (vol. %)	13 – 18	45 – 55	25 – 30
Carbon dioxide (vol. %)	12 – 16	10 – 15	20 – 25
Hydrogen (vol. %)	11 – 16	23 – 28	35 – 40
Methane (vol. %)	2 – 6	0 – 1	9 – 11
Nitrogen (vol. %)	45 – 60	0 – 1	0 – 5
Heating value (MJ/Nm^3)	4 – 6	10 – 12	12 – 18

engage with other substances present in the syngas, generally forming chlorides, hydroxides, and sulfates. These resultant compounds have the potential to induce fouling and corrosion within downstream equipment [33,35,62].

Besides biomass, numerous catalysts employed to eliminate contaminants or alter the composition of syngas also introduce alkali metals into the system. Some of these catalysts, such as rubidium (Rb), cesium (Cs), and lithium (Li), can include alkali metals as essential components. These metals can vaporize in conjunction with the K and Na from the biomass in the high-temperature regions of the reactor. They subsequently condense in cooler sections, where they might trigger equipment corrosion or fouling [35,62]. Furthermore, the presence of alkali metals in the syngas can lead to catalyst deactivation [35,52]. Consequently, the removal of alkali metals from the syngas is imperative to prevent operational complications.

As detailed in Table 3, numerous final applications of syngas need particle removal exceeding 99 %. For instance, ICE tolerate particle concentrations up to 50 mg/Nm^3. Elevated concentration levels cause operational issues in the engine, such as nozzle deposits and blockages in the gas injection system, ultimately shortening the lifespan of the engine

Table 3
Examples of technical specifications of the syngas for different applications [33,36,59].

Applications	Particulate	Tars	Sulfur	Nitrogen	Alkali	Chlorine
IC Engine	< 50 mg/m^3	< 100 mg/m^3	n/a	n/a	n/a	n/a
Gas turbine	< 30 mg/m^3	< 5.0 mg/m^3	< 20 ppbV	< 50 ppbV	< 0.02 ppbV	< 1 ppbV
FT synthesis	< 0.1 ppm	below dew point	< 100 ppb Fe catalysts < 60 ppb Co catalysts	< 10 ppb	< 100 ppb	< 10 ppb
Methanol synthesis	< 0.02 mg/m^3	< 0.1 mg/m^3	< 1 mg/m^3	< 0.1 mg/m^3	n/a	< 0.1 mg/m^3
Solid oxide fuel cell	10 – 100 ppm	< 2000 ppm	< 1 ppm	n/a	<1 ppm	< 1 ppm
Alkaline fuel cell	< 100 ppm	Poison	Poison	n/a	Poison	Poison

n/a means not available.

and elevating maintenance expenses. In the context of GT, particle concentrations in the syngas should not exceed 30 mg/Nm^3. Increased concentration levels have adverse effects on the blades of the turbine due to abrasion. Additionally, these particles can persist in the combustion gas of ICE and GT, surpassing the emission limits set by environmental regulations [35,49].

3.2. *Tar*

Tar stands as a major undesirable component in syngas, leading to significant problems in both the process and subsequent gas utilization. Tar-related problems include a decrease in energy efficiency, the occurrence of condensation resulting in the obstruction of downstream equipment, the formation of tar aerosols, and polymerization into more intricate structures [45,62].

Tar formation is primarily initiated during the pyrolysis stage, arising from the decomposition of lignocellulosic biomass. It involves a complex mixture of high molecular weight hydrocarbons, including aromatic compounds extending up to five rings, which might also feature oxygenation. Polycyclic aromatic hydrocarbons (PAHs) are also present [34,36,49,53,62]. Though the term "tar" lacks a universally precise definition, consensus has been reached to encompass hydrocarbons with molecular weights surpassing benzene (C_6H_6) [63]. Tar compounds are also classified as primary, secondary, or tertiary, contingent on the conditions of their formation [33]. Primary tars include organic compounds like levoglucosan and furfurals, released in the early pyrolysis stages. With escalating temperatures and residence times, secondary tars form, including phenolics and olefins. Subsequent increases in temperature and residence time produce tertiary tars [42]. The prevailing classification of tars encompasses five classes as detailed in Table 4.

Class 1 tar compounds are characterized by an extremely high molecular weight and undetectability via gas chromatography, are they are typically present at less than 2 wt% of the tar composition. Class 2 encompasses oxygenated compounds that are readily soluble in water, constituting approximately 7 wt% of the tar composition. Single-ring aromatics (Class 3) and PAHs distributed over two to seven aromatic rings (Classes 4 and 5), may exhibit significant variations in concentration. Factors such as temperature, gasifying agent, and the presence of catalysts can contribute to considerable variations in tar content in syngas, although their exact composition may vary widely between different processes [34,42,62]. The increased presence of Class 3, 4, and 5 compounds is attributed to the decomposition of Class 1 and 2 compounds as the particle undergoes elevated pyrolysis temperatures [64].

Table 4
Tar classification based on molecular weight of tar compounds [42,62,64].

Class	Name	Characteristics	wt.% of the total tar composition*
1	GC-undetectable	High molecular weight tars that condense at high temperature and have very low concentrations; (Calculated by subtracting the GC-detectable tar fraction from total).	2
2	Heterocyclic aromatics	Tars containing heteroatoms, highly water-soluble compounds (e.g., Pyridine, phenol, cresols, quinoline, isoquinoline, dibenzophenol).	7
3	Light aromatic (1 ring)	Typically, light hydrocarbons with a single ring; their condensability and solubility are generally not problematic (e.g., Toluene, ethylbenzene, xylenes, styrene).	46
4	Light PAH compounds (2 to 3 rings)	Light polyaromatic hydrocarbon compounds (2–3 rings); they condense even at low concentrations and temperatures (e.g., Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene).	34
5	Heavy PAH compounds (4 to 7 rings)	Heavy polyaromatic hydrocarbon compounds (>3 rings) that condense at high temperatures and low concentrations (e.g., Fluoranthene, pyrene, chrysene, perylene, coronene).	11

Various techniques can be used to measure tar in the producer gas. The flame ionization detection (FID) tar analyzer can detect tar levels in the range of 0–120 g/Nm^3. On the other hand, a tar analyzer with photoionization detector detects tar contents between 0–50 g/Nm^3. This technique is very sensitive to low concentrations and has a linear response to tar compounds. Laser-induced fluorescence can detect some tar species between 0–20 g/Nm^3, mainly PAHs. Mass spectrometry is another technique that has been applied to measure tar compounds and is very sensitive. In this case, to measure tars, the mass spectrometer configurations are coupled to molecular beam (MB) and ion molecule reaction (IMR). Ion molecule reaction mass spectrometry is capable of measuring BTX (Benzene-Toluene-Xylene) and PAHs at low and high concentrations [26].

The presence of tar in raw syngas significantly influences its prospective direct applications and necessitates specific gas treatment for advanced utilization (e.g., refer to Table 3). For direct syngas combustion, there are no stringent limitations on tar concentration if condensation within processing equipment is averted. However, the resultant flue gas from the combustion process must comply with emission requirements for this technology [34]. For employment in ICE, the syngas needs cooling to temperatures below 100 °C, because at these temperatures tar compounds typically condense within the fuel injection system, causing substantial operational challenges. To mitigate these difficulties, the tar concentration in syngas for ICE applications should remain below 100 mg/Nm^3 [47]. In the context of GT, although syngas can be utilized at elevated temperatures (e.g., exceeding 400 °C) the potential for tar condensation exists. This may lead to subsequent dehydration reactions, resulting in the formation of solid coke, which contributes to fouling, blockages, and abrasion of turbine blades. Therefore, the permissible tar concentration level is below 5 mg/Nm^3 [49]. For other syngas applications such as fuel cells, in particular Solid Oxide Fuel Cells (SOFC), and secondary conversion through FT synthesis (e.g., methanol or synthetic fuels), the presence of a catalyst will promote the conversion of tar into compounds that block its surface, resulting in its permanent deactivation [65]. Both SOFC and FT synthesis exhibit greater sensitivity to impurities compared to ICE or GT, underscoring the requirement for rigorous syngas cleaning and testing to achieve tar levels below 1 ppm [66]. Recent progress in developing tar tolerant anode materials of SOFC involve the development of improved Ni-based electrocatalysts by adding another metal or oxide. Coking can be also reduced through the modification of the cell structure by adding barrier layers of porous inert materials which prevent coking forming gases reaching the active sites of the Ni-SOFC anode [67,68]. *In situ* reforming of tar compounds in SOFC is also a promising approach to overcome tar-related issues, since it allows not only to avoid gas cleaning tar removal stage, but also to increase the overall efficiency of the process [69]. The technical feasibility of direct internal tar steam reforming in SOFC as an effective tool to minimize degradation of the Ni-anodes of the SOFC caused by tar deposition has been proven by thermodynamic simulations when increasing current density or steam content [70].

3.3. *Sulfur*

Biomass generally exhibits a low sulfur concentration, typically ranging from 0.1 to 0.5 g/kg. However, specific forms of biomass like certain grasses and black liquor (a byproduct of the pulp and paper industry) can present sulfur concentrations surpassing 1.0 g/kg [49,71]. H_2S constitutes the main sulfur compound found in producer gas during biomass gasification, although trace amounts of carbonyl sulfide (COS) can also emerge, albeit in low concentrations [36]. The H_2S concentration varies between 100 mg/Nm^3 to over 3000 mg/Nm^3, contingent upon the inherent characteristics of the fed biomass. Sulfur compounds, mainly H_2S, introduce several issues involving corrosion of metal surfaces, catalyst deactivation, and environmental pollution. When syngas is employed in combustion systems, the reduced sulfur compounds undergo transformation into sulfur dioxide (SO_2), a regulated environmental pollutant [72,73]. To avert these complications, numerous final syngas applications mandate extremely low sulfur concentrations in the gas (as shown in Table 1).

3.4. Nitrogen compounds

Biomass typically exhibits a wide range of nitrogen concentrations [74]. Throughout gasification, NH_3 emerges as the primary nitrogen compound present in the syngas, with minor concentrations of HCN [75]. These compounds result from the release of nitrogen from protein structures or heterocyclic aromatic compounds present in the biomass, occurring during the pyrolysis, gasification, and combustion stages of the process [36]. NH_3 formation is favored at temperatures below 800 °C, with over 60 wt% of the biomass' nitrogen content converting into NH_3 [34]. However, at higher temperatures and under oxygen-limited conditions during gasification, chemical equilibrium reveals that nitrogen gas (N_2) prevails as the dominant nitrogen-containing species in the producer gas [36].

NH_3 concentrations in producer gas can span from 363 to 578 mg/Nm^3, contingent upon the nitrogen content of the feedstock [76]. These concentrations might be detrimental in certain applications. For instance, in GT, NH_3 concentrations must not surpass 34.8 mg/Nm^3 to manage NO_x emissions. On the other hand, even concentrations lower than $<$ 0.002 mg/Nm^3 can inhibit certain catalysts employed to enhance syngas quality [33,36].

3.5. Chlorine

In raw syngas, the prevalent chlorine species are HCl, ammonium chloride (NH_4Cl), and alkaline chlorides (primarily sodium chloride (NaCl) and potassium chloride (KCl)), which can exist in vapor or solid form depending on system operating temperatures [35]. HCl is the predominant chlorine species in raw syngas, reaching several milligrams per normal cubic meter of syngas, dependent on biomass composition [12]. In various final syngas applications, these HCl concentrations can cause significant issues, for example, concentrations exceeding $>$ 0.003 mg/Nm^3 cause corrosion in GT pipes and blades [33,35]. In other contexts, such as fuel cells, chlorine concentrations must remain well below $<$ 20 mL/L, as higher levels lead to performance degradation of the Ni anode of molten carbonate fuel cells (MCFC) and SOFC [77]. Alkaline chlorides, particularly NaCl and KCl, undergo condensation and deposition on cold surfaces and equipment downstream of the gasification process, culminating in fouling and obstructions in systems [35]. Furthermore, chlorine poses challenges related to catalyst poisoning, which affects syngas upgrading processes such as NH_3 and other compound removal [33].

4. Syngas cleaning processes

The methods used to clean syngas contaminants can be categorized into two primary groups based on the working fluid: wet gas cleaning and dry gas cleaning [39].

4.1. Wet gas cleaning

Wet gas cleaning (WGC) is regarded as an efficient and cost-effective gas-cleaning technology that effectively reduces the concentration of relevant contaminants to the desired low limits. This approach is widely adopted for removing contaminants from raw syngas due to its established reliability and high efficiency [33]. Notably, WGC is performed at temperatures typically below 100 °C [47]. Since the gasification process occurs at elevated temperatures (700 to 900 °C), a drawback of this method is the energy efficiency penalty due to the cooling of the syngas. Additionally, there are added costs associated with treating or disposing of contaminants retained in the product streams originating from the cleaning process [33].

In general, WGC technologies employ wet scrubbers (such as spray and wash towers, cyclonic and dynamic scrubbers, venturi scrubbers, and wet electrostatic precipitators (Wet-ESPs) that use water to remove contaminants from the syngas stream [33,78]. Although other cleaning fluids like motor oil and vegetable oils can also be employed water is the predominant choice [79]. Among these technologies, spray scrubber systems are the simplest and utilize inertial forces to separate impurities from the gas stream. Dynamic and cyclonic systems can be integrated into a single device, as depicted in Fig. 2a. In this configuration, the tangential inlet first removes larger impurities through inertial separation, followed by a moistened paddle to capture smaller impurities. After the dynamic section, the remaining impurities are eliminated through final cyclonic motion [36,39].

The Venturi scrubber consists of a convergent-divergent channel where the cross-sectional area decreases and then increases, with the narrowest part referred to as the throat. In the converging section, the area decrease accelerates the velocity and turbulence of the gas. The scrubbing fluid is injected slightly before or directly into the throat. The turbulence leads to liquid atomization, enhancing gas–liquid contact. As the mixture decelerates in the diverging section, it induces particle and droplet impacts and droplet agglomeration [80]. The Venturi scrubber is often integrated with a cyclone separator in the stripping section, as shown in Fig. 2b. Here, centrifugal forces exerted by the cyclone separate liquid droplets from the gas stream.

Electrostatic precipitators (ESPs) are commonly utilized for particle collection in various industries due to their low energy consumption, minimal pressure drop, and high particle removal efficiency. ESPs employ electrical forces to direct particles from the gas stream to collection plates. Two primary types of ESPs exist: Dry-ESP (Fig. 3a) and Wet-ESP (Fig. 3b). Wet-ESPs function through three stages: charging, particle collection, and cleaning of the collecting electrode surfaces. These systems involve a vertical or horizontal chamber with parallel tubes or plates through which an electric current pass. They also often incorporate a wet scrubber either before or after the chamber. The mixture of water and particles gains electric charge as they traverse the chamber, and the particles are then separated from the gas stream upon collision with the collecting electrode. Cleaning of the collecting electrode involves rinsing with water. Operating within a humid environment, Wet-ESPs can remove particles as well as other pollutants like tar and acid gases present in the syngas. Further detailed information about wet gas scrubbing systems can be found in references [33,36,80].

Scrubbing media must have characteristics such as high efficiency in removing tars and water-soluble compounds and high durability. When the purification medium is water, water-soluble compounds (NH_3, HCl, and H_2S) are removed. However, only part of the tars are removed (phenols) as most of the organic substances that make up tar have low solubility in water (e.g. benzene, toluene, xylene, styrene, and indene). Due to the significant presence of these compounds in tar, they are easier to dissolve in non-polar adsorbents such as vegetable oil than in polar solvents such as water. It has been reported that vegetable oil is 60 % more efficient at removing tars than water (32 %) [81]. Furthermore, it is important to note that using water in tar removal will originate a tar-contaminated water that will necessarily need further treatment. This

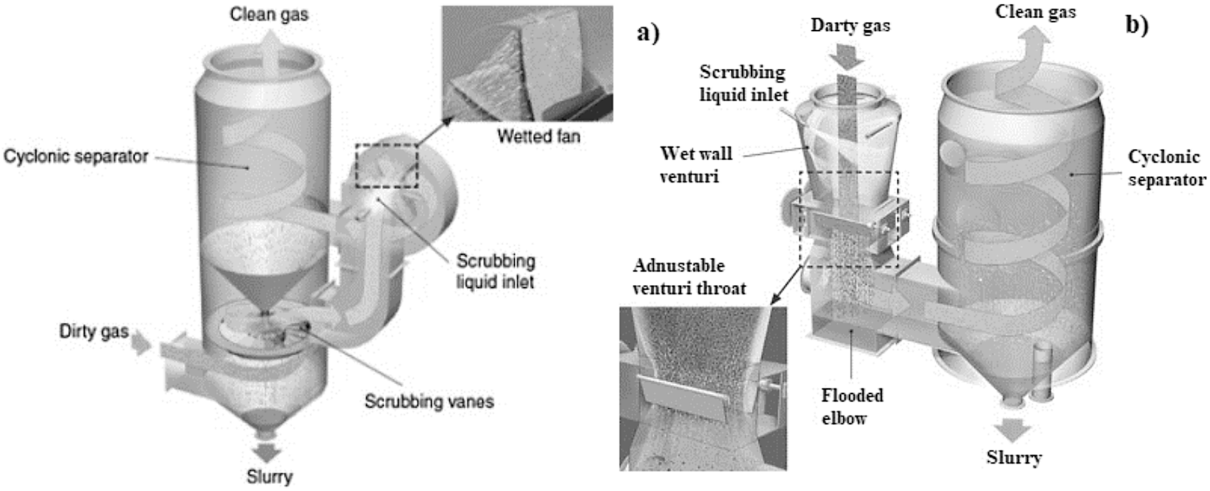

Fig. 2. Wet scrubbers: (a) Integrating wet dynamic and cyclonic scrubbers; (b) Venturi wet scrubber [80].

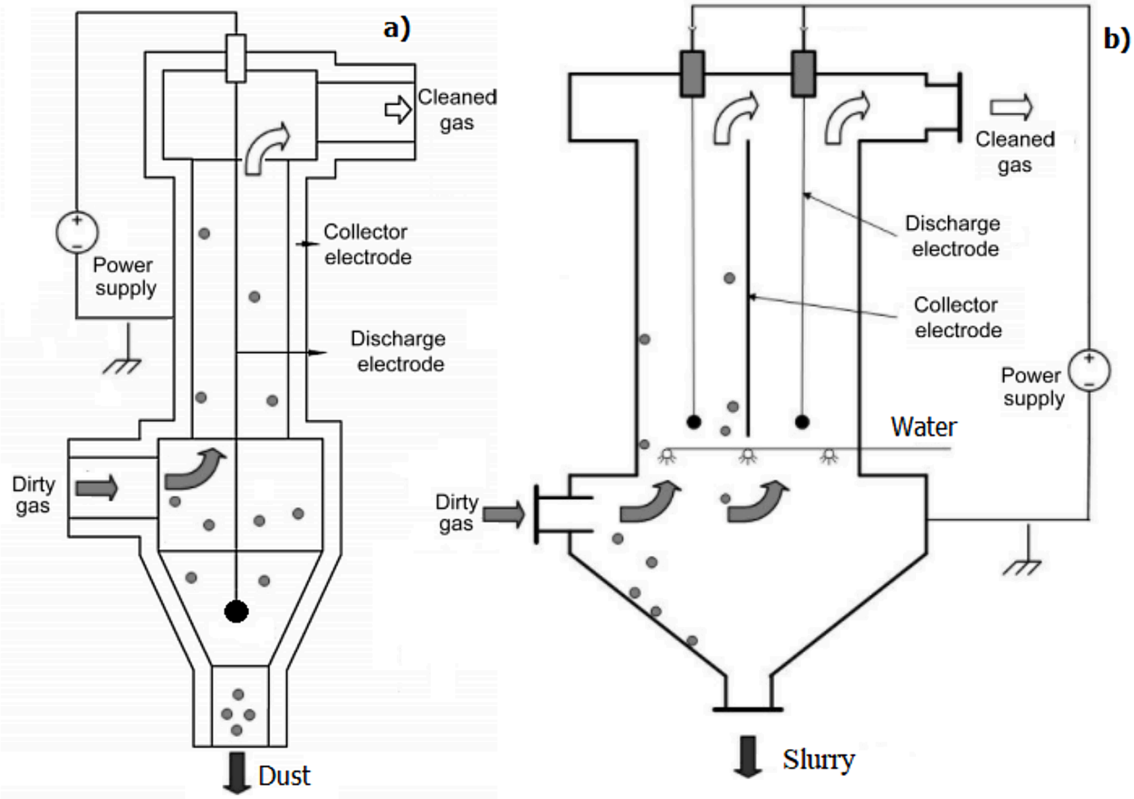

Fig. 3. Electrostatic precipitators: a) Dry-EPS, b) Wet-EPS.

additional treatment is crucial to prevent environmental contamination and may involve complex and costly wastewater treatment processes. Therefore, selecting the cleaning method should be based on the specific nature of the contaminants present in the syngas to ensure effective and economically viable removal [34].

4.1.1. *Particulate matter and alkali compounds*

The WGC method demonstrates a particle removal efficiency exceeding 90 % for particle sizes larger than 5 μm and ranging between 60 and 70 % for submicron particles [38]. For alkali compounds, the removal efficiency exceeds 95 % [82]. Parihar et al. [83] studied the efficiency of particle removal from the syngas stream using a tube-type Wet-EPS with a gas processing capacity of 100 Nm^3/h. The gas was generated in a downdraft gasifier, and the maximum particle concentration observed was 700 mg/Nm^3. The Wet-EPS managed to reduce particle volume to 36 mg/Nm^3, a value below permissible limits for naturally aspirated reciprocating engines (50 mg/Nm^3). However, this performance did not meet the allowed limits for GT applications (30 mg/Nm^3, see Table 1). The Wet-EPS achieved a maximum particle removal efficiency of 83 %. In another study, Corrêa Jr et al. [84] examined the effect of using syngas derived from rice husk as a complement to natural gas in a microturbine. Prior to using the gas in the microturbine, it underwent a cleaning process involving a dry cyclone filter for larger particles and a Venturi-type scrubber for smaller particles. The results demonstrated that this system effectively reduced particle levels to below 30 mg/Nm^3, ensuring compatibility with microturbine performance. While wet scrubbers are mature technologies for particle removal, especially for particle sizes greater than 5 µm, submicron particles require more complex techniques with higher energy consumption and greater economic costs.

4.1.2. Tars

The Wet-ESP system, as seen in the study by Parihar et al. [83], achieves a tar removal efficiency of 62 %. Similarly, Corrêa Jr et al. [84] reported a tar concentration lower than 100 mg/Nm^3 after passing through the Venturi scrubber. Water-based wet scrubbers exhibit high removal efficiency for light, oxygenated, and polar compounds constituting tar. However, they have lower efficiency for heavy and non-polar heterocyclic compounds [39,82]. These non-polar compounds are also removed by condensation due to the wet scrubber's cooling effect, causing them to reach the dew point. As previously stated, wet scrubbers generate highly contaminated water streams, needing complex and costly treatment and purification systems, which is a drawback of water-based syngas cleaning [33]. Oil-based scrubbing liquids offer benefits such as efficient removal of heavy and heterocyclic tars, operation at higher temperatures for enhanced process efficiency, and the potential for regenerating scrubbing oil with hot gas for concentrating and recovering or disposing of contaminants [36]. Nonetheless, downsides include process complexity and increased production costs due to expensive oils [33]. Fig. 4 illustrates a comparison of tar compound removal efficiency for various scrubbing liquids.

4.1.3. Sulfur

Desulfurization technologies fall into three categories based on the addition of water and the state of the product: wet, dry, and semi-dry methods. Wet sulfur removal from syngas typically involves physical absorption, chemical reactions, or a combination of both. This technique enjoys widespread commercial use across various industrial processes. Common sorbents include water, alkanolamines, alkali salts, aqueous ammonia, and organic solvents with high affinity for acid gases [36,49,85]. Wet methods for sulfur removal achieve desulfurization efficiencies exceeding 90 % and can also remove some heavy metals, making them suitable for GT applications where sulfur concentrations must be less than 30 mg/Nm^3 to comply with SO_2 emission limits in stack emissions [86]. Specific sulfur removal methods, such as methyldiethanolamine (MDEA)-based chemical solvents, can achieve 95 % H_2S removal efficiency, and the wet sulfuric acid (WSA) process, achieves sulfur conversion rates of up to 98 % to H_2SO_4 and up to 99 % sulfur recovery [87]. However, for downstream syngas applications requiring extremely low sulfur concentrations of less than 0.1 mg/Nm^3 to avoid catalyst poisoning, the wet removal method might be insufficient. Although some physical absorption solvents, such as Selexol® and Rectisol®, have shown excellent results in sulfur removal, the semi-dry method is typically employed to achieve these extremely low levels [88]. Semi-dry desulfurization technology involves mixing CaO or $Ca(OH)_2$ powder with water to achieve the appropriate concentrations and spraying it into the reaction tower to react with the SOx in the syngas. The calcium salt produced is collected at the bottom of the tower, and the water in the suspension evaporates using the latent heat of the syngas [89].

Removal of H_2S and COS from the gas stream presents distinct challenges. While H_2S can be efficiently removed using wet methods, COS removal often requires additional steps due to its lower reactivity and solubility. For COS removal, hydrolysis to H_2S is a common method, often using catalytic hydrolysis with alumina or titanium oxide as the catalyst. This converts COS to H_2S and CO_2, which can then be removed using conventional desulfurization methods [90]. Additionally, physical absorption using solvents like Selexol® or Rectisol® and chemical absorption using optimized amines can aid in COS removal, although they are typically more effective for H_2S [91]. For instance, Yin et al. [92], implemented a wet desulfurization process in the purification system of an MSW gasification project effectively removing SO_2. They also employed a semi-dry desulfurization process to remove H_2S. Moreover, since the methanization process requires trace sulfur content in the feed gas, they installed a fine desulfurization reaction tower before the methanation reactor to strictly control the total sulfur content below 0.05 ppm [89,93].

4.1.4. Nitrogen

Nitrogen pollutants in cold gas are primarily removed through wet scrubbing by absorption in water. The main nitrogen-derived compounds in the syngas stream are NH_3 and HCN, both of which are highly soluble in water, making water an effective medium for their elimination. Even the condensation of water vapor in the syngas significantly reduces NH_3 and HCN contents. Resnik & Pennline [94] reported significant reduction in NH_3 concentrations, with removal efficiency

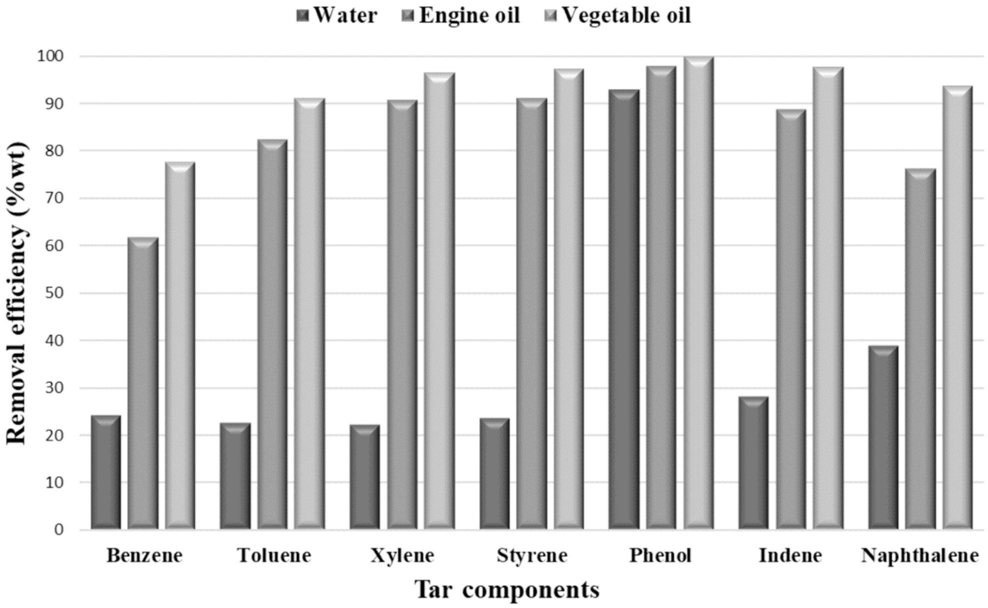

Fig. 4. Tar compounds removal efficiency for different scrubbing liquids [33,36].

exceeding 99 % when utilizing a water-based wet scrubber. Acid-based scrubbing is an advancement over water-based scrubbing, capable of removing NH_3, HCN, and other nitrogen contaminants. The efficiency of these acid absorbents varies widely and is influenced by NH_3 concentration. The benefits of acid scrubbing include the absorption of acid gases like H_2S, thereby enhancing NH_3 removal efficiency with increased absorbent acidity over time. However, limitations include increased corrosivity and lower efficiency at very high NH_3 concentrations (>500 mg/Nm^3) often seen in biomass with high nitrogen content [33,36].

4.1.5. Chlorine

Many syngas applications require extremely low chlorine contaminant levels. Wet scrubbing, commonly using water or a caustic solution, is employed to remove chlorine contaminants. Gaseous HCl and solid NH_4Cl compounds are the main chlorine species in the raw syngas stream. These species are highly soluble in water, rendering water-based wet scrubbing suitable. Water is widely used for chlorine removal, although it needs an expensive ionic exchanger for chlorine solution removal. The addition of sodium hydroxide (NaOH) to water improves chlorine species elimination by enhancing the reaction between HCl and NaOH, producing NaCl which can be precipitated for removal. Caustic scrubbing also benefits by removing other pollutants like COS and CO_2 [36,95,96].

4.2. Dry gas cleaning

In recent years, significant attention has been directed toward dry gas cleaning (DGC) due to its substantial energy and environmental benefits. This approach is particularly noteworthy for its capacity to perform gasification residue cleaning and conditioning at temperatures close to the gasification process, resulting in reduced overall energy losses [40,73,97-100]. DGC offers additional advantages, including the mitigation of waste streams and the potential conversion of certain contaminants into valuable products. For instance, tar can be transformed into combustible gases such as CO, H_2, and CH_4. DGC can be categorized into three fundamental groups: mechanical-physical processes (primarily targeting particle elimination), thermal processes (mainly designed for tar elimination), and catalytic processes (primarily addressing the removal of tar, sulfur, nitrogen, alkali, and chlorine). The subsequent sections will examine the application of these processes for eliminating specific contaminants within biomass gasification-derived syngas.

4.2.1. Particulate removal

On an industrial scale, the elimination of particles from the dry, contaminated gas stream typically employs physical–mechanical systems. These systems find wide application in biomass or coal combustion facilities [101,102]. Consequently, with appropriate adjustments to operational specifications, they can be effectively employed for cleaning syngas resulting from biomass gasification. The underlying principles of physical–mechanical gas cleaning processes are rooted in one or more of the following physical mechanisms: inertial separation, barrier filtration, and electrostatic interaction [37].

4.2.1.1. Inertial separation. Inertial and impact separation processes encompass the utilization of inertial forces applied to particles, thereby inducing their detachment from the gas stream [39]. The most renowned and extensively employed apparatus within this category is the cyclone, although alternatives like impact separators and dust agglomerators can also be employed [37]. Cyclones use centrifugal force to separate particles from the gas stream. These mechanisms can operate at temperatures surpassing 1000 °C, rendering them suitable for the extraction of solid particles from high-temperature gaseous streams. This obviates the likelihood of compound condensation, including substances like tar and acidic species. The operating temperature is primarily constrained by the material strength of the construction, serving as the primary limiting factor [47]. Cyclone designs characterized by high efficiency achieve particle removal efficiencies over 95 % for particles exceeding 5 μm in diameter [37,39]. Fig. 5 provides a comparative assessment of particle removal efficiencies between cyclones and other physical–mechanical separation systems. One limitation of these devices lies in their diminished efficacy for smaller particle sizes. Nevertheless, they can be employed as precursory separators for larger particles.

4.2.1.2. Barrier filtration. Barrier filtration, commonly referred to as filtration, stands as one of the most prevalent methods for the removal of particles from gaseous streams. This process materializes when a gas stream traverses fibers, granules, or a porous monolithic solid. Four distinct mechanisms (diffusion, inertial impact, direct interception, and gravitational settlement) collaboratively effectuate the removal of particles from the gas stream. Particles are gathered due to stochastic collisions with the filter medium, brought about by diffusion, inertial impact, and gravitational settlement as they veer away from the gas flow paths. Additionally, particles following the gas flow paths can be captured through direct interception if their paths draw close to the filter medium. Porous media further contribute to particle elimination by restraining particles larger than the designated pore size [39].

As particles amass on the contact surface of the filter medium, a layer of dust, termed a filter cake, forms and augments filtration efficiency by impeding the passage of smaller particles. Upon reaching a maximum tolerable pressure drop, the filter cake is dislodged through mechanical agitation or a reverse flow of compressed gas pulses [36,39]. Several filtration device types exist, encompassing bag filters, rigid filters, and both fixed and mobile bed granular filters.

Bag filters (Fig. 6a) achieve particle capture through inertial impact, interception, and diffusion within the filter media. Design considerations encompass factors such as the permissible maximum pressure drop before filter cake removal and the methodology for dislodging the filter cake (mechanical agitation, reverse flow, tapping, or compressed gas pulses). Another pivotal facet in fabric filter design pertains to determining an acceptable filtration velocity, usually quantified as the flow rate per fabric area (e.g., m^3/s/m^2) [36].

Materials deployed for filter media encompass polyester, polypropylene, polypeptide (wool), and others. These systems function within the temperature range of 90 °C to 250 °C to forestall contact with liquids and remain within material temperature tolerance. It is feasible

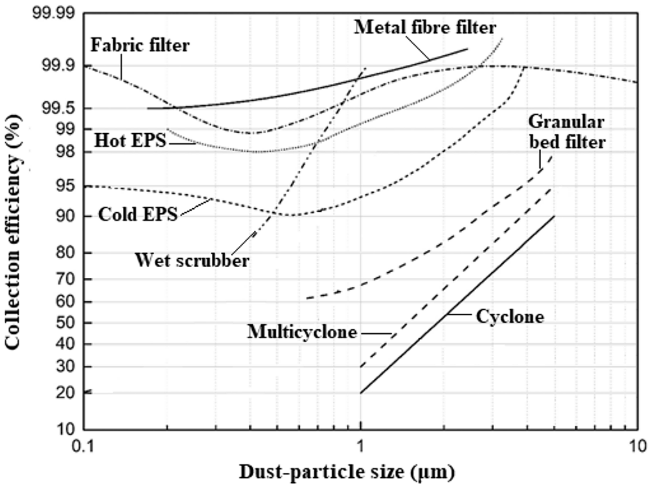

Fig. 5. Particle separation efficiencies of mechanical-physical gas cleaning systems (adapted from [101]).

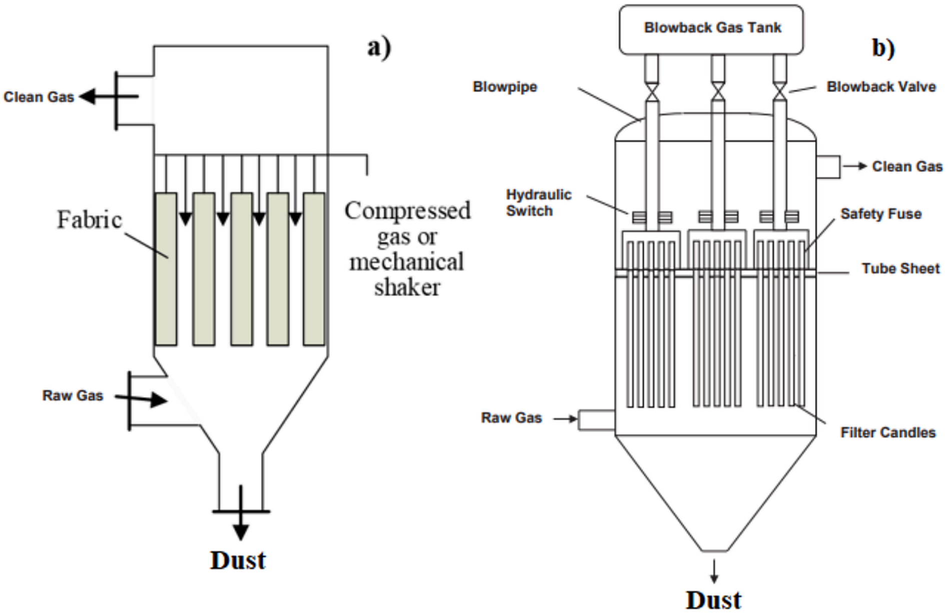

Fig. 6. Barrier filtration: a) Fabric filters, b) Candle filter.

to devise high-temperature bag filters (up to 700 °C) using specialized materials like 3 M's Nextel (a compound of aluminum, boron, and silica oxide). Nevertheless, the primary drawback is their elevated cost [36].

Fabric filter efficiency spans between 70 % and 99.8 % for particles > 0.3 μm [85]. They are also capable of removing alkaline compounds that condense as particles at temperatures below 300 °C. Yet, these filters exhibit sensitivity to tar accumulation, which is difficult to cleanse and consequently leads to filter clogging and reduced operational lifespan [40]. For this reason, cloth filters are typically deployed in the final stage of syngas cleaning systems [103].

Rigid filters, typically crafted from ceramic or metallic materials, possess the main advantage of withstanding high temperatures, rendering them suitable for hot gas filtration. A prevalent example of rigid filters is the candle filter. Installed on a tube plate in vertically spaced groups, each group suspended separately from others and the filter container's sidewalls (Fig. 6b), candle filters facilitate gas flow from the exterior to the interior through the porous wall of the candle filter. Dust accumulates on the external surface of the candles, generating a dust cake. Upon attaining the maximum acceptable pressure drop, a reverse pulse of clean compressed gas, usually nitrogen, removes the filter cake. While one group of candles undergoes cleaning, other groups remain operational, enabling continuous filter functionality [104,105]. Ceramic candle filters can be fabricated from ceramic grains, ceramic fibers, or ceramic fibers embedded with ceramic grains. Their density ranges from roughly 40 % for pure grain ceramics (termed high-density ceramics) to approximately 90 % for pure ceramic fiber (referred to as low-density ceramics). High-density ceramic filter elements can achieve particle collection efficiency of up to 99.9 %, even for submicron particles at temperatures exceeding 1000 °C. Nonetheless, concerns exist about the reliability of ceramic candles when operated at extremely high temperatures (>1000 °C), as they could undergo chemical degradation, creep, and static fatigue over time [105].

To address these concerns, sintered metal candles have been developed, crafted from metallic fibers or metallic powders. Metal powder candles are typically fabricated through pressing and subsequent sintering under vacuum or within an inert gas atmosphere. Metallic fibers are drawn through several steps to attain the desired diameter, followed by cutting, weaving into a web, and sintering. They are then rolled and pressed to the defined thickness, with adjustments made to permeability and average filtration level. Metal candle filters can achieve high porosities (up to 85 %), exhibit low pressure drops (6–10 mbar for fibers and 15–50 mbar for powder), and demonstrate high efficiencies in collecting micrometric-sized dust particles (approximately 99 %). They also exhibit robust mechanical resilience under constant and transient loads [106,107].

Metal candle filters are manufactured using diverse metal alloys selected for their thermal and chemical stability, contingent upon the material to be filtered. This selection aims to avert oxidation and corrosion that could irreparably damage the candle structure. In instances where the gas to be filtered contains sulfur, chlorides, or hydrogen sulfide, such as in the case of syngas, special alloys like Inconel 600, Monel, Hastelloy X, HR 1601, FeCr-alloy, or specialized iron aluminide alloys must be employed. Iron aluminide metal alloys can endure temperatures up to 780 °C, while FeCr-alloy-made candles can withstand temperatures of around 1000 °C [104].

Granular filters, used for particle removal, employ filter media composed of refractory granular materials (such as quartz sand, fine sand, ceramics, and others) through which the contaminated gas is passed. The refractory nature of the bed material enables the filtration of hot gases. As the contaminated gas flows through the filter media, several forces (such as van der Waals forces, capillary forces, gravity, and electrostatic forces) act upon particles, leading to their deposition on the surface of the granules. The collection mechanisms involve interception, inertial impaction, diffusion, gravitational settling, and electrostatic attraction [108].

Granular bed filters (GBFs) can be categorized into two groups: fixed bed and moving bed configurations. The fixed granular bed filter (Fig. 7a) consists of a stainless-steel structure with a defined diameter supporting one or multiple layers of the filter medium forming the packed bed. During filtration, the contaminated gas flows through the media, where a significant proportion of particles are captured. With the accumulation of particles on the granules, a dust cake forms, enhancing collection efficiency but also elevating the pressure drop across the filter media. For regeneration, a back-flow initiates fluidization of the filter bed, entraining previously trapped dust in the fluidized gas stream and rejuvenating the filter media. The fixed granular bed exhibits high filtration efficiency, surpassing 99 %, but is hindered by the necessity to intermittently halt gas flow for cleaning [109,110].

The Moving Bed Filter (MGBF) circumvents the need for periodic gas flow interruptions by continually renewing dirty filter granules with clean ones. The granular material within the bed advances gradually through the filter, maintaining a pace conducive to high-efficiency

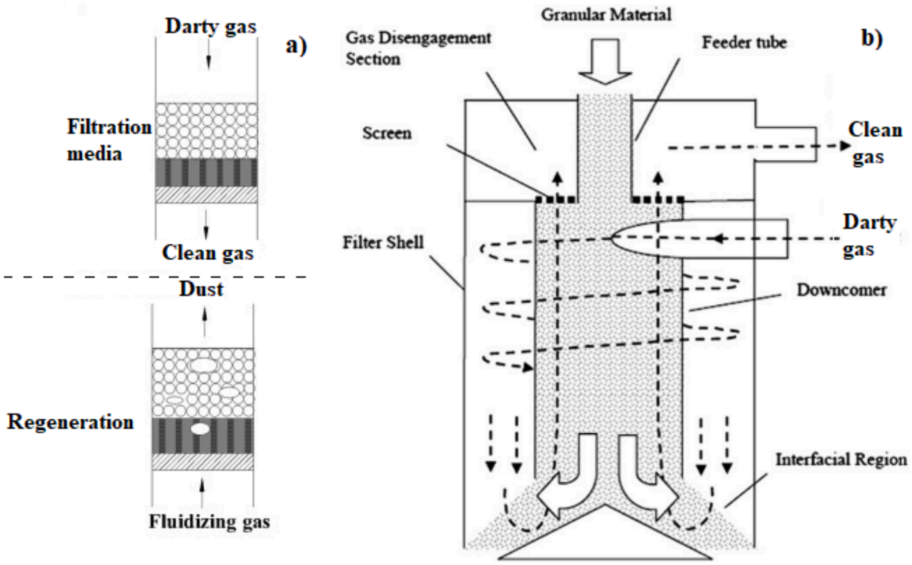

Fig. 7. Granular bed filter (GBF): a) Fixed-bed granular filter, b) Moving-bed granular filter (adapted from [108]).

filtration. This setup balances the ongoing accumulation of particulate material with the continuous replacement of clean media within the bed (Fig. 7b). The outcome is a consistent and acceptable pressure drop [108].

Primary factors influencing MGBF efficiency include the average bed speed, granule size, and the gas velocity to be filtered. These factors affect pore size, available surface area for particle impaction, and pressure drop due to the thickness of the dust cake forming at the interfacial region, where most cleaning occurs. MGBFs have demonstrated efficiencies surpassing 99 % for removing 4 μm particles and up to 93 % for 0.3 μm particles, even at high temperatures up to 840 °C. This filter type exhibits promise for high-temperature gas cleaning due to its robustness and minimal maintenance requirements [36,111,112].

4.2.1.3. Electrostatic interaction. Dry-ESPs operate through three sequential stages: charging, particle collection, and subsequent cleaning of particles from the collecting electrode. The Dry-ESP arrangement, depicted in Fig. 3a, comprises a box with a hopper bottom containing rows of tubes through which contaminated gas flows. Within each tube, high voltage negatively polarized electrodes (ranging from 45 to 70 kV) operate under direct current (DC), facilitated by a transformer-rectifier assembly. These electrodes are surrounded by grounded collector electrodes [113]. The passage of electric current charges solid particles, which, due to their dissimilar dielectric properties compared to gas molecules, are separated from the gas stream, and amassed on the collecting electrode surfaces [36]. Subsequently, charged particles deposited on the collector electrode surfaces are periodically dislodged through mechanical impacts [114].

Dry-ESPs offer a range of advantages. They function across a broad temperature spectrum, typically spanning from 200 to 1000 °C, contingent upon the specific application. However, temperatures exceeding 200 °C can potentially affect process efficiency due to alterations in gas physical properties, such as density, viscosity, and resistivity [35,39,114,115]. Moreover, they exhibit high efficacy, capturing over 99 % of total particles > 10 μm and between 80 to 95 % of > 2.5 μm particles [113].

The major challenge associated with Dry-ESP deployment for syngas cleaning is the potential for generating electrical sparks during operation, which could lead to explosions. Sparks might stem from imperfections in metal surfaces that magnify electric field strength or from a layer of highly resistive particulate material inducing positive ions to migrate toward the negative discharge electrode, thus triggering sparks. To mitigate this risk, strict control over the operational voltage of the device is imperative [37]. In-depth descriptions of ESP technology can be found in the literature [35,39,113,114].

4.2.2. *Tar removal*

4.2.2.1. Mechanical-physical processes. Numerous mechanical-physical systems also demonstrate effective tar separation from the gas stream. However, designing these systems for such a purpose presents formidable complexities and costs, particularly when aiming for low-tar syngas [39,116]. These systems can segregate tars from syngas, yet they do not eliminate them, rather they translocate tars to a distinct phase, needing intricate supplementary treatments for ultimate eradication [34,98]. Rigorous safety protocols must govern the operation of mechanical-physical cleaning systems, as a substantial portion of the generated waste is highly toxic due to the presence of aromatic hydrocarbons, compounds identified as carcinogens, mutagens, and teratogens [34,117].

For instance, filter systems can incorporate absorbents or catalysts to eliminate gas phase contaminants from the syngas stream. Ma & Baron [118] demonstrated this by developing a catalytic filter, enhancing a typical α–alumina (Al_2O_3) candle filter material with active nickel (Ni) and magnesium oxide (MgO) components within its pores. The outcome exhibited a reduction in benzene and naphthalene concentrations by 95 % and 99.5 % respectively, indicating a reduction in tar concentrations, as these components represent key tar constituents [119]. Similarly, Rapagnà et al. [109] positioned a silicon carbide candle filter impregnated with a Ni-supported catalyst MgO-Al_2O_3 within the freeboard of a fluidized bed reactor to mitigate tar concentration. Comparative to a non-catalytic filter, catalytic candles increased gas yield from 1.35 to 1.55 Nm^3/kg of dry biomass, while converting 58 % of product tar and 23 % of product methane.

4.2.2.2. Thermal processes. Thermal processes encompass the deconstruction of large molecules at elevated temperatures into smaller, noncondensable gaseous molecules at reduced temperatures. Standard temperatures for thermal processes typically range from 1000 °C to 1300 °C. Elevating temperatures and extending residence periods enhance the fragmentation of sizable organic molecules, thereby augmenting both the production and quality of gas. Thermal processes are executed through methods such as thermal cracking and plasma cracking [49,117]. Thermal cracking is centered on the fragmentation of substantial tar molecules, leading to the conversion into smaller permanent gas molecules such as H_2 and CO [47]. This conversion facilitates the recovery of energy content mainly through the resultant smaller molecules [65]. Nonetheless, the process necessitates subjecting tar to high temperatures, reaching up to 1300 °C [117]. These elevated temperatures are particularly vital for tar sourced from biomass, given its refractory characteristics. To efficiently break down the tar, several approaches have been proposed: prolonging residence time, such as employing a fluidized bed reactor freeboard, albeit with only partial effectiveness; direct contact with a separately heated high-temperature surface, entailing a considerable energy input and a subsequent reduction in overall efficiency – a method which also exhibits partial efficacy and relies on effective mixing; partial oxidation by introducing air or oxygen, potentially elevating CO levels at the cost of decreased system efficiency [120].

Among the advantages of thermal cracking are its easy control and relatively straightforward integration into low-temperature gasification systems. However, its application leads to heat dissipation, reduced efficiency, and elevated soot production [65]. While thermal cracking eliminates a substantial portion of the tar within the gasified product, it is recognized that complete removal is unattainable, and the post-treatment tar content generally surpasses acceptable levels for most final gasification product applications [39,49].

Researchers have experimentally investigated the partial tar thermal oxidation-based treatment. For instance, Houben et al. [121] conducted experiments involving tar reduction through a partial combustion burner for fuel gas. Naphthalene was introduced as a model tar component. The outcomes demonstrated that the partial combustion burner achieved over 90 % reduction in tar content by means of cracking, using an air/fuel ratio of 0.2. In a recent study, Hu et al. [122] scrutinized the thermal cracking of tar, employing quartz sand, across a temperature span of 1023 K to 1223 K, in a micro fluidized bed reactor analyzer (MFBRA). The findings of this study indicated an enhancement in total tar conversion with escalating temperatures, rising from approximately 30.6 % at 750 °C to 48.9 % at 950 °C, corresponding to an increase of 18.3 %. The results also underscored that even at 950 °C, the ultimate conversion achieved by thermal cracking remained modest, barely reaching 50 %. This highlights the partial efficacy of thermal cracking in tar removal.

Plasma-based tar reforming has garnered considerable interest in the quest for more efficient tar reforming techniques. The plasma reactor presents an efficient approach to tar reforming mechanisms. Unlike catalytic or thermal degradation, the plasma reformer achieves heightened reactivity rates, coupled with the achievement of steady-state speed. Consequently, it offers improved efficiency in tar conversion [123]. The plasma reactor can generate a high-temperature electric discharge arc, reaching temperatures of up to 10,000 °C. This discharge induces atomic decomposition of materials under varying conditions and atmospheres [120]. Tar reforming in biomass gasification product treatment can be categorized into two groups, contingent upon temperature, electron density, and energy concentration: thermal plasma and non-thermal or imbalanced plasma [124].

In thermal plasma, the reactor can sustain high gas temperatures ranging from 1600 °C to 1800 °C, enabling the establishment of thermal equilibrium for energetic and neutral species [125]. Within this temperature range, the tar present in biomass gasification products can transform into enduring combustible gases like H_2 and CO. However, the main challenge in employing thermal plasma for tar reforming remains the elevated specific energy consumption and the degradation and erosion of electrodes, alongside the incompatibility with catalyst integration due to the exceedingly high temperatures [126].

Non-thermal plasma (NTP) or imbalanced plasma favors hydrocarbon decomposition at lower temperatures. The tar decomposition via this approach showcases exceptional efficiency across various biomass materials due to its efficient design and a substantial abundance of excited particles, characterized by an electron temperature of 105 °C and an energy range of 1–10 eV. This facilitates the cleavage of light hydrocarbon chemical bonds, overcoming the limitations of high temperatures observed in thermal decomposition and catalytic cracking [127]. There are numerous NTP reactors described in literature for biomass tar decomposition including gliding arc discharge (GAD), pulse discharge (PD), corona discharge (CD), microwave plasma (MW), glow discharge (GD), and dielectric barrier discharge (DBD) [127,128]. Table 5 provides a summary of diverse NTP applications in tar reforming.

4.2.2.3. Catalytic processes. Owing to the benefits of converting tar into valuable gases and tailoring the composition of gasification products, catalytic cracking has garnered significant attention, with particular emphasis over the last 20 years [137–140]. The catalytic elimination of tar at elevated post-gasification temperatures entails subjecting the raw gas to secondary treatment in a reactor, commonly featuring a fixed or monolithic bed [141]. Catalytic cracking operates at lower temperatures than thermal cracking (700–900 °C), which is achieved by reducing the activation energy required for tar compound breakdown [142,143]. This bears the potential to curtail thermal inefficiencies and the expenses linked to operation at higher temperatures. Conversely, catalysts pose operational challenges due to a decrease in catalyst activity, often caused by poisoning, fragmentation, or carbon deposition [144].

Catalyst poisoning occurs by the irreversible adsorption of molecules, particularly tainted with sulfur (H_2S), which notably impacts metal catalysts (e.g., nickel, iron) [35,145]. Fragmentation can result from physical or chemical forces, such as extreme temperatures, elevated pressures, and abrasive surroundings, leading to the division of the catalyst into smaller fragments that can be easily entrained by the gas flow. Corrosive agents like H_2S, NH_3, and HCl present in the gas stream can also chemically remove the active components of the catalyst, predominantly in the case of metal catalysts [35]. Carbon deposition (coking) represents another phenomenon affecting catalyst efficiency, occurring when organic compounds dehydrate and transform into fine carbon particles possessing refractory properties. These particles are deposited and accumulate on the active catalyst surface, hindering its efficacy [145].

Narnaware & Panwar [146] and Argyle & Bartholomew [147] have summarized the attributes of an ideal catalyst as follows: effectiveness in tar removal within an environment containing high concentrations of H_2, CO, CO_2, H_2O, and temperatures ranging between 700 and 900 °C; robust stability against deactivation from coke, poisoning, or sintering; easy regeneration; high wear resistance; affordability; and environmental non-toxicity.

The potential for tar cracking hinges on catalyst composition and type. The performance of heterogeneous catalysts depends on the type of metal impregnated, the promoter (which heightens activity and/or stability), and the support. Catalysts employed for tar removal can be

Table 5
Non-thermal plasma (NTP) tar removal applications and corresponding performance [124].

Plasma reactor	Tar comp.	Tar conc. (g/Nm^3)	Carrier gas	Conversion (%)	Ref.
GAD	$C_{10}H_8$	1.1–2.0	Humid N_2	84.0	[129]
	C_6H_6	4.3		82.6	[130]
	C_7H_8/$C_{10}H_8$	17.3		80.2	[131]
	C_7H_8	14.0	Dry N_2	83.2	[132]
CD	Real tar	0.7	Real syngas	62.0	[133]
DBD	$C_{10}H_8$	0.4	Air	95.0	[134]
	C_7H_8	51.9	Humid N_2	64.0	[135]
MW	C_7H_8	4.2	20 % Ar/N_2	99.0	[136]

categorized in various ways. For instance, Abu El-Rub et al. [148] proposed a straightforward classification based on catalyst origin (natural or synthetic). Natural catalysts encompass minerals like dolomite, olivine, clay minerals, and ferrous metal oxides. Synthetic catalysts encompass chars, fluid catalytic cracking catalysts, alkali metal carbonates, activated alumina, and transition metals. In another approach, Chen et al. [139] subdivides catalysts into three groups: nickel catalysts, dolomite catalysts, alkali metal catalysts, and other metal catalysts. In this study, we will classify catalysts into six groups, as outlined by Guan et al. [58], which will be expanded upon below:

i *Nickel-based catalysts*

Nickel (Ni), classified as a transition metal within Group VIII of the periodic table, has gained significant attention for its catalytic attributes and extensive industrial application in processes like steam and dry reforming [149]. Ni-based catalysts, typically supported on metal oxides, have been extensively investigated for their efficacy in tar removal generated during biomass gasification [150–153]. These catalysts exhibit heightened activity in steam reforming of heavier tars (comprising more than three rings) while showing relatively diminished effectiveness against lighter tars [149]. Wu et al. [154] discovered that nickel-based catalysts facilitated the conversion of tar into unsaturated hydrocarbons and oxygen-containing organics. However, these catalysts lacked stability, could not be regenerated, and a significant drawback is their swift deactivation due to coke formation and susceptibility to poisoning by sulfides, metal chlorides, and alkaline oxides, rendering them less suitable as primary catalysts [31,155]. Nevertheless, they demonstrate remarkable secondary catalytic activity [35]. Ni demonstrates compatibility with a range of materials, among which zeolite, Al_2O_3, ZrO_2, TiO_2, CeO_2, MgO, olivine, and dolomite have been extensively explored [31,156]. Buchireddy et al. [157] examined the influence of nickel impregnation on zeolite catalysts, reporting a notable enhancement in steam reforming of tars, attributed to the catalytic effects of nickel. Miyazawa et al. [126] explored the catalytic activity of Ni supported on various materials (Al_2O_3, ZrO_2, TiO_2, CeO_2, and MgO), ranking their efficacy as follows: $Ni/Al_2O_3 > Ni/ZrO_2 > Ni/TiO_2 > Ni/CeO_2 > Ni/MgO$. This suggests that the support material can enhance the catalytic performance of nickel catalysts. Irfan et al. [158] evaluated the impact of Ni loading on the cracking behavior of Municipal Solid Wastes (MSW) gasification tar within the ($Ni–CaO–TiO_2$) system. They observed that increasing the Ni content to 30 % significantly accelerated tar decomposition. Su et al. [159] utilized lanthanum (La) to enhance the Ni/Al_2O_3 supercritical catalytic gasification of kitchen waste, finding that La increased catalytic activity by improving metal dispersion and reducing catalyst deactivation. This suggests that the support material can enhance the catalytic performance of nickel catalysts. Ferella et al. [160] investigated several Ni and Fe bimetallic catalysts supported on Al_2O_3, revealing that bimetallic catalysts exhibit higher catalytic activity than nickel supported on Al_2O_3. Koike et al. [161] delved into the steam reforming of tar model compounds (benzene, toluene, and phenol) using Ni-Fe/Mg/Al bimetallic catalysts prepared through calcination and reduction of a hydrotalcite-like precursor. The study noted that phenol is strongly adsorbed on the surface of iron and nickel, forming coke, which leads to reduced catalyst activity against benzene and toluene. Ruivo et al. [141] investigated a novel Fe_2-xNixTiO$_5$ catalyst for biomass gasification gas cleaning and upgrading applications. The study demonstrated that the catalyst exhibited high activity in converting tar model compounds at temperatures above 700 °C. Additionally, the conversion of biomass-derived gas tar from a bubbling fluidized bed gasifier exceeded 78 % at 800 °C. In another study, Heo et al. [162] examined the effect of adding Ca, K, and Mn to Ni-based catalysts supported on dolomite for toluene steam reforming. Results indicated that dolomite was the most promising support material for toluene conversion and selective hydrogen formation. The catalytic performance order for Ni/dolomite was Ni-Mn/dolomite > Ni-Ca/dolomite > Ni-K/dolomite > Ni/dolomite, with the highest catalytic yield achieved by Ni-Mn/dolomite at 754 °C.

Synthesis methods like wet impregnation or co-precipitation were applied to several Ni-supported catalysts, resulting in slight enhancements in tar conversion attributed to better dispersion of the active metal within the catalyst support [163–165]. Similarly, wet impregnation of Ni in dolomite and olivine catalysts led to noticeable improvements in catalytic activity following the addition of Ni [166].

ii *Non-nickel transition metal catalysts*

Apart from nickel, various other transition metals (such as Rh, Ru, Pd, Pt, Co, Fe, etc.) have undergone investigation for their catalytic potential in reforming biomass gasification tar. Numerous studies have highlighted the remarkable catalytic activity, elevated sulfide resistance, and enduring stability of certain noble transition metals (Ru, Rh, and Pt) utilized in tar reforming [62,167,168]. Tomoshige et al. [169] studied the catalytic activity of these noble metals, supported on CeO_2/SiO_2 for tar steam reforming, comparing their performance to Ni-based catalysts. The study revealed that the $Rh/CeO_2/SiO_2$ catalyst exhibited substantial tar conversion, outperforming commercial Ni-based catalysts. The same study ranked the catalytic efficacy of noble metals (Rh > Pt > Pd > Ru = Ni), with Rh being the most catalytically active. Ammendola et al. [170] examined a synthetic Rh-based catalyst (Rh-La/CoO_3) supported on Al_2O_3 in a dual fixed-bed reactor at the laboratory scale. The results demonstrated complete conversion of condensable tars, superior catalytic activity relative to Ni/Al_2O_3 catalysts, and heightened resistance to coke deactivation. Guan et al. [62] reviewed the catalytic steam reforming of biomass tar, highlighting various catalysts' strengths and weaknesses. Nickel-based catalysts are effective but prone to coking. Noble metals like Rh, Ru, and Pt offer high activity and stability but are expensive. Other transition metals such as Fe, Co, and Cu perform well but suffer from carbon deposition. The study underscores the challenges in developing optimal catalysts for tar reforming. Iida et al. [171] scrutinized the impact of a Ru precursor on the steam reforming of aromatic compounds, using toluene as a model, for various $12SrO\text{-}7Al_2O_3$ catalysts. The results indicated that Ru/$12SrO\text{-}7Al_2O_3$ exhibited superior catalytic performance and pronounced resistance to coke deactivation. While noble transition metal catalysts can substantially reduce tar content, their higher cost compared to conventional nickel catalysts poses a challenge for large-scale commercial implementation [62].

The catalytic activity of additional transition metals (Co, Fe, Zn, Cu) has also been explored for steam reforming of tar, with some showcasing greater catalytic efficacy than Ni-based catalysts [34]. Wu et al. [172] investigated the catalytic performance of magnesium oxide (MgO) loaded with cobalt (Co) and nickel (Ni) for naphthalene conversion. They observed significantly higher catalytic activity for Co-MgO compared to Ni-MgO. In one experiment, Co-MgO achieved a 23 % naphthalene conversion, while Ni-MgO only reached 12 %. This enhanced performance can be attributed to the superior oxygen absorption capacity of Co and its stronger interaction with MgO, leading to improved catalytic efficiency and stability. Additionally, Niazi et al. [173] explored the effects of incorporating Fe, Cu, and Mg into nickel-ceria supported catalysts, discovering that these modifications markedly enhanced both performance and stability in reforming reactions. Recent studies further support these findings. Wu et al. [174] reported that integrating Fe into Ni-based catalysts boosts activity and resistance to deactivation during low-temperature ethanol steam reforming, which is closely related to tar reforming. This implies potential similar enhancements in tar steam reforming. Landi et al. [175] and Fedorov et al. [175] demonstrated that adding Cu to Fe-based catalysts enhances catalytic performance, leading to improved activity and stability under high-temperature conditions. This modification facilitates better naphthalene conversion and greater resistance to coke deposition. The synergistic effects of Cu with Fe-based catalysts significantly enhance catalytic properties, underscoring Cu's role in promoting effective steam reforming processes.

iii *Alkali metal catalysts*

Alkali metals, categorized within Group 1A of the periodic table, encompass elements like Li, Na, and K. Multiple studies have evidenced the effectiveness of alkali metal catalysts in tar steam reforming, contributing to improved syngas quality [176,177]. However, a significant drawback of these catalysts lies in their tendency to vaporize at typical gasification reaction temperatures and the challenges involved in their downstream recovery. Guo & Wang [178] explored the catalytic effects of metal catalysts like CaO, NiO, and K_2CO_3 on the pyrolysis and gasification of waste bamboo biomass. Their study optimized process conditions and analyzed syngas production using thermal analysis and gas chromatography. The results indicated that K_2CO_3 was the most effective catalyst, increasing char yield from 20.2 % to 26.8 % and reducing tar yield from 44.3 % to 38.6 %. Nearly all biomass components were fully converted at 800 °C. Kim et al. [179] explored the catalytic activity of K_2CO_3 supported on perovskite oxide (LaMn(1-x) Cu_xO_3) and Al_2O_3 for *in-situ* tar removal in a fluidized bed gasifier. With 10 wt% K_2CO_3 supported on Al_2O_3 and perovskite oxide, tar concentration decreased by 53 % and 59 %, respectively, at a low gasification temperature of 700 °C. Unsupported K_2CO_3 exhibited lesser effectiveness, resulting in a mere 20 % reduction in tar content. Conversely, alkaline species inherently present in biomass play a pivotal catalytic role in thermal conversion processes, with released alkali species potentially catalyzing steam reforming of tar within the gasification process [95]. Hognon et al. [180] studied the impact of inorganic elements within the biomass itself on steam biomass gasification, affirming that the reactivity variance among diverse biomass types is influenced by their respective inorganic elements. Biomass samples rich in potassium exhibited heightened reactivity, known to act as a catalyst in both char gasification and tar reforming. Pio et al. [181] assessed the influence of three low-cost catalysts: bottom bed ashes from residual forest biomass combustion (eucalyptus-derived), carbon particles resulting from wood pellet direct gasification, and synthetic fayalite (Fe_2SiO_4), within a pilot-scale bubbling fluidized bed gasifier. The study revealed a substantial impact on H_2 and CO concentrations, which increased by over 300 % compared to results without catalysts. Additionally, carbon conversion efficiency and cold gasification system efficiency improved. Besides serving as a cost-effective natural catalyst, biomass ash usage circumvents waste handling challenges [165].

iv *Natural catalysts*

Natural minerals like dolomite and olivine can serve as catalysts either directly or after certain treatments such as calcination. These natural catalysts are cost-effective, abundant, and exhibit significant catalytic activity for tar reforming [34,62]. Dolomite, a Ca and Mg mineral with the chemical formula $MgCO_3$-$CaCO_3$, has been extensively researched as a primary and/or secondary catalyst in biomass gasification due to its affordability, accessibility, and effective tar reduction capabilities [33,39,182]. Calcination enhances the catalytic potency of dolomite for tar removal by increasing pore size and surface area [62,183]. The addition of other metal oxides like Fe_2O_3 also improves the catalytic activity of dolomite [39]. According to Cortazar et al. [184], calcinated dolomite catalysts exhibit enhanced tar reduction activity when steam is employed as a gasifying agent, suggesting that dolomite primarily removes tars through steam reforming. A drawback when used as a primary catalyst is its abrasive nature, which can lead to reactor wall erosion, particularly in fluidized bed gasifiers [185]. Olivine, a magnesium iron silicate ($(Mg1\text{-}xFe_x)_2SiO_4$), typically varies in size from 100 to 400 μm and has a density similar to sand (2500–2900 kg/m^3) [73]. Soomro et al. [166] noted that olivine exhibits slightly lower tar reforming efficiency compared to dolomite, yet its wear resistance is notably higher, making it suitable for use alongside sand in fluidized bed gasifiers.

v *Zeolites catalysts*

Zeolites, also referred to as "molecular sieves" are crystalline silicates $[SiO_4]^{4-}$ and aluminosilicates $[AlO_4]^{5-}$ linked via oxygen atoms, creating a three-dimensional network with molecular-scale channels and cavities [186–188]. Due to their well-defined pore structure, remarkably high surface area, and surface acidity, zeolites have found extensive use in the petrochemical industry for cracking complex hydrocarbons, and when modified with dispersed metals, they become catalysts for hydrogenation and the breaking of aromatic hydrocarbon rings [182,183]. These attributes make zeolites promising candidates for tar cracking, as they can break down hydrocarbons akin to those found in biomass gasification syngas [30].

El-Rub et al. [189] investigated the application of natural zeolite as a catalyst for toluene conversion, a model compound for tar, in biomass gasification systems. They evaluated its performance at temperatures between 700 °C and 900 °C. Their findings demonstrate that natural zeolite significantly enhances toluene conversion compared to thermal cracking alone. At 900 °C, the catalyst achieved a conversion efficiency of up to 79 %. In another study, Ahmed et al. [190] investigated the efficacy of Ni/Fe/Mg zeolite-supported catalysts for steam reforming of toluene. They examined the influence of adding MgO and Fe on the catalytic activity of Ni/zeolite, Ni-Fe/zeolite, and Ni-Fe-Mg/zeolite configurations. Their findings revealed that Ni-Fe-Mg/zeolite catalysts with optimal compositions exhibited superior performance compared to their monometallic and bimetallic counterparts. Zeolite catalytic activity correlates with increased acidity and pore size. Advantages of zeolite use include strong catalytic support due to high thermal/hydrothermal stability, increased catalytic activity with acid strength, better resistance to nitrogen and sulfur compounds, and ease of regeneration [62]. However, their main drawback lies in rapid deactivation due to coke deposition [191].

vi *Carbon-supported catalysts*

Activated carbon (AC), along with biomass-derived char (biochar), and mineral coal, have gained significant attention as catalytic supports for hydrocarbon conversion and tar cracking due to their highly porous structures [117,192]. The catalytic efficacy of these carbon materials in tar removal is closely linked to factors like pore size, surface area, and ash or mineral content. Their use is particularly attractive due to their low-cost nature as natural products [193].

Several studies have explored the performance of these catalysts in tar conversion. Lu et al. [194] examined AC derived from coconut husks for toluene decomposition. This AC was employed as a support for three Cu precursors (Cu nitrate, Cu acetate, and Cu sulfate), and the influence of Cu loadings and reaction temperatures was investigated. Tests were conducted using 200 ppm of toluene in an N_2 gas containing 10 % O_2. The copper nitrate precursor yielded the highest toluene conversion at lower temperatures. The catalytic activities of AC-supported copper catalysts followed the sequence Cu nitrate (99 %) > Cu acetate (97 %) > Cu sulfate (80 %) for 1 wt% Cu loading. The favorable toluene conversion was attributed to the effective dispersion of active phases and the nanoscale size of Cu particles. In another study, Takaoka et al. [195] employed AC derived from coconut shells for pentachlorobenzene (PeCB) decomposition. Catalysts were prepared by mixing AC with hydrogen peroxide (H_2O_2) and nitric acid (HNO_3) as oxidizing agents for different durations. Oxidizing AC resulted in an increased number of larger pores with larger pore diameters. PeCB decomposition tests were conducted at temperatures ranging from 300 °C to 400 °C for 30 min. AC samples treated with HNO_3 for 24 h exhibited high PeCB conversions at 300 °C, while at 400 °C, all catalyst samples, including untreated AC, achieved complete PeCB conversion. Bhandari et al. [196] evaluated the catalytic performances of three synthesized catalysts: biochar, activated carbon, and acidic surface-activated carbon. They found all three to be effective in tar removal, with removal efficiencies ranging from 69 % to 92 %. AC catalysts exhibited higher toluene removal efficiency due to their superior surface area, larger pore diameter, and greater pore volume compared to biochar catalysts.

Feng et al. [197] explored the use of biochar as a catalyst and investigated its impact on homogeneous and heterogeneous conversion of biomass tar in the presence of H_2O and CO_2 reformers. Results indicated that temperatures of 700–900 °C were necessary for the homogeneous transformation of tar, particularly PAHs, in the presence of H_2. In the heterogeneous tar reforming with biochar at 800 °C, tar reduction increased with rising H_2O and CO_2 concentrations. Trung et al. [198] investigated dual-functional materials by dispersing nanometer-sized noble metals (Au, Pd, and Au-Pd) within a granular carbon-ceria support matrix using the metal-sol method. The study demonstrated the high efficiency of these novel catalysts in achieving effective toluene removal at low temperatures, underscoring their potential for application in industrial tar treatment systems. Zhang et al. [199] studied the utilization of advanced catalytic materials for biomass gasification, specifically focusing on tar cracking efficiency by synthesizing a biochar-supported Fe-Mo carbides catalyst through an impregnation method coupled with *in-situ* carbothermal reduction. The catalyst exhibited promising performance in tar cracking efficiency, notably achieving an efficiency of 91.05 % with Fe-$Mo_{0.5}$@C catalyst and retaining 84.77 % efficiency over 5 cycles. The authors proposed a tar catalytic cracking mechanism, elucidating the role of Fe_3C-Mo_2C active sites in generating stable light aromatic hydrocarbons and phenolic substances. Khajeh et al. [200] also described the tar removal from carbon-supported iron catalysts using biochars prepared from woody sawdust, reaching a removal efficiency of 76.2 %. Biochar was impregnated with Fe and K and the authors mentioned that the syngas yield almost doubled with the incorporation of catalyst in the pyrolysis of biomass. Yang et al. [201] developed novel biochar-based nanocatalysts loaded with Ni/Ca/Fe nanoparticles via a one-step impregnation method. The introduction of nanoparticles notably increased H_2 yield and tar conversion in cotton stalk gasification. Among the catalysts tested, Fe-loaded biochar exhibited the most promising catalytic gasification performance, achieving 87 % tar conversion and 42.46 mmol/g H_2 production.

Overall, biochar stands out as a promising catalyst candidate for tar reforming due to its abundance and cost-effectiveness. Frainetti et al. [193] emphasized its catalytic activity for tar removal and the potential for enhancement through modification and activation processes. However, commercialization hinges on addressing key challenges such as understanding the impact of varying tar compositions, refining activation methods, and ensuring catalyst stability. While metal loading shows potential, its economic feasibility and resistance to deactivation require further investigation. Co-loading metals presents a promising avenue for future exploration, highlighting the need for continued research to optimize biochar catalysts for tar reforming applications.

4.2.3. *Removal of sulfur compounds*

In the gasification process, the sulfur present in biomass is primarily converted into H_2S, with smaller amounts of CS_2, COS, and elemental sulfur (S_x) [202]. The concentration of H_2S in the syngas depends on the sulfur content of the feedstock, as depicted in Fig. 8. It is important to note that this relationship does not seem to be linear but exhibits a slight polynomial character [38].

The removal of sulfur contaminants from syngas is commonly achieved through adsorption at high temperatures. Adsorption involves the physical or chemical binding of gaseous species to solid materials. The process can be reversible or irreversible. Reversible adsorption allows for solvent regeneration but often employs more expensive synthetic materials. Irreversible adsorption, while cheaper, does not permit recovery and results in the permanent removal of adsorbed contaminants [36]. Sulfur adsorption can occur either *in situ* (within the gasifier bed) or downstream (post-gasification). *In situ* capture is often achieved using natural calcium-based sorbents like limestone or dolomite, or commercial sorbents like calcium acetate, magnesium acetate, and calcium [39]. For dry desulfurization downstream of the gasifier, regenerable metal oxide sorbents are employed, utilizing metals such as Zn, Fe, Cu, Mn, Mo, Co, and V [203]. These sorbents, whether single, mixed, or supported metal oxides on microporous structures, can effectively reduce H_2S concentrations to below 100 ppmv [202]. Metal oxide sorbents must fulfill specific criteria, including high equilibrium constants and fast kinetics for sulfidation, selectivity towards sulfur capture to minimize side reactions, resistance to H_2 reduction to preserve the syngas lower heating value (LHV), mechanical robustness to reduce wear-induced mass losses, and cost-effective regeneration capabilities [204]. Zinc oxide (ZnO) and its derivatives are well-known for their effectiveness in H_2S removal. Numerous studies have demonstrated that ZnO catalysts can reduce H_2S to levels below 1 ppmv. However, regeneration poses a challenge. To prevent the formation of zinc sulfate ($ZnSO_4$), regeneration must occur under a reducing gas stream, which can lead to the reduction of ZnO to elemental zinc. Moreover, ZnO can volatilize at temperatures exceeding 600 °C, limiting its long-term performance. Incorporating iron and titanium oxides into the structure of the ZnO catalyst has been explored to mitigate these issues [205,206].

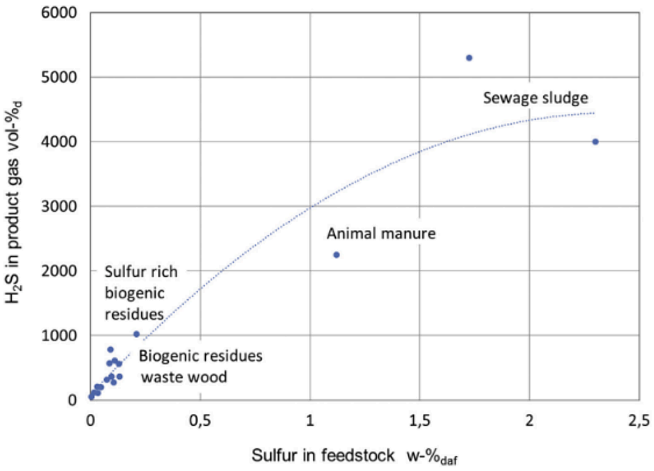

Fig. 8. H_2S content in the dry syngas dependent on the nitrogen content in the feedstock ash-free [38].

Copper oxide (CuO) catalysts have also been extensively studied for H_2S reduction, displaying favorable thermodynamics and rapid sorption rates under reducing and oxidizing conditions. CuO can significantly reduce H_2S from several thousand ppmv to sub-ppmv levels. However, unsupported CuO is prone to reduction to elemental copper in the gasification environment, resulting in lower sorbent efficiency. This can be addressed by dispersing CuO onto a support to enhance stability and surface area. Still, even supported copper-based catalysts may be affected by hydrogen presence in the syngas, limiting their utility [202,207].

Other transition metal oxide catalysts, such as iron oxide (FeO), have been tested for H_2S sorption due to their thermodynamic favorability and relatively low cost. However, at elevated temperatures (>600 °C), iron oxide catalyzes the Boudouard reaction, potentially leading to catalyst deactivation through coke formation [205].

4.2.4. *Removal of nitrogen compounds*

During the gasification process, nitrogen pollutants are mainly in the form of NH_3, with smaller amounts of HCN, isocyanic acid (HNCO), and nitrogen oxides (NOx) [38,208]. These pollutants originate from protein structures and heterocyclic aromatic compounds in the biomass, leading to their presence in the syngas. The concentration of NH_3 in the syngas varies depending on the nitrogen content of the raw biomass material, as illustrated in Fig. 9. However, the relationship between NH_3 content and feedstock nitrogen content (daf) is not strictly linear, it exhibits a slight polynomial nature [38].

Dry cleaning of nitrogen compounds in gasification primarily focuses on the decomposition of NH_3, rather than its removal from the gas stream. Decomposing NH_3 into N_2 and H_2 is highly desirable as it does not introduce additional contaminants into the gas stream [209]. Like other pollutants, NH_3 decomposition can be conducted either *in situ* (within the gasifier bed) or downstream (post-gasification). For *in situ* decomposition, alkali metal derivatives such as dolomite, olivine, CaO, and MgO are primarily used. For catalytic decomposition downstream of the gasifier, catalysts based on transition metals like iron, nickel, ruthenium, zirconium, and others are employed.

Iron-based catalysts are well-documented for their activity in NH_3 decomposition. Tsubouchi et al. [210] used iron dispersed in charcoal to decompose NH_3 in various gas mixtures. They achieved 100 % NH_3 conversion to N_2 at 850 °C in a (N_2 + H_2) mixture. Another study by Tsubouchi et al. [211] explored limonite for NH_3 conversion at elevated temperatures. They reported nearly complete NH_3 conversion at 500 °C in an inert environment. However, when primary gases (CO, H_2, H_2O) were present, the catalytic activity of limonite decreased, requiring temperatures exceeding 750 °C to achieve more than 90 % conversion. Iron catalysts can exhibit undesirable reactions between NH_3 and CO, leading to the production of HCN or HNC.

Nickel-based catalysts are highly effective in NH_3 decomposition at temperatures above 600 °C, with efficiencies exceeding 95 % [208,212,213]. However, these catalysts are susceptible to deactivation due to coking and/or poisoning, particularly by H_2S in the syngas [160]. The activity of nickel catalysts can be enhanced when they are supported on transition metal oxides, such as ZrO_2, MoO_3, and Al_2O_3. These supports can be combined with other metals to improve performance and stability. Bimetallic Ni-Pt/Al_2O_3 catalysts have shown high NH_3 conversion efficiency [214].

Ruthenium (Ru) catalysts supported on various metal oxides have also been explored for NH_3 decomposition [215]. Ru-based catalysts exhibited good activity, with NH_3 conversion performance surpassing that of Ni-based catalysts. However, like Ni, Ru-based catalysts are susceptible to deactivation through coking and H_2S poisoning [157].

Selective catalytic oxidation is another strategy for NH_3 elimination, involving the controlled addition of an oxidant (O_2, NO, or a mixture) to convert NH_3 to N_2. Thermal catalytic decomposition of NH_3 occurs through a mechanism opposite to NH_3 formation, where NH_3 molecules dehydrogenate, forming N* and H* radicals that combine to produce N_2 and H_2 [36]. Thermal catalytic oxidation has an advantage as it occurs at lower temperatures compared to decomposition (around 500 °C). However, it may lead to undesirable reactions depleting H_2 in the syngas [208].

4.2.5. *Removal of halide compounds*

Removing chlorine contaminants from dry syngas is typically achieved through adsorption, with a focus on eliminating HCl due to its abundance compared to other chlorine components [206]. HCl adsorption can be performed *in situ* (within the gasifier bed) or downstream (post-gasification). *In situ* removal often involves the use of solid sorbents like dolomite, which contains CaO and $Ca(OH)_2$, reducing HCl content [39]. Downstream removal of HCl employs alkali metals (Li, Na, K), alkaline earth metals (Mg, Ca, Sr, Ba), and transition metal oxides (MnO, CoO, ZnO, NiO, Y_2O_3, Cu_2O, FeO) [85].

The HCl adsorption capacity of alkaline oxides at high temperatures follows the trend $Na_2O \approx K_2O \gg Li_2O$. Na_2O and K_2O are more effective at temperatures up to 600 °C and HCl concentrations below 5 ppmv, while Li_2O is efficient only at lower temperatures around 200 °C [163]. Alkaline oxides combine with CO_2 in the syngas to form carbonates (Li_2CO_3, Na_2CO_3, K_2CO_3). Na_2CO_3 has been tested for HCl removal in carbon-rich syngas, showing the ability to reduce HCl to as low as 1 ppmv at 400 °C [206].

Alkaline earth metal oxides, which include BaO, SrO, CaO, and MgO, exhibit different adsorption capacities for HCl, with BaO having the highest adsorption capacity, followed by SrO, CaO, and MgO. These sorbents are more effective when they do not transform into their corresponding carbonates [33]. The adsorption of HCl by alkaline and alkaline earth metal oxides plays a crucial role in reducing its concentration in the syngas, thus mitigating issues related to high-temperature corrosion and catalyst deactivation.

5. Developments in biomass gasification

Emerging developments in biomass gasification encompass notable advancements in integrated gasification, supercritical-water gasification, and chemical looping gasification. These concepts hold significant promise as they aim to minimize syngas production costs and enhance the efficiency of gasification systems. This is achieved through the strategic integration of diverse processes, showcasing their potential to revolutionize the field.

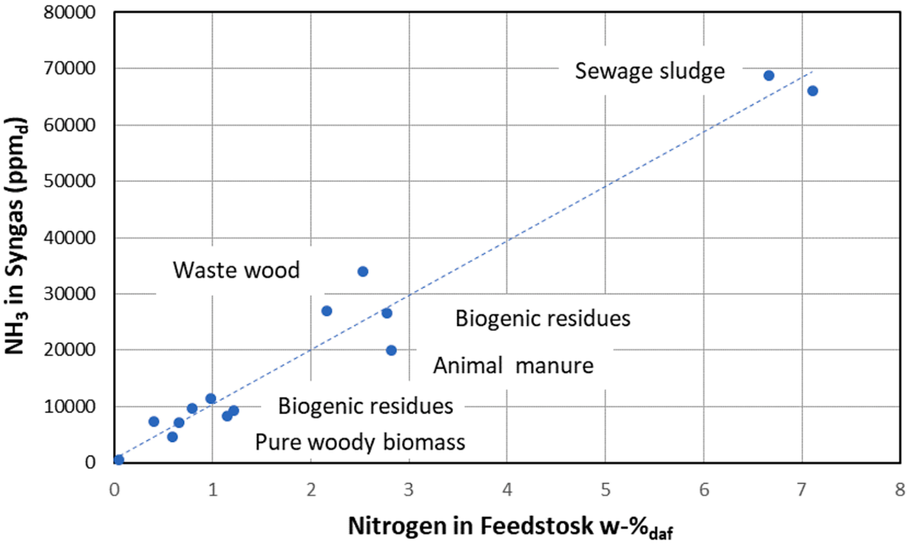

Fig. 9. NH_3 content in the dry syngas dependent on the nitrogen content in the feedstock ash-free [38].

5.1. Progress in gasification technologies for a cleaner syngas

5.1.1. Integrated processes

Syngas cleaning and conditioning in fluidized bed gasification plants typically occurs downstream of the gasifier, applying additional equipment specially designed for this purpose. This process involves the deployment of filters and catalysts at temperatures lower than the gasification temperature [216]. The integrated process concept, illustrated in Fig. 10, introduces an advanced approach by consolidating the fluidized bed gasifier with the hot syngas conditioning and cleaning systems within a unified structure. This approach enables the concurrent reduction of particles and tar through a synergistic amalgamation of filters and catalysts. These catalytic filters are strategically positioned within the freeboard of the gasifier [39,43]. Moreover, synthesized sorbents are introduced alongside the bed material to effectively eliminate traces of elements such as H_2S, HCl, and alkalis, thereby preventing catalyst deactivation [217].

The integrated process concept was initially documented through two patents and extensively investigated within various European projects (NOVACAT, PYROCHAR, UNIQUE, UNIFHY) [217,218]. These initiatives encompassed a range of scales, spanning laboratory, pilot, and industrial applications, thanks to collaborative efforts involving numerous research institutions and private enterprises across Europe [38,43,216,219].

On a laboratory scale, Rapàgna et al. [220] and D'Orazio et al. [221] tested catalytic filters by placing a candle filter in the freeboard of a fluidized bed gasifier. Their studies reported remarkable improvements, including dry gas yield enhancements of 70 % to 100 %, nearly complete elimination of gas-borne particle content at the gasifier exit, and reduction of total tar content to as low as 0.14 g/Nm^3. This tar content was significantly lower than that observed without the use of a catalytic filter (6 g/Nm^3).

In actual operational conditions, Gallucci & Foscolo [219] and Heidenreich & Foscolo [43] integrated a catalytic candle filter featuring nickel compounds as catalytic elements within the freeboard of the dual fluidized bed gasifier known as "Güssing" [222]. This filter incorporated a preheated nitrogen feedback mechanism to periodically dislodge dust cake adhered to the outer candle surface, thus preventing substantial pressure drops across the filter. Consequently, particle content accompanying the syngas at the gasifier exit was reduced by approximately 50 %, accompanied by a substantial decrease in tar levels (approximately 95 %) and a slight reduction in methane content (from 10.1 to 8.1 %).

The integration of the syngas cleaning and conditioning system into the fluidized bed gasifier can significantly curtail investment costs associated with gas cleaning and conditioning equipment. As a result, implementation and energy production costs for biomass gasification plants can be lowered, rendering the generated kWh competitive with other energy sources. Notably, this approach offers the dual advantages of renewability and minimal environmental impact. In sum, the integrated process gasifier concept for cleaning and conditioning hot gas constitutes a tangible contribution to the overarching goal of reducing the cost of electricity derived from advanced biomass power generation systems [216].

Moreover, other works explore integration with other types of technologies. For instance, Freda et al.[223] investigated the gasification of hazelnut shells grains using air as a gasifying agent at 800 °C in a bench-scale rotary kiln. The authors directly treated the producer gas in a thermal cleaning unit operating at 800–1100 °C to reduce contaminants. Results showed that at high temperatures, CO_2 reacted with tar and particulates to produce CO, enhancing the producer gas quality in terms of heating value, yield, and contaminants content. Benzene, the most abundant organic contaminant, was significantly reduced by thermal treatment. This study integrated a bench-scale rotary kiln gasifier with lignocellulosic biomass feedstock with a thermal cleaning

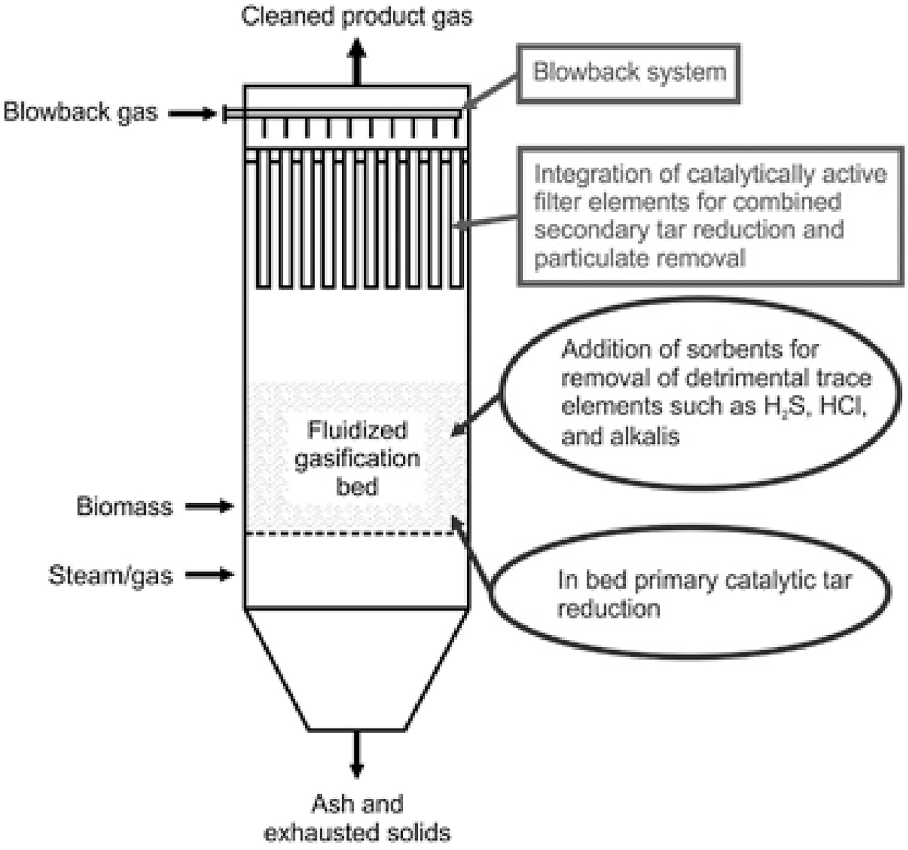

Fig. 10. Scheme of the integrated process gasifier concept [216].

unit, demonstrating the suitability of rotary kilns for air gasification and thermal integration. The authors also state that their approach could be applied with other gasifier types, but further research is needed to understand contaminant removal mechanisms and optimize operational conditions, considering biomass feedstock variations.

Modular or small-scale facilities and systems represent good options for reducing the cost and risk often associated with biomass gasification projects, particularly those interested in producing power, renewable gases, biofuels, and chemicals [224]. Integrated and intensified gasification/cleaning processes fall into this category. In this framework, Frilund et al. [225], presented an innovative low- to medium-temperature final gas-cleaning process based on the adsorption and organic solvent-free scrubbing methods. The developed system was coupled to a bubbling-fluidized bed gasifier with a hot filter, a reformer, and a downstream FT system. More recently the same group confirmed the feasibility of its cleaning concept in a pilot-scale fixed-bed gasification unit to obtain ultraclean syngas for the FT synthesis [226]. Their results proved efficient impurities removal (e.g., ammonia, benzene, H_2S, COS, and HCN) during the scrubbing and adsorption steps, which preserved the performance of the Cu-based catalyst during long-term stability tests. Barisano et al. [227] proposed a novel and intensified steam/oxygen biomass gasification process, integrating directly into the reactor freeboard of a bundle of ceramic candles for high-temperature syngas cleaning. This system benefits from the integration of steam/oxygen gasification and hot gas cleaning into a single compact fluidized-bed unit. Later work by these authors [228], focused on coupling a prototype gasification plant based on this concept to a portable purification system for the generation of high-purity hydrogen (fuel cell vehicle grade, 99.99 % vol. H_2).

Other researchers applied the intensified gasification methodology to upgrade syngas into SNG. An interesting study by Bartik et al. [229], compares different integrated routes for SNG production, based on the combination of three main processes, namely, direct methanation of the gasification syngas, a hybrid process with hydrogen addition to the syngas, and the methanation of the H_2-rich gasification syngas with *in situ* CO_2 removal (SER concept). The choice of the optimal SNG production pathway is likely dependent on the SNG final end-use but the specific context of the production facility must also be considered, i.e., location –greenfield or brownfield-, availability of renewable hydrogen and electricity on site or nearby, sustainability, etc. Overall, additional upgrading is required to produce SNG with quality standards for grid injection, although gasification with H_2 addition and the SER configuration may offer better economic perspectives.

In line with the above strategy, the European project HYFUELUP (*Hybrid Biomethane Production from Integrated Biomass Conversion*) [230] aims to demonstrate, at a pre-commercial scale (TRL 7), an innovative pathway for efficient and cost-effective SNG production, by integrating a Sorption Enhanced Gasification (SEG)/Oxy-SEG technology, gas cleaning and fluidized-bed methanation. The integrated process results in syngas with a high H_2 content (>65 %) and a CO_2-rich flue gas suitable for catalytic methanation.

Another emerging strategy, particularly explored in the Integrated Gasification Combined Cycle (IGCC), involves integrated gasification-membrane cleaning technologies as an alternative to chemical and physical gas–liquid absorption and cryogenic separation methods [231,232]. The utilization of membrane technology in IGCC plants takes advantage of the high-pressure syngas, which increases the efficiency and decreases the costs of the overall process. In this regard, a techno-economic and environmental analysis of membrane separation technology for selective CO_2 separation in a gasification power facility is reported in [231]. The study compares the application of a membrane unit for CO_2 capture before the combined cycle gas turbine (single membrane approach) with the implementation of a hybrid system comprising a CO_2-selective membrane placed at the top of the chemical scrubber (combined membrane chemical gas–liquid absorption approach). The membrane technology has proven economic, and environmental benefits compared to traditional chemical and physical absorption methods, such as lower CAPEX and OPEX (~10 %), a reduction of about 7 % of the electricity production costs, and lower CO_2 capture costs (down to 50 %). Among the two considered options, the single membrane configuration provided higher benefits. Moreover, the work by Das et al. [232] focuses on the integration of the ion transport membrane technology (ITM) with conventional IGCC as a novel and effective approach to producing sustainable energy. ITM is coupled to the gasification unit to decrease energy loss in the air separation system while increasing the overall efficiency of the power generation unit. The ITM configuration outperforms conventional cryogenic air separators in terms of net efficiency. According to the authors, the efficiency of the power plant facility can be further improved through the integration of a CO_2 capture unit. Recent developments concerning the coupling of membrane technologies to gasification systems have also been reported by Malsegna et al. [233]. This study examined the technical feasibility of integrating a 5-column sorption-enhanced water gas shift (SEWGS) pilot unit in a waste gasification plant for the generation of fuel cell-grade hydrogen. Their proposed configuration enables the production of high-purity H_2 (99.5 %) although it does not meet the strict specifications for direct use in fuel cells, requiring additional purification for this purpose. However, the novel integrated system shows potential for simultaneous carbon capture (CO_2 purity of 99.9 %) and renewable high-purity H_2 generation.

5.1.2. *Supercritical-water gasification*

Supercritical water gasification (SCWG) is a thermochemical process that converts biomass into H_2 and CO_2 by means of catalytic cracking and steam reforming under supercritical-water conditions ($T \geq 374.2\ ^\circ C$, $P \geq 22.1$ MPa) [234,235]. In these conditions, water acts as an oxidant and reacts with biomass [236], resulting in a steam-reforming reaction that yields H_2, CH_4, CO, and CO_2. Subsequently, homogeneous gas–gas reactions take place, resulting in the generation of H_2 and CO_2 [237,238]. This process involves the use of water as both the reaction and reagent medium, thus obviating the need to dry the raw material before the process. This results in a significant reduction in energy consumption [239]. Consequently, this technique holds great promise for the gasification of biomass with high moisture content [235]. Furthermore, it can achieve high biomass conversion rates (up to 100 %), high volumetric hydrogen content in final gaseous products (≥50 %) and produce no tar or other by-products [240]. Achieving these high yields requires the optimization of several parameters, including the operating temperature, operating pressure, reagent concentration, and reaction time [241].

According to Lee et al. [242], several review papers investigated SCWG. These papers are dedicated to studying conversion pathways of model compounds and specific biomass into gaseous products, degradation pathways of biomass model compounds, catalyst types employed in this process, reaction mechanisms, and the impact of process parameters on gasification efficiency, design strategies and operational hurdles encountered in laboratory-scale continuous flow reactors. Nonetheless, there is still a limited number of works examining real biomass, microalgae, sewage sludge, and industrial wastewater as feedstock sources. Moreover, significant advancements have been achieved in this process, particularly regarding reactor configurations (e.g., diamond anvil cell autoclaves batch reactor, quartz capillaries batch reactor, micro-tuber reactor, tubular and hybrid reactors, Y-shape reactor, and bubbling fluidized bed reactor) [243].

Given the current European focus on hydrogen production, SCWG presents an intriguing avenue due to its effectiveness in generating hydrogen. Chen et al. [243], studied SCWG from various angles, including thermodynamics, economics, and environmental impact. The authors reveal that there is still a significant need to enhance reaction temperature, slurry concentration, and heat transfer efficiency to improve overall process energy efficiency. The study also demonstrates that SCWG shows moderate environmental impact on hydrogen production but lacks significant advantages over alternative methods, leading to the need for further optimization of SCWG technology to align with the demand for sustainable, cost-effective, and efficient hydrogen production.

The high costs associated with SCWG represent an important limitation towards its commercialization. A strategy to overcome this issue and improve the cost-efficiency of this process is the integration of SCWG with other technologies [244]. The Dutch company SCW Systems is the global leading SCWG developer with the largest industrial installation capable of processing up to 16 tons of feedstock per hour. This technology presents different levels of maturity around the world. For instance, in Europe SCWG developers have built different types of plants, including prototypes (TRL≤4), pre-industrial units (TRL 4–6), and demonstrators (TRL 7–9). SCWG facilities are operating continuously in Germany, France, Spain, the Netherlands, and Switzerland [235]. SCWG is becoming a key technology for the generation of renewable gases, as such, it is attracting increased attention from academia and industry with initiatives projected in several European countries for the coming years [245]. The potential to scale up this technology is very large in the medium term.

5.1.3. *Chemical looping gasification*

Chemical looping gasification involves the utilization of lattice oxygen in oxygen carriers (OC) for the gasification of biomass [246]. The oxygen carriers employed must adhere to certain general principles, exhibiting diverse oxide states to facilitate redox reactions, low activation energies for association/dissociation reactions, robust abrasion resistance, high redundancy for prolonged use, non-toxicity, and cost-effectiveness [247].

Numerous combinations of raw materials and oxygen carriers are conceivable for testing, including rice husk with Fe-based OC [248], sawdust with manganese OC and iron ore [249], lignocellulosic biomass with Fe_2O_3 OC, biomass with pristine/doped brownmillerite, biomass with Fe_2O_3/Al_2O_3 OC or microalgae biomass with perovskite OC La-Fe-O [201]. Nevertheless, iron oxide is commonly employed as an oxygen carrier due to its advantages over other precious metal oxides [247].

In-depth knowledge of reaction mechanisms is crucial for enhancing the design and operation of the loop chemical gasification process. Yan et al. [250] estimated the activation energy of the chemical looping gasification process to be within the range of 81.6–140.9 kJ/mol, indicating the preferential role of oxygen carriers as catalysts. The loop chemical gasification process introduces additional control and maintenance costs compared to direct gasification.

The key advantages of loop chemical gasification include the minimal energy loss during the process and the reduced separation costs associated with the syngas obtained post-production, as most of the N_2 is excluded from the air stream to mitigate dilution effects [247]. The economic viability of biomass loop chemical gasification can be further enhanced by obtaining value-added end products. However, it is essential to acknowledge that the use of loop chemical gasification involves the consumption of the reduced products obtained in the syngas to recycle the spent oxygen carriers, consequently reducing the syngas yield [251].

5.1.4. *Carbon capture technologies: CO_2 removal and high-value products*

In the transition to a net zero energy system, carbon capture (CC) technologies are gaining increased relevance. The implementation of CC technologies in biomass gasification plants contributes to lowering their carbon footprint, turning gasification-based processes into more environmentally friendly routes [252,253]. Carbon Capture Storage and Utilization (CCSU) technologies allow for the simultaneous removal and conversion of CO_2 into renewable high-value products, like methane, methanol, and liquid fuels, facilitating the decarbonization of some high-emitting sectors, such as transportation, heating-and-cooling, and chemical industry.

Syngas conversion to renewable fuels and chemicals include methanation, methanol synthesis, and FT processes. Although in some specific cases, a small amount of CO_2 (<10 vol% dry basis) in the syngas can be beneficial [254,255], for most of these syngas conversion processes CO_2 must be removed to increase product purity, improve reaction kinetics, and prevent catalyst deactivation [224,256–257]. Moreover, CO_2 is often removed from the syngas to decrease the volume of the syngas enabling the use of smaller equipment. Adjustment of the H_2-to-CO ratio in syngas via WGS or by adding extra hydrogen is also required [258].

In the case of gasification facilities, CO_2 capture is easier and cheaper to implement compared to other sectors because of the high pressure of the obtained syngas, which leads to higher CO_2 concentration levels [224]. Captured CO_2 can be used on-site to synthesize high-value products, as indicated previously, but it can be also sold generating additional revenues. Applications of CO_2 comprise building materials, carbonated beverages, mineralization of hard water, flame retardants (fire extinguishers), and pneumatic gas in pressure-based tools and mechanisms.

Gasification-CC coupling can provide not only environmental gains but also economic benefits, although deep research and demonstration of these processes are still needed, some works have been recently published on this topic. For instance, a comparative analysis of forestry residue utilization routes, including combined heat and power (CHP), gasification, and hydrothermal liquefaction (HTL), to produce liquid biofuels is reported in [259]. The greenhouse gas (GHG) reduction potential of CHP, HTL, and gasification with CCS or CCU (Carbon Capture and Utilization) using a consequential life cycle analysis (LCA) approach is assessed in this study. The CCU approach shows the highest potential for GHG savings if hydrogen comes exclusively from renewable electricity. CCS routes are much less affected by variations in the electricity mix, and all show emissions reductions. Interestingly, in a renewable electricity scenario, gasification coupled with CCU exhibits the highest GHG reduction potential. Biomass gasification combined with CC technologies has been mostly investigated for renewable hydrogen production. This is an efficient path to obtain renewable hydrogen, and since it can generate net-negative CO_2 emissions, it is a cleaner process than the state-of-the-art route of water electrolysis [260–262]. However, this approach can be also applied to the synthesis of fuels and chemicals. Methanol is one of the most-traded chemicals produced globally, therefore, innovative strategies aimed at reducing the emissions of traditional methanol synthesis based on fossil fuels will have a major impact on reaching the zero-emission target. In this context, biomass gasification-to-methanol is a topic of research interest. Bobadilla et al. [263], reviewed the conversion of biogenic wastes into biomethanol employing a combination of developed and innovative technologies, involving gasification, microchannel reactors, and membranes. The authors conclude that this technological approach is a sustainable and cost-effective way for biomethanol production. Obtaining the suitable H_2-to-CO ratio represents a challenge to produce methanol from biomass, as the gasification syngas has a low H_2-to-CO ratio (typically < 1) and cannot be directly utilized for methanol synthesis (H_2-to-CO at least 2) and conventional routes involving WGS often results in complex processes. In recent work by Liu et al. [264], CCU technologies combined with sorption-enhanced biomass gasification are proposed as a means to produce tunable syngas for methanol synthesis.

As previously reported throughout this work, biomass gasification is also being studied for the generation of SNG, but this process requires H_2-to-CO ratios even higher than those employed for the methanol synthesis, thus, strategies to increase the H_2 content in the syngas gasification are essential. CO methanation requires a theoretical H_2-to-CO ratio of 3:1, but higher values lead to increased CO conversion and CH_4 selectivity while reducing carbon deposition. Like the methanol synthesis, WGS and the addition of external hydrogen can be used to enhance the H_2-to-CO ratio. Ruggiero et al. [265], have recently conducted a thermodynamic analysis to study the influence of working conditions and the composition of gasification syngas on the production of SNG. The combination of steam gasification and catalytic methanation with a steam-to-biomass ratio of 0.3 provides the best results in terms of yield and quality of SNG, but additional hydrogen feeding is always required. Giglio et al. [266] studied and modeled two different configurations based on the integration between biomass gasification, solid oxide electrolysis (SOEC), and catalytic methanation for SNG production. This study also explores the integration of a WGS reactor and a CCS unit to adjust the syngas composition. The SOEC-coupled-gasification comprising the WGS/CCS system outperforms biomass gasification in terms of SNG production.

Biomass gasification in combination with CC technologies represents a promising approach for the generation of added-value products, such as hydrogen, methane, and methanol. However, more research to develop innovative solutions is needed to pave the way for the deployment of these technologies, which will a key role in decarbonizing energy.

5.2. Advancements in syngas cleaning strategies

In recent times, there have been several efforts to improve and develop strategies for enhancing the quality of syngas produced from biomass gasification, concerning both primary and secondary processes for cleaning syngas [267]. Furthermore, several pre-treatments such as torrefaction, water washing, and alkali impregnation can be applied to minimize harmful gas emissions and tar formation during gasification [268].

Torrefaction of biomass waste before gasification has shown benefits such as reducing moisture content and particle size, while torrefied biomass has shown increased production of H_2 and CO during gasification [269]. Additionally, torrefied biomass requires less energy to be converted in the gasification process, resulting in a syngas with fewer tars and improved fuel properties [270].

Zhao et al. [271] applied a water washing pretreatment in the raw biomass to obtain lower alkali metal content and a decrease in tar yield on the syngas. On the other hand, Umeki et al. [272] reported the reduction in tar and soot formation by the impregnation of K_2CO_3 on biomass samples prior to gasification, indicating that potassium inhibited the growth of PAHs and promoted the composition of light tar.

The co-gasification of biomass with other waste streams is another potential pathway to reduce contaminants release, avoid tar formation, and enhance combustible gas yield. Saini et al. [273] reported a higher H_2 and CH_4 production with a reduction in CO_2 yield after the co-gasification of biomass waste with lignite. Qi et al. [274] suggested the co-gasification of biomass and MSW improved syngas quality and reduced environmental pollution of MSW management. Erdem et al. [275] also pointed out the improvement in H_2 yield and the increase in the syngas calorific value after the co-gasification of biomass and plastic waste.

Tar reforming using biochar as a catalyst has gained more attention recently due to the high adsorption capacity of biochar after activation associated with the low-cost. As a by-product of the gasification process, biochar as a catalyst appears as an inexpensive and sustainable way to enhance the syngas composition and increase the process efficiency. Much research has been focused on tar removal from syngas using biochar produced from biomass wastes with metal catalysts impregnation [193]. Liu et al. [276] reported increased generation gas product and higher H_2 yield derived from tar destruction and hydrocarbon reforming through the synergetic effect of steam and K-biochar catalyst on syngas upgrading. Furthermore, Frilund et al. [225] reported reducing in the syngas contaminants with the complete elimination of H_2S and COS by the catalytic effect of activated biochar with a ZnO-based absorbent. Singh et al. [277] achieved high removal of smaller aromatic compounds, which leads to the risk of clogging in downstream equipment, during tar reforming by applying an integrated two-step process using biochar from gasification of malle wood chips. One approach to boost the catalytic effect of biochars on tar removal and increase H_2 yield relies on partial oxidation, which can minimize pore block for the coke particles avoiding catalyst deactivation [278]. The use of waste-derived catalysts supported on spheres of γ-Al_2O_3 is an interesting strategy to reduce syngas treatment costs as well as promote a valuable alternative to waste valorization [193]. Peck et al. [279] demonstrated high naphthalene conversion (78 %) into syngas using a nickel-based catalytic filter on ceramic support which acted as both a particulate filter and tar reformer. Medeiros et al. [280] observed a high CO_2 conversion and an increase in H_2/CO after one-step upgrading of the flue gas over alumina-based catalysts. Chan et al. [35] also demonstrated a 90 % removal efficiency in tar and sulfur and a 14 % increase in total syngas yield by a nano-structured nickel catalyst support on alumina during tar reforming of hot syngas from MSW gasification.

Recently, the above-mentioned NTP approach has gained more attention in tar removal from syngas since it promotes tar cracking with lower energy consumption compared to the thermal plasma process and avoids costs with catalysts. However, the syngas upgrading by NTP can be combined with catalysts to enhance conversion in a process named "catalytic assisted non-thermal plasma", which increases tar removal and adds costs with catalysts that may be justified from an economic perspective [267]. Sasujit et al. [281] found that non-thermal plasma was responsible for a maximum removal efficiency of 85 % for naphthalene, whereas Sallen et al. [282] obtained a maximum removal of toluene of 89 % using a dielectric barrier discharge (DBD) reactor using N_2 as a carrier gas. In addition, Sallen at al. [283] reported the high decomposition of benzene (82.9 %) with H_2 and light hydrocarbon production using CH_4 as a carrier gas. The catalytic-assisted non-thermal plasma process was also described to promote CO_2 conversion in fuel and chemicals with enhanced value in DBD reactors with moderate reaction conditions [284].

Achieving high tar removal and syngas upgrading depends on several parameters that drive the biomass conversion in the gasification process and the combination of primary and secondary methods may lead to enhanced syngas cleaning. It is worth noting that the viability of applying one or more syngas cleaning methods relies on the feedstock properties and gasification conditions and must be supported by techno-economic and LCA studies to assess its economic and environmental feasibility.

6. Demonstration and commercial scale of syngas cleaning systems

In numerous commercial applications, the integration of wet and dry-cleaning methods yields high-performance, low-temperature solutions for the removal of tar. A pertinent illustration of this on a commercial scale is exemplified by the downdraft gasification facilities of the Indiana-based company ANKUR [285]. This company offers an array of solutions for generating modest-scale electrical and thermal energy across a wide spectrum of capacities. For syngas cleaning, they employ a blend of wet and dry-cleaning techniques, encompassing cyclones, wet scrubbers, and diverse filters.

The syngas stream traverses a cyclone situated at the outlet of the gasifier to set up the elimination of larger particles (such as ash and coal), following which it is directed to a Venturi-type wet scrubber dependent on water. This scrubber removes particles, tar, and other impurities. Subsequently, moisture is extracted from the gas and channeled into a filtration system, as depicted in Fig. 11 [286]. The filtration arrangement has three or more stages, with the initial stages employing sand, sawdust, or carbon as filter media, culminating in a fabric filter. This purification regimen ends in a tar and particulate content below 25 mg/Nm^3, meeting the required purity for employment in ICE. However, the utilization of water for cleaning yields substantial quantities of tar-laden wastewater, approximately 0.6 kg per kilogram of biomass [39]. Consequently, the need for a multifaceted and costly wastewater treatment and refinement system emerges as the main drawback of this

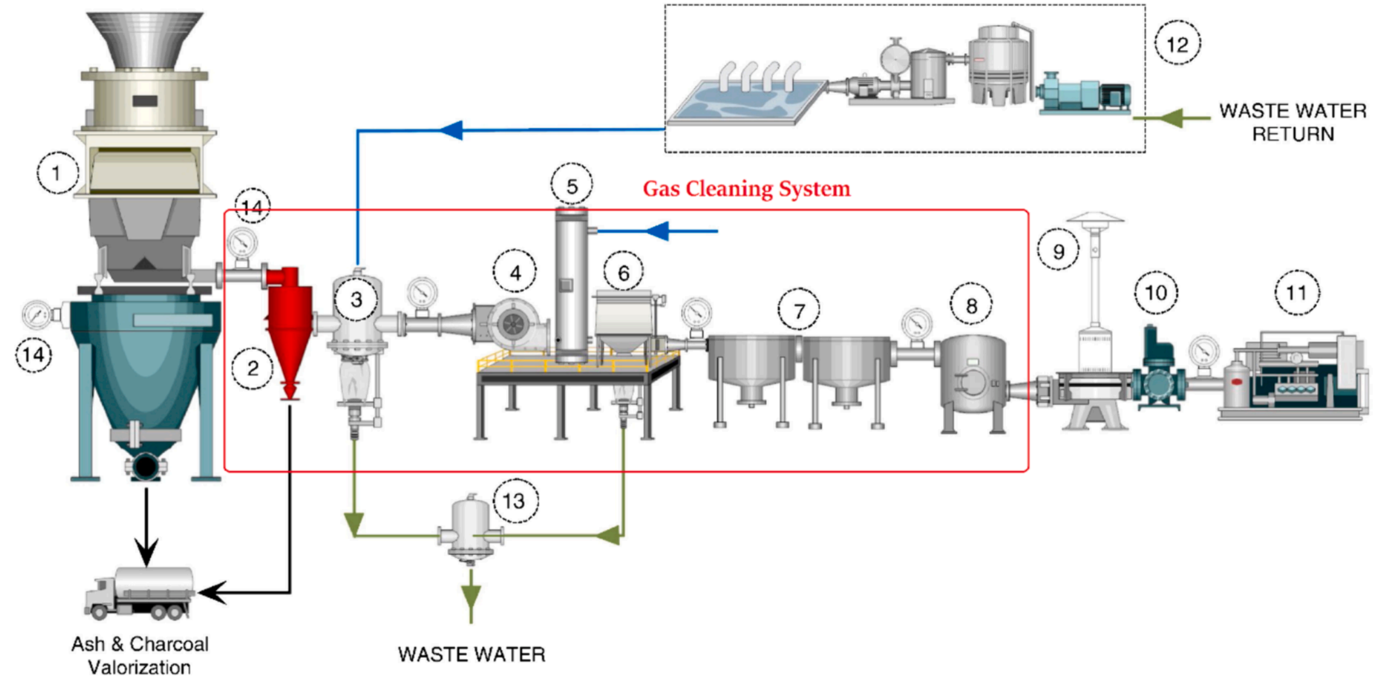

Fig. 11. Scheme for the ANKUR gas cleaning system with cyclone, water-based tar Venturi scrubber and filter system: 1. gasifier; 2. cyclone and ash collection box; 3. Venturi scrubber and drain box; 4. wet blower; 5. heat exchanger; 6. mist eliminator; 7. fine filters; 8. pleated filter; 9. flare; 10. header box; 11. gas engine; 12. waste water treatment; 13. combo tank; 14. different pressure points. [286].

cleaning technology.

Another technology harmonizing wet and dry-cleaning methodologies has been pioneered by the Center for Energy Research in the Netherlands (now TNO, previously known as ECN) [78]. This system encompasses a cyclone, oil-based multi-stage wet scrubbers (OLGA), and water-based wet scrubbers [287]. Operating within the temperature range of 60 to 450 °C, this technology achieves an efficacy exceeding 99 % in purging contaminants from raw syngas, surpassing conventional water scrubbers operating at efficiencies ranging between 49 to 79 %. Comparable superiority is demonstrated even against Wet-ESP, which attains a peak efficiency of 99 % for the heaviest contaminants and up to 74 % for lighter impurities [33,34,39]. The OLGA technology is established into four pivotal stages, as depicted in Fig. 12. The initial stage involves the passage of gas through a cyclone that exploits centrifugal force to effectuate the removal of the largest particles. Subsequently, the syngas is cooled in the second stage (the collector) by means of scrubbing oil. The heaviest contaminants, including tars comprising more than three rings and fine particles, undergo condensation and separation from the scrubbing oil via filtration. These components are then introduced into the gasifier along with the biomass [34,39]. In the third stage, the scrubbing oil assimilates lighter contaminants, mainly tar compounds with one to two rings, within the absorber. The oil laden with light tars undergoes regeneration in the stripper, allowing for the recuperation of approximately 99 % of the oil employed in the gas purification process. The light tars are co-fed with the gasifying agent into the reactor. A valuable side of the OLGA process is the potential for recycling both light and heavy tars back into the gasifier, thereby enhancing the energy efficiency of the technology [78]. Furthermore, this process has minimal impact on the lighter components such as CH_4, CO, and H_2. Nonetheless, a notable disadvantage pertains to the elevated costs associated with oil-based absorbents. It is noteworthy to mention that the OLGA technology is presently accessible in the commercial domain [39].

7. Concluding remarks

Biomass is gaining prominence as a viable energy source that can help balance energy supply and demand worldwide. Gasification stands out as a key technology for converting biomass into versatile fuel gas suitable for fuel and chemical synthesis. However, the raw syngas

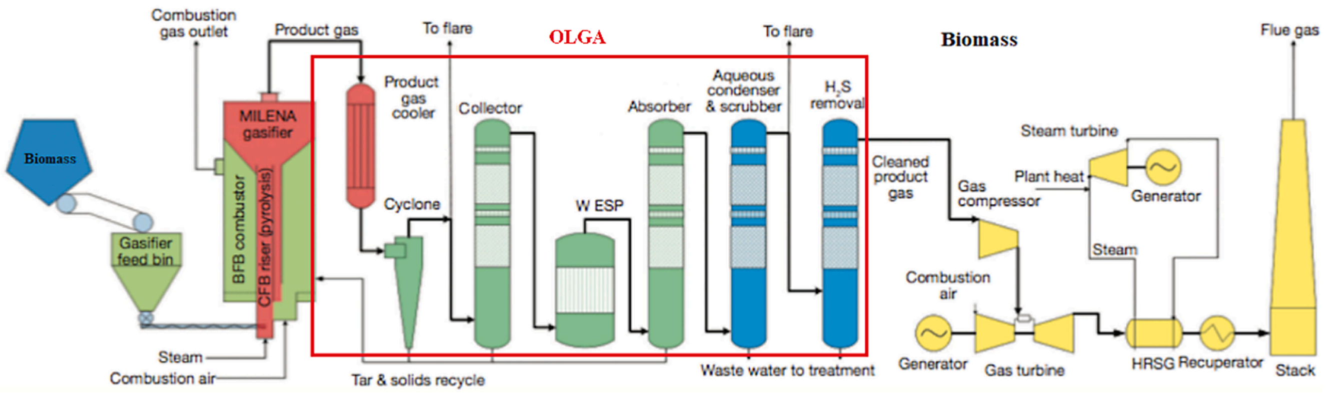

Fig. 12. Syngas cleaning with heat exchanger and OLGA system at the Güssing Plant [288].

produced through gasification contains impurities, needing effective purification and conditioning to make it viable for its numerous applications. This work discussed the status, advancements and challenges in biomass gasification, specifically regarding syngas cleaning strategies, shedding a light on technological developments from each syngas contaminant, to gasification systems that can deliver cleaner syngas.

Wet gas cleaning (WGC) and dry gas cleaning (DGC) are the two main methods for syngas purification. WGC, often using water in wet scrubbers, is cost-effective and straightforward but comes with challenges such as reduced efficiency from cooling and high costs associated with effluent treatment. One very prominent approach within WGC is the oil-based OLGA system, which reintegrates waste materials into the gasifier, offering both economic and environmental benefits. On the other hand, DGC processes contaminants at high temperatures, presenting energy and environmental advantages. This method includes physical–mechanical, thermal, and catalytic treatments to eliminate particulates, tar, and acid gases. Technologies like cyclones, filters, and dry scrubbers effectively remove particulates, while thermal cracking and catalytic treatments convert tars and adjust gas composition. However, these methods face challenges such as reduced catalytic activity, catalyst poisoning, and operational complexity.

Recent advancements in syngas cleaning have focused on both primary and secondary methods. Primary methods minimize tar formation during gasification by controlling operational parameters, while secondary methods treat the produced gas. Pre-treatments such as torrefaction, water washing, and alkali impregnation have shown promise in reducing emissions and tar formation. For instance, torrefied biomass requires less energy for gasification, resulting in higher H_2 and CO production with fewer tars. The co-gasification of biomass with other waste streams also shows potential in reducing contaminants and enhancing syngas quality, with demonstrated improvements in H_2 and CH_4 production and reduced CO_2 yield when co-gasifying biomass with lignite, MSW, or plastic waste. Innovative strategies like using biochar as a catalyst for tar reforming have also gained attention due to biochar's high adsorption capacity and low cost. In addition, non-thermal plasma (NTP) technology is emerging as an efficient method for tar removal, offering lower energy consumption and cost savings compared to traditional thermal plasma processes.

As for recent developments in the gasification technology that allow for a cleaner syngas, the integrated gasification concept, which optimizes gasification by combining multiple treatment methods both *in situ* and downstream, presents itself as a promising concept also as a retrofitting concept. Supercritical water gasification (SCWG) and chemical loop gasification are also promising. SCWG, which uses water as both a reaction medium and reagent, is effective for biomass with high moisture content, achieving high conversion rates without tar generation. Chemical loop gasification employs redox reactions with iron oxide, offering strong abrasion resistance and cost-effectiveness but requires additional control and maintenance.

Moreover, carbon capture technologies (CC) are gaining relevance in the transition to a net-zero energy system. Implementing CC technologies in biomass gasification plants reduces their carbon footprint, making gasification processes more environmentally friendly. These technologies enable the simultaneous removal and conversion of CO_2 into renewable high-value products like methane, methanol, and liquid fuels, aiding the decarbonization of high-emitting sectors such as transportation, heating and cooling, and the chemical industry. Syngas conversion to renewable fuels and chemicals, including methanation, methanol synthesis, and Fischer-Tropsch processes, requires CO_2 removal to enhance product purity and reaction kinetics. Therefore, gasification facilities find CO_2 capture easier and cheaper due to the high pressure and CO_2 concentration in syngas. Also, this captured CO_2 can be used on-site for high-value products or sold, generating additional revenue. Overall, biomass gasification combined with advanced cleaning and carbon capture technologies holds significant promise for sustainable energy production. While challenges remain, ongoing research and technological advancements are paving the way for more efficient, economically viable, and environmentally friendly gasification processes. These developments are crucial for achieving a decarbonized energy future.

CRediT authorship contribution statement

J.R.C. Rey: Writing – original draft, Investigation, Data curation, Conceptualization. **A. Longo:** Writing – review & editing. **B. Rijo:** Writing – review & editing, Validation. **C.M. Pedrero:** Writing – review & editing. **L.A.C. Tarelho:** Writing – review & editing, Supervision, Conceptualization. **P.S.D. Brito:** Writing – review & editing, Supervision, Conceptualization. **C. Nobre:** Writing – review & editing, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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