

# A comprehensive review of primary strategies for tar removal in biomass gasification

M. Cortazar<sup>a</sup>, L. Santamaria<sup>a</sup>, G. Lopez<sup>a,b,\*</sup>, J. Alvarez<sup>c</sup>, L. Zhang<sup>d</sup>, R. Wang<sup>d</sup>, X. Bi<sup>d</sup>, M. Olazar<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644, E48080 Bilbao, Spain

<sup>b</sup> IKERBASQUE, Basque Foundation for Science, Bilbao, Spain

<sup>c</sup> Department of Chemical and Environmental Engineering, University of the Basque Country UPV/EHU, Nieves Cano 12, 01006 Vitoria-Gasteiz, Spain

<sup>d</sup> Department of Chemical and Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver V6T 1Z3, B.C., Canada

## ARTICLE INFO

### Keywords:

Biomass  
Gasification  
Primary strategies  
Tar removal  
In situ catalysts  
Reactor design

## ABSTRACT

In the current energy scenario, the production of heat, power and biofuels from biomass has become of major interest. Amongst diverse thermochemical routes, gasification has stood out as a key technology for the large-scale application of biomass. However, the development of biomass gasification is subjected to the efficient conversion of the biochar and the mitigation of troublesome by-products, such as tar. Syngas with high tar content can cause pipeline fouling, downstream corrosion, catalyst deactivation, as well as adverse impact on health and environment, which obstruct the commercialization of biomass gasification technologies. Since the reduction of tar formation is a key challenge in biomass gasification, a comprehensive overview is provided on the following aspects, which particularly include the definition and complementary classifications of tar, as well as possible tar formation and transformation mechanisms. Moreover, the adverse effects of tar on downstream applications, human health or environment, and tar analyzing techniques (online and off-line) are discussed. Finally, the primary tar removal strategies are summarized. In this respect, the effect of key operation parameters (temperature, ER and S/B), catalysts utilization (natural and supported metal catalysts) and the improvement of reactor design on tar formation and elimination was thoroughly analyzed.

## 1. Introduction to biomass gasification

Since the Industrial Revolution, fossil fuels have become the dominant source of energy globally, which has strongly contributed to global warming [1]. Nowadays, three-quarters of the greenhouse gas emissions emerge from the combustion of fossil fuels for power generation [2]. Renewable energy and fuels come to the fore with the aim to reduce CO<sub>2</sub> emissions [3]. EU's 2030 climate target plan proposes to reduce greenhouse gas emissions from energy, industry and transport sectors by at least 55 % by 2023 and become climate neutral by 2050 [4].

Achieving net-zero emissions by 2050 will entail the transformation of the energy structure, in which carbon-neutral or carbon-negative technologies will play a crucial role. Hydrogen is one of the carbon-free energy carriers, as it only produces water after combustion. However, up to now it is far from being the key pillar of the global energy system in decarbonisation. It only represents a modest fraction of the worldwide energy mix and is mainly produced from non-renewable

resources. In fact, hydrogen production was responsible for the emission of 830 million tons CO<sub>2</sub> in the year 2020 [5]. Therefore, the future prospect of the H<sub>2</sub> production technologies is driven by the need to cut down CO<sub>2</sub> emissions, which demands its production from cleaner technologies (electrolysis, fossil fuels with carbon capture, utilization, and storage or bioenergy). In this scenario, the development of hydrogen production from biomass or wastes has been considered as a vital strategy to achieve the European Green Deal [5–7].

Renewable energy will be the key in the decarbonisation of our energy systems in the next decades. In 2019, around 14 % of the global primary energy came from renewable sources, with the share of biomass-based sources including municipal and industrial waste, solid biomass, liquid biofuels and biogas being around 67 % [8]. Thus, sustainable managed biomass stands out as one of the best alternative energy candidates to produce heat, power and biofuels without contributing to a net rise in CO<sub>2</sub> level; that is, the CO<sub>2</sub> emitted during its use is compensated by the carbon stock accumulated during its growing

\* Corresponding author at: Department of Chemical Engineering, University of the Basque Country UPV/EHU, P.O. Box 644, E48080 Bilbao, Spain.

E-mail addresses: [gartzen.lopez@ehu.es](mailto:gartzen.lopez@ehu.es), [gartzen.lopez@ehu.es](mailto:gartzen.lopez@ehu.es), [gartzen.lopez@ehu.es](mailto:gartzen.lopez@ehu.es) (G. Lopez).

<https://doi.org/10.1016/j.enconman.2022.116496>

Received 19 September 2022; Received in revised form 9 November 2022; Accepted 16 November 2022

Available online 1 December 2022

0196-8904/© 2022 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

stage [9].

According to the Directive 2009/28/EC from the European Parliament, published on 23 April 2009, on the promotion of the use of energy from renewable sources [10], biomass is defined as the biodegradable fraction of products, wastes and residues from biological origin such as agriculture (including vegetal and animal substances), forestry and related industries including fisheries and aquaculture, as well as the biodegradable fraction of industrial and municipal wastes.

Biomass can be converted into H<sub>2</sub> or syngas through thermochemical and biological processes. Thermochemical processes use heat to break down the biomass and generate hydrogen, whereas biological processes use several microorganisms, such as bacteria and algae in the presence of sunlight or organic matter. Amongst all the thermochemical routes, gasification is a key technology for the large-scale exploitation of biomass, as it may allow for a more effective conversion of biomass compared to pyrolysis. Generally, biomass gasification takes place at high temperatures (in 700–1200 °C temperature range) and in the presence of gasification agents (air, O<sub>2</sub>, steam, CO<sub>2</sub> or their mixtures). The main product of the process is a gaseous mixture, mainly H<sub>2</sub>, CO, CO<sub>2</sub> and CH<sub>4</sub>. Gasification also produces solid residues (char and/or soot) and other undesired products such, as tar (heavy hydrocarbons). The obtained syngas could be used as fuel for heating and power generation or as an intermediate for the production of other fuels and chemicals, such as methanol, dimethyl ether and ammonia. Moreover, hydrogen-rich syngas can be produced from adsorption enhanced gasification [11,12] or obtained by the further conversion of CO in syngas [13] through water–gas-shift reaction. Fig. 1 shows a scheme for the biomass gasification process.

As mentioned above, different combinations or concentrations of gasification agents are applied in biomass gasification technologies. The use of one or another gasification agent leads to a different composition of product gas, so the choice among them is made based on a balance between the final product gas specification (for downstream application) and process costs [14].

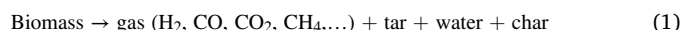
Air is the mostly used gasification agent due to its availability and low cost. It promotes combustion and partial oxidation reactions, supplying the energy required for the gasification process. A typical composition of the air gasification gaseous product is made up of 15 % H<sub>2</sub>, 20 % CO, 2 % CH<sub>4</sub>, 15 % CO<sub>2</sub> and 48 % N<sub>2</sub>, which accounts for a low heating value gas (4–6 MJ Nm<sup>-3</sup>) and moderate char and tar content [15]. Using pure O<sub>2</sub> with steam as the gasification agent has been investigated in order to mitigate the N<sub>2</sub> concentration in syngas. The use of O<sub>2</sub> yields a high quality gas composed of 40 % H<sub>2</sub>, 40 % CO and 20 % CO<sub>2</sub> and negligible tar and char content associated with the higher temperatures reached, which leads to a heating value in the 10–15 MJ Nm<sup>-3</sup> range. However, the operating costs are high due to those involved by O<sub>2</sub> production [16]. Use of pure steam rather than air produces a syngas with high H<sub>2</sub> concentration (of around 40 %) and improves the high heating value of the gas to 15–20 MJ m<sup>-3</sup> range, with the amount of tar generated being moderate. The typical product gas composition obtained in biomass steam gasification is as follows: 40 % H<sub>2</sub>, 25 % CO, 25 % CO<sub>2</sub> and 8 % CH<sub>4</sub>. Nevertheless, the endothermic nature of steam gasification reactions entails additional heat and

thereby, depending on the technology, the process costs increase [15]. According to Karl and Pröll [17], the high H<sub>2</sub> concentration and high heating value syngas obtained in the steam gasification make this technology promising for the conversion of biomass into second generation fuels, such as Fischer-Tropsch diesel, methanol, dimethyl ether (DME) or synthetic natural gas (SNG).

### 1.1. Chemical reactions in biomass gasification

Biomass gasification is a complex process, which involves several elementary gas–solid (heterogeneous reactions) and gas-phase reactions (homogeneous reactions) [18]. Independent of the gasifier configuration, the gasification process consists of the following stages: drying, pyrolysis, oxidation and reduction [19]. In a typical gasifier, drying occurs at temperatures below 150 °C. In this stage, the moisture of the biomass is evaporated, and consequently steam is released. The effect of the drying step on the gasification process is rather limited [20].

The pyrolysis step corresponds to the thermal decomposition (devolatilization) of the dry biomass, generating volatile compounds (mainly CO, H<sub>2</sub>, CO<sub>2</sub>, light hydrocarbons/oxygenates and tar) and char. Biomass pyrolysis reaction is shown by Eq. (1).



In the pyrolysis step products are released from biomass to the gas phase in a series of reactions taking place at temperatures between 150 and 700 °C. This step highly depends on temperature, heating rate, biomass composition and particle size. At temperatures below 600 °C, biomass is initially decomposed into volatiles, char and gas, whereas at higher temperatures tar is cracked (Eq. (2)) or reformed into light hydrocarbons (Eq. (3)), or evolve towards more stable aromatic structures.



The products of the pyrolysis steps react with the externally supplied gasification agent (air, steam, CO<sub>2</sub> or their mixture). In the air blown gasification, the exothermic nature of the oxidation reactions make the temperature rise in the gasifier to 800–1000 °C range. Char and hydrogen are usually the principal reactants, converting rapidly into CO<sub>2</sub> and H<sub>2</sub>O as shown in Eqs. (4–6).



Finally, in the reduction stage, the pyrolysis and oxidation products (gas and char) react to produce the final product stream. H<sub>2</sub>, CO and CH<sub>4</sub> are yielded through water gas shift (Eq. (7)), methane reforming (Eq. (8)), char CO<sub>2</sub> gasification (Eq. (9)) and char steam gasification (Eq. (10)) reactions.

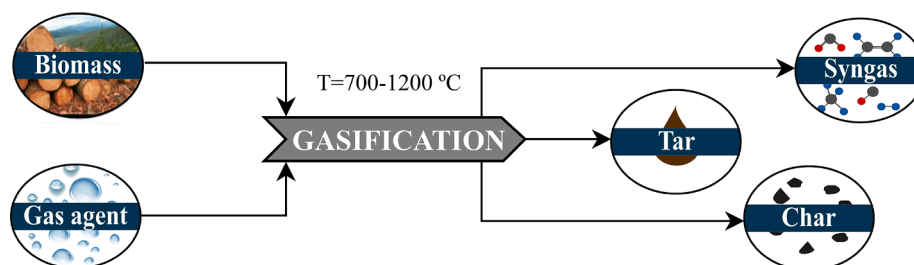
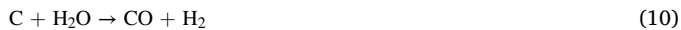


Fig. 1. Schematic representation of the biomass gasification.



Char gasification reaction is the rate-limiting step in the overall gasification process especially when relatively low gasification temperature is selected [21]. This is especially true for  $\text{CO}_2$  gasification, which is between 2 and 5 times slower than steam gasification [22]. Thus, char gasification is the controlling step in biomass gasification, since its reaction rate is much lower than the other reactions involved in biomass gasification [23,24].

## 1.2. Gasification technologies

The gasifier, as the main element of a gasification plant, provides the space for biomass and gasification agent to be mixed to a certain extent, in some cases in the presence of primary catalysts and/or additives. According to Sansaniwal et al. [15], the design of a biomass gasifier depends on the fuel availability, particle shape, size and moisture content, ash content and end user applications. Thus, a large number of gasifiers have been designed, as are fixed bed (updraft and downdraft), fluidized bed (bubbling, circulating, dual and multi-stages), entrained flow, spouted bed or plasma reactors, with the most commonly used being the first three [25]. Fig. 2 illustrates schematically the reactors used in biomass steam gasification.

Fixed bed gasifiers are traditionally used for biomass gasification and they could be classified as updraft and downdraft, depending on the upward or downward flow of the gasification agent [15]. Those gasifiers have a simple and robust design, lead to high carbon conversion rates and long residence time, and operate at low gas velocities, which make them suitable for small-scale heat and power generation applications [25]. In the updraft gasifiers, the gasification agent enters from the bottom, whereas biomass is fed from the top, and therefore the interaction between the biomass and produced volatiles with the gasification agent is in a counter-current mode. Among their strengths, those worth mentioning are high thermal efficiency, small pressure drop and low tendency to form slag. However, they are very sensitive to the biomass moisture content and lead to the formation of high amount of tar and low syngas yield. In the downdraft gasifier, both gasification agent and

biomass flow downwards, which results in a co-current flow. In comparison with updraft gasifiers, downdraft ones produce less tar, and therefore a syngas of much better quality. Nevertheless, they cannot process biomass with low density and high moisture and ash content, and the thermal efficiency is lower than that in the updraft gasifier [26–28]. Although fixed bed reactors involve simple design and, furthermore, the downdraft gasifiers lead to low tar contents due to the catalytic effect of the char, they have obvious drawbacks, such as low and non-uniform heat and mass transfer between the solid biomass and gasification agent within the reactor, which hinder their scaling up, and so applications at large scale [14,29,30].

Fluidized beds are based on the fluidization principles, so the bed particles are brought into dynamic “fluid-like” state when the fluidization medium passes through the bed. This feature provides high mixing and gas–solid contact between phases, increasing the reaction rates and conversion efficiencies. Moreover, heat and mass transfer are enhanced, which enables a high operational flexibility and bed isothermicity [18]. Thus, this technology is more attractive and economical for large-scale applications. Fluidized beds are categorized into two types depending on the fluidization velocity and the bed height: bubbling fluidized beds and circulating fluidized beds. Bubbling fluidized beds operate at low gas velocities ( $1\text{--}3 \text{ m s}^{-1}$ ), which is usually slightly greater than the minimum fluidization velocity, whereas circulating fluidized beds are designed to operate at high gas velocities (between  $3$  and  $10 \text{ m s}^{-1}$ ), which means that the bed material is vigorously fluidized [26]. Thus, the high fluidization gas velocity makes some of the bed material entrained from the reactor, which is captured by a cyclone located at the gas outlet and returned to the bottom of the reactor. Although higher conversion efficiencies have been achieved in circulating fluidized beds than in bubbling ones, both reactors encounter tar and dust related problems due to the short residence time of the volatiles in the reactor [15].

The main features (versatility for using different types of biomass, high heat and mass transfer rates between phases, and bed isothermicity) of fluidized beds for biomass gasification have been well proven in large scale dual fluidized bed (DFB) reactors. The DFB consists of two interconnected fluidized bed reactors: one reactor is used for gasification, whereas the other one is used to produce the heat required for the gasification process through char combustion [31–34]. The heat generated is transported to the gasification chamber by circulating the

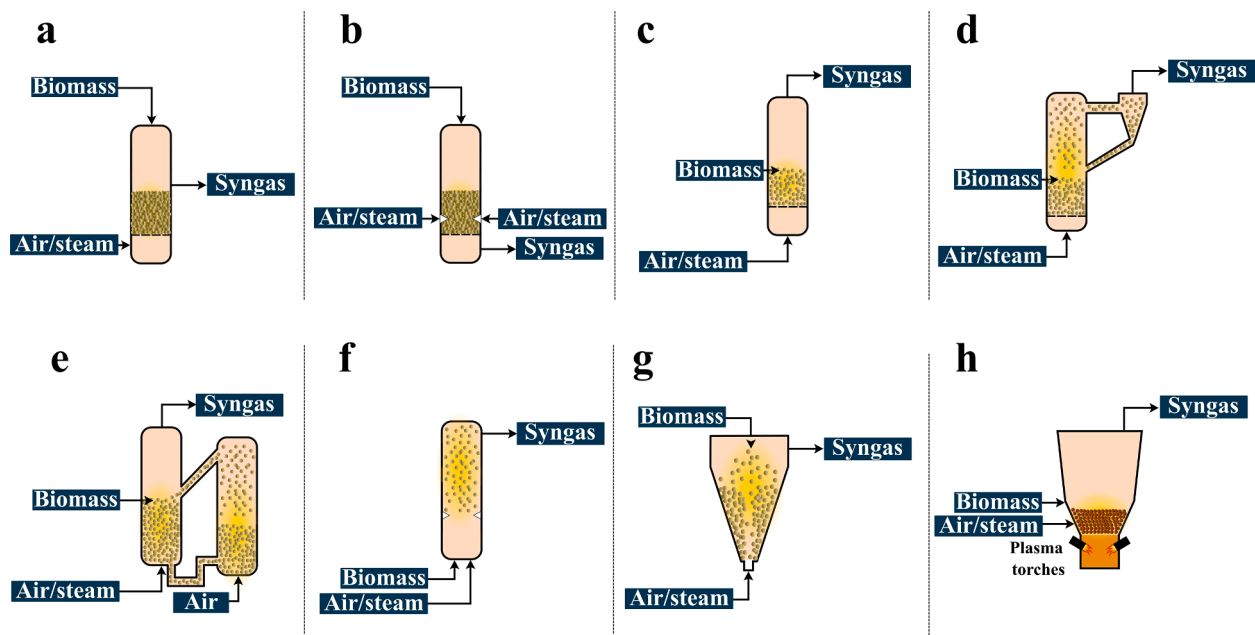


Fig. 2. Reactor configurations for biomass gasification: (a) updraft fixed bed; (b) downdraft fixed bed; (c) bubbling fluidized bed; (d) circulating fluidized bed; (e) dual fluidized bed; (f) entrained flow; (g) spouted bed and (h) plasma reactors.

bed material. Up to now, the vast majority of the current biomass steam gasification demonstration or industrial scale plants are based on this technology [17,35]. The research status of the DFB system was recently reviewed by Hanchate et al. [36]. Güssing (8 MWth) plant was running successfully since the year 2001 [37], as well as industrial scale units in Oberwart (8.5 MWth) [38] and Ulm (15 MWth). Moreover, a GoBiGas plant has been recently commissioned and tested in Sweden [39], but subsequently closed due mainly to economic reasons.

Entrained flow reactors operate at temperatures above 1000 °C and high pressures (20–70 bar). They are highly efficient as they enhance carbon conversion, producing a low tar content gas [40]. However, they require a very small particle size (<0.4 mm) and almost fully dried biomass, which involves high capital and maintenance costs, and so restricted for their scaling [30].

Regarding plasma reactors, they consist of two electrodes, usually Cu or carbon electrodes, through which an electrical energy is coupled to the gas through gas ions [41]. These reactors generate an arc of electric discharge at temperatures of up to 10,000 °C, and generated gas ions trigger the decomposition of the biomass and hydrocarbons. Although a good tar removal efficiency might be obtained, especially for heavy compounds, this technology involves high capital investment and maintenance (lifetime of pulse power supplier is limited), as well as high operational costs (high energy demand) [26].

Conical spouted bed reactors stand out as an alternative to conventional fluidized beds. This technology allows handling larger particle sizes than those used in fluidized beds, including those with irregular texture, fine materials, and sticky solids, with no agglomeration or segregation problems [42]. Moreover, the countercurrent displacement of the solids in the annulus and the gas in the spout zone leads to high heat and mass transfer rates between gas and particle phases [43]. It is noteworthy that this reactor has also a simple design (no distributor plate) and requires lower volumes than fluidized beds for the same capacity (a lower sand/biomass ratio is required). However, this technology is characterized by short gas residence times, which hinder tar conversion, and therefore overall process efficiency [44].

Although the reaction steps of the gasification process are independent of the gasifier configuration, the location of the reaction zones described in Section 1.1 is clearly identified in a fixed bed reactor (Fig. 3), as there is little mixing in this type of reactor. However, given the intense mixing in a fluidized bed, the locations of the reaction zones depend on the geometry of the reactor and the distribution of the feeding points. Typically, reactor designs aim to optimize the char combustion zone close to the oxidant feed point(s) in order to enhance the carbon conversion efficiency and produce the heat required to carry out the gasification reactions, as well as the negative impact of partial oxidation on the cold gas efficiency [45]. Thus, the development of biomass gasification is conditioned by the efficient conversion of the feed and the avoidance of troublesome by-products [46].

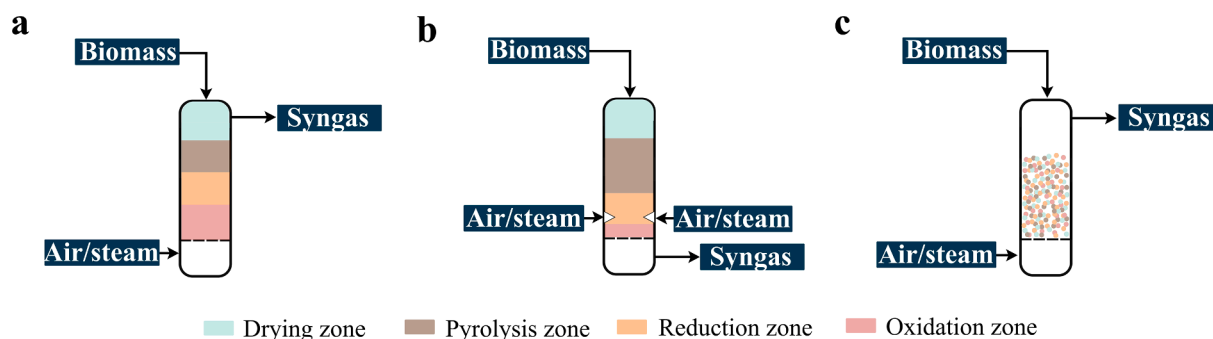
### 1.3. Tar generated in biomass gasification

Although syngas is the main product stream in the biomass gasification, other undesired compounds are also formed, such as tar (condensable aromatic and polyaromatic hydrocarbons) and other trace contaminants including nitrogen compounds (NH<sub>3</sub> and HCN), sulphur-containing inorganic compounds (H<sub>2</sub>S, COS and CS<sub>2</sub>), halogen compounds (HCl and Cl) and alkali (Na, K) and heavy metals [47,48].

The composition yields and characteristics of the gasification products depend on the composition and structure of the biomass, process conditions (such as temperature, gasification agent, pressure, residence time or use of catalyst) and reactor type [49]. Even small changes in process conditions could affect the overall performance of the gasification process, and therefore the quality of the final product gas [50]. Thus, clean woody biomass leads to a product gas with very low concentrations of NH<sub>3</sub>, H<sub>2</sub>S and HCl, as it contains low amounts of sulphur, nitrogen and chlorine compounds, whereas the use of low-cost residual biomass, such as agricultural residues, manure [51], sewage sludge [52] or waste [53], leads to much higher concentrations. In comparison with the latter contaminants, tar is present in higher amounts in the product

**Table 1**  
Impurities formed in biomass gasification and the associated problems [54,55].

Type of impurities	More common compounds	Associated problems
Nitrogen	Mainly NH <sub>3</sub> and HCN Traces of pyridines, quinolines...	NO <sub>x</sub> Emissions Gas conditioning needed Poisoning of downstream catalyst
Sulphur	Mainly H <sub>2</sub> S and COS Traces of thiophenes, mercaptans...	Interaction with alkali metals leads to emissions, deposits and corrosion Gas conditioning needed Poisoning of downstream catalyst
Chlorine	Mainly HCl Traces of CH <sub>3</sub> Cl	Emissions, corrosion and ash sintering Interaction with K leads to deposition and agglomeration. Ash softening temperature decreased
Alkali and alkaline earth metals	Forming salts	Involved in ash deposition and deposit formation. Ash melting temperatures lowered (Na, K) or increased (Mg, Ca). Reaction with Si and S leads to deposition, agglomeration, fouling and corrosion Ash disposal Ash melting behaviour
Heavy metals	Traces of Hg, Cd	Emissions Ash disposal costs increase
Tar	Aromatic and polyaromatic hydrocarbons	Ease for condensing Corrosion, fouling and clogging on downstream equipment Gas conditioning needed Deactivation of downstream catalyst



**Fig. 3.** Fixed bed updraft (a) and downdraft (b), and fluidized bed (c), with their reaction zones.

gas, and special attention will therefore be paid in the following sections. Table 1 shows the major impurities present in the product gas and their effect on the gasification process.

Tar is a complex mixture of high molecular weight aromatic hydrocarbons (containing single-ring to multiple-ring aromatic compounds), which are especially problematic, as they may cause fouling, corrosion and blocking of downstream equipment and many environmental problems [56]. Nevertheless, the tar contains a significant amount of energy that could be transformed into syngas [57]. Therefore, tar removal strategies have been extensively developed. Fig. 4 shows a schematic representation of those methods. Overall, those strategies may be classified as follows: i) primary, to remove tar in the gasifier, or ii) secondary, the in-line cleaning of the syngas produced. Regarding the primary methods, the first-line measures usually involve the design of the gasifier, the use of in situ catalysts, and the adequate control of operating conditions (temperature, equivalence ratio, and gasification agent) [58]. The secondary-line methods do not interfere with the gasifier operation and they could be classified into physical (cyclones, cooling towers/wash columns, electrostatic precipitators and so on) and chemical treatments (thermal and catalytic process and partial oxidation) [59]. Primary tar elimination methods significantly reduce the process cost, but they may not be efficient enough to remove all tar. In those cases, the combination of in situ and ex situ methods may be a good option [60].

This review provides a comprehensive overview of the tar issue and examines literature on the primary measures for tar removal in the biomass gasification. A critical literature survey has been carried out in order to assess the effect of operating conditions (temperature, ER (equivalence ratio) and S/B (steam to biomass ratio)), biomass characteristics, primary catalysts (natural and supported metal catalysts) and modifications and improvements in reactor design (injection of secondary air/O<sub>2</sub>, changes in reactor design and feeding mode, use of filter candles in the freeboard and staged gasification) on the tar content in the produced gas.

## 2. Tar issue

### 2.1. Tar definition and classifications

Tar is an ambiguous term that describes a complex mixture of condensable hydrocarbons. Given the diversity of institutions and

researchers working on biomass gasification, there are a large number of tar definitions and tar sampling techniques. Thus, the Gasification Task from the IEA Bioenergy Agreement, US Department of energy (DOE) and the DGXVII from the European Commission agreed to define tar as hydrocarbons with molecular weight higher than benzene [61]. To sum up, tar is a thick brown-black colored highly viscous liquid, which contains single-ring to multiple-ring aromatic compounds along with other oxygen containing hydrocarbons and complex polycyclic hydrocarbons [62].

Two different tar classification methods can be found in the literature. The first one was reported by Evans and Milne [63] and grouped tar compounds into 4 lumps according to their reactivity (primary, secondary, alkyl-tertiary and condensed tertiary tar) as shown in Table 2. However, the distinction between secondary and tertiary compounds is not always straightforward, as they may overlap [61]. Thus, Energy Research Center of the Netherlands (ECN) proposed a more clear tar classification, which also ranks the large amount of unconverted tar compounds. According to this classification, tar compounds are divided into five classes based on their molecular weight, solubility and condensability (Table 2): GC undetectable tar, light aromatics, heterocycles, light and heavy PAHs. Both methods are commonly used to classify tar depending on the subsequent application, and they are in fact complementary.

### 2.2. Tar formation and transformation mechanisms

To reduce tar production, a thorough understanding of its formation and transformation is essential. However, elucidation of tar formation and transformation mechanisms remains challenging, as they involve very fast and complicated processes [65]. This is probably associated with the complex nature of biomass, as it has a heterogeneous chemical composition, including different polymeric units and cross-linkages in its constituents (lignin, cellulose and hemicellulose), and the competing reactions involving highly reactive species (radicals with complex chemistry), producing a large number of PAH isomers [66]. Apart from being the main compounds of tar, PAHs are very problematic, especially the heavier ones. Therefore, knowledge of their formation mechanism and evolution is of vital importance for the optimization of the gasification process [67].

Lignin is considered as the potential precursor of PAH formation, since it is the only fraction in the biomass with an aromatic ring

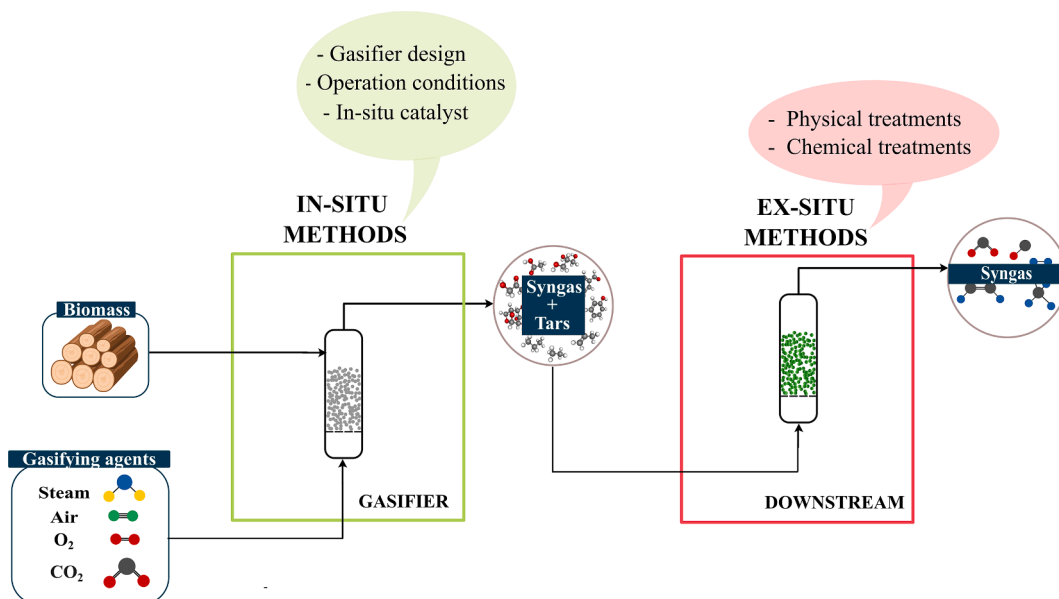


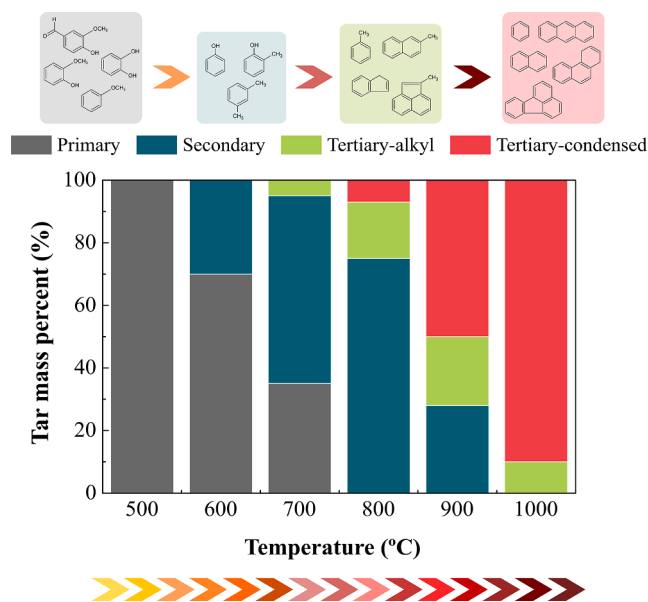
Fig. 4. Schematic representation of tar removal strategies.

**Table 2**  
Tar classification methods, their properties and typical compounds [57,59,60,64].

Classification method	Basis of classification	Nomenclature	Description	Properties	Typical compounds
Milne	Reactivity, appearance	Primary	Cellulose, hemicellulose and lignin derived oxygenated compounds	Low molecular weight oxygenated hydrocarbons	Acids, sugars, alcohols, ketones, aldehydes, catechol, guaiacol, anisol, vanillin
		Secondary	Product from the conversion of primary products (phenolic and olefin compounds)	Alkyl phenols Singles-ring aromatics	Phenol, cresol, xylene
		Alkyl tertiary	Aromatic compounds with methyl branches	Methyl derivative aromatics with one or more rings	Methyl acenaphthylene, methyl naphthalene, toluene, indene
		Condensed tertiary	Polycyclic aromatic compounds without branches	Polynuclear aromatic hydrocarbon (PAH) series without substituents	Benzene, naphthalene, acenaphthylene, anthracene, phenanthrene, pyrene
ECN-TNO-UT	Molecular weight, solubility and condensability	Class I	GC undetectable compounds	Very heavy compounds with 8 or more rings Not detected by GC Calculated by subtracting the GC detectable tar from the total gravimetric tar	
		Class II	Heterocyclic compounds	Single ring aromatics containing heteroatoms High solubility in water	Pyridine, phenol, cresol, quinoline, isoquinoline
		Class III	Light aromatic compounds	Single ring aromatic compounds Without condensability and solubility problems	Toluene, ethylbenzene, xylenes, styrene
		Class IV	Light PAHs	2–3 ring aromatic compounds Condense at low temperatures	Indene, naphthalene, methylnaphthalene, biphenyl, acenaphthalene, fluorene, phenanthrene, anthracene
		Class V	Heavy PAHs	More than 3 ring aromatic compounds Condense at very low temperatures	Pyrene, fluoranthene, benzo(b)fluoranthene, benzo(a)pyrene, benzo(k)fluoranthene

structure. Tar formation during biomass gasification follows several sequential steps. When biomass is fed into the gasifier, it first dries and then starts to decompose (Eq. (1)). The operating temperature is responsible for the nature of the tar produced. Temperatures below 500 °C lead to a tar mainly formed from oxygenated organic compounds, which are usually known as primary tar. Examples of primary tar are vanillin (4-hydroxy-3-methoxybenzaldehyde, C<sub>8</sub>H<sub>8</sub>O<sub>3</sub>), catechol (1,2-dihydroxybenzene, C<sub>6</sub>H<sub>6</sub>O<sub>2</sub>), guaiacol (2-methoxyphenol, C<sub>7</sub>H<sub>8</sub>O<sub>2</sub>) and anisol (methoxybenzene, C<sub>7</sub>H<sub>8</sub>O) [68]. However, temperatures above 500 °C are capable of converting primary tar into secondary tar, since dehydroxylation, demethoxylation and demethylation reactions take place simultaneously [69]. Secondary tar is mainly made up of branched and heteroatom compounds. Higher temperatures result in the further bond breaking and reforming on the tar matrix, which make tar evolve to more stable PAH compounds (tertiary tar), through ring condensation and polymerization [60]. Fig. 5 shows the tar evolution in the 500–1000 °C temperature range.

The formation of PAHs and their transformation is initiated when the PAH precursors are produced. There are two main pathways for PAH formation: one considers benzene as the precursor, whereas the other considers phenol [67,70]. Benzene could be produced by the primary pyrolysis of lignin or by the combination of light alkenes through dehydrogenation and Diels-Alder condensation reactions. In the case of phenol, it is generated when the ether bond in the lignin breaks under acid conditions. With benzene as precursor, PAHs could be formed by its ring condensation reaction or hydrogen abstraction and addition reactions of unsaturated light hydrocarbons, such as acetylene, vinyl, methyl... The PAH formation from benzene precursors is shown in Fig. 6. However, when phenol is the precursor, phenolic compounds lose the CO radical to form cyclopentadiene, which in turn loses one H atom to generate a cyclopentadienyl radical. Then two cyclopentadienyl radicals combine into naphthalene. Naphthalene loses an H radical to give indenyl, which reacts with cyclopentadiene generating aromatic compounds with more than two rings. This reaction pathway could be seen



**Fig. 5.** Tar compound distribution in the 500–1000 °C temperature range.

in Fig. 7.

Thus, to reduce the yield of PAH tar, the formation of the precursors or the transformation of PAH tar from the precursors needs to be reduced [72]. According to Qin et al. [67], H<sub>2</sub> suppresses the formation of large PAH, as hydrogen radicals preferably saturated carbon-containing intermediates, reducing the possibility of reactions involving carbon containing species to produce larger compounds.

The growth mechanism of tar is still under investigation and many research have been done to understand it. Several authors have reported

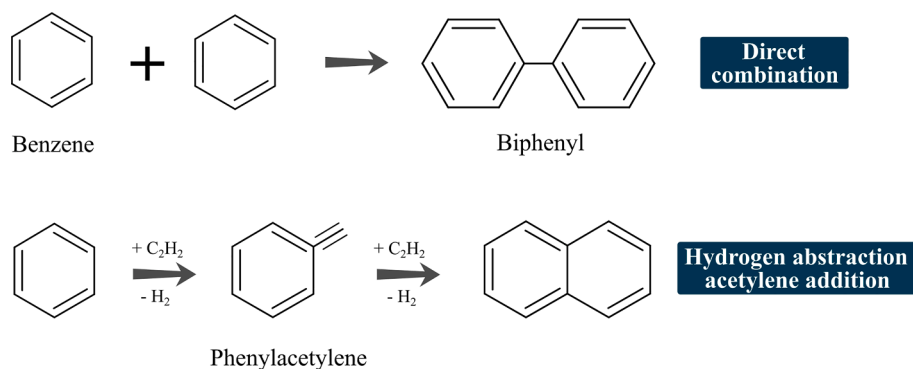


Fig. 6. PAH formation from benzene precursors [62].

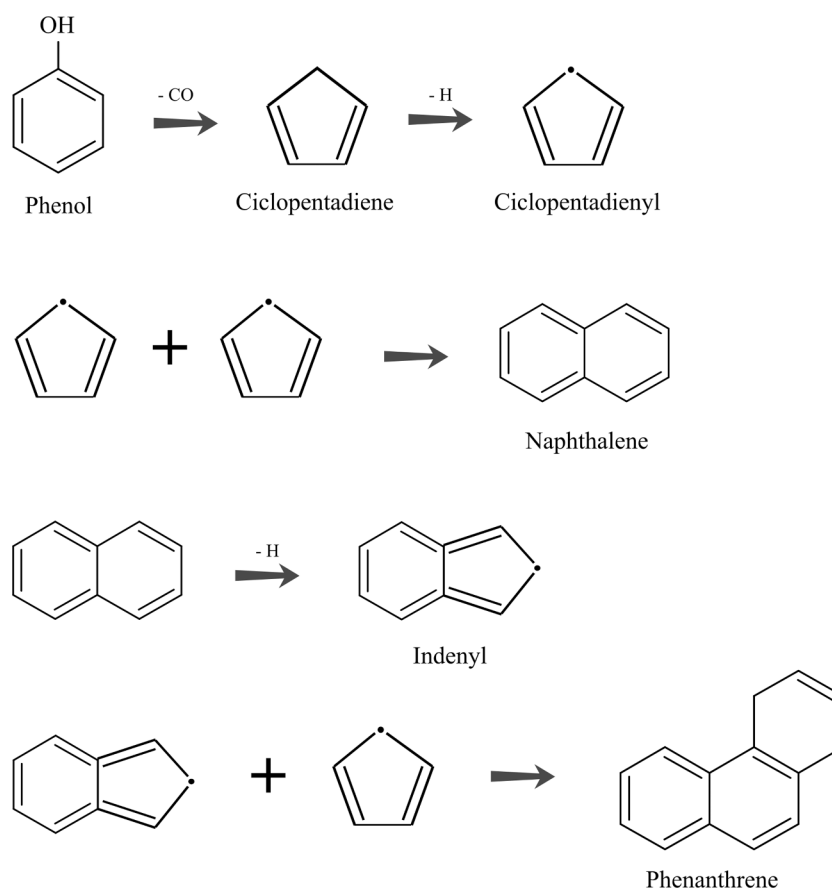


Fig. 7. PAH formation from phenol precursors [71].

different possible mechanisms for tar growth, such as aromatic ring-ring condensation and acetylene addition [73], particle filler model [74], aryl-aryl combination followed by  $H_2$  elimination and ring cyclization [75] and condensation of aromatic radicals with neutral species. The hydrogen-abstraction/acetylene-addition (HACA) mechanism has been widely used to describe the evolution of PAHs [62,76,77] although other researchers point out that it is a rather slow mechanism [65,78]. Additionally, Shukla and Koshi [65] proposed several tar growing pathways based on reactions involving radical mechanisms: HAVA (hydrogen abstraction and vinyl radical addition) [79], PAC (phenyl addition and cyclization) [80,81] and MAC (methyl addition and cyclization) [82]. The studies carried out by the same authors pointed out that PAC is the most efficient mechanism for PAH growth, MAC is more efficient than HACA, but less than PAC and HAVA is faster than HACA [79]. It seems that the formation of PAHs and their role may be related to the complex

combination of the mechanisms described above and their efficient pathways. Overall, those mechanisms are based on consecutive dealkylation/decarboxylation (tar aromaticity is enhanced by the cleavage of alkyl groups attached to the aromatic rings), dimerization (direct combination of aromatic rings) and cyclization reactions that may occur simultaneously, which lead to the growth of light aromatic compounds to heavier ones [83].

### 2.3. Tar drawbacks on the commercialization of gasification technologies

The major challenge of biomass gasification is related to tar formation, as it requires cleaning and upgrading of the product gas, which restricts its industrial viability [56]. Technical and economic problems concerning tar have given rise to the cancellation of several investments in the past [84]. Overcoming tar-associated problems is crucial for

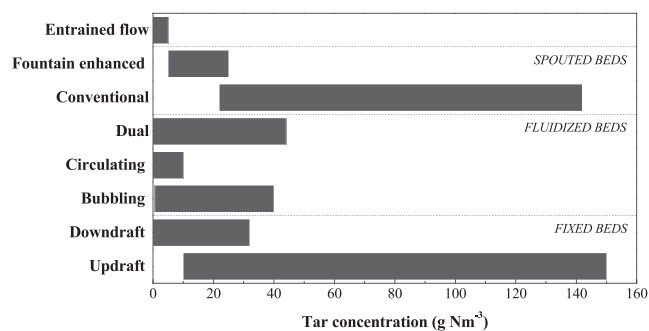
achieving economically and environmentally efficient energy recovery from biomass gasification [85]. In fact, tar formation wastes 5–15 % of the effective energy from biomass gasification, reducing the process efficiency [67]. All tar compounds are undesired in the product gas, as they may polymerize into more complex structures on downstream pipelines, heat exchangers or filters, leading to corrosion, fouling and clogging. Consequently, process efficiency decreases and emissions and operational costs increase. Thus, the tar issue is closely linked to operational problems, gas downstream applications and human and environmental risks, as summarized in Table 3.

Tar amount and its composition are influenced by the type of gasifier (which determines the contact mode and mass and heat transfer rates), composition of the biomass used as feedstock and, especially, operating conditions (such as temperature, gasification agent, pressure, residence time or use of catalyst), as will be discussed in Section 3. Tar concentration depends on the gasification technology, as shown in Fig. 8. Tar content for entrained flow and circulating fluidized bed reactors is low, with a range of 0–5 g Nm<sup>-3</sup> and 0–10 g Nm<sup>-3</sup>, respectively. However, much higher tar concentrations are produced in conventional spouted beds and updraft fixed bed, up to 140 g Nm<sup>-3</sup>. Fountain enhanced spouted beds, dual and bubbling fluidized beds and downdraft fixed beds lead to moderate tar levels, with an upper value of 50 g Nm<sup>-3</sup> [22,46,60,86]. The total amount of tar in the product gas determines the downstream application. Thus, applications directed towards the production of motor fuels, such as H<sub>2</sub> production, Fischer-Tropsch synthesis, methanol and natural gas synthesis, only accept a very low tar level, below 1 mg Nm<sup>-3</sup>, whereas power generation equipment, such as gas turbines, gas engines, fuel cells or boilers, accept higher limits (<1–100 mg Nm<sup>-3</sup>) [87]. As observed in Fig. 8, tar concentrations in the standard gasification technologies remain above the acceptable range for mentioned applications. Thus, tar needs to be removed or converted in order to avoid unacceptable levels of maintenance in the upgrading processes.

Likewise, not only does the total tar concentration indicate the suitability of the end-use application, but tar forming compounds also play a key role, as all tar components present in the product gas contribute to the overall tar dew point. Tar dew point is the temperature at which the partial pressure of the tar equals the tar saturation pressure. Thus, as the tar dew point is kept at very low levels, fouling problems by tar condensation are minimized. Undoubtedly, heavy PAHs dominate tar dew point. Even for concentrations below 1 mg Nm<sup>-3</sup>, a dew point below 100 °C is impossible to obtain. However, light aromatics are not condensable even at concentrations of 10 g Nm<sup>-3</sup>. In the case of heterocycles and light PAHs, they need to be partially removed to keep the dew point at approximately 25 °C. As light aromatic compounds do not play an important role in this matter, tar removal strategies must focus

**Table 3**  
Side effects of tar in the biomass gasification process [48,57,59,64].

Side effects	Explanation
Pipeline blockage at low temperatures	Below 300 °C, tar in the gaseous stream may condense quickly and attach easily to the gas pipelines, resulting in their obstruction and operational disruption
Corrosion on downstream equipment	The acid nature of the tar may cause severe corrosion in downstream equipment
Catalyst deactivation in downstream reactor (if used)	Tar could deposit on the catalyst surface and block the active sites, shortening its lifetime
Reduction of process efficiency	Tar accounts for 3–5 % of the total energy in the feedstock or 10–15 % of the energy in the product gas, reducing the total energy utilization and process efficiency
Production of phenolic wastewater	As phenolic compounds are abundant in the tar, a great deal of wastewater is produced in the gas cleaning, which must be treated
Human and environmental risks	Most of tar compounds are carcinogenic, so the human and environmental health is in danger when released



**Fig. 8.** Tar concentration obtained in different gasification reactors [22,46,60,86].

on reducing heterocycles and light and heavy PAHs in order to ensure a successful application of the product gas [48,59,60].

### 2.3.1. Effect of tar on the applications of the gaseous product

The product gas from biomass gasification could be used in the power generation and chemical synthesis. The processes for the synthesis of chemicals are promising, but the relevant technologies using biomass as feedstock are still under development [88]. Table 4 gives an overview of the tar limits, as well as the problems and challenges associated with both applications.

**2.3.1.1. For power generation.** Currently, gas produced in biomass gasification is mainly used for power generation. There are different technologies to integrate biomass gasification with other technologies such as steam turbines, gas turbines, gas engine and fuel cells for electricity generation. The tar containing gas obtained at the exit of the gasifier may not be directly coupled with those equipments because it may cause corrosion in the cylinder, blockage of the gas flow line and valves, piston choking, blade corrosion and erosion, high consumption of lubricating oil and so on. Thus, the gas must meet specific

**Table 4**  
Tar limitations and problems and challenges associated with power generation devices and fuel synthesis processes [15,27,47,88,90,91].

	Tar limits	Problems	Solutions
<b>Power generation</b>			
Boiler/steam turbine	No specific restrictions	Although there is little chance for tar condensation, the gas produced after burning should meet local emission requirements	Obtaining higher energy efficiency with smaller boilers (<150 MWth)
Gas turbine	5 mg Nm <sup>-3</sup>	As they used hot gas, carbon deposits could be formed. Turbine blades are very sensitive to tar	Improving abrasion and erosion resistance of turbine blades
Gas engine	100 mg Nm <sup>-3</sup>	Heavy tar could deposit on the engine manifold and cylinder wall	Modification of the gas injection system
Fuel cells	< 1 mg Nm <sup>-3</sup>	Tar could condensate in fuel injection system. Tar could cause corrosion and carbon deposition, and consequently degrade the anodes	Development of anodes resistant to carbon deposition. Improving durability of the fuel cells
<b>Chemical/fuel synthesis</b>			
Fischer-Tropsch synthesis	< 1 mg Nm <sup>-3</sup>	Catalyst deactivation by coke formation	Development of high activity catalyst with excellent resistance to coke without high cost
Methanol synthesis	< 1 mg Nm <sup>-3</sup>		Improving process energy integration
Methanation	< 1 mg Nm <sup>-3</sup>		



requirements (further discussed below) regarding tar concentration after conditioning for smooth operation of these devices [89].

The main advantage of boiler and steam turbine combination is that the expanding fluid is completely isolated from the gas combustion fumes. Consequently, there is no specific tar limitation and the product gas can be used directly without further treatment and it will not cause corrosion, fouling and plugging of the rotating parts [90]. However, commercially available steam turbines have an extremely low efficiency of electricity generation, in the 10–20 % range, and they are expensive, which make them an unviable option [85].

In the case of gas turbines, the turbine components are exposed to combustion products and their electrical efficiency is higher than those of boiler and steam turbine combination. Gas turbines can accept hot gas for combustion and, as temperature is higher than the dew point of the tar, tar could stay in vapor phase [85]. Due to high exhaust gas temperatures, they are ideal for adding an additional energy recovery system, such as a steam cycle, i.e., Integrated Gasification Combined Cycle (IGCC). To date, the IGCC electrical efficiency has reached over 42 % [91]. Nevertheless, at 400 °C tar may dehydrate and form carbon deposits, which cause fouling, plugging and abrasion of turbine blades. Thus, the tar level must be below 5 mg Nm<sup>-3</sup> to meet the manufacturer's specification [86].

Regarding gas engine, it is not so sensitive to gas impurities compared to gas turbine, allowing a gas with 100 mg Nm<sup>-3</sup> of tar concentration. On the one hand, special attention should be paid to heavy tar species, as they could deposit on the engine manifold and cylinder wall. On the other hand, polycyclic aromatic hydrocarbons do not tend to deposit, although they may influence gas emissions from engine exhausts and wastewater from the gas conditioning units [92]. In this case, the decontamination of the gas could be achieved with quite inexpensive equipment, which makes the solution viable and competitive. Its advantages include low investment, maintenance and operating costs, reliability, high operating efficiency, compact and [93] robust structure and simple operation and maintenance [85]. However, the engines are designed for gasoline and diesel, and consequently the injection systems require some modifications [27]. Many co-generation units for the production of thermal energy with electricity using gas engines have been installed and working successfully in the world, using biomass as feedstock [47].

Solid oxide fuel cells (SOFC) produce electricity via electrochemical conversion of H<sub>2</sub> and CO in the product gas, whereas CH<sub>4</sub> is internally reformed to H<sub>2</sub> and CO. This electrochemical conversion is possible thanks to their operation at high temperature and a catalyst contained in the anode. They offer the possibility of highly efficient electricity production (over 40 % electric conversion efficiency could be obtained), which could reach 60 % or more when the exhaust heat from SOFC is used in combined cycle application or cogeneration. Moreover, compared to traditional power generation devices, fuel cells have lower impact to the environment, as the product gas is not burned [94]. However, feeding tar containing product gas could result in significant deactivation from carbon deposition, which hinders the fuel transport, blocks active sites of anodes and, as a result, reduces the electrical efficiency and durability of the fuel cell [95]. Understanding the degradation mechanisms in the anode, identifying the optimal operation conditions and developing advanced SOFC materials, as well as regeneration methods and diagnosis tools, are essential for a stable, efficient and eco-friendly SOFC systems [93]. Thus, the tar limits are even more stringent than for gas turbines. Below 1 mg Nm<sup>-3</sup> is recommended, which leads to the absence of large scale applications [96].

**2.3.1.2. For chemical/fuel synthesis.** Concerning chemical synthesis processes, such as Fisher-Tropsch and methanation, tar containing product gas causes similar problems, as all of them are catalytic process. The catalyst employed in each case can be deactivated by tar through coke formation. Since coke blocks the active sites of the catalyst, the

overall reactive sites of the catalyst decrease until the entire catalyst becomes inactive [27,86]. Therefore, the product gas should be cleaned before feeding into these synthesis processes with the tar concentration limit being below 1 mg Nm<sup>-3</sup>. Up to date, there is limited applications in large-scale by using biomass as feedstock for chemical and fuel production, although it may be of great interest due to the rise in the prices of fossil fuel, as well as the introduction of carbon taxes and the increasing energy demand in the energy-intensive sectors [88,97].

### 2.3.2. Effect of tar on health and environment

There is a growing interest in developing biomass gasification for sustainable energy production. Due to the relatively short reproduction time and the consumption of CO<sub>2</sub> through photosynthesis during the growth of woody biomass, the use of them for power generation is net neutral in CO<sub>2</sub> emissions [98]. However, power generation from biomass gasification poses several health and environmental hazards. Tar contains a great amount of highly toxic and carcinogenic aromatic hydrocarbons, which could be risky for creatures and environment if disposed into water sources, such as rivers and underground water.

There are stipulated concentrations from which tar compounds are deemed toxic and carcinogenic. The limit concentrations vary depending on the exposure time. The US Occupational Safety and Health Administration (OSHA) has established the exposure limits of the following tar compounds: toluene, 200 ppm (753.70 mg m<sup>-3</sup>), whereas the values for naphthalene and phenol are much lower, 10 ppm (52.35 mg m<sup>-3</sup>) and 5 ppm (19.23 mg m<sup>-3</sup>), respectively. In the case of anthracene, pyrene and fluoranthrene, OSHA has identified them as typical components of the benzene-soluble fraction of coal tar pitch volatiles, with their limit being 0.2 mg m<sup>-3</sup>.

## 2.4. Tar content determination methods

Since tar concentration determines the downstream processes and impacts on the health and environment, the measurement of its content in the product gas and/or its online monitoring over time are crucial for process control [48]. Qualitative and quantitative measurements of tar in the gaseous stream can assist in assessing the effectiveness of the cleanup and conditioning processes, and verifying the adequacy of the gas quality for its final use [99]. Operating conditions, the peripheral equipment of the gasification plant, as well as the experience of the operators influence the tar formation, detection and sampling results. Therefore, standardized tar analysis methods are essential for comparison purposes [84].

Various approaches have been applied for measuring the tar content in the product gas, which could be divided into two groups: off-line and online methods. Conventional off-line analysis characterizes tar content by sampling a known amount of the sample from the main gas stream and bringing condensed or dissolved tar to an analytical laboratory for further chemical analysis, whereas the online methods allow measuring the tar content directly in the product gas [55].

Since there are numerous methods for tar measurement, their selection should be based on the information desired (qualitative or quantitative results; accuracy; interested chemical compound), final use of this information (industrial monitoring or R&D), reliability of the technique and cost. In the case of industrial monitoring and analysis, they should be reliable, fast, not expensive and preferably online, and they should need low staffing without specific expertise.

### 2.4.1. Off-line methods

The overall process of off-line analysis comprises the following common steps: tar sampling, sample preparation (depending on the analytical technique, conditioning may include drying or filtering particulates) and analysis of the sample which is generally carried out by gas chromatography (GC) or high pressure liquid chromatography (HPLC). The most relevant off-line tar determination methods are the tar guideline/protocol, the solid phase adsorption (SPA) and solid phase

micro-extraction (SPME). The procedure of each method is listed below and summarized in Table 5.

**2.4.1.1. Tar protocol.** The tar guideline/protocol was the first technical guideline for sampling and analyzing biomass gasification tar and was developed by the European Committee for standardization (ECN) with the help of different European Research Institutes (VTT, KTH, DTI, MTG, NRE). Nowadays, it is a reference procedure for tar measurement and is standardized by the tentative standard CEN/TS 15,439 [100]. It has a sampling unit to adjust the gas temperature and pressure, a subsequent high temperature filter to remove particles, tar collector (consisting of six impinger bottles with solvents placed in a temperature controlled bath) and an isokinetic gas pump which provides a constant gas flow rate. In the series of impinger bottles, the first one acts as moisture collector, in which water condenses from the product gas by adsorption in isopropanol. After the moisture collector, the gases pass through four impinger bottles with solvent (usually isopropanol) and a final empty bottle. The first two bottles are kept at a temperature of 20 °C approximately in a water bath, whereas the following two bottles are cooled to -20 °C in a salt and ice bath in order to capture aerosols. Fig. 9 shows a scheme of the tar protocol impinger train. Several authors studied the configuration of the impinger train in order to optimize the temperature profile of the gas flowing through the bottles, the type of solvent and its amount in each bottle [92,101–105].

In order to determine the tar content in the product gas, the evaporation of the solvent in the four impinger bottles and weighing the residue tar is required. Although the tar protocol quantifies the total tar amount, it does not provide information about its composition, as this requires an additional analysis in GC or GC/MS.

This is a reliable method for the quantification of the total tar

**Table 5**  
Comparison of off-line tar measuring techniques [48,55,101,129].

	Tar protocol	SPA	SPME
Principle	Cold trapping in liquid solvent (isopropanol)	Adsorption in a solid phase (amino-based, active carbon...)	Adsorption in a solid stationary phase (silica fiber with PDMS)
Sampling time	1 h	1–2 min	10 min
Desorption time	–	1 h	–
Analysis time	1 h	1 h	1 h
Advantages	Robust method Measures the total tar	Easy and fast sampling Small amounts of solvent No loss of tar adsorbed by solvent evaporation and aerosol formation High accuracy and reproducibility	Easy and rather fast sampling Solvent-free sampling Suitable for measuring very low tar amounts
Shortcomings	Long sampling times Bulky and complicated sampling Large solvent volumes Loss of adsorbed tar by solvent evaporation and aerosol formation Inadequate for low tar concentration Low precision	Only measures GC detectable compounds Inadequate for heavy tar BTX must be analyzed within few hours to avoid their desorption	Under development Application in raw product gas uncertain Only measures GC detectable compounds Non-aromatic C <sub>5+</sub> hydrocarbons might compete with tar compounds on the adsorption sites Not standard procedure available
Tar detection limit	>5 mg Nm <sup>-3</sup>	>2.5 mg Nm <sup>-3</sup>	<0.1 mg Nm <sup>-3</sup>
Application	Laboratory use	Laboratory use	Laboratory use

amount. However, the implementation is difficult as it is a very time consuming method (the sampling time may be as long as 1 h) and requires specific knowledge and instrumentation, which makes the analysis expensive. Moreover, it is not a suitable method when tar concentrations are low (below 1 mg Nm<sup>-3</sup>) and the handling of large volumes of solvents may pose safety concerns [84,106].

The tar guideline also includes the Petersen column as an alternative analytical method for the impinger train. It consists of two washing stages filled with acetone, which is surrounded by a cooling jacket. In the first stage, the gas is washed using an impinger and in the second stage, washing efficiency is improved by generating a large amount of small bubbles in order to retain tar droplets. The outlet of the column is connected to a gas pump and a gas flow meter during sampling. As Petersen column is a single unit, it makes the tar sampling easier than the standard tar protocol method [48,56,100].

**2.4.1.2. Solid phase adsorption (SPA).** SPA method was originally developed by KTH in the 1990's [107], with the main objective for shortening the time of tar sampling and sample preparation. It is based on tar extraction from the gas sample by adsorption onto a solid-phase column and subsequent off-line desorption from the loaded solid cartridge. The tar containing gas sample crosses the sorbent (amino-based, activated carbon or a combination) which retains the tar compounds. Afterwards, the column is desorbed using a solvent. Then, tar compounds are analyzed using GC [108]. The tar sampling is carried out by inserting a syringe needle (attached to the solid phase extraction column) into the process line via a rubber septum, which reduces the tar sampling time to 1 min. However, the total time invested for one measurement is long, as the column needs to be prepared before each sampling and the final laboratory analysis is laborious [107].

The selection of the sorbent column is vital, as the reliability of the tar quantification depends on it. There are different types of SPA columns, which differ in composition and size. The 100 and 500 mg amino-based LC-NH<sub>2</sub> column is the most used one, as it is reliable for tar compounds ranging from naphthalene to pyrene [107–110]. However, as agreed by Gonzalez et al. [111] and Osipovs et al. [112] this column is not able to capture organic compounds, such as benzene, toluene and xylenes, nor tar compounds heavier than pyrene. Some studies showed that the volatile organic compounds produced during biomass gasification might be collected by modifying the column with some amount of activated carbon in series [113–115]. Moreover, some research groups have adapted the methodology of SPA sampling to meet their analysis requirements by varying the sorbent of the column, the sampling conditions, the sample storage and the elution procedure of tar compounds from the column [101,111,115,116].

According to several studies [101,107,112,115], the values of tar obtained with tar protocol and SPA sampling procedures are consistent. Thus, they concluded that SPA technique is simple for use, inexpensive, fast and allows high accuracy and reproducibility in the results, which make it an adequate method for sampling gas with low tar concentration.

**2.4.1.3. Solid phase micro-extraction (SPME).** SPME was developed by KTH with the aim of improving SPA method for the analysis of tar compounds in the product gas with low tar content. Before that, the method was applied for the analysis of organic compounds in water, air or solid matrices by several research groups [117–125]. Similar to SPA, this method is based on extracting analytes from a sample by adsorption onto a solid stationary phase and subsequent desorption of the analytes in an analytical equipment. The stationary phase used is silica fiber coated with 50 μm polydimethylsiloxane (PDMS). As the fiber is small and cylindrically shaped, it is possible to integrate it into a device that works like a standard syringe, which fits into the injector of a gas chromatography. Once tar compounds have been adsorbed onto the PDMS phase, the fiber is placed in the GC injector, where the analytes

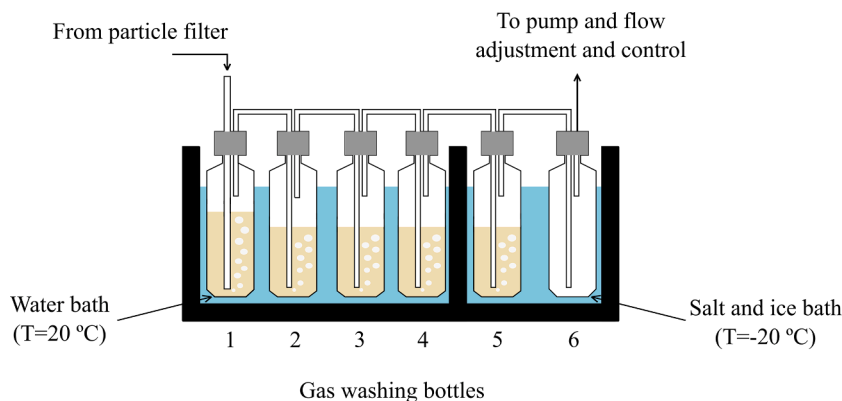


Fig. 9. Scheme of the tar protocol impringer train. Adapted from Li et al. [56]

are directly desorbed without needing a solvent extraction step. This technique is suitable for the analysis of a gas with very low tar content (clean syngas), as it ensures attaining lower detection limits than SPA analysis [126].

To achieve correct measurement, the selection of the solid stationary phase and sampling temperature are critical [127]. The adsorption capacity of tar compounds on the stationary phase depends on the affinity between the fiber and the tar compounds, i.e., their polarity. Since PDMS is a non-polar phase, the affinity increases as the polarity of the compounds decreases [128]. Moreover, the sampling temperature greatly influences the adsorption on the fiber, as each compound has an optimum temperature that maximizes sensitivity while condensation is avoided. The optimum temperature for light and polar compounds is set

at 21 °C, which shifts to higher temperatures for heavier tar compounds to be condensed. Thus, this technique is suitable to measure very low tar concentrations [126]. The main differences among off-line techniques are summarized in Table 5.

#### 2.4.2. Online methods

As shown in Section 2.4.1, off-line methods are generally time consuming (long sampling or preparation time) and require specific knowledge and instrumentation. Moreover, they need further laboratory analysis, which may require days or even weeks after sampling, making these methods inadequate for process monitoring. A robust analytical device capable of monitoring the tar concentration online for process control is needed [84,103,130]. Online tar analysis could be employed

Table 6  
Comparison between online tar measurement techniques [55,106,129–131,133].

Technique	Detected tar compounds	Tar detection limit	Advantages	Limitations	Status
FID online tar analyzer	Total tar concentration	0–120 g Nm <sup>-3</sup>	Fast and easy quantification of tar concentration Short measurement time: 60–90 s Easy to use Simple maintenance Light and robust	Maximum operating temperature: 300 °C Impossibility of determine individual tar composition Filter change	Discontinuation
PID online tar analyzer	Total tar concentration	0–50 g Nm <sup>-3</sup>	Short response time: few seconds Very sensitive to low concentrations Linear response to tar compounds Non-destructive analysis	Maximum operating temperature: 300 °C Impossibility of determining individual tar composition Fouling of the excitation chamber Changes in tar composition negatively affect the accuracy of the quantification	On hold
Laser induced fluorescence	Some tar species	0–20 g Nm <sup>-3</sup>	High-precision High fluorescence signals Linear correlation between fluorescence signal and tar content Non-invasive	Very expensive (not suitable for industrial applications)	On hold
Led induced fluorescence	Some tar species	0.5– >10 g Nm <sup>-3</sup>	Low price: promising for industrial applications Stability of optical power Linear correlation between fluorescence signal and tar content Non-invasive	Low optical power Limited tar compounds can be detected at a single wavelength It is difficult to translate the absorbance into tar concentration (more than one tar species causes absorbance at the same wavelength) Fouling on optical windows is problematic Only can measure light and heavy polyaromatics	On hold
Molecular beam mass spectrometer	Some tar species	Near-universal detection	Robust equipment for monitoring hot raw product gas High reproducibility and sensibility Near-universal detection Commercially available	Complex system Expensive equipment Quantification could be complicated Possible interference with other gas compounds	Commercial
Ion molecule reaction mass spectrometry	Some tar species	Near-universal detection	Capable of measuring BTX and PAHs at low and high concentrations Commercially available	Need for building a fragmentation database for low ionization potential Expensive equipment	Commercial

to monitor the gasification process, the efficiency of tar scrubbers or catalytic tar cracker/reformer, which can assist the operators to find the optimum experimental conditions in fewer runs than the off-line methods. In the commercial operation, online methods can help the gas quality control, which extends the life of gas engines and other downstream equipment [106]. Several universities and research institutions have developed their own online tools for measuring tar, which have been applied in many scientific works [84,131–133]. However, it is important to have simple and robust devices for commercial operation. The technologies used for this aim are designed based on molecule ionization and detection by flame (FID) or photons (PID), optical methods, such as laser and UV-LED induced fluorescence and mass spectroscopy, i.e., molecular beam mass spectroscopy (MBMS) and ion molecular reaction spectroscopy (IMR-MS). Other techniques has also been tested for the online tar monitoring, such as tar dew point analyzer, high temperature reactor (HTR) [134], liquid UV-vis spectroscopy [135,136] and volatility tandem differential mobility analyzer (VTDMA) [137]. These techniques are further introduced below. Table 6 is produced to compare different online tar measuring techniques.

**2.4.2.1. FID analyzer.** FID online tar analyzer was initially developed by the Institute of Combustion and Power Plant Technology (IFK) and refined in the past years together with Ratfisch Analysensysteme GmbH for commercialization. In fact, it was commercialized with the name of TA120-3, although nowadays this device is discontinued. The measurement principle is based on a differential measurement of the organically bound carbon compounds present in the product gas, which is carried out using a flame ionization detector (FID). This device has two sample loops independently connected to FID. The only difference between the two loops is the cooled filter located before the FID in one of the loops, where tar is retained. Thus, the unaltered gas sample passing through the FID gives information about the total hydrocarbon content, whereas the gas sample crossing the filter indicates the total non-condensable hydrocarbon content. Detailed technical measurement principles and specifications of this device could be found elsewhere [84,106]. It enables a fast and simple quantification of the total hydrocarbon concentration, non-condensable hydrocarbon concentration and tar concentration (by difference). Tar contents in the product gas in the 0–120 g Nm<sup>-3</sup> range are detectable and each analysis takes around 60–90 s. Moreover, as a commercial product, it is easy to operate. Furthermore, it is portable and can be used in multiple sampling points as it is light (around 10 kg). One of the major challenges of this analyzer is the selection of an adequate tar filter, since the calculation of tar is performed through difference. If tar is not properly adsorbed or if other compounds are also adsorbed (such as benzene) the accuracy of the tar concentration measurement can be adversely affected [106]. Overall, filter changing and the maintenance of the equipment are quite easy. The online tar analyzer was tested and compared with off-line techniques, such solid phase adsorption [99] and tar protocol [84,103].

**2.4.2.2. Photo ionization detector (PID) analyzer.** PID based online tar analyzer was developed jointly by BTG and KTH. The fundamental element of the detector is an ultraviolet lamp filled with a gas, which generates photons and excites tar compounds. As a result, positively charged molecules produce a current directly proportional to the concentration of the compounds. The gas filling the UV lamp plays a key role in the detection of the compounds, as the emitted light has different wavelengths, and therefore different compounds could be detected. In this way, the lamp filled with xenon can detect aromatic compounds, such as toluene, phenol, naphthalene, acenaphthene, biphenyl, flourene, anthracene and pyrene. The recorded PID signal accounts for the total signal from all excited compounds, i.e., the total tar concentration, but is unable to quantify individual tar compounds. However, PID based tar analyzer could be suitable for online qualitative monitoring of tar, as PID signal stabilizes within a minute, the response time is of a few

seconds and is very sensitive to low tar concentrations (<10 mg Nm<sup>-3</sup>). In fact, the PID sensitivity is between 10 and 50 times higher than that of FID. The bottleneck of this method is the fouling of the excitation chamber, which leads to a decrease in the PID response over time, and therefore the operation must be interrupted for periodic cleaning [131,138].

**2.4.2.3. Optical analyzer.** The optical online tar monitoring systems are based on fluorescence spectroscopy. The principle behind fluorescence spectroscopy for online tar measurement is a linear correlation between fluorescence signal and the tar concentration in a gas. In the first setup, Nd:YAG laser was used as the light source for analyte excitation. However, in the last few years light emitting diodes (LED) have been used to reduce the equipment cost (laser, spectrograph and CCD camera) and reinforce the robustness of the system for industrial application. UV-photons emitted from the LED are absorbed by tar compounds, raising their electronic state to excited ones. PAHs in the tar are excited by wavelengths longer than 250 nm and release fluorescence upon relaxation. The optical setup is composed of a heated (up to 350 °C) measurement cell, which allows optical access to tar containing gaseous streams through quartz glass windows constantly flushed by nitrogen to avoid tar condensation. The fluorescence light emitted by tar compounds in the cell is directed by an optical fiber to a UV/vis spectrometer, where the signals are detected. The whole measurement equipment is placed into a box to avoid ambient light interference. Several universities and research centers have developed laser and LED induced fluorescence based devices [99,103,130,132,139–142]. However, none of them has been capable of running for a long time-frame in a plant environment. Thus, long-term stability of the laser is a challenge and fouling of the optical windows is troublesome even if the windows are heated up to 300 °C [143]. More recently, Borgmeyer and Behrendt [130] have setup their LED-based system cooled by water, which exhibited no fluctuations regardless of the environmental conditions. Moreover, optical window purging with hot nitrogen during operation enabled continuous operation for several weeks, as no tar was condensed on the cell windows.

**2.4.2.4. Online mass spectrometers.** Online mass spectrometers have also been applied for continuously measuring a wide range of tar compounds with high sensitivity. Unlike most of the analytic mass spectrometers, which are coupled to a GC that separates gaseous compounds, the online mass spectrometers setups are coupled to molecular beam (MB) and ion molecule reaction (IMR).

In the molecular beam mass spectrometers (MBMS), a small portion of the gases is expanded continuously in a vacuum environment using a tiny nozzle which causes the fast cooling of the sample, inhibiting condensation or reaction. Thus, the analyte is preserved in its original state, allowing light gases to be sampled simultaneously with heavier condensable and reactive species. The subsequent mass spectrometry analysis generates instantaneously the chemical fingerprint of the sample, enabling the observation of its time-resolved behavior. The MBMS online analyzer was originally developed to study prompt thermochemical phenomena and has been extensively used by US National Renewable Energy Laboratory (NREL) in several other applications [144–147]. Carpenter et al. [133] investigated the use of a molecular beam mass spectrometer as an alternative method for quantifying real-time tar concentrations in biomass gasification and compared the results with those obtained with tar protocol, which showed consistent results. This device could be used to sample directly from harsh environments, including high-temperature, wet and particulate-laden gas streams. However, there is no pre-separation of the observed peaks, and isomers cannot be distinguished, making it difficult to interpret the mass spectra. Moreover, this system is quite complex, big in size and expensive, which obstructs its use in industrial applications.

The French Alternative Energies and Atomic Energy Commission

(CEA) have adapted IMR-MS setup for online tar measurement. A low ionization energy inert gas (Xe or Kr) is used as ion source because high ionization energies fragment molecules and lead to more complex mass spectra and multiple overlapping intensities. In this technique, an inert gas is ionized by electron impact, which reacts under vacuum conditions with the sample gas according to the ion molecule reaction in a reaction chamber. The ionized sample gas is then conducted to a classical quadrupole and mass spectrometer. Defoort et al. [148] tested this equipment in biomass steam gasification, measuring the released wet and dry gases. In the case of wet gas, it was diluted with nitrogen, which led to less consistent results, as the values were close the detection limit of the equipment. However, the masses corresponding to benzene, toluene, thiophene, phenol, indene, acenaphthylene, biphenyl + acenaphthene, fluorene, phenanthrene + anthracene were well defined. As soft ionization is used, fragmentation of molecules is avoided, but the need for building a fragmentation database at such low ionization potential arises.

The status of the presented techniques for tar sampling and measuring is diverse. The development of some of them has been suspended, whereas others are commercially available or still under development. Tar protocol and SPA off-line techniques are actively used. Although SPA method is less time consuming and cumbersome than tar protocol and provides adequate results, tar protocol is still more frequently used in both industrial and research environments. Many research groups have reported the use of this technique to measure the amount of tar in the biomass gasification processes [105,149–155]. In the case of SPME technology, it seems that it was abandoned after its first demonstration with clean syngas. Regarding the online methods, only MBMS and IMR-MS setups are commercially available up to now. MBMS and IMR-MS equipment for online quantification of tar during biomass gasification are being commercialized by Extrel and V&F (Airsense model) companies respectively. However, both setups are so expensive (around 300,000 \$) that they are not used to monitor and control tar concentration in gasification processes. Some years ago, a FID online analyzer was commercialized by Ratfisch Analysensysteme GmbH with the name of TA120-3, but nowadays the purchase of this device is no longer possible. Technical challenges and restrictions hindered the scientific and commercial success, and therefore further development of the technique is still needed [84]. At this time, the development of a PID based commercially available device is stopped because the fouling problems of the UV lamp have not been solved yet. However, it may have a great potential when they are solved. In the case of optical methods, UV-LED based ones seem to be more promising for process control than laser ones as they are much cheaper, but there is still a lot of work ahead to eliminate the associated problems.

### 3. Primary strategies for tar elimination

Tar removal is one of the main challenges in biomass gasification, since it leads to the blockage and fouling of pipelines, heat exchangers and particle filters [22]. In this regard, several strategies have been proposed and analyzed in order to reduce or even completely eliminate the tar compounds in the gas. These measures can be classified into two groups: i) primary methods, wherein the tar is removed inside the gasifier by selecting optimum operating conditions, using special bed materials, catalysts or with an improved design of the gasifier, and; ii) secondary methods, where the tar is reduced at the downstream of the gasifier. The latter one can be divided into physical/mechanical (filters, cyclones and scrubbers) and chemical methods (thermal and catalytic tar cracking) [59]. Despite these strategies have been proved to be effective for tar elimination, they are hardly economically feasible [46].

This section provides an overview of the main primary strategies for tar elimination in biomass gasification. Accordingly, different operating conditions (temperature, S/B and ER and gasification agent), biomass characteristics and primary catalysts used in the existing studies are analyzed in Sections 3.1, 3.2 and 3.3, respectively. Moreover, the

advantages in reactor design development and the new strategies implemented in the reactor itself for tar removal will be discussed in Section 3.4.

#### 3.1. Operating conditions

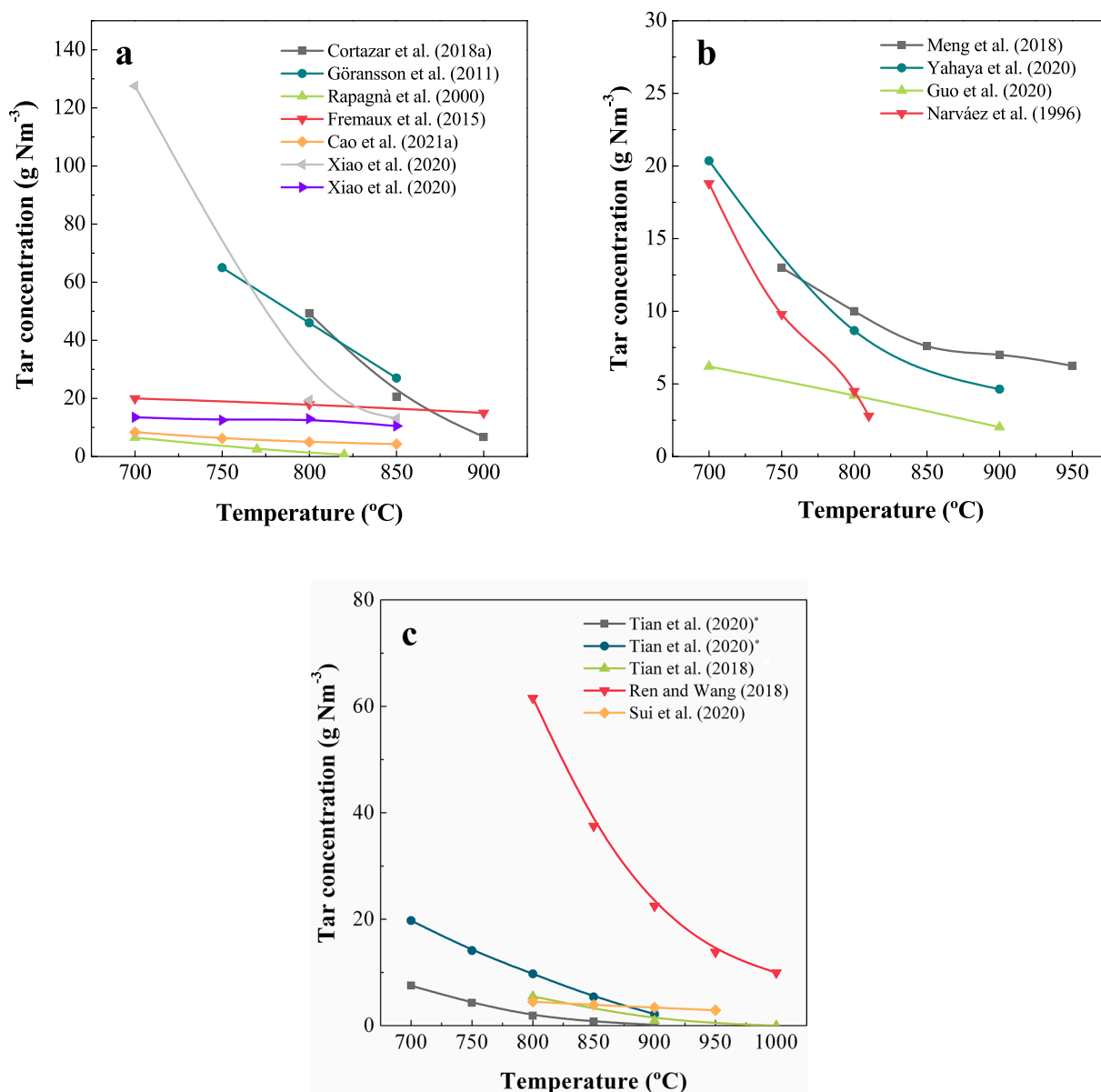
The selection and control of the operating conditions during biomass gasification is of uttermost importance for the reduction or elimination of tar in the gaseous stream. Among the operating parameters that affect the gasification performance, the most influential ones are as follows: temperature, gasification agent, S/B ratio, ER, residence time and pressure. Moreover, the type of biomass and its features (ash content, particle size and moisture) may greatly influence the distribution of the products obtained in the process [16]. It should be noted that the optimum operating conditions vary in different types of gasifiers [58]. In fact, the gasifier design determines the main process conditions. The residence time of the biomass derived volatile product stream on the reactor plays a key role on its performance. In fact, remarkable difference in biomass conversion efficiency and tar concentration can be observed among different gasification technologies. Whereas fluidized beds, spouted beds and entrained flow reactors are characterized by short or medium residence times, fixed beds, especially, downdraft fixed beds, have much longer residence times.

##### 3.1.1. Temperature

Gasification temperature is one of the most influential parameter in terms of tar formation and H<sub>2</sub> production [16]. The temperature range at which gasification is usually conducted varies from 700 to 1200 °C, although most of the research on biomass gasification selected the temperatures between 800 and 1000 °C due to the low melting point of biomass ash and high biochar reactivity [36]. It should be noted that the temperature range selected also depends on the gasification agent used (air, oxygen, steam or their mixtures) and the type of gasifier, with a correct fluidization regime being essential for a homogeneous temperature profile inside the gasifier in order to ensure suitable operation [58]. At low gasification temperatures, high tar concentrations are obtained, whereas at higher temperatures, tar content is significantly reduced due to the promotion and acceleration of tar cracking and reforming reactions [156]. The latter positively enriches the H<sub>2</sub> content in the syngas, with the lower values of CO and CH<sub>4</sub> contents [16]. However, it must be taken into account that for industrial size gasifiers, higher temperatures may cause fouling and reduce the cold gas efficiency of the gaseous stream as a greater amount of air needs to be fed.

The impact of temperature on the tar content in the gaseous stream has been analyzed in several researches [157–161]. Accordingly, a wide range of reactor configurations have been employed, with the most common ones being fixed bed (updraft, downdraft and crossdraft), fluidized bed, entrained flow, spouted bed, rotary kiln and plasma reactors [22,26,162]. Fig. 10 compares results reported in literatures wherein the influence of gasification temperature on tar content is analyzed. As will be shown later, (Section 3.1.2), the tar content is considerably affected by the type of gasification agent. For the sake of clarity, the graphs in Fig. 10 have been ordered according to the gasification agent used, i.e., steam (Fig. 10a), air or O<sub>2</sub> (Fig. 10b), and their mixtures (Fig. 10c).

As observed in Fig. 10, regardless the gasification agent used, the tar content is reduced as temperature is increased. Tian et al. [168] investigated the influence of reaction temperature (700–900 °C) on the gas composition, lower heating value (LHV), tar content, gas yield and H<sub>2</sub>/CO ratio of gaseous stream with a fluidized bed gasifier for the air–steam gasification of rice husk. Two bed materials were tested and a considerable tar reduction was attained when gasification runs were conducted at 900 °C (they reported tar values of 2.17 and 0.15 g Nm<sup>-3</sup> with silica sand and coal bottom ash, respectively). Guo et al. [166] reported a tar reduction to one third (from 6.2 g Nm<sup>-3</sup> at 700 °C to 2.02 g Nm<sup>-3</sup> at 900 °C) in the corn straw gasification conducted in a bench-scale internal circulating fluidized bed at the ER of 0.21. Rapagnà et al. [163]



**Fig. 10.** Influence of gasification temperature on tar content. Gasification agent: a) steam, b) air/O<sub>2</sub> and c) mixtures of steam-air [157,158,160,161,163–172]. \*Results not given on a dry basis.

conducted the steam gasification of almond shells in a fluidized bed using olivine as bed material. A decrease in tar content from 6.1 to 0.5 g Nm<sup>-3</sup> was observed as temperature was increased from 770 to 820 °C. A conical spouted bed reactor (CSBR) was used by Erkiaga et al. [44] to analyze the influence of temperature in the pinewood sawdust steam gasification using sand as bed material. The tar content was significantly reduced from 364 to 142 g Nm<sup>-3</sup> as temperature was increased from 800 to 900 °C due to the enhancement of tar cracking and reforming reactions. Cortazar et al. [161] investigated the influence of gasification temperature on product distribution and composition in a fountain confined conical spouted bed reactor using olivine as primary catalyst. This new configuration enhanced the spouting regime in the CSBR, leading to an improvement on the overall gasification efficiency. They reported a reduction on tar concentration from 49.2 g Nm<sup>-3</sup> at 800 °C to 6.7 g Nm<sup>-3</sup> at 900 °C.

Moreover, gasification temperature not only affects the tar content, but also influences tar composition [157]. It is noted that the diversity of tar classification by the researchers hampers the straight comparison of the literature results. In general, as gasification temperature increases,

tar is mainly formed from highly stable species (light and heavy polycyclic aromatic compounds (PAHs)) because light aromatics (1 ring) and heterocyclic compounds are considerably removed [58,60,157,173]. Mayerhofer et al. [174] analyzed the influence of temperature (750–840 °C) on tar composition using a fluidized bed reactor for the steam gasification of wood pellets. They observed that high temperatures were essential for the formation of secondary and tertiary aromatic and polyaromatic tar species. The composition of the tar (FTIR and GC/MS) at different gasification temperatures was also analyzed by Cortazar et al. [161], who proposed a mechanism of tar formation and its evolution with temperature. They observed that tar composition evolves with increasing temperature to more stable species in the range of secondary and tertiary tar (of higher molecular weight) due to the rearrangement reactions at the expense of the reduction or absence of tar containing branched or heteroatom compounds. Similar results have been reported in the literature [166,175,176].

### 3.1.2. Gasification agent

The gasification agent greatly influences the tar content and its

composition in the gaseous stream, as well as the reaction rate and the heating value of the produced gas, as a result of the different gasification reactions involved when different gasification agents are selected. The choice of gasification agent depends on the balance between the required syngas quality and process costs [36,58,177]. Several gasification agents have been employed in the literature, with the most common ones being steam, air, O<sub>2</sub>, CO<sub>2</sub> and their mixtures. To obtain a gas with low tar content, oxygen is the best candidate. However, the operating costs are high due to the energy required for oxygen production. Thus, air-blown gasifier is most widely used, although higher tar concentrations are produced than with O<sub>2</sub>. Attention has also been paid to the steam gasification of biomass because it generates syngas with relatively high hydrogen content, although higher tar concentrations are also produced. Nevertheless, steam gasification reactions are highly endothermic and an external energy supply is required. In view of these facts, air and steam mixtures seem to be promising from both economy and chemistry points of view, since the partial combustion of the biomass particle inside the gasifier supplies the heat required for the process, with tar formation and hydrogen production being moderate [156,178,179]. Moreover, CO<sub>2</sub> gasification seems to be very promising, as it improves the cold gas efficiency when added to the inlet air, at the same time as allows valorizing CO<sub>2</sub> [180]. Fig. 11 shows some literature results on the effect of air, steam and O<sub>2</sub>-air/steam mixtures on tar concentration. The main aim of this section is not to compare the results obtained by the different authors as diverse operating conditions, biomass type and gasification technologies were used. Thus, the results obtained for the same authors under the same conditions were compared below.

When comparing the results obtained with different gasification agents, it is fair to compare the gas yield under a dry and inert-gas-free basis to avoid the dilution effect of N<sub>2</sub>. As shown in Fig. 11, Gil et al. [181] and Pinto et al. [183] studied the effect of the type of gasification agent on tar concentration and recorded the highest tar concentrations for steam, 80 and 15 g Nm<sup>-3</sup>, respectively. In addition, both authors obtained lower tar concentrations with air and O<sub>2</sub>/steam mixtures. However, much lower differences could be observed for the tar concentrations obtained by Pinto et al. [183]. With regard to the research carried out by Gil et al. [181] involving air and O<sub>2</sub>/steam gasification, the gas yield was not measured on a N<sub>2</sub> free basis, which certainly explains the higher influence noticed. Jeremiáš et al. [187] also compared the influence of air and O<sub>2</sub>/steam on the gasification of wood chips in a fluidized bed and showed that the mixture was slightly more effective in tar reduction. As for Kitzler et al. [184], the comparison was done

between mixtures, concluding that the one with O<sub>2</sub> is the best to reduce the tar concentration. However, the high cost of O<sub>2</sub> does not balance that small decrease in tar. Pinto et al. [183] drew the same conclusion when adding O<sub>2</sub> to steam, as tar reduction was only 5 %.

Furthermore, Huynh and Kong [186] and Kihedu et al. [185] noted the same declining trend as the previous authors when they used air and air/steam mixtures, with the tar concentration being higher for the mixture. Both authors reported that tar was reduced by around 26 % when air was used. The results from Fig. 11 bring to light that O<sub>2</sub>-rich mixtures led to the lowest tar concentration followed by air.

There is no much literature regarding how tar composition is affected by the gasification agent. Jeremiáš et al. [187] reported that steam mixtures resulted in a tar with a lower amount of heavy PAHs compared to air-only gasification. In fact, the amount of this lump was reduced by almost half, from 11 wt% in air gasification to 6 wt% in O<sub>2</sub>/steam gasification. In the same line, Corella et al. [188] reported that tar produced in the steam gasification was easier to be removed than the tar obtained in air gasification. In the study carried out by Jeremiáš et al. [187], the amounts of heterocycles and light aromatics obtained with O<sub>2</sub>/steam mixture and air were almost the same, around 3 wt% for heterocycles and 41 wt% for light aromatics. Consequently, the amount of light PAHs was higher for O<sub>2</sub>/steam mixture (51 wt%) than for the air gasification (45 wt%). According to Gil-Lalaguna et al. [156], steam containing gasification mixtures led to a decrease in the fraction of light PAHs, as it seems that polymerization reactions were prevented when steam was used. The same authors [156] analyzed the composition of the gasification medium for gasification of sewage sludge in a fluidized bed and stated that *N*-aromatics and light PAHs were the most sensitive tar lumps to the steam/O<sub>2</sub> ratio.

It should be noted that the fuel mass ratio and gasification agent, i.e., S/B, ER and gasifying ratio (GR) when steam, air or O<sub>2</sub>-steam mixtures are used, respectively, are the key influential parameters in the formation of tar, and they are therefore discussed in detail in the following subsections.

**3.1.2.1. Influence of S/B ratio.** Steam is regarded as the most suitable gasification agent for the production of H<sub>2</sub> rich syngas [13]. Moreover, with steam gasification, syngas with a high heating value in the range of 10–15 MJ m<sup>-3</sup> is obtained, which makes its use attractive for energy production [16]. The endothermic nature of steam gasification reactions may involve an increase in the energy requirements of this process, thereby increasing the costs compared to the use of other gasification agents such as air. Moreover, the use of steam provides the additional

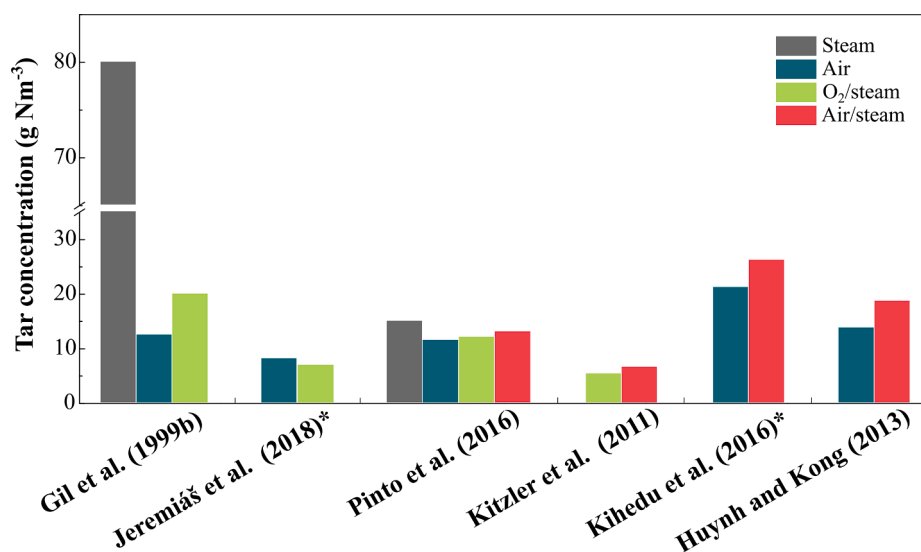


Fig. 11. Influence of the gasification agent on tar concentration [181–186]. \*Results not given in dry basis.

advantage of avoiding a costly separation process [22]. The main reactions involved in the biomass steam gasification are as follows: drying, pyrolysis, char gasification, reforming, cracking and Water Gas Shift (WGS) reactions [13,44,189].

S/B ratio is one of the key parameters involved in steam gasification. It is defined as the mass flow rate of the steam fed into reactor divided by the biomass mass flow rate. An increase in S/B ratio promotes the displacement of WGS reaction equilibrium and enhances steam reforming and heterogeneous char gasification reactions rate, and therefore a higher gas yield is obtained at the same time as tar reforming and char gasification reactions are promoted. However, an excess of steam could lead to a reduction in temperature, and consequently enhance tar formation. Fig. 12 shows some studies wherein the influence of S/B ratio on tar concentration is analyzed.

As shown in Fig. 12, high S/B ratios lead to an improvement in tar reduction. Among all the studies, the one by Goransson et al. [158] shows that tar concentration is mostly influenced by the S/B ratio. They studied the effect of S/B ratio in the 0.3–0.9 range in a dual fluidized bed and reported that the tar concentration was reduced by more than half, from 46.0 to 20.5 g Nm<sup>-3</sup>. Furthermore, Tian et al. [169] and Ren and Wang [170] observed a more moderate decrease in tar concentration when S/B ratio was varied from 0.6 to 1 and from 0.5 to 1.5, revealing that the amount of tar gradually declined from 5.5 to 1.8 g Nm<sup>-3</sup> and from 14.3 to 5.4 g Nm<sup>-3</sup>, respectively. However, other authors [163,164,166,191], see Fig. 12, concluded that slight increases in S/B ratio affect tar concentration. In fact, Luo et al. [190] did not note any tar for S/B ratios higher than 0.73 in a fixed bed reactor, whereas they recorded a tar concentration of 47.8 g Nm<sup>-3</sup> when no steam was in the feed. Taking the results of these studies into account, it could be concluded that there is an optimum S/B ratio that strikes a balance among high H<sub>2</sub> production, low tar concentration and external energy requirement, given that higher amounts of water must be vaporized and unreacted steam must be cooled and condensed. In this respect, Kaushal and Tyagi [192] suggested an optimum S/B ratio between 0.6 and 0.85 to ensure the thermal efficiency of the process and, at the same time, high steam partial pressure to promote steam reforming reactions.

Studies dealing with the influence of S/B ratio on tar composition are scarce and mostly the comparison between them turns to be difficult, as tar definitions are usually diverse. In general, it is agreed that the addition of steam changes tar composition, leading to a decline in the amount of light tar compounds [158,193]. Erkiaga et al. [44] and Guo et al. [166] conducted a detailed study in which the influence of S/B ratio was analyzed for the different tar lumps. However, different

conclusions were drawn, which might be related with the different operating conditions used. On the one hand, Guo et al. [166] varied the S/B ratio in the 0–0.6 range maintaining the reaction temperature at 700 °C and ER = 0.21 in air–steam gasification experiments. They concluded that an increase in the S/B ratio led to a decrease in the amount of heterocycles and light aromatics from 5 and 64 wt% to 2.5 and 47 wt%, respectively, whereas those of light and heavy PAHs increased from 11 and 1 wt% to 28 and 5 wt%, respectively, and the content of GC undetectable compounds decreased slightly from 19 to 17.5 wt%. On the other hand, Erkiaga et al. [44] analyzed the influence of S/B ratio between 0 and 2 at 900 °C in the biomass steam gasification and observed the opposite trend for the heterocyclic compounds and the light PAH fraction. They concluded that the main effect of increasing the amount of steam (S/B ratio from 0 to 1) was an increase in heterocyclic compounds (from 10 to 15.5 wt%) and a reduction in light PAHs (from 70 to 66 wt%), although the effect was rather limited. In addition, further increasing the S/B ratio from 1 to 2 did not change the tar composition.

**3.1.2.2. Influence of ER.** Air and pure oxygen have been extensively used as gasification agent, since it promotes combustion and partial oxidation reactions, providing the energy required for the gasification process. However, a syngas of low heating value is produced in the air gasification of biomass due to the dilution with N<sub>2</sub> [15].

ER is a crucial factor affecting the air/oxygen gasification performance. It is defined as the actual air/oxygen supply divided by the stoichiometric flow rate required for complete combustion [194]. In biomass gasification, it usually varies from 0.20 to 0.40. ER values below 0.2 result in incomplete gasification and a low heating value gas, and therefore more tar and char are formed [29,46,47]. Fig. 13 compares some results obtained in different studies in which the tar concentration was monitored by increasing ER. All selected studies gasify lignocellulosic biomass, although they applied different reactors, operating conditions (mainly gasifier temperature), and heat supply methods (allothermal or autothermal). When a gasifier is autothermal, a higher ER implies a higher reaction temperature, so it may be difficult to distinguish between the temperature or ER effect on the tar concentration [195]. Moreover, it is to note that all of the authors carried out air gasification, except Sui et al. [171] and Guo et al. [166], who conducted out steam/air experiments.

As observed in Fig. 13, an increase in ER leads to a reduction in tar concentration. When increasing ER, oxidation and exothermic reactions are enhanced, which promote the oxidation of volatiles and carbon.

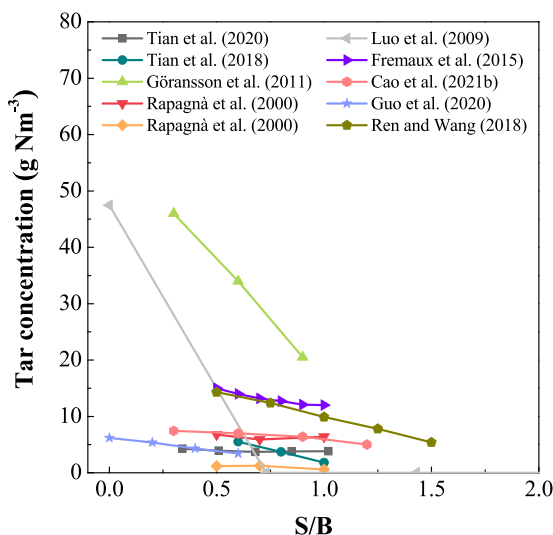


Fig. 12. Influence of S/B ratio on tar concentration in the syngas [158,163,164,166,169,170,190,191].

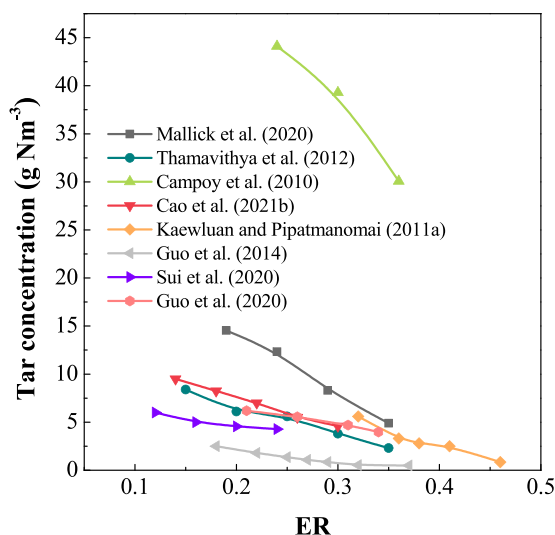


Fig. 13. Influence of ER on tar concentration in the syngas [166,171,191,194–198].



Thus, oxidative reactions of tar are favoured and so the reaction between tar and moisture in the raw material, producing more  $H_2$ , CO and other light gases [166]. However, excessively high ER values result in higher gas yields (though more diluted in air gasification) and shorter residence time, which avoids tar reduction. An optimum ER should strike a balance between high calorific value gas and low tar concentrations [191]. In this line, Sui et al. [171] varied ER from 0.12 to 0.24 at 800 °C in a fluidized bed gasifier and considered ER of 0.2 as an optimum value, as tar content did not significantly change when ER was further increased to 0.24. Furthermore, Guo et al. [194] reported a higher ER (0.32) as the optimum one. In fact, these authors studied the effect of ER between 0.18 and 0.37 in a downdraft fixed bed, which has poorer heat and mass transfer rates than fluidized beds, and noted that tar content dropped from 2.5 to 0.52  $g\ Nm^{-3}$  when the ER was increased to 0.32, but it hardly changed for higher ERs. Due to the dilution effect of  $N_2$ , high ER ratios involve high amounts of  $N_2$ , which reduces the tar concentration. Therefore, in those cases it would be necessary to check the tar yields (defined as the amount of tar produced in mass divided by the amount of biomass in the feed) to determine the real effect of ER in tar elimination.

Regarding the influence of ER on tar composition, Guo et al. [166] varied it between 0.21 and 0.34 in an autothermal fluidized bed and monitored the amounts of different tar lumps. The contents of heterocyclic compounds and light aromatics decreased with an increase in the ER, whereas those of light and heavy PAHs increased. According to those authors, as the ER increased, the  $O_2$  in the air promoted the oxidation of heterocycles and light aromatics, leading to the cleavage of C—H and C—O bonds and formation of free H and O radicals. Those free radicals enhanced dimerization reactions and  $H_2$ -abstraction- $C_2H_2$  addition sequence reactions, forming aromatics with a higher number of rings. Mallick et al. [196] gave also a very similar explanation.

### 3.1.3. Pressure

Gasification process may be carried out at atmospheric pressure or under higher pressures. In fact, special attention should be paid to the operating pressure as it might provide certain advantages from a chemical point of view, but also some challenges from an operational perspective as it was reported by several authors [36,89,177,199].

Following Le Chatelier's principle, some reactions are accelerated at high operating pressures due to chemical equilibrium shift towards the side with fewer moles. Thus, an increase in the amount of tar is expected with increasing pressure [18,174]. However, according to Mayerhofer et al. [174], the total gas pressure also influences the release of primary/secondary tar, as evaporation decrease leads to longer residence times of primary/secondary tar, and therefore cracking is enhanced and tar composition changed. As for Wolfesberger et al. [200], they pointed out that pressure has an influence on tar concentration depending on the gasifier design. Thus, pressurized operation is suitable for large-scale processes since heat transfer in the bed is much more efficient, and consequently gasification performance improves, reducing tar formation [18]. One of the advantages of the pressurized operation is that, depending on the final application of the produced syngas, it might not require an additional compression. With regards to the challenges involving the pressurized gasification, operation is more expensive and significant amount of purging gas is needed. Although the equipment size is smaller when higher pressures are employed because lower gas volumes are treated, they are 4 times more expensive than the equipment used in atmospheric gasification [199]. Therefore, pressurized gasification is only advisable if the syngas needs to be compressed for its final application [46,89,177,199].

In the literature, there is a discrepancy regarding the effect of pressure on tar concentration. As shown in Fig. 14, some authors reported that elevated pressures reduce the tar concentration, whereas others concluded that tar content increases by increasing pressure. Thus, Wolfesberger et al. [200] carried out biomass gasification at 825 °C in a 70 kW air-blown pressurized unit and found that the tar content declined from 4.4 to 1.7  $g\ Nm^{-3}$  when the pressure was increased from 1

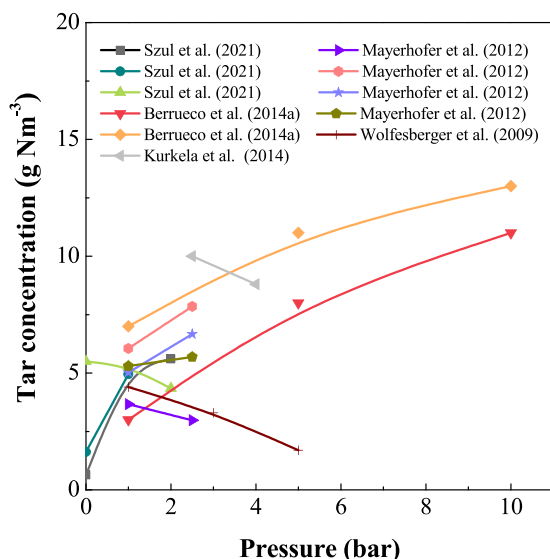


Fig. 14. Influence of the operating pressure on tar concentration [174,200,202–204].

to 5 bar. These authors suggested that as the pressure increases, the gas linear velocity declines due to the influence of pressure on the density of the gaseous phase, and therefore the residence time increases and the tar concentration decreases.

Mayerhofer et al. [174] changed the pressure from 1 to 2.5 bar in an allothermal bubbling fluidized bed gasifier operated at 750 and 800 °C with S/B ratios of 0.8 and 1.2. They reported a raising tendency for tar concentration under all the conditions studied with increasing pressure, except for the experiment at 800 °C and using a S/B ratio of 2. Likewise, Berruoco et al. [201] also revealed that elevating the pressure from 1 to 10 bar in a fluidized bed reactor, tar concentration increased from 3 to 11  $g\ Nm^{-3}$  for Norwegian spruce and from 7 to 13  $g\ Nm^{-3}$  for Norwegian forest residue. However, Szul et al. [202] used an autothermal fluidized bed reactor to analyse the influence of pressure in the 0–2 bar range on the gasification of softwood, bark and lignin at 850 °C, and found that tar concentration increased with pressure for bark and lignin, from 0.64 to 5.6  $g\ Nm^{-3}$  and from 1.62 to 4.95  $g\ Nm^{-3}$ , respectively, whereas a slightly decreasing trend was observed for the softwood, from 5.50 to 4.34  $g\ Nm^{-3}$ . Kurkela et al. [203] also reported a slightly declining trend for tar concentration (from 10 to 8.8  $g\ Nm^{-3}$ ) when the pressure increased from 2.5 to 4 bar, although they pointed out that the gasifier became unstable and operational changes were needed. They suggested that a bubbling fluidized bed would be more adequate for operating at high pressures than a circulating fluidized bed.

Regarding the effect of pressure on tar composition, Mayerhofer et al. [174] observed that heterocyclic compounds were hardly affected or slightly reduced with increasing pressure, whereas the concentration of light PAHs increased. The most significant change was reported for naphthalene, which rose from 0.61  $g\ Nm^{-3}$  to 1.79  $g\ Nm^{-3}$ . However, Wolfesberger et al. [200] found the opposite tendency for tar concentration, reporting that the amount of naphthalene and heterocycles increased from 40 and 3 wt% to 52 and 6 wt%, respectively and that of light PAHs decreased from 35 to 20 wt%, with that of light aromatics remaining steady.

### 3.1.4. Gas residence time

Gas residence time determines how many, and to what extent, consecutive reactions can take place at certain temperature [205]. Thus, residence time is a crucial parameter, which should be considered in the design of a gasifier. Short residence times hinder tar cracking and reforming reactions and lower conversion efficiencies, whereas high residence times allow greater exposure of tar to the gasification agent,

which reduces tar formation and leads to higher process efficiency [206].

Fixed bed reactors are characterized by long residence times, which make them so efficient for tar elimination, especially the downdraft gasifiers. In the case of updraft fixed beds, they produce a gas with a higher amount of tar than downdraft ones. Nevertheless, fluid beds have usually much shorter residence times. Regarding entrained bed gasifiers, they have a very short residence time, even lower than fluidized beds [207]. Spouted beds are also characterized by short residence times, below 0.5 s. Erkiaga et al. [44] showed that tar cracking and reforming was limited (very high tar concentration in the gaseous stream) in the biomass steam gasification carried out in a conical spouted bed reactor. In order to improve the efficiency of this reactor for biomass steam gasification, it was modified by inserting a fountain confiner and draft tube [208]. Cortazar et al. [209] showed that lower tar concentrations were obtained working with the fountain confiner and under fountain enhanced regime, as the distribution of the gas residence time was improved.

However, the literature has barely studied the influence of residence time on the gasification performance. That is, the studies were not mainly focused on tar concentration, although a few ones deal with experimental and simulation runs analyzing the effect of residence time on syngas compositions [210–212]. Paasen and Kiel [205] studied the effect of gas residence time by sampling the gas at different freeboard heights, which corresponded to 1.2 and 5.4 s, and reported that tar concentration decreased from 22.63 to 17.54 g Nm<sup>-3</sup>. Regarding individual tar lumps, the concentration of light and heavy PAHs increased, whereas the concentration of heterocyclic and light aromatic compounds decreased with increasing residence time, which is in agreement with the results of Kinoshita and Wang [213]. The latter adjusted the residence time between 3.2 and 4.8 s by varying the nitrogen flowrate at 800 °C and concluded that tar concentration was hardly influenced by residence time.

### 3.2. Biomass characteristics

The main biomass characteristics influencing gasification performance are biomass type, moisture content and particle size. The following subsections deal with the effect of biomass type and its features (moisture and particle size) on the product distribution, mainly tar concentration.

#### 3.2.1. Biomass type

Biomass could be classified into different groups according to their origin: agricultural biomass, forest biomass, municipal biomass and biological biomass [36]. Lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin, and their proportion depends on the original biomass type [16]. These principal components play a crucial role in biomass gasification, which also applies to the ashes produced. In fact, the proportion between these biomass components determines process performance. Thus, the cellulose and hemicellulose amount is associated with the gas yield and the lignin amount is correlated with the tar yield. Generally, biomass with high amounts of lignin lead to high tar yields, whereas those with high amounts of cellulose or fixed carbon lead to low tar contents [47]. Moreover, ash content and its composition play a remarkable role both in determining biomass char gasification kinetics [214] and causing the problems associated with ash melting in the gasifier [215].

Fig. 15 shows the variation in the tar concentration for different types of biomass based on the investigations reported in the literature. As observed, there is no clear tendency. It seems that other factors, such as reactor type and operating conditions, may have a major influence on tar composition than the biomass type. Accordingly, studies performed under the same experimental conditions should be considered for the evaluation of biomass composition. Schmid et al. [216] studied the steam gasification of different biomass pellets in a dual fluidized bed

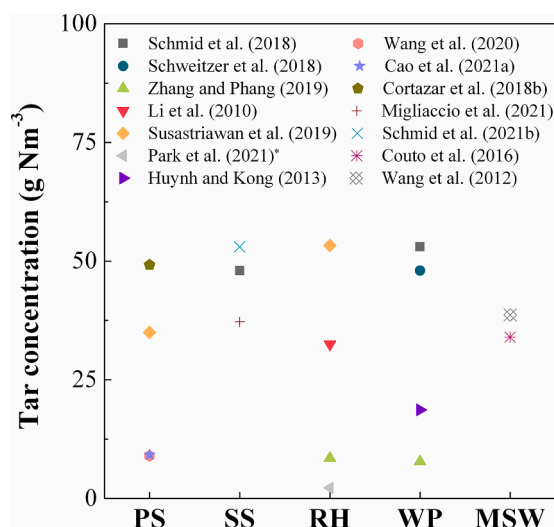


Fig. 15. Tar concentration for various biomass feedstocks (PS: pine sawdust; SS: sewage sludge; RH: rice husk; WP: wood pellets; MSW: municipal solid wastes) [51,172,186,209,218–227]. \*Results not given in dry basis.

gasifier. The tar formation differences were found to be mainly associated with the tar cracking activity of the ashes contained in some specific biomass as straw and sewage sludge. However, Schweitzer et al. [51] obtained higher tar yields for sewage sludge pellets than that for lignocellulosic biomass, this result was attributed to the presence of aromatic structures in sewage sludge. Herguido et al. [217] observed minor differences in the steam gasification of different lignocellulosic biomass wastes in a fluidized bed gasifier.

#### 3.2.2. Moisture

Generally, woody and some herbaceous biomass contain a moisture content below 15 wt%. However, some freshly harvested biomass could have moisture contents of up to 60 wt% [47].

The moisture content of the biomass has a great effect on the energy balance of the reactor. When a biomass with high amount of moisture (above 40 wt%) is fed, gasification temperature decreases, and therefore the process efficiency is reduced, as water evaporation is a highly endothermic process. In fact, an extra of 2260 kJ are needed to vaporize one kilogram of moisture in the biomass. According to the literature [13,18,47], biomass with less than 35 wt% of moisture should be treated to strike a balance between high quality syngas with low tar concentration and costs-benefits. Feeding biomass with a moisture content in the 10–15 wt% range is ideal for an adequate operation of the feeder and gasification performance, as the presence of some moisture in the feed could be advantageous [228].

In the case of handling high moisture content biomass, low feeding rates are advisable in order to maintain bed conditions stable, and therefore operate with high efficiency in the process [229]. Moreover, additional heat must also be supplied, either externally or by introducing some air or O<sub>2</sub> [47]. Regarding the reactor configuration, updraft fixed bed could be operated with 60 wt% of moisture, whereas the downdraft ones could only efficiently handle a moisture content of up to 25 wt% [15]. Thus, co-gasification is gaining attention in order to handle high moisture content biomass [183,230,231]. Furthermore, pre-treatments, such as drying, torrefaction or hydrothermal upgrading are also recommended in these cases [18,232].

Fig. 16 shows some of the studies in which the influence of the biomass moisture content on tar concentration was reported. The studies carried out by Paasen and Kiel [205] in a bubbling fluidized bed by varying the moisture content in the 10–43 wt% range showed that some moisture could be beneficial to the gasification process, as the enhancement of WGS and CH<sub>4</sub> and tar steam reforming reactions

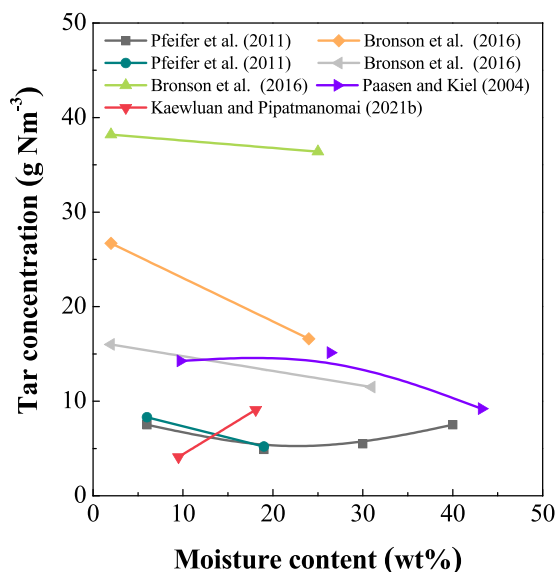


Fig. 16. Influence of the biomass moisture content on tar concentration [38,205,229,230].

reduced tar concentration from 14.3 to 9.2 g Nm<sup>-3</sup>. Likewise, Pfeifer et al. [38] in a dual fluidized bed reactor reported over a range of moisture contents (6–40 wt%) that the highest tar concentration (7.5 g Nm<sup>-3</sup>) was measured when the biomass with the lowest moisture content (6 wt%) was fed and the lowest (4.9 g Nm<sup>-3</sup>) when the biomass with 20 wt% moisture content was fed. For moisture contents of up to 40 wt%, tar concentration increased slightly, but these values were still below those for 6 wt% moisture content. Furthermore, Bronson et al. [229] did not observe a significant reduction in the tar concentration (from 38.2 to 36.4 g Nm<sup>-3</sup>) when wet fine biomass was gasified, whereas the reduction was more remarkable, from 26.7 and 16.0 g Nm<sup>-3</sup> to 16.6 and 11.5 g Nm<sup>-3</sup>, respectively, for moderate and coarse wet biomass particles. Unlike the previous authors, who supplied extra heat to keep the reactor temperature constant, Kaewluan and Pipatmanomai [230] experienced a reduction of 60 °C in both bed and freeboard temperatures when increasing the moisture content from 9.5 to 18.1 wt%, which led to higher tar concentrations. As for the evolution of tar composition with increasing biomass moisture content, no clear trend can be deduced from the results shown by Bronson et al. [229] and Paasen and Kiel [205].

### 3.2.3. Particle size

Biomass particle size is closely related to the limitations of the initial steps in the gasification process, such as the heating of the particle, pyrolysis and diffusion of gaseous products inside the biomass particle, and therefore to the process efficiency. Since smaller biomass particle sizes have larger surface area per unit mass, which means higher heat and mass transfer rates between phases, it can be foreseen that biomass size will enhance the gasification performance [16]. Moreover, small particles lead to less intraparticle reaction between tar and char, which affects the products yields [233]. However, reducing biomass particle size below 1 mm increases energy consumption exponentially, which accounts for around 10 % of the output energy obtained in the gasification process [234,235]. Therefore, it is essential to develop a versatile gasification technology that may handle large biomass particles without compromising heat and mass transfer phenomena [22].

Although the effect of biomass particle size has only been studied by few researchers using a variety of reactors, different trends and impact levels could be observed on tar concentration. On the one hand, Luo et al. [190], Lv et al. [236], Tian et al. [169] and Hernandez et al. [210] have reported that particle size reduction improved the gasification

performance by increasing gas production, and at the same time tar amount was reduced. On the other hand, other authors [44,237–239] stated that the influence of particle size in tar removal is negligible. Thus, Erkiaga et al. [44] studied the effect of particle size on biomass steam gasification using 0.3–1 mm (fine), 1–2 mm (medium) and 2–4 mm (coarse) sawdust particles in a conical spouted bed reactor, and concluded that particle size played a minor role at 850 °C because heat transfer rates in the bed were so high that the limitations of the physical steps were negligible. Thus, tar concentration increased only slightly as biomass particle size was increased, from around 243 g Nm<sup>-3</sup> for fine and medium sawdust to 263 g Nm<sup>-3</sup> for coarse sawdust. Regarding the influence of biomass particle size on tar composition, the same authors observed almost the same composition for all the biomass fractions (20–25 wt% for heterocycles, 5–8 wt% for light aromatics, 58–62 wt% for light PAHs and 10–12 wt% for heavy PAHs), concluding that particle size has no influence on the subsequent tar cracking process.

Particle size could play a significant role when other technologies are used, probably due to their lower heat and mass transfer rates. Some other researchers [229,240,241] found that fine particles could have a negative impact on gasification performance as they yielded a gaseous product with the highest tar loading. According to those authors, the presence of a greater amount of tar when fine biomass particles were fed could be partially ascribed to their entrainment. A fraction of the biomass particles was entrained from the bed just after feeding because their terminal velocity was lower than the operating velocity. As the volatiles are mostly released in the freeboard of the gasifier, they are less likely to be reformed, and tar formation is therefore enhanced. In relation to the tar composition, Bronson et al. [229] gasified three different size forest residues (<3.1755 mm, 3.175–6.35 mm and 6.35–19.05 mm) in an air-blown fluidized bed and they only observed differences in tar composition for the gravimetric tar.

### 3.3. Primary catalysts

The use of catalysts also has a positive impact on reducing the amount of tar generated in biomass gasification, since they enhance cracking and reforming reactions. The selection of a suitable catalyst with proper reforming and cracking activity could eliminate tar compounds and precursors [47]. These catalysts may be used as primary catalysts directly in the gasifier, or as secondary catalysts in downstream catalytic processes. The use of in situ primary catalysts is a promising method to reduce the tar concentration in comparison with the use of a more expensive secondary catalytic cracking reactor downstream [58,242,243]. A large number of materials with significant activity for tar cracking and reforming have been examined as primary catalysts. In the following subsections, the roles of different primary catalysts have on tar reduction will be reviewed. Those catalysts have been divided into three main groups: natural catalysts, metal catalysts and others.

#### 3.3.1. Natural catalysts

A wide variety of inexpensive natural catalysts have been thoroughly researched as primary catalysts, with olivine, dolomite and limestone having received much attention, due to their low cost, abundance and moderate activity. However, other minerals have also been used as primary catalysts, such as magnesite [110,244–246], ilmenite [247–250], limonite [251,252], bauxite [253,254], feldspar [255,256] and siderite [257].

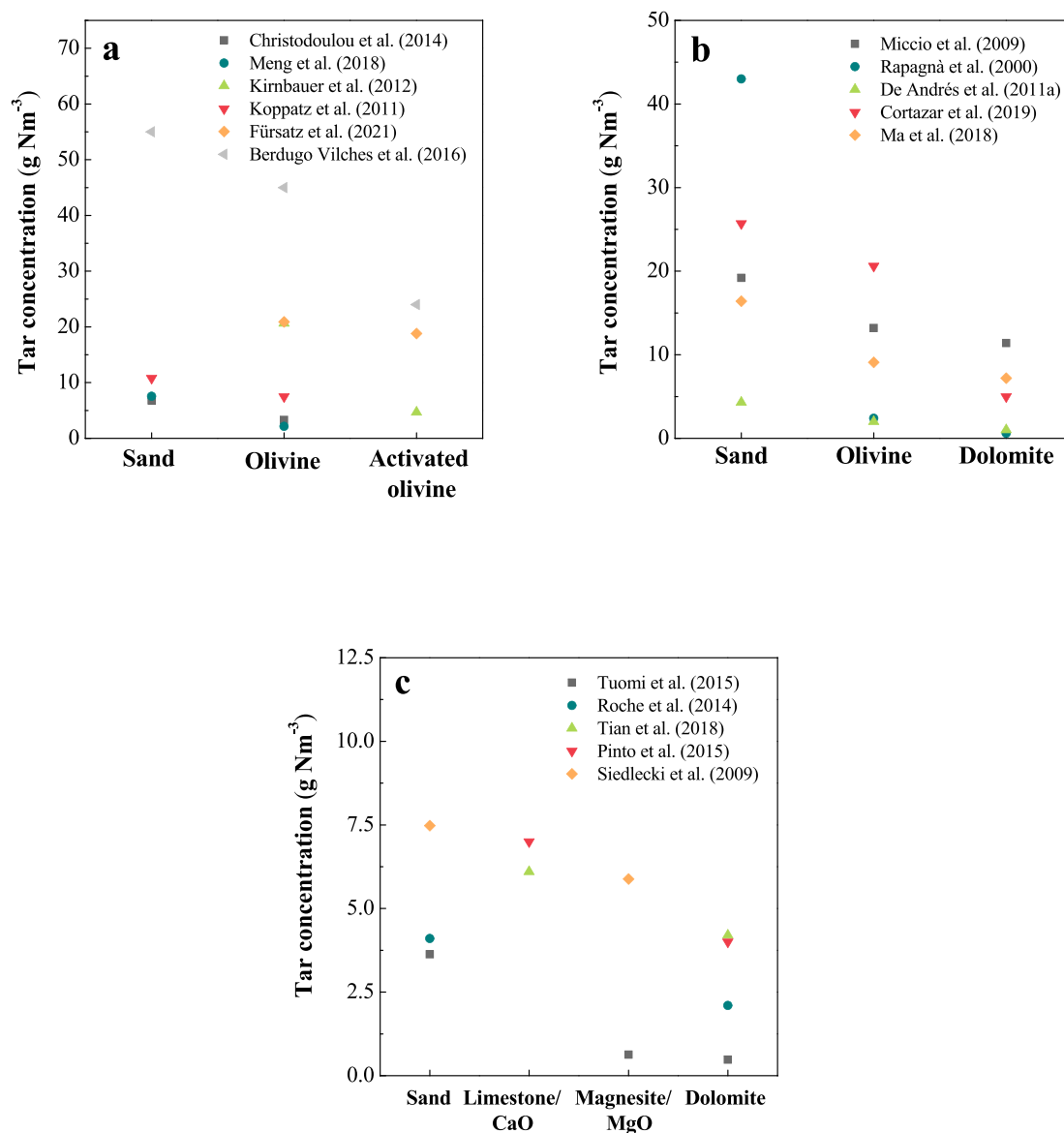
Dolomite is a calcium and magnesium carbonate mineral, ideally CaMg(CO<sub>3</sub>)<sub>2</sub>, olivine is a magnesium and iron silicate represented by the general formula (Mg, Fe)<sub>2</sub>SiO<sub>4</sub> and limestone is a carbonate sedimentary rock, mostly composed of calcite and aragonite minerals (CaCO<sub>3</sub>). All of them may also contain other trace metals. The chemical composition of those natural catalysts varies from source to source, as well as their surface areas, pore sizes and their distribution. Moreover, their catalytic activity can be improved by calcination at temperatures above 900 °C, as decarbonate (only for dolomite and limestone) and the oxides migrate to

the surface [57,242,258–260]. Thus, the catalytic activity of those natural catalysts in the biomass gasification seems to be related to CaO-MgO in the dolomite, MgO and  $\text{Fe}_2\text{O}_3$  phases in the olivine and CaO in the limestone. Regarding their performance, olivine has an outstanding mechanical resistance, comparable to that of both dolomite and limestone that may undergo severe attrition when used in fluidized bed reactors. However, as reported by Devi et al. [261], Koppatz et al. [262] and Kook et al. [263] the activity of dolomite is higher than that of olivine.

Typically, industrial-size plants use olivine as bed material, as calcium-rich layers on the surface of the particles appear after days of operation [264]. These layers emerge from the interaction of the bed material particles with the woody biomass ash, which improve the catalytic activity of the olivine, and therefore enhance tar reduction [265]. Fig. 17 compares the tar concentration results obtained by several authors when using diverse natural materials as primary catalysts in the biomass air/steam gasification. As shown, the results acquired with inert sand have been taken as a reference (associated with the thermal cracking effect). In order to shed light on the efficiency of these catalysts for removing tar, Fig. 17a shows the role of olivine and activated olivine,

Fig. 17b compares the performance between olivine and dolomite, while Fig. 17c illustrates the difference among dolomite, magnesite/MgO and limestone/CaO.

As observed in Fig. 17a, the use of olivine and activated olivine as in-bed catalysts improved tar conversion, thus, tar content values were remarkably lower than those obtained with the silica sand. Christodoulou et al. [266] and Meng et al. [157] obtained very similar tar concentrations for both sand and olivine in the biomass air gasification carried out in a circulating fluidized bed, accounting 51.5 and 71.7 % of tar reduction with olivine. In the same line, Koppatz et al. [262] reported a bit higher tar values and a lower tar removal capacity of olivine in a dual fluidized bed reactor at 850 °C, from 10.8 to 7.7  $\text{g Nm}^{-3}$  (tar reduction of 30.5 %). However, Berdugo-Vilches et al. [249] reported much higher tar contents in their experiments conducted at 800 °C, although the introduction of olivine as primary catalysts significantly reduced tar concentration by approximately 18 %. The differences observed in the capacity of olivine for tar removal might be related to the iron species present in the olivine surface [273,274]. Regarding the use of activated olivine, a noticeable tar reduction was reported by Kirnbauer et al. [267] with spent olivine (rich in Ca) and Berdugo-



**Fig. 17.** The influence of different natural catalysts on tar concentration. Natural catalysts: a) sand, olivine and activated olivine, b) sand, olivine and dolomite and c) sand, dolomite, magnesite/MgO and limestone/CaO. [110,151,157,163,169,245,249,256,262,266–272].

Velches et al. [249] with K-loaded olivine, from 20.6 and 46 g Nm<sup>-3</sup> to 4.6 and 25 g Nm<sup>-3</sup>, respectively. Nevertheless, Fürsatz et al. [256] observed negligible catalytic effect by applying olivine (with a non-negligible content of heavy metals), as tar concentration only decreased by approximately 10 %, from 20.9 to 18.8 g Nm<sup>-3</sup>.

Fig. 17b confirms that dolomite is more catalytically active for tar reduction than olivine. Rapagnà et al. [163] compared the use of sand, olivine and dolomite at 770 °C in a fluidized bed reactor and reported a drastic tar reduction from 43 g Nm<sup>-3</sup> with sand to 2.4 g Nm<sup>-3</sup> with olivine and 0.6 g Nm<sup>-3</sup> with dolomite. Other authors also observed that dolomite performed better than that of olivine, with the tar content being reduced from 13.2 to 11.4 g Nm<sup>-3</sup> [268], 2.1 to 1.0 g Nm<sup>-3</sup> [151] and 9.1 to 7.2 g Nm<sup>-3</sup> [269] in a fluidized bed reactor. In the case of Cortazar et al. [272], they noticed a more outstanding behavior of dolomite compared to olivine as tar concentration was decreased from 20.6 to 5.0 g Nm<sup>-3</sup>.

Fig. 17c aims to determine the effect of dolomite or its individual components, i.e., MgO and CaO, on tar reduction. As observed, better results were obtained with dolomite in comparison with magnesite/MgO or limestone/CaO. Those three natural catalysts enhanced tar removal comparing to the use of inert sand. Tuomi et al. [245] tested the performance of MgO and dolomite in a fixed bed reactor at 850 °C and obtained a lower amount of tar by using dolomite, 0.48 g Nm<sup>-3</sup>, than using MgO, 0.63 g Nm<sup>-3</sup> (tar concentration was 3.63 g Nm<sup>-3</sup> with sand). Similarly, Siedlecki et al. [110] reported that magnesite reduced tar concentration by 21 % compared to sand. Furthermore, Tian et al. [169] and Pinto et al. [271] analyzed the effectiveness of the in-bed use of limestone and dolomite in air/steam gasification carried out in a fluidized bed and reported that tar concentration decreased from 6.1 and 7 g Nm<sup>-3</sup> (with limestone) to 4.2 and 4.0 g Nm<sup>-3</sup>, respectively, when a dolomite bed is used instead of limestone.

The use of in situ primary catalysts not only affects the tar content, but also influences its composition. According to Cortazar et al. [272] the distribution of the various tar fractions depends on the catalyst characteristics (acid or basic). Independent of the natural primary catalyst used, reported studies [31,244,268] show that light PAHs were the main compounds in tar, among which naphthalene, acenaphthylene, fluorene, phenanthrene and indene are noteworthy. Moreover, heavy PAH still remained, with fluoranthene and pyrene being the most abundant compounds. To sum up, primary natural catalysts lead to a tar made up of highly stable compounds.

The in situ use of natural catalysts is an attractive method to remove tar, although the tar content in the product gas may not meet the requirements for use in downstream applications. However, they can act as a guard catalyst to avoid the rapid deactivation of an expensive secondary catalyst by carbon deposits.

### 3.3.2. Metal catalysts

Supported metal catalysts have been extensively used in the steam reforming of biomass tar model compounds, especially transition metal catalysts [259,260,275]. Amongst them, nickel based catalysts are the most used ones in both research and industrial processes. In fact, there are a lot of commercially available Ni catalysts and they are supported on a wide variety of materials, such as Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, MgO and even olivine and dolomite natural ores [276–282]. Those catalysts have a high catalytic activity for tar removal. They are also active for methane reforming and WGS reactions, which leads to an increase in the syngas and hydrogen yields [259]. However, catalysts containing nickel are very toxic and undergo a rapid deactivation caused by carbon deposits on the catalyst surface [57,283–285]. Thus, iron based catalysts have recently attracted an increasing attention for tar reduction, as iron is cheaper and less toxic than nickel. The activity of iron based catalysts is related to the tar cracking and reforming capacity of metallic iron and WGS reaction enhancement capacity of magnetite (Fe<sub>3</sub>O<sub>4</sub>) [105,286–290].

In spite of the great research effort in the catalyst development for tar

elimination working with tar model compounds, the literature dealing with in situ metal catalysts for the biomass air and/or steam gasification is still scarce, with Al<sub>2</sub>O<sub>3</sub> and olivine supports being the most studied. Miccio et al. [268,291] impregnated Fe and Ni on Al<sub>2</sub>O<sub>3</sub> and tested in the air/steam gasification of spruce wood pellets (ER = 0.17 and S/B = 0.66) in a bubbling fluidized bed. They reported similar tar concentrations for both catalysts, i.e., 8.4 g Nm<sup>-3</sup> for Fe/Al<sub>2</sub>O<sub>3</sub> and 8 g Nm<sup>-3</sup> for Ni/Al<sub>2</sub>O<sub>3</sub>. Besides, Assadullah et al. [292] tested the performance of Rh/CeO<sub>2</sub>/SiO<sub>2</sub> catalyst and a commercial steam reforming catalyst G-91 (14 wt%Ni) in air gasification of cedar wood, and obtained a negligible tar amount when Rh/CeO<sub>2</sub>/SiO<sub>2</sub> catalyst was used, whereas tar concentration was of about 30 g Nm<sup>-3</sup> when G-91 catalyst was used. Dolomite was also used as catalyst support by Chaiprasert and Vitidsant [293] and tested in coconut shell steam gasification at 800 °C in a fluidized bed reactor, with Ni and small amounts of Pt, Co and Fe impregnated as promoters.

Fig. 18 shows the influence of iron and nickel based in situ catalysts on tar concentration and compares with that of pure olivine. As observed, metal loading to olivine reduces the tar amount in the process. Virginie et al. [105] studied the performance of 10 wt%Fe/olivine catalyst in the biomass steam gasification at 850 °C in a dual fluidized bed and reported that tar reduction was more significant in the presence of Fe/olivine in the bed than with olivine (5.1 and 2.6 g Nm<sup>-3</sup> of tar content for olivine and Fe/olivine respectively). Moreover, Barisano et al. [150] used the same catalysts in the biomass steam/O<sub>2</sub> gasification at 890 °C in an internally circulating bubbling fluidized bed and noted the total content was reduced by 38 % (from 10.1 to 6.2 g Nm<sup>-3</sup>). The same trend was observed by Cortazar et al. [294] with a lower Fe load catalysts (5 wt%), who reported that tar concentration was reduced approximately by half, from 20.6 to 10.4 g Nm<sup>-3</sup>.

Regarding Ni incorporation, Pfeifer et al. [31] added 20 % of 5 wt% Ni/olivine catalyst to a bed of olivine to study tar removal in a 100 kWth dual fluidized bed reactor, and obtained a tar concentration as low as of 0.5 g Nm<sup>-3</sup>. Meng et al. [157] reported a slightly higher value of tar concentration (0.86 g Nm<sup>-3</sup>) when Ni-Fe/olivine catalyst was used for pine sawdust air gasification in a circulating fluidized bed. The literature data compared in Fig. 18 reveal that the Ni/olivine catalyst is the most effective in terms of tar removal.

With respect to tar composition, Barisano et al. [295] and Cortazar et al. [294] reported that naphthalene was the major tar compound using Fe/olivine catalyst, with its amount being still very high. Furthermore, they observed a significant removal of phenol, methyl phenol, 1-methyl phenol, 1-methyl naphthalene, dibenzofuran, 1-H

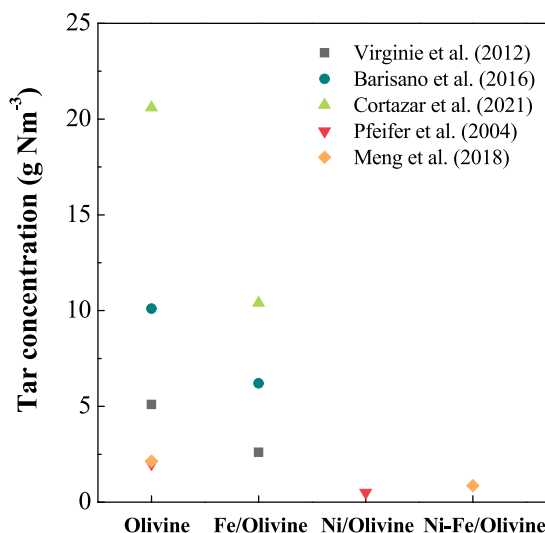


Fig. 18. The influence of olivine based metal catalysts on tar concentration. [31,105,150,157,294].

phenalene, 2-phenyl naphthalene and pyrene. Thus, they concluded that the more stable tar compounds are more difficult to be removed even with the Fe/olivine catalyst.

### 3.3.3. Other types of catalysts

Researchers are searching for other low cost in situ catalysts with high catalytic activity for tar abatement. Apart from natural catalysts, other materials, such as  $\gamma$ -alumina, spent FCC catalyst or cement have also been examined. The  $\gamma$ -alumina and the spent FCC catalyst are of acid character, whereas cement is basic. As  $\gamma$ -alumina has been widely used as catalyst support, it has also been explored in biomass gasification. Kuramoto et al. [296] and Matsuoka et al. [297] verified the effectiveness of  $\gamma$ -alumina for removing tar and yielding hydrogen. Concerning the use of the spent FCC catalyst, it is a highly interesting application, since it allows prolonging the lifetime of a refinery waste material [298,299].

Fig. 19 compares the research work carried out by various authors wherein the above materials were employed as primary catalysts. However, the comparison of the results is not straightforward due to different operating conditions and technologies used, which led to unclear trends. In any case, it is noteworthy that the use of those catalysts in-bed improved tar removal over that corresponding to the inert sand. In addition, this figure also shows that alumina has been the most tested material, probably due to its suitable mechanical properties and cracking activity [300]. In the case of Cortazar et al. [272], they compared the behaviour of  $\gamma$ -alumina and spent FCC catalyst in the biomass steam gasification at 850 °C and observed that  $\gamma$ -alumina led to much lower tar concentration (16.2 g Nm<sup>-3</sup> with FCC catalyst vs 5.0 g Nm<sup>-3</sup>).

### 3.3.4. Primary catalyst deactivation

Catalysts stability has been widely investigated in the literature for steam reforming processes, especially using tar model compounds or two-stage processes. However, there is scarce information in the literature dealing with the stability of primary catalysts and the main causes of deactivation.

Regarding natural primary catalysts, most of the research groups stated that they did not notice any activity loss after many experimental runs. Nevertheless, Kirnbauer and Hofbauer [37] and Berdugo-Vilches et al. [249] observed that when biomass gasification runs were conducted on olivine as primary catalysts, it was activated due to the deposition of biomass ash on the surface of the bed material. Berdugo-Vilches et al. [249] reported that the bed material was more active for

tar removal after 1 week of operation than in the initial runs.

Concerning metal primary catalysts, a stable activity of the catalysts was observed by different authors. Thus, Miccio et al. [268] reported that Ni/Al<sub>2</sub>O<sub>3</sub> catalysts remained stable for the whole duration of the test, suggesting no deactivation phenomena due to coke deposition or structure modifications. Likewise, Pfeifer et al. [31] reported no noticeable deactivation in two tests of 30 and 45 h for Ni catalyst, and Virginie et al. [105] confirmed that Fe/olivine catalysts was fairly stable during 48 h of continuous operation. Moreover, Assadullah et al. [292] noticed a slight decrease in the surface area of Rh/CeO<sub>2</sub>/SiO<sub>2</sub> catalysts after use for at least in 20 experiments, but reported that deactivation was not severe. Nevertheless, other authors reported deactivation of the primary catalysts [293,294]. Cortazar et al. [294] observed significant deactivation of Fe/olivine catalysts after 140 min on stream in a bench scale gasification plant due to metal iron oxidation to Fe<sub>3</sub>O<sub>4</sub>. Chairprasert and Vitidsant [293] showed coke deposition on Ni/dolomite catalysts. A small amount of Pt, Co and Fe as promoters reduced the amount of coke compared with the catalyst without promoter, with the amount of coke formation in the catalysts being according to the following order: Ni/Pt/dolomite (6.5 wt%) < Ni/Fe/dolomite (8.3 wt%) < Ni/Co/dolomite (9.3 wt%) < Ni/dolomite (16 wt%).

### 3.4. Modifications in reactors and innovative designs

Although the use of in-bed catalysts and the optimization of the operating conditions (temperature, ER and S/B) allow improving the gasification process performance, they may not be sufficient to attain the gas purity required for downstream gas applications (Table 4). In this context, further measures involving redesign of the gasifier or development of innovative designs are needed to obtain a clean product gas [306].

According to Bridgwater [307], there are three key strategies which may improve the reactor performance in terms of tar reduction and obtain high process efficiencies. The first one is the injection of some air or pure O<sub>2</sub> along the reactor to promote the partial oxidation of tar by creating various thermal levels in the gasifier. The next one is the use of heated bed materials to favour the tar cracking. The last one is to increase the residence time of the tar inside the reactor, as with some technologies most volatiles are directly carried out by the gas flow without contacting the bed material. Accordingly, several attempts have been proposed in the literature to decrease tar concentration, such as the injection of secondary air/O<sub>2</sub>, changes in reactor design and feeding mode, use of filter candles in the freeboard and staged gasification (drastic zone division of pyrolysis and reduction stages). Those strategies will be discussed in the following subsections.

#### 3.4.1. Secondary air/O<sub>2</sub> injection

Air staging has been widely applied in the coal combustion field. Although the main target for both processes is different (reduce the emissions of sulphur and nitrogen compounds in combustion but tar elimination in gasification), both aim to promote the partial oxidation of the undesirable compounds [308–312]. In the gasification process, the staging injection of air/O<sub>2</sub> can significantly raise the temperature in the upper section of the reactor, and consequently improve the gasification performance to a great extent due to the oxidative atmosphere. In that way, a more uniform temperature profile is achieved in the gasifier. However, raising the temperature through secondary air injection in the freeboard may have a negative impact on the gas heating value [167,197,198,313,314].

Thamavithya et al. [197] placed the secondary air supply port 1100 mm above the primary air distributor in a spout-fluid bed and used secondary air to primary air ratios of 10, 20 and 30 % by keeping primary air flow rate constant. The temperature of the partial oxidation zone increased from 578 °C with no secondary air to 742 °C with 30 % secondary air supply, which caused tar content to reduce from 5.63 to 1.53 g Nm<sup>-3</sup>. Likewise, Campoy et al. [198] investigated the effect of

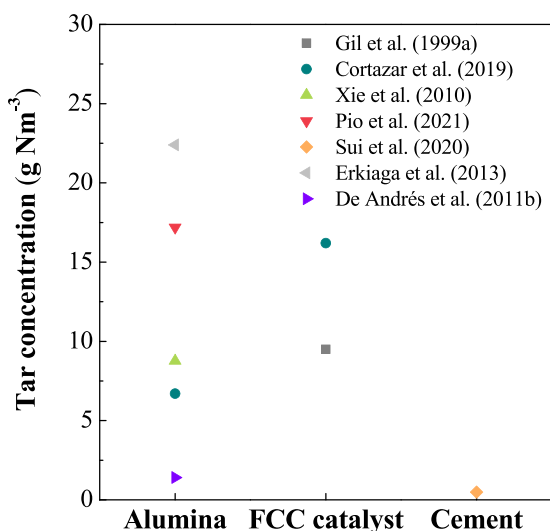


Fig. 19. The influence of  $\gamma$ -alumina, spent FCC catalyst and cement as primary catalysts on tar concentration [171,272,301–305].

some primary measures on the performance of an air-blown fluidized bed gasifier and reported that the injection of secondary air (keeping SR constant and fixing the secondary to total air ratio at 11 %) reduced the gravimetric tar and the water-soluble tar compounds by 20 and 30 %, respectively. However, the total tar concentration was still high (20–23 g Nm<sup>-3</sup>) and the fraction of stable aromatic tar compounds in the gas increased significantly. Recently, Tsekos et al. [315] investigated the effect of secondary air injection in a novel indirectly heated bubbling fluidized bed and achieved a 91 % reduction in the total tar content (from 45 to 4 g Nm<sup>-3</sup>) when 8 kg h<sup>-1</sup> of secondary air was injected. Regarding tar composition, naphthalene, acenaphthylene, anthracene and toluene were the most abundant tar species, with naphthalene being the prevailing one by far. Even so, the secondary air injection entailed more than 87 % reduction in naphthalene concentration. Wang et al. [314] conducted a more extensive research on the effect of the injection point and direction for coal gasification in a circulating fluidized bed. They concluded that higher injecting points led to a more remarkable improvement in the gasification performance and the tangential injection was more effective than the radial injection because of the preferable contact between gasification agents and char particles.

Although secondary air/O<sub>2</sub> injection reduces tar concentration, in most cases it is not enough for the gas to meet the requirements in downstream applications. Thus, many research groups have decided to take some other complementary measures to further reduce tar concentration.

### 3.4.2. Candle filters in the freeboard

Under UNIFHY (UNIQUE gasifier for hydrogen Production) European Project framework, joint R&D efforts by several research organizations and private companies throughout Europe managed to integrate biomass gasification and hot syngas cleaning and conditioning into one reactor vessel [316]. With this in mind, they placed a catalytic hot gas filter (a commercially available ceramic candle filter) in the freeboard of a fluidized bed (Fig. 20). The first record of inserting a catalytic filter within the biomass gasifier and testing it in real process conditions was published by Rapagnà et al. [317], although several previous studies dealing with hot gas catalytic filtration under simulated biomass gasification conditions can be found in the literature [318–320]. The main objectives of placing a filter candle in the freeboard were to improve the thermal efficiency of the whole process, allow tar conversion, remove trace elements and avoid particle entrainment in the gas at the reactor outlet, so delivering high purity syngas [317,321]. Regarding the advantages of this innovative solution, the operating temperature of the catalytic filter candle was close to the process temperature, which favoured tar reforming reactions towards permanent gases, and at the same time particles and other trace elements, such as ammonia, were eliminated.

Experimental tests in fluidized bed gasifiers at laboratory and industrial scale using different types of filter candles (catalytic and non-catalytic) demonstrated their efficiency in tar reduction. Almost all

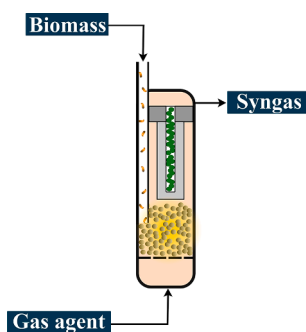


Fig. 20. Scheme of a catalytic candle filter located in the freeboard of a fluidized bed reactor.

effort was devoted to the development of adequate filtering material. At the beginning, Rapagnà et al. [317] tested a commercially available DIA-SCHUMALITH type N filter supported on SiC with outer mullite membrane activated with Ni/MgO-Al<sub>2</sub>O<sub>3</sub> catalyst (catalytic filter) or without being activated (non-catalytic filter) in the biomass steam gasification at 830 °C with an S/B ratio of 1. They reported that the catalytic filter activation reduced tar concentration from 1.9 to 0.7 g Nm<sup>-3</sup>. Subsequently, Rapagnà et al. [321] used the previous non-catalytic filter with the hollow-cylindrical space filled with 6 wt%Ni/MgO catalysts and obtained similar tar concentration as with the catalytically active filter (of around 0.7 g Nm<sup>-3</sup>). They reported that, although the reduction in methane and tar conversion was rather low, the catalytic performance of this filter element remained stable for a total gasification time of 22 h.

Al<sub>2</sub>O<sub>3</sub> based grain-sintered candle filters showed a great improvement in the gasification performance. Thus, Rapagnà et al. [322] compared the non-catalytic option of Al<sub>2</sub>O<sub>3</sub> based filter with one in which Ni was integrated and observed a stable catalytic activity over 20 h of continuous steam biomass gasification, achieving an average tar conversion of 93.5 % (0.15 g Nm<sup>-3</sup> of tar concentration was reported for the Ni impregnated catalytic filter). Moreover, Rapagnà et al. [149] tested the performance of a new catalytically activated Al<sub>2</sub>O<sub>3</sub> based hot gas filter candle, which was improved with an Al<sub>2</sub>O<sub>3</sub> outer membrane and an integrated catalytic ceramic foam. In this candle, a MgO-NiO catalytic layer system was applied on the filter support and a MgO-Al<sub>2</sub>O<sub>3</sub>-NiO based catalytic layer system was applied on the integrated catalytic ceramic foam. They obtained a product gas with a very low amount of tar (0.057 g Nm<sup>-3</sup>) and free of dust when 20 % of dolomite was added to the olivine bed.

However, the main technical problem associated with the use of filter candles is related to the difficulty to impregnate the metal active phase directly on the ceramic filters due to their considerable size (the typical length of this filtering device is 1.5 m). Thus, with the aim of making the overall process more feasible in practice, Savuto et al. [323] followed the strategy by Rapagnà et al. [321] and proposed to fill the inner empty space of commercial Al<sub>2</sub>O<sub>3</sub> filtering candles with pellets of a steam reforming catalyst available in the market. They studied three different configurations: i) empty candle, ii) candle partially filled with catalyst pellets and iii) candle totally filled with catalyst pellets, and concluded that the runs with the partially filled candle led to the best results in terms of tar elimination (0.3 g Nm<sup>-3</sup>). Moreover, the Ni catalyst was very stable for approximately 4 h, with no lower performance or degradation being observed over this time period.

Although coking and clogging are critical in the performance of candle filters in the freeboard, they have been hardly studied yet. Rapagnà et al. [317] measured the pressure drop through the catalytic filter candle under different operating conditions and reported a linear increase with time until a plateau was reached. Thus, they conducted 22 h gasification tests and detected fine particles being attached to the filter and forming a layer of increasing thickness. However, the increasing amount of fines attached to the filter did not lead to a substantial change in pressure drop, as it remained below reasonable limits until the end of the test. Moreover, they confirmed that periodical cleaning of the dust cake by conventional back pulsing system is enough for the adequate operation of the candle filters. They advise N<sub>2</sub> as blowback gas for the regeneration, once it has been preheated to avoid possible condensation problems.

### 3.4.3. Location of the feeding point

In bench- and lab-scale fluidized bed reactors, the feeding point is usually above the bed or on a middle location in the bed [149,172,204], whereas in large pilot plants, the feeding point is at the lower part of the bed, more specifically near the gas distributor plate [249,256,262,324].

According to Corella et al. [325], the location of the feeding point depends on the differences in biomass features, bed material and produced char/ash densities. In fact, biomass has a bulk density 2–5 times

lower than silica sand and this difference is 10 times or even higher for the char and/or ash formed in the biomass gasification. Therefore, there is a big tendency for biomass, char and ash to move upward in the bed and segregate at the top. Thus, these authors investigated the effect of the feeding location on tar concentration and reported lower tar yields when biomass was fed at the lower section in the bed than from the top (4.5 wt% vs 13 wt%) in a bubbling fluidized bed. Thus, when biomass is fed from the top of the reactor, the contact between the fluidizing gas and bed material is very poor and the volatiles directly leave the reactor (with low residence time). Consequently, a big amount of undesirable byproducts, such as tar and char, are formed. However, when the biomass is fed at the lower end of the bed, although a priori it could entail more operational problems than feeding from the top, there is sufficient time for the biomass to interact with the bed material and the gasification agent, enabling efficient carbon conversion and less tar formation. This is consistent with the results by Gómez-Barea et al. [306], who stated that feeding the biomass at the bottom increases the residence time for tar conversion, thereby reducing the tar concentration, at the same time leading to more stable and heavy (aromatic) tar compounds in the gas.

Other researches also selected in-bed feeding as the optimum one [314,326,327]. Kern et al. [326] studied the influence of the position at which the biomass must be fed into a DFB gasifier. Steam gasification experiments of wood pellets carried out at 850 °C and  $S/B = 0.6$  concluded that much lower tar contents were observed with in-bed feeding than with on-bed feeding, as tar concentration was reduced from 26.5 to 8.7 g Nm<sup>-3</sup>. Likewise, Wilk et al. [327] also showed that in-bed feeding was more favorable for wood pellet gasification in a DFB, although they hardly observed differences for the co-gasification of plastic waste and wood pellets. Wang et al. [314] performed coal gasification in a CFB in order to compare on-bed feeding and feeding from the loop seal (the feed was injected into the bed), and reported that coal feeding by loop seal was an effective way to improve the gasification performance because the residence time was prolonged by making the coal to circulate through the whole furnace. The same conclusion was drawn by [328] based on a CPFD model for a fluidized bed reactor.

#### 3.4.4. Multi-staged gasifiers

As explained in Section 1.1, the gasification process consists of several overlapped steps, such as heating and drying, pyrolysis, oxidation and gasification itself, making it impossible to control and optimize the different steps separately in a conventional gasifier. Multi-stage gasification processes separate and combine the pyrolysis and the gasification steps in a single controlled one. Thus, a better understanding of the complex thermal conversion process, as well as the optimization of the conditions in the entire process, is needed [329].

The most common strategy is to combine pyrolysis and gasification in a two- or three-stage gasification process, either in one unit or in separate reactor units combined in series. With both reactor configurations, high process efficiencies with high char conversion rates and high purity syngas with low tar concentration are possible. However, the complexity of the process is increased by combining different reactors [316]. According to Gómez-Barea et al. [306], staged gasification is the only method capable of maximizing process efficiency and minimizing secondary gas treatment (by avoiding complex tar cleaning) with reasonable simplicity and cost. Recently, Kargbo et al. [330] evaluated the economic feasibility of two-stage gasification systems and reported they are around 25 % more economical than single-stage ones.

Several two-stage gasification concepts have been recently developed by separating pyrolysis and gasification zones. Thus, biomass is pyrolyzed in the first reactor (1st stage), and the produced volatiles and char are then directed to the second reactor (2nd stage), where the tar is cracked and reformed and the char is gasified. According to Spath et al. [331], efficiencies of around 90–95 % are obtained in two-step gasification processes, whereas only 70–72 % are attained in single-stage fluidized bed gasifiers. Different reactors were combined, such as two

downdraft fixed beds, updraft and downdraft fixed beds, bubbling fluidized bed and fixed bed, fluidized bed and entrained flow reactor and bubbling fluidized bed and riser.

Regarding the different reactor configurations based on fixed beds, Bui et al. [332] developed the two-stage throatless reactor combining two single-stage downdraft gasifiers (one above the other) and reported that tar content was about 40 times lower (about 50 mg Nm<sup>-3</sup>) than for a single-stage reactor operating under similar conditions. More recently, Restrepo et al. [333] designed, built and operated a 50 kWe two-stage downdraft gasifier with an extensive gas cleaning system, and reported that the quality of the gas is good enough for use in SOFCs. Sulc et al. [334] also used a fixed-bed based reactor arrangement, but in this case the first stage was an updraft fixed bed reactor. Fixing the temperature at 670 °C for the first stage and at 950 °C for the second one, they reported that tar content was reduced from 6.8 g Nm<sup>-3</sup> to 45.1 mg Nm<sup>-3</sup>. Furthermore, the Biomass Gasification Group in the Technical University of Denmark [335–337] designed the “Viking” gasifier consisting of a screw conveyer pyrolysis unit and a downdraft fixed bed (scaled up to 200 kWe), which operated successfully more than 4000 h. In this technology, the biomass pyrolysis takes place on the screw conveyor and the produced volatiles and char are directed to the gasification unit, which allowed obtaining a gas with a tar content below 15 mg Nm<sup>-3</sup> with no heavy compounds. In the same line, Mun et al. [338] and Choi et al. [339], from the University of Seoul, developed the first generation UOS gasifier comprised of a bubbling fluidized bed and a fixed bed in series for the dried sewage sludge gasification. They noticed that, using activated carbon in the fixed bed, a tar free syngas was obtained when the temperature was kept at around 800 °C in both stages.

With regards to fluidized bed combinations, Niu et al. [40] and Pei et al. [340] developed a novel two-stage gasifier, consisting of a fluidized bed and an entrained flow bed connected in series. The fluidized bed was used in the first stage for converting biomass into raw gas, tar and char at approximately 650–700 °C, while a swirl-melting furnace with liquid slagging was provided with temperatures above 1250 °C for tar cracking, char reforming and ash melting in the second stage. Continuous steady operation of the pilot plant demonstrated the feasibility of this two-stage gasification technology, as a significant improvement in fuel gas quality was obtained, i.e., the tar content was reduced from 14.25 to 0.95 g Nm<sup>-3</sup> with the addition of the second stage in which an ER of 0.19 was used [40]. As for Zeng et al. [30] and Wang et al. [324], they also used a two-stage gasification system, but in this case both opted for using a fluidized bed in the first stage and a riser in the second one. Zeng et al. [30] reported tar values as low as 0.4 g Nm<sup>-3</sup> in the air gasification of herb residues, with the temperatures in the pyrolyzer and gasifier being of around 700 and 850 °C, whereas Wang et al. [324] obtained higher values (of around 4.35 g Nm<sup>-3</sup>) in the oxygen-rich air gasification of pine chips. Fig. 21 shows these two novel two stage gasification systems.

Likewise, it is worth mentioning the biomass pyrolysis and in-line reforming strategy for producing a H<sub>2</sub>-rich syngas without tar [341]. In this process biomass thermal degradation and the catalytic gasification of pyrolysis volatiles (mainly bio-oil) are performed in two different reactors. Besides sharing some advantages of the multi-stage processes such as the possibility to select the optimum conditions in the pyrolysis and in-line reforming steps separately [342], they may operate at lower temperatures than those in gasification process, which makes possible the use of highly active reforming catalysts which completely remove tar. Moreover, milder temperatures prevent catalyst deactivation by sintering [343].

The pyrolysis step is usually carried out at around 500 °C to ensure full devolatilization of the biomass. Furthermore, the catalytic steam reforming step is performed at the 600–800 °C temperature range on metal supported catalysts. Temperatures below 600 °C lead to low reaction rates, whereas higher temperatures than 800 °C cause catalyst deactivation due to metal sintering. In this step, the volatile stream leaving the pyrolysis reactor passes through the catalytic bed and reacts



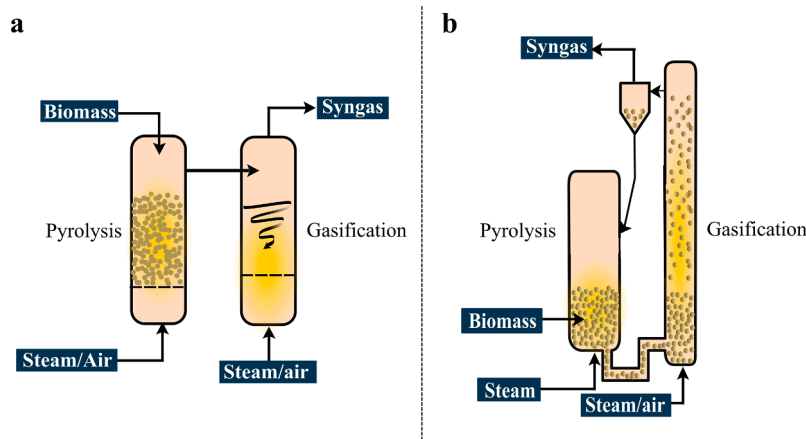


Fig. 21. Reactor configurations for two-stage gasifiers connected in series based on a) fluidized and entrained bed reactors developed by Niu et al. [40] and Pei et al. [340], and b) bubbling fluidized bed and riser developed by Zeng et al. [30] and Wang et al. [324].

with the steam on the active sites of the catalyst [344]. Due to the high endothermicity of this step, a small amount of  $O_2$  is commonly introduced. Although the presence of  $O_2$  in the reforming reactor reduces  $H_2$  production, it contributes to in situ combustion of the coke, which improves catalyst stability [345,346].

A wide variety of reactor configurations has been used in the literature for biomass pyrolysis and in-line reforming such as a combination of two fixed beds [347,348], fluidized and fixed bed [349], screw kiln and fixed bed [350], spouted and fluidized bed [351,352] and spouted and fixed bed [353]. Fig. 22 shows the combination of conical spouted bed and fluidized bed reactors for the pyrolysis-reforming strategy. It should be pointed out that most of the pyrolysis-reforming studies are conducted in batch laboratory units, particularly fixed beds [354,355]. However, when continuous operation is preferred, these results may be extrapolated to the conditions of industrial reactors, with catalyst stability being controlled. Operation in fluidized beds and spouted beds in continuous operation has been reported by several authors [349,356,357]. Performing the first step in a fast pyrolysis reactor, which is characterized by high heating rates and very short residence times (below 1 s), ensures an efficient conversion of the biomass into volatiles with low char yields (the liquid fraction or bio-oil is maximized), increasing the  $H_2$  potential of the process [344]. Moreover, this combination allows a better control of the process operating conditions, especially temperature [358].

This process has shown an outstanding capacity for  $H_2$  production, obtaining values around 10 wt% once process operating conditions and catalysts were optimized [351,352,354,359,360]. The selection of a suitable catalytic material and preparation method, as well as the design of an adequate catalyst, are essential aspects for ensuring its good

performance. As reforming catalysts have a vital role on process conversion efficiency and product yields, several studies dealt with catalysts synthesis using different supports, promoters and active metallic phases as well as their proportion in the catalyst [347,348,350,351,361,362].

When it comes to the selection of active metals, they should promote reforming and WGS reactions in order to enhance  $H_2$  production in the reforming step. Ni catalysts have been widely used in the literature, as their activity for reforming  $CH_4$  [363], naphta [364] and pyrolysis volatiles [365,366] is well known. Other transition metals, such as Co or Fe and noble metals (Rh, Ir, Pt and Ru), have also been studied [361,367,368]. Regarding the catalyst support, it must provide a high surface area, adequate pore distribution, mechanical strength and good thermal stability, promoting the dispersion of the active phase and modulating catalysts activity. An active catalyst is not enough for a satisfactory process performance, the stability of the catalyst must also be considered [369].

Thus, catalyst lifetime lies in its capacity for avoiding deactivation by coke deposition, metal sintering and poisoning. In fact, the pyrolysis-reforming process is considerably limited by the fast deactivation rate of the catalysts. The addition of promoters enhances the activity, selectivity and stability of the catalyst, as was proven by Kimura et al. [370] and Sánchez-Sánchez et al. [371]. Furthermore, fluidized bed reactors allow implementing advanced catalyst regeneration strategies [372].

Gómez-Barea [373], Choi et al. [374] and Pan et al. [375], among others, implemented three-stage gasification. Usually-three-stage gasifiers comprise pyrolysis, reforming and combustion steps separately. However, Choi et al. [374] developed a three-stage gasifier (UOS gasifier) consisting of an auger for biomass devolatilization, as well as fluidized and fixed bed reactors placed in series for reforming and cracking, but none of the reactors was used for char combustion. In an experiment they performed by feeding sewage sludge on activated carbon in the fixed bed, in which the temperature in the auger reactor was  $710\text{ }^\circ\text{C}$  and in the fluidized bed and fixed bed reactors  $830\text{ }^\circ\text{C}$ , the tar content in the gas stream was  $22\text{ mg Nm}^{-3}$  (including  $N_2$  flow). A scheme of this reactor combination is shown in Fig. 23a. Pan et al. [375] used a different reactor configuration based on three separated reactors called DTBG (decoupled triple bed gasifier), which consisted of a gas–solid countercurrent and solid–solid concurrent moving bed for pyrolysis, a gas–solid crosscurrent moving bed for the gasification/reforming of the volatiles on a catalyst, and a fast fluidized bed for char and catalyst coke combustion. This reactor configuration system was used in the steam co-gasification of sawdust and bituminous coal, which reduced the tar content from  $25.35$  to  $4.87\text{ g Nm}^{-3}$  when Fe/olivine catalyst was used instead of sand. Gómez-Barea et al. [373] also proposed a three-stage gasification (FLETGAS) process based on fluidized

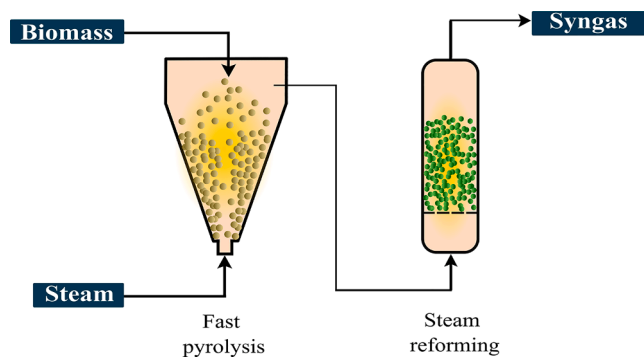


Fig. 22. Reactor configuration for pyrolysis and steam reforming strategy based on conical spouted bed and fluidized bed reactors, developed by Arregi et al. [352] and Santamaria et al. [351].

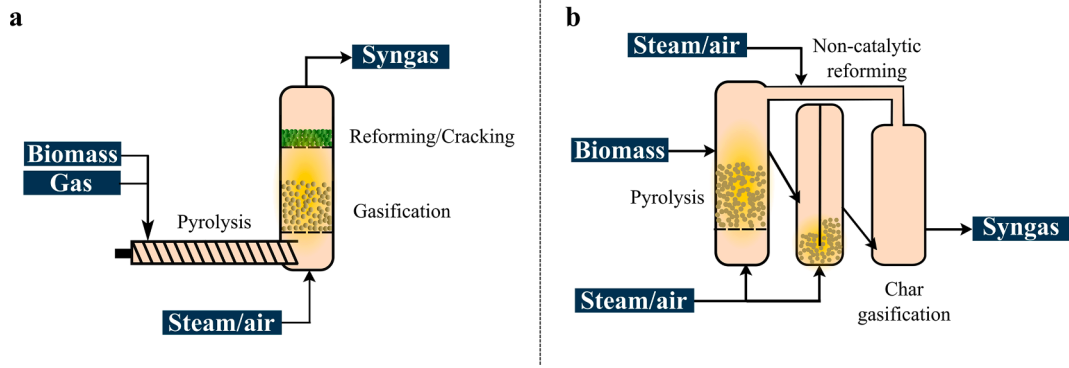


Fig. 23. Configurations for three-stage gasification systems, developed by a) Choi et al. [374] and b) Gomez-Barea et al. [373].

bed devolatilization, non-catalytic air/steam reforming of the gas coming from the devolatilizer, and chemical filtering of the gas and gasification of the char generated in the devolatilizer in a moving bed (shown in Fig. 23b). Moreover, these authors compared their results with those obtained in the one-stage process and observed that tar content was reduced from 31 to 0.01 g Nm<sup>-3</sup> under similar conditions.

Researchers from Fraunhofer-Institute for Solar Energy Systems [376] developed a novel fixed-bed gasifier consisting of four independent zones (gasification and cracking of the tar, reduction and oxidation) separated by moving grates, which allow controlling the residence time in every zone. This novel technology was employed in the air gasification of biomass. They managed to reduce the tar content of the product gas throughout 60 h operation by increasing temperature and bed height in the cracking zone, which led to tar contents below 50 mg Nm<sup>-3</sup> without the need of costly gas clean-up systems.

3.4.5. Modifications in reactor design

This section describes the most innovative modifications and re-designs carried out in DFB, spouted bed and fixed bed gasifiers with the aim to improve the gasification performance, specifically from the perspective of tar removal.

3.4.5.1. Changes in DFBs. Researchers from TU Wien [256,265,377,378] proposed an advanced concept for gasification following the DFB technology. Fig. 24 compares the classic and advanced designs of their DFB reactor. The classic design (Fig. 24a),

which is typically used at the existing industrial sized plants, consists of a bubbling fluidized bed as gasification reactor and a fast fluidized bed as combustion reactor. Both reactors are connected via two loop seals from their lower and upper parts. The bed material leaving the combustion reactor is separated from the flue gas via a cyclone and then introduced into the gasification reactor again, as it works as heat carrier for the overall endothermic gasification. The produced char is used as fuel and transported to the combustion reactor, where it is burned with air. Additional fuel can be introduced into the combustion reactor to control the gasification temperature and compensate the relatively high heat losses of the experimental pilot plant. In this process, the flue gas stream and the product gas stream are separated, leading to a N<sub>2</sub>-free product gas.

In order to improve the gas–solid contact within the gasification reactor, an advanced design was developed (Fig. 24b). This innovative design is equipped with two gravity separators on top of the reactors. Compared to the use of cyclones, the gas and particle velocities are lower, which leads to smooth separation of the bed material from the gas streams, allowing the use of relatively low abrasion resistance materials, such as calcite. Therefore, calcite can also be used without profuse continuous replacement of the bed material. Besides those developments regarding separators, the key innovation is related to the design of the gasification reactor. The gasification reactor consists of two main parts: the lower part with the biomass feeding point, which works as a bubbling fluidized bed, and the upper part operating as a countercurrent column with turbulent fluidized bed zones. The countercurrent column

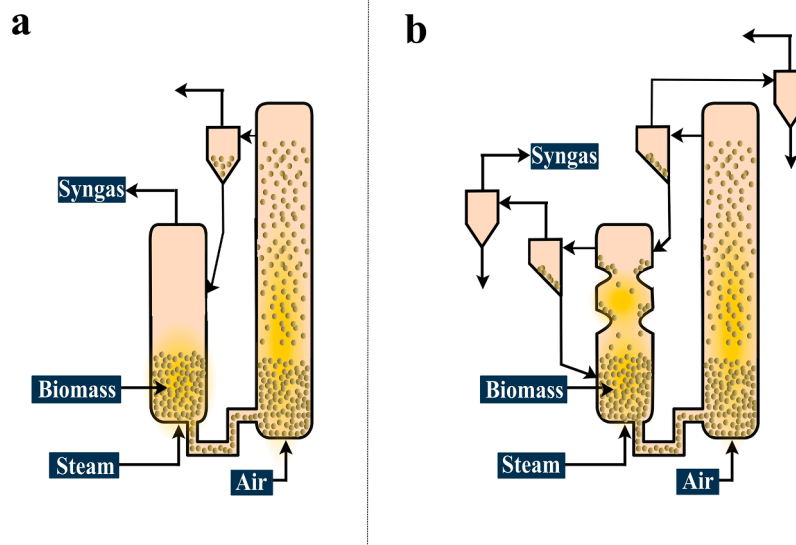


Fig. 24. Traditional (a) and advanced (b) designs of the 100 kWth BFB pilot plant at TU Wien.

results from the hot bed material, which is separated from the flue gas stream and introduced into this column. Furthermore, the column is equipped with constrictions, which lead to a distribution of the bed material hold-up over the height of the column. As a result, the interaction of bed material and the product gas in the upper part of the gasification reactor is increased significantly. To sum up, this innovative design allows the use of soft materials due to the gentle separation units and, furthermore, increases the gas–solid contact and residence time of the product gas through geometrical modifications in the gasification reactor.

Benedikt et al. [377] conducted gasification tests with wood and calcite as bed material in their novel plant and compared the results with those corresponding to a conventional plant using olivine under similar conditions. The results showed that the new configuration led to a product gas with remarkably lower tar content ( $1.87 \text{ g Nm}^{-3}$  rather than  $8.65 \text{ g Nm}^{-3}$ ), i.e., a decrease of 78 %. The higher tar conversion in the new configuration was explained by the coupling of two effects: (i) The more active bed material (calcium oxide) enhanced steam reforming reactions and (ii) the higher temperatures in the countercurrent column for cracking reactions. Moreover, no heterocyclic tar components were detected in the runs with calcite and the percentage of class 5 tar was significantly lower in the runs conducted in the improved pilot plant. Since the development of this innovative design, great effort and work have been devoted to testing the performance of the plant using a great variety of lignocellulosic materials (softwood, hazelnut sheels, bark, sugarcane bagasse, rice husk, straw and so on), biogenic residual (chicken manure), bed materials (limestone, feldspar, quartz and mixtures) under different operating conditions, as reviewed by Schmid et al. [379].

More recently, Di Carlo et al. [380] proposed a cold model of a novel pilot scale dual bubbling fluidized bed gasifier-HBF2.0 (100 kWth of biomass input). It consists of two concentric cylindrical fluidized beds inside a single vessel; the external is for gasification and the internal for combustion. The two fluidized beds are interconnected with a baffle plate, which contains an opening at the base and another one at the bed surface, to allow bed material circulation and operation at different temperatures and superficial velocities. Heat is exchanged between the combustor and the gasifier by the circulation of the bed material: sand and residual char in the slow bed (gasifier) flow into the fast bed through the lower orifice and hot sand is recycled back into the slow bed through the upper orifice. The main novelties of this design are i) the system is compact, and thus suitable for small scale applications, with both reaction chambers (gasification and combustion) being integrated in one cylindrical body; ii) the heat exchange between the two chambers occurs by the circulation of the bed material and also by conduction/convection through the wall of the internal cylinder; iii) the higher temperature chamber (combustor), operating at  $900\text{--}950 \text{ }^\circ\text{C}$ , is thermally insulated; this reduces the drawback of thermal losses in small scale applications; iv) the longer residence time in the combustor (bubbling bed) allows complete burning of char particles.

Kuba et al. [381] implemented two measures on-site to optimize the Senden DFB power plant. The first measure was based on bed particle activation through ash layer formation. According to Kuba et al. [264] and Fürsatz et al. [256], layered olivine particles (used) have higher catalytic activity compared to those of fresh olivine, as they have Ca-rich surfaces active for tar reduction. Thus, a new line for recycling layered olivine and a hopper were installed. This recycling line connects the combustion reactor with the hopper, where the spent olivine is discharged and stored, and afterwards, used to compensate the bed material losses. Regarding the second measure, separately regulated additional fluidization nozzles were introduced into the inclined wall of the gasifier to improve the mixing of the biomass and catalytically active bed material, and so to avoid segregation, which led to further decrease in the tar content in the product gas. After implementing these two modifications, those authors reported that the layered olivine reduced tar concentration from  $17.7$  (before optimization) to  $14.2 \text{ g Nm}^{-3}$ , and

even a more significant reduction when nozzles were installed (to  $10.3 \text{ g Nm}^{-3}$ ). These two operation points for optimizing long-term running were suggested by Kuba and Hofbauer [175].

**3.4.5.2. Changes in spouted beds.** The research group lead by Professor Olazar developed a novel reactor configuration based on a conical spouted bed, called fountain enhanced spouted bed. Fig. 25 shows a scheme of the conventional and novel spouted beds. Conventional conical spouted beds (Fig. 25a) are characterized by short gas residence time, which is a key strength for pyrolysis process since secondary reactions are minimized and so, the bio-oil yield is maximized. Multiple studies supported the suitability of spouted beds for pyrolysis [382–384]. However, this is a serious drawback for gasification, hindering tar conversion and consequently, the overall process efficiency [44]. In order to overcome this issue, the incorporation of the fountain confiner was proposed. The fountain confiner is a tube welded to the lid of the reactor, which has its lower end close to the bed material. By inserting the fountain confiner two main objectives were pursued: increase the gas residence time and improve the contact of biomass derived gases and catalyst particles. Both objectives were successfully achieved with the hydrodynamic regime attained with the incorporation of a fountain confiner in the conical spouted bed reactor [208,209].

In the conventional spouted bed the volatiles leave the reactor straight away through the outlet located in the upper section of the reactor, which lead to short residence time of tar and very little contact with the bed material. However, the novel fountain confined spouted bed (Fig. 25b) prevents volatiles from leaving directly the gasifier as they must flow downwards and then upwards through the shell between the confiner and reactor wall to get out. Thus, the extended gas flow path narrows the residence time distribution and improves the contact with the bed material. Moreover, this reactor operates under fountain enhanced regime (approximately 4 times the minimum velocity of the conventional spouted beds), being characterized by a great expansion and turbulence of the bed. This novel reactor provides a highly flexible and stable hydrodynamic regime and the possibility of operating with fine materials and high fountain heights with a negligible particle entrainment [208,209].

Cortazar et al. [209] checked the advantages of the fountain enhanced spouted bed reactor in biomass steam gasification and compared with the performance of the conventional reactor. In both cases the same operation conditions were employed:  $850 \text{ }^\circ\text{C}$ , S/B ratio of 2 and olivine as primary catalyst. Tar content was reduced from  $49.2 \text{ g Nm}^{-3}$  using the conventional configuration to  $20.6 \text{ g Nm}^{-3}$  when operating with the fountain enhanced spouted bed. Moreover, a great improvement in the process conversion efficiency was achieved, with gas and  $\text{H}_2$  productions reaching  $1.3 \text{ Nm}^3 \text{ kg}^{-1}$  and  $5 \text{ wt}\%$  [209]. The use of the fountain confiner also allowed for operating with dolomite without fine particle elutriation even when dolomite attrition was substantial [272]. In fact, this device was originally design to avoid entrainment problems when fine powders were used [385,386]. Thus, tar value as low as  $5.0 \text{ g Nm}^{-3}$  and gas and  $\text{H}_2$  productions of  $1.6 \text{ Nm}^3 \text{ kg}^{-1}$  and  $7.3 \text{ wt}\%$  were obtained using dolomite as primary catalysts [272].

**3.4.5.3. Changes in fixed beds.** The installation of additional nozzles is a strategy that has also been used in downdraft gasifiers to avoid the bypass of volatiles through relatively cold zones, and consequently improve gasification performance [387–389]. According to Susanto and Beenackers [389], multiple air nozzles or ring type oxidation zones are only valid up to a few hundred  $\text{kg h}^{-1}$  capacity at best. With the aim of scaling up a concurrent gasifier, these authors installed a separate combustion chamber within the reactor and developed a downdraft moving bed gasifier with internal recycle. By establishing a recycle gas flow countercurrently with the solids feed, the heat transfer to the bed above the oxidation zone is greatly improved, which resulted in a more

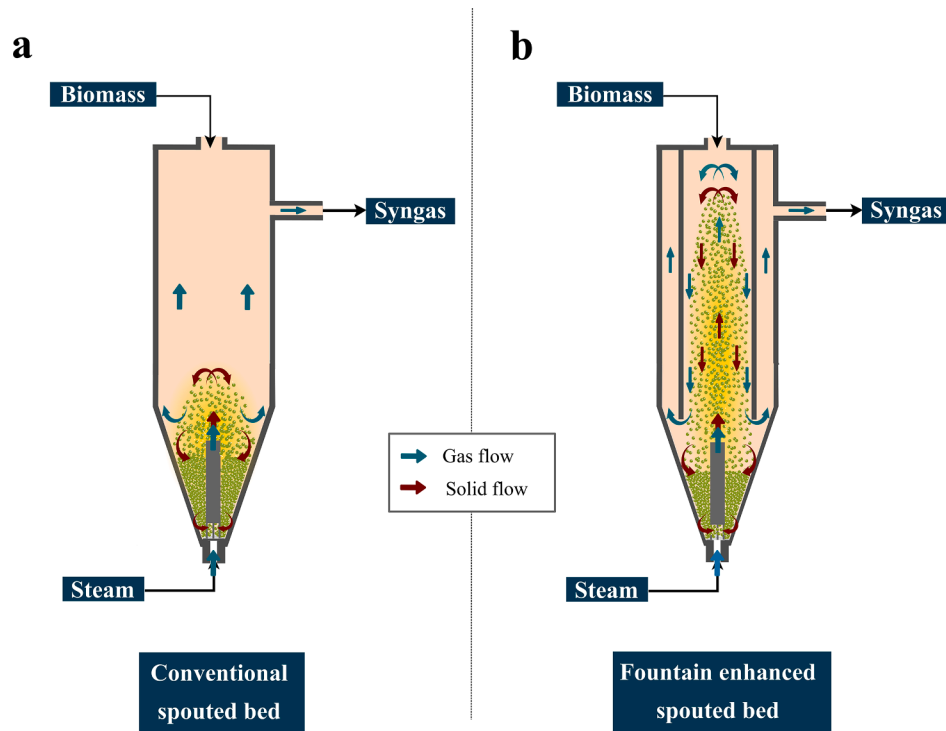


Fig. 25. Schematic representation of conventional (a) and fountain enhanced (b) spouted beds and their respective gas flow patterns.

complete pyrolysis of the solids upon entering the reduction zone. Thus, the recycle system greatly reduced the tar content in the produced gas to values below  $0.1 \text{ g Nm}^{-3}$ . They also observed that tar content decreased by increasing the recycle ratio (recycle gas to gasification air) to 0.6, but no further tar reduction was observed for higher ratios. Furthermore, Machin et al. [387] changed the entry angle of the gasification agent to the combustion chamber from  $90^\circ$  to  $72^\circ$ , creating a swirl flow. This altered fluid dynamic behaviour promoted mixing of the gasification agent with the pyrolysis gases. Consequently, the temperature inside the combustion chamber was homogenized, thus diminishing the formation of cool areas between the nozzles. In addition, this modification increased the residence time of the gas inside the combustion chamber, thereby increasing the thermal cracking of tar in this zone and decreasing the tar concentration in the producer gas. The tar in this new configuration did not exceed  $10 \text{ mg Nm}^{-3}$ . More recently, Rahman et al. [388,390] gathered the modifications of the previous two authors and proposed a low-tar biomass (LTB) gasifier. This reactor is provided with a separate combustor inside the reactor in the partial oxidation zone and the gasification agent is fed into the combustor from the top of the reactor by three nozzles inclined  $120^\circ$  and oriented towards the center of the combustor. The use of wood chips with a moisture content of 11–34 wt% resulted in a very low tar content of  $10.6 \text{ mg Nm}^{-3}$ .

Kurkela et al. [391] introduced a catalytic modification in their reactor design. The gasifier is a combination of the updraft gasification and a second catalytic step integrated within the upper part of gasifier, which is VTT's third fixed-bed gasifier design called staged fixed-bed gasifier (SXB). The primary gasification stage takes place in a traditional counter-current fixed bed reactor, whereas tar reforming and cracking reactions are catalytically enhanced in the secondary stage. A steel plate separates both stages, which has four holes. Those holes are equipped with Venturi-type inlet distributors, which allow feeding a small amount of air into their axes in order to avoid the formation of tar deposits that may gradually block the distributor holes. The secondary stage is made up of horizontal baskets filled with catalyst and assembled at four vertical levels, each having four catalyst wings, resulting in a total of 16 catalyst wings. The raw gas from the lower updraft bed flows

through the holes of the division plate into the secondary gasification zone and joins the secondary gasification gases (to induce partial combustion reactions and increase temperature), which are introduced through a catalytic distributor system. The scheme of this reactor is shown in Fig. 26.

#### 4. Research gaps and future recommendations

Overall, the development degree of gasification technologies is rather high, with several pilot scale plants and even certain industrial scale ones in operation. This is especially true when comparing gasification with other thermochemical processes, such as hydrothermal conversion or pyrolysis. Thus, the latter processes are considerably less mature, i.e., with studies being usually performed in batch laboratory scale units. One of the main challenges that gasification plants should face to be operative at large scale lies in the flexibility of the process.

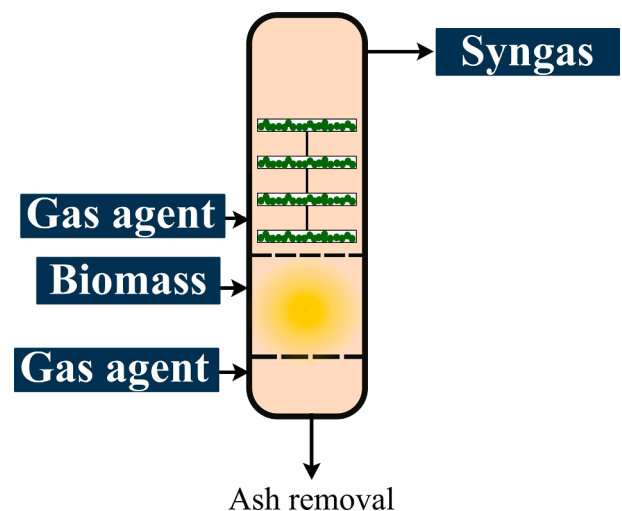


Fig. 26. Scheme of VTT's staged fixed-bed gasifier.

That is, large scale gasification plants should be able to process different biomass types and, at the same time, avoid their great impact on both process and products. Thus, biomass composition is very heterogeneous and has a great influence on the process operation, but also on the products stream, especially on tar formation. Therefore, points to be studied should involve versatile and efficient gasification technologies in order to overcome the seasonal nature of biomass wastes.

Another point that deserves a better understanding is related to the stability of primary catalysts in order to adopt different strategies for their regeneration. This aspect is especially evident in the multi-staged process or in the pyrolysis and in-line reforming process. Although the conversion efficiency of this processes is high and tar can be completely converted into syngas, the metallic catalysts undergo rapid deactivation by coke deposition. Thus, the development of a continuous regeneration system for these catalysts is crucial for their application in large scale units.

Another research gap is related to the knowledge on the biomass gasification reaction mechanisms, namely, tar formation and biomass conversion mechanisms, which are closely related to the design of the gasifiers. Thus, use of rigorous kinetic models of biomass gasification, together with simulation tools, such as CFD/DEM, is an encouraging alternative for optimizing the inner flow in industrial gasifiers at the same time as ensuring efficient designs.

As aforementioned, none of the primary strategies revised in this paper leads to fully avoid tar formation. The best option is to combine suitable strategies, which involves optimizing operating conditions and progressing on the joint design of reactors and catalysts.

## 5. Conclusions

The major challenge in biomass gasification is the reduction of tar formation. Tar, apart from being extremely problematic (fouling, corrosion and blocking in downstream equipment and human and environmental problems), contains a significant amount of energy, reducing the process efficiency and syngas production. Moreover, syngas applications are limited by strict tar content requirement. Therefore, this review provides a complete overview about the tar issue, its formation mechanism, analytical procedures and main primary strategies for tar elimination in biomass gasification since an efficient tar removal is mandatory in order to use gas in downstream applications.

The formation and transformation of tar as well as the analytical techniques for tar determination have been thoroughly discussed. Understanding the tar formation and transformation mechanism is essential to prevent tar production. Although it is well known that consecutive and simultaneous dealkylation/decarboxylation, dimerization and cyclization reactions lead to the growth of light aromatic compounds into heavier ones, the mechanism itself is not fully clear yet. Undoubtedly, more research in this area is needed. Regarding tar sampling and analyzing techniques, the appropriate selection is important to assess the effectiveness of the cleanup and conditioning processes and to verify the adequacy of the cleaned gas for its final use. Among all analytical techniques, tar protocol is actively used in both industrial and scientific environments.

Tar amount and its composition are influenced by the type of gasifier, biomass composition and, especially, operating conditions (such as temperature, gasification agent, pressure, residence time or use of catalyst). The use of in-bed catalysts and the optimization of the operating conditions improve the gasification process performance to produce a cleaner product gas. Thus, the increase of temperature, the gasification agent concentration (S/B and ER values) and residence time promote tar cracking and reforming reactions and therefore improve the overall efficiency of the process. Regarding the operating conditions, temperature is the most influential parameter in tar reduction whereas the effect of S/B or ER is less dominant. However, the influence of pressure or biomass composition on gasification performance is not so clear with inconsistent results reported in the literature. Moreover, the

use of inexpensive catalysts represents an interesting approach due to their high cracking activity and availability. In spite of the poor physical properties, dolomite has demonstrated a suitable activity for tar abatement. In addition, other natural minerals such as olivine, magnesite or bauxite have also showed promising performances as primary catalyst. In order to further enhance activity for the steam reforming and WGS reactions, the impregnation of primary catalysts with active metallic species (e.g. Fe and Ni) was proposed. In general, Ni is more active than Fe, but the interest of Fe lies in its lower price and toxicity. Those catalysts significantly improved tar conversion and syngas composition, although their application is constrained by the fast deactivation.

Gasifier design determines the main process conditions and remarkable differences in biomass conversion efficiency and tar formation have been observed between different reactor designs, fixed bed (updraft and downdraft), fluidized bed (bubbling, circulating and dual), entrained flow, spouted bed or plasma reactors. Likewise, further measures involving redesign of the gasifier or development of innovative designs are also essential to promote tar abatement. The aim of those reactor modifications usually pursues the improvement of residence time, temperature profiles in the gasifier and the gas–solid contact. The existing research efforts have been focusing on the fluidized beds, with the most common approaches including the secondary air injections or candle filters and the optimization of the feeding location or hydrodynamic regime. However, the implementation of all kind of primary strategies may not be efficient enough to remove tar in order to be used in downstream applications. In fact, under fine-tuned conditions the obtained tar concentration could be 2 or even 3 orders of magnitude higher than those required for synthesis ( $<1 \text{ mg Nm}^{-3}$ ) or heat and power ( $<1 \text{ -}100 \text{ mg Nm}^{-3}$ ) applications. In order to meet the requirements for the different syngas applications, the combination of in situ and ex situ strategies may be used. Secondary catalytic treatments may obtain tar removal efficiencies close to 100 % using Ni-based catalysts but they are deactivated quickly by coke deposition. Thus, the in situ use of natural catalysts is an attractive method as they can act as a guard catalyst to avoid the rapid deactivation of an expensive secondary catalyst. It is to be noted that although several secondary strategies have been investigated in lab scale, industrial plants still used oxidation reactors, electrostatic precipitators, bag filters, cyclones and scrubbers for tar control.

## 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.

## Acknowledgements

This work was carried out with the financial support from Spanish Ministries of Science, Innovation and Universities (RTI2018-098283-J-I00 (MCIU/AEI/FEDER, UE)) and Science and Innovation (PID2019-107357RB-I00 (MCIU/AEI/FEDER, UE) and TED2021-132056B-I00 (MCIU/AEI/FEDER, UE)) and the Basque Government (IT1645-22). Moreover, this project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 823745.

## References

- [1] Hafner M, Raimondi PP. Priorities and challenges of the EU energy transition: From the European Green Package to the new Green Deal. *Russ J Econ* 2021;6: 374–89.
- [2] WBA, Global Bionergy Statistics 2021 (2021).

- [3] Skjærseth JB. Towards a European Green Deal: The evolution of EU climate and energy policy mixes. *Int Envir Agreem Polit Law Econ* 2021;21:25–41.
- [4] Pietzcker RC, Osorio S, Rodrigues R. Tightening EU ETS targets in line with the European Green Deal: Impacts on the decarbonization of the EU power sector. *Appl Energy* 2021;293:116914.
- [5] IEA, *Global Hydrogen Review 2021* (2021).
- [6] Kakoulaki G, Kougiass I, Taylor N, Dolci F, Moya J, Jäger-Waldau A. Green hydrogen in Europe – A regional assessment: Substituting existing production with electrolysis powered by renewables. *Energy Convers Manage* 2021;228:113649.
- [7] Kovač A, Paranos M, Marcius D. Hydrogen in energy transition: A review. *Int J Hydrogen Energy* 2021;46:10016–35.
- [8] WBA, *Global Bioenergy Statistics 2020* (2020).
- [9] Ong HC, Chen WH, Farooq A, Gan YY, Lee KT, Ashokkumar V. Catalytic thermochemical conversion of biomass for biofuel production: A comprehensive review. *Renew Sustain Energy Rev* 2019;113:109266.
- [10] European Parliament, Directive 2009/28/EC of the European Parliament and of the Council of 23 April 2009 on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC (2009).
- [11] Mbeugang CFM, Li B, Lin D, Xie X, Wang S, Wang S, et al. Hydrogen rich syngas production from sorption enhanced gasification of cellulose in the presence of calcium oxide. *Energy* 2021;228:120659.
- [12] Chen S, Zhao Z, Soomro A, Ma S, Wu M, Sun Z, et al. Hydrogen-rich syngas production via sorption-enhanced steam gasification of sewage sludge. *Biomass Bioenergy* 2020;138:105607.
- [13] Cao L, Yu IKM, Xiong X, Tsang DCW, Zhang S, Clark JH, et al. Biorenewable hydrogen production through biomass gasification: A review and future prospects. *Environ Res* 2020;186:109547.
- [14] Mishra S, Upadhyay RK. Review on biomass gasification: Gasifiers, gasifying mediums, and operational parameters. *Mater Sci Energy Technol* 2021;4:329–40.
- [15] Sansaniwal SK, Pal K, Rosen MA, Tyagi SK. Recent advances in the development of biomass gasification technology: A comprehensive review. *Renew Sustain Energy Rev* 2017;72:363–84.
- [16] Parthasarathy P, Narayanan KS. Hydrogen production from steam gasification of biomass: Influence of process parameters on hydrogen yield - A review. *Renew Energy* 2014;66:570–9.
- [17] Karl J, Pröll T. Steam gasification of biomass in dual fluidized bed gasifiers: A review. *Renew Sustain Energy Rev* 2018;98:64–78.
- [18] Motta IL, Miranda NT, Maciel Filho R, Wolf Maciel MR. Biomass gasification in fluidized beds: A review of biomass moisture content and operating pressure effects. *Renewable Sustainable Energy Rev* 2018;94:998–1023.
- [19] Susastriawan AAP, Saptoadi H. Purnomo, Small-scale downdraft gasifiers for biomass gasification: A review. *Renewable Sustainable Energy Rev* 2017;76:989–1003.
- [20] Baruah D, Baruah DC. Modeling of biomass gasification: A review. *Renewable Sustainable Energy Rev* 2014;39:806–15.
- [21] Alvarez J, Lopez G, Amutio M, Bilbao J, Olazar M. Evolution of biomass char features and their role in the reactivity during steam gasification in a conical spouted bed reactor. *Energy Convers Manage* 2019;181:214–22.
- [22] Arregi A, Amutio M, Lopez G, Bilbao J, Olazar M. Evaluation of thermochemical routes for hydrogen production from biomass: A review. *Energy Convers Manage* 2018;165:696–719.
- [23] Cortazar M, Lopez G, Alvarez J, Arregi A, Amutio M, Bilbao J, et al. Experimental study and modeling of biomass char gasification kinetics in a novel thermogravimetric flow reactor. *Chem Eng J* 2020;396:125200.
- [24] Di Blasi C. Combustion and gasification rates of lignocellulosic chars. *Prog Energy Combust Sci* 2009;35:121–40.
- [25] Sikarwar VS, Zhao M. Biomass Gasification. In: Abraham MA, editor. *Encyclopedia of Sustainable Technologies*. Oxford: Elsevier; 2017. p. 205–16.
- [26] Ren J, Cao JP, Zhao XY, Yang FL, Wei XY. Recent advances in syngas production from biomass catalytic gasification: A critical review on reactors, catalysts, catalytic mechanisms and mathematical models. *Renewable Sustainable Energy Rev* 2019;116:109426.
- [27] Molino A, Chianese S, Musmarra D. Biomass gasification technology: The state of the art overview. *J Energy Chem* 2016;25:10–25.
- [28] Pereira EG, Martins MA. Gasification Technologies. In: Abraham MA, editor. *Encyclopedia of Sustainable Technologies*. Oxford: Elsevier; 2017. p. 315–25.
- [29] Alauddin ZABZ, Lahijani P, Mohammadi M, Mohamed AR. Gasification of lignocellulosic biomass in fluidized beds for renewable energy development: A review. *Renewable Sustainable Energy Rev* 2010;14:2852–62.
- [30] Zeng X, Shao R, Wang F, Dong P, Yu J, Xu G. Industrial demonstration plant for the gasification of herb residue by fluidized bed two-stage process. *Bioresour Technol* 2016;206:93–8.
- [31] Pfeifer C, Rauch R, Hofbauer H. In-Bed Catalytic Tar Reduction in a Dual Fluidized Bed Biomass Steam Gasifier. *Ind Eng Chem Res* 2004;43:1634–40.
- [32] Hejazi B, Grace JR, Bi X, Mahecha-Botero A. Kinetic Model of Steam Gasification of Biomass in a Dual Fluidized Bed Reactor: Comparison with Pilot-Plant Experimental Results. *Energy Fuels* 2017;31:12141–55.
- [33] Li YH, Chen Z, Watkinson P, Bi X, Grace J, Lim CJ, et al. A novel dual-bed for steam gasification of biomass. *Biomass Convers Biorefin* 2018;8:357–67.
- [34] Zhou C, Chen L, Liu C, Wang J, Xing X, Liu Y, et al. Interconnected pyrolysis and gasification of typical biomass in a novel dual fluidized bed. *Energy Convers Manage* 2022;271:116323.
- [35] Larsson A, Kuba M, Berdugo Vilches T, Seemann M, Hofbauer H, Thunman H. Steam gasification of biomass – Typical gas quality and operational strategies derived from industrial-scale plants. *Fuel Process Technol* 2021;212:106609.
- [36] Hanchate N, Ramani S, Mathpati CS, Dalvi VH. Biomass gasification using dual fluidized bed gasification systems: A review. *J Clean Prod* 2021;280:123148.
- [37] Kirnbauer F, Hofbauer H. Investigations on bed material changes in a dual fluidized bed steam gasification plant in Güssing, Austria. *Energy Fuels* 2011;25:3793–8.
- [38] Pfeifer C, Koppatz S, Hofbauer H. Steam gasification of various feedstocks at a dual fluidized bed gasifier: Impacts of operation conditions and bed materials. *Biomass Convers Biorefin* 2011;1:39–53.
- [39] Thunman H, Seemann M, Berdugo Vilches T, Maric J, Pallares D, Ström H, et al. Advanced biofuel production via gasification – lessons learned from 200 man-years of research activity with Chalmers' research gasifier and the GoBiGas demonstration plant. *Energy Sci Eng* 2018;6:6–34.
- [40] Niu M, Huang Y, Jin B, Liang S, Dong Q, Gu H, et al. A novel two-stage enriched air biomass gasification for producing low-tar high heating value fuel gas: Pilot verification and performance analysis. *Energy* 2019;173:511–22.
- [41] Gao N, Milandile MH, Quan C, Rundong L. Critical assessment of plasma tar reforming during biomass gasification: A review on advancement in plasma technology. *J Hazard Mater* 2022;421:126764.
- [42] Aguado R, Alvarez S, San José MJ, Olazar M, Bilbao J. Gas flow distribution modelling in conical spouted beds. *Comput. Aided. Chem Eng* 2005;20:613–8.
- [43] Makibar J, Fernandez-Akregi AR, Alava I, Cueva F, Lopez G, Olazar M. Investigations on heat transfer and hydrodynamics under pyrolysis conditions of a pilot-plant draft tube conical spouted bed reactor. *Chem Eng Process Process Intensif* 2011;50:790–8.
- [44] Erkiaga A, Lopez G, Amutio M, Bilbao J, Olazar M. Influence of operating conditions on the steam gasification of biomass in a conical spouted bed reactor. *Chem Eng J* 2014;237:259–67.
- [45] Siedlecki M, de Jong W, Verkoijen AHM. Fluidized bed gasification as a mature and reliable technology for the production of bio-syngas and applied in the production of liquid transportation fuels—a review. *Energies* 2011;4:389–434.
- [46] Claude V, Courson C, Köhler M, Lambert SD. Overview and Essentials of Biomass Gasification Technologies and Their Catalytic Cleaning Methods. *Energy Fuels* 2016;30:8791–814.
- [47] Sikarwar VS, Zhao M, Clough P, Yao J, Zhong X, Memon MZ, et al. An overview of advances in biomass gasification. *Energy Environ Sci* 2016;9:2939–77.
- [48] Rakesh N, Dasappa S. A critical assessment of tar generated during biomass gasification - Formation, evaluation, issues and mitigation strategies. *Renewable Sustainable Energy Rev* 2018;91:1045–64.
- [49] Shayan E, Zare V, Mirzaee I. Hydrogen production from biomass gasification; a theoretical comparison of using different gasification agents. *Energy Convers Manage* 2018;159:30–41.
- [50] Suryawanshi SJ, Shewale VC, Thakare RS, Yarasu RB. Parametric study of different biomass feedstocks used for gasification process of gasifier—a literature review. *Biomass Convers. Bioref.* 2021 In press.
- [51] Schweitzer D, Gredinger A, Schmid M, Waizmann G, Beirw M, Spörl R, et al. Steam gasification of wood pellets, sewage sludge and manure: Gasification performance and concentration of impurities. *Biomass Bioenergy* 2018;111:308–19.
- [52] Pinto F, André RN, Lopes H, Dias M, Gulyurtlu I, Cabrita I. Effect of experimental conditions on gas quality and solids produced by sewage sludge cogasification. 2. Sewage sludge mixed with biomass. *Energy Fuels* 2008;22:2314–25.
- [53] De Almeida VF, Gómez-Barea A, Arroyo-Caire J, Pardo I. On the Measurement of the Main Inorganic Contaminants Derived from Cl, S and N in Simulated Waste-Derived Syngas. *Waste Biomass Valoriz* 2020;11:6869–84.
- [54] Bioenergy IEA. Biomass as gasification feedstock. Factsheet 2017.
- [55] Bioenergy IEA. Gas analysis in gasification of biomass and waste. Guideline report 2018;1.
- [56] Li C, Suzuki K. Tar property, analysis, reforming mechanism and model for biomass gasification—An overview. *Renewable Sustainable Energy Rev* 2009;13:594–604.
- [57] Guan G, Kaewpanha M, Hao X, Abudula A. Catalytic steam reforming of biomass tar: Prospects and challenges. *Renewable Sustainable Energy Rev* 2016;58:450–61.
- [58] Devi L, Ptasiński KJ, Janssen FJJG. A review of the primary measures for tar elimination in biomass gasification processes. *Biomass Bioenergy* 2003;24:125–40.
- [59] Anis S, Zainal ZA. Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review. *Renewable Sustainable Energy Rev* 2011;15:2355–77.
- [60] Valderrama Rios ML, González AM, Lora EES, Almazán del Olmo OA. Reduction of tar generated during biomass gasification: A review. *Biomass Bioenergy* 2018;108:345–70.
- [61] Rabou LPLM, Zwart RWR, Vreugdenhil BJ, Bos L. Tar in Biomass Producer Gas, the Energy research Centre of The Netherlands (ECN) Experience: An Enduring Challenge. *Energy Fuels* 2009;23:6189–98.
- [62] Font Palma C. Modelling of tar formation and evolution for biomass gasification: A review. *Appl Energy* 2013;111:129–41.
- [63] Evans RJ, Milne TA. Chemistry of Tar Formation and Maturation in the Thermochemical Conversion of Biomass. In: Bridgwater AV, Boocock DGB, editors. *Developments in Thermochemical Biomass Conversion: Volume 1 / Volume 2*. Netherlands, Dordrecht: Springer; 1997. p. 803–16.

- [64] Zeng X, Ueki Y, Yoshie R, Naruse I, Wang F, Han Z, et al. Recent progress in tar removal by char and the applications: A comprehensive analysis. *Carbon Resour Convers* 2020;3:1–18.
- [65] Shukla B, Koshi M. Comparative study on the growth mechanisms of PAHs. *Combust Flame* 2011;158:369–75.
- [66] Zhou H, Wu C, Onwudili JA, Meng A, Zhang Y, Williams PT. Polycyclic aromatic hydrocarbon formation from the pyrolysis/gasification of lignin at different reaction conditions. *Energy Fuels* 2014;28:6371–9.
- [67] Qin Y, Campen A, Wiltowski T, Feng J, Li W. The influence of different chemical compositions in biomass on gasification tar formation. *Biomass Bioenergy* 2015; 83:77–84.
- [68] Shen Y, Zhao P, Shao Q, Ma D, Takahashi F, Yoshikawa K. In-situ catalytic conversion of tar using rice husk char-supported nickel-iron catalysts for biomass pyrolysis/gasification. *Appl Catal, B* 2014;152–153:140–51.
- [69] Zhou B, Dichiaro A, Zhang Y, Zhang Q, Zhou J. Tar formation and evolution during biomass gasification: An experimental and theoretical study. *Fuel* 2018; 234:944–53.
- [70] Yu H, Zhang Z, Li Z, Chen D. Characteristics of tar formation during cellulose, hemicellulose and lignin gasification. *Fuel* 2014;118:250–6.
- [71] Sharma RK, Hajaligol MR. Effect of pyrolysis conditions on the formation of polycyclic aromatic hydrocarbons (PAHs) from polyphenolic compounds. *J Anal Appl Pyrolysis* 2003;66:123–44.
- [72] Nguyen HNT, Seemann M, Thunman H. Fate of Polycyclic Aromatic Hydrocarbons during Tertiary Tar Formation in Steam Gasification of Biomass. *Energy Fuels* 2018;32:3499–509.
- [73] Böhm H, Jander H, Tanke D. PAH growth and soot formation in the pyrolysis of acetylene and benzene at high temperatures and pressures: Modeling and experiment. *Symp Int Combust* 1998;27:1605–12.
- [74] Dong GL, Hüttinger KJ. Consideration of reaction mechanisms leading to pyrolytic carbon of different textures. *Carbon* 2002;40:2515–28.
- [75] Unterreiner BV, Sierka M, Ahlrichs R. Reaction pathways for growth of polycyclic aromatic hydrocarbons under combustion conditions, a DFT study. *Phys Chem Chem Phys* 2004;6:4377–84.
- [76] Wang H, Frenklach M. A detailed kinetic modeling study of aromatics formation in laminar premixed acetylene and ethylene flames. *Combust Flame* 1997;110: 173–221.
- [77] Liu P, Li Z, Bennett A, Lin H, Sarathy SM, Roberts WL. The site effect on PAHs formation in HACA-based mass growth process. *Combust Flame* 2019;199:54–68.
- [78] Reizer E, Csizmadia IG, Palotás Á, B., V. Viskolcz, B. Fiser., Formation Mechanism of Benzo(a)pyrene: One of the Most Carcinogenic Polycyclic Aromatic Hydrocarbons (PAH). *Molecules* 2019;24:1040.
- [79] Shukla B, Koshi M. A novel route for PAH growth in HACA based mechanisms. *Combust Flame* 2012;159:3589–96.
- [80] Shukla B, Susa A, Miyoshi A, Koshi M. Role of Phenyl Radicals in the Growth of Polycyclic Aromatic Hydrocarbons. *J Phys Chem A* 2008;112:2362–9.
- [81] Shukla B, Koshi M. A highly efficient growth mechanism of polycyclic aromatic hydrocarbons. *Phys Chem Chem Phys* 2010;12:2427–37.
- [82] Shukla B, Miyoshi A, Koshi M. Role of Methyl Radicals in the Growth of PAHs. *J Am Soc Mass Spectrom* 2010;21:534–44.
- [83] Fuentes-Cano D, Gómez-Barea A, Nilsson S, Ollero P. The influence of temperature and steam on the yields of tar and light hydrocarbon compounds during devolatilization of dried sewage sludge in a fluidized bed. *Fuel* 2013;108: 341–50.
- [84] Gredinger A, Spörl R, Scheffknecht G. Comparison measurements of tar content in gasification systems between an online method and the tar protocol. *Biomass Bioenergy* 2018;111:301–7.
- [85] Arena U, Di Gregorio F, Santonastasi M. A techno-economic comparison between two design configurations for a small scale, biomass-to-energy gasification based system. *Chem Eng J* 2010;162:580–90.
- [86] Asadullah M. Biomass gasification gas cleaning for downstream applications: A comparative critical review. *Renewable Sustainable Energy Rev* 2014;40:118–32.
- [87] Harb R, Rivera-Tinoco R, Nemer M, Zeghony B, Bouallou C. Towards synthetic fuels production from biomass gasification: Tar content at low temperatures. *Biomass Bioenergy* 2020;137:105540.
- [88] Engvall K, Kusar H, Sjöström K, Pettersson LJ. Upgrading of Raw Gas from Biomass and Waste Gasification: Challenges and Opportunities. *Top Catal* 2011; 54:949.
- [89] Sansaniwal SK, Rosen MA, Tyagi SK. Global challenges in the sustainable development of biomass gasification: An overview. *Renewable Sustainable Energy Rev* 2017;80:23–43.
- [90] Asadullah M. Barriers of commercial power generation using biomass gasification gas: A review. *Renewable Sustainable Energy Rev* 2014;29:201–15.
- [91] Situmorang YA, Zhao Z, Yoshida A, Abudula A, Guan G. Small-scale biomass gasification systems for power generation: A review. *Renewable Sustainable Energy Rev* 2020;117:109486.
- [92] Prando D, Shivananda Ail S, Chiaramonti D, Baratieri M, Dasappa S. Characterisation of the producer gas from an open top gasifier: Assessment of different tar analysis approaches. *Fuel* 2016;181:566–72.
- [93] Li Y, Pang Y, Tu H, Torrigino F, Biollaz SMA, Li Z, et al. Impact of syngas from biomass gasification on solid oxide fuel cells: A review study for the energy transition. *Energy Convers Manage* 2021;250:114894.
- [94] Ud Din Z, Zainal ZA. The fate of SOFC anodes under biomass producer gas contaminants. *Renewable Sustainable Energy Rev* 2017;72:1050–66.
- [95] Lorente E, Millan M, Brandon NP. Use of gasification syngas in SOFC: Impact of real tar on anode materials. *Int J Hydrogen Energy* 2012;37:7271–8.
- [96] Liu M, Aravind PV. The fate of tars under solid oxide fuel cell conditions: A review. *Appl Therm Eng* 2014;70:687–93.
- [97] Rauch R, Hrbek J, Hofbauer H. Biomass Gasification for Synthesis Gas Production and Applications of the Syngas, in: *Advances in Bioenergy. The Sustainability Challenge* 2016:73–91.
- [98] Luo X, Wu T, Shi K, Song M, Rao Y. Biomass Gasification: An Overview of Technological Barriers and Socio-Environmental Impact, 2018.
- [99] Meng X, Mitsakis P, Mayerhofer M, de Jong W, Gaderer M, Verkooijen AHM, et al. Tar formation in a steam-O<sub>2</sub> blown CFB gasifier and a steam blown PBFB gasifier (BabyHPR): Comparison between different on-line measurement techniques and the off-line SPA sampling and analysis method. *Fuel Process Technol* 2012;100: 16–29.
- [100] Neef J, Knoef H, Buffinga GJ, Zielke U, Sjöström K, Brage C, et al. Guideline for Sampling and Analysis of Tars and Particles in Biomass Producer Gases 2008: 162–75.
- [101] Neubert M, Reil S, Wolff M, Pöcher D, Stork H, Ultsch C, et al. Experimental comparison of solid phase adsorption (SPA), activated carbon test tubes and tar protocol (DIN CEN/TS 15439) for tar analysis of biomass derived syngas. *Biomass Bioenergy* 2017;105:443–52.
- [102] Patuzzi F, Prando D, Vakalis S, Rizzo AM, Chiaramonti D, Tirlir W, et al. Small-scale biomass gasification CHP systems: Comparative performance assessment and monitoring experiences in South Tyrol [Italy]. *Energy* 2016;112:285–93.
- [103] Neubauer Y, Gredinger A, Borgmeyer J, Kleinhappel M, Biollaz SMA. Comparison of two on-line tar-monitoring devices with off-line liquid sample tar-analysis operated on a test gas generation system applying ethene pyrolysis. *Biomass Bioenergy* 2018;117:63–70.
- [104] Mahapatra S, Dasappa S. Influence of surface area to volume ratio of fuel particles on gasification process in a fixed bed, *Energy. Sustainable Dev* 2014;19:122–9.
- [105] Virginie M, Adánez J, Courson C, De Diego LF, García-Labiano F, Niznansky D, et al. Effect of Fe-olivine on the tar content during biomass gasification in a dual fluidized bed. *Appl Catal, B* 2012;121:214–22.
- [106] Gredinger A, Schweitzer D, Dieter H, Scheffknecht G. A Measurement Device for Online Monitoring of Total Tar in Gasification Systems. *J Energy Res Technol* 2016;138:042205.
- [107] Brage C, Yu Q, Chen G, Sjöström K. Use of amino phase adsorbent for biomass tar sampling and separation. *Fuel* 1997;76:137–42.
- [108] Israelsson M, Seemann M, Thunman H. Assessment of the solid-phase adsorption method for sampling biomass-derived tar in industrial environments. *Energy Fuels* 2013;27:7569–78.
- [109] Horvat A, Kwapinska M, Xue G, Dooley S, Kwapinski W, Leahy JJ. Detailed Measurement Uncertainty Analysis of Solid-Phase Adsorption-Total Gas Chromatography (GC)-Detectable Tar from Biomass Gasification. *Energy Fuels* 2016;30:2187–97.
- [110] Siedlecke M, Nieuwstraten R, Simeone E, de Jong W, Verkooijen AHM. Effect of Magnesite as Bed Material in a 100 kWth Steam-Oxygen Blown Circulating Fluidized-Bed Biomass Gasifier on Gas Composition and Tar Formation. *Energy Fuels* 2009;23:5643–54.
- [111] González IO, Pastor RMP, Hervás JM. Sampling of tar from sewage sludge gasification using solid phase adsorption. *Anal Bioanal Chem* 2012;403:2039–46.
- [112] Osipov S. Comparison of efficiency of two methods for tar sampling in the syngas. *Fuel* 2013;103:387–92.
- [113] Osipov S. Sampling of benzene in tar matrices from biomass gasification using two different solid-phase sorbents. *Anal Bioanal Chem* 2008;391:1409–17.
- [114] Osipov S. Use of two different adsorbents for sampling tar in gas obtained from peat gasification. *Int J Environ Anal Chem* 2009;89:871–80.
- [115] Dufour A, Girods P, Masson E, Normand S, Rogaume Y, Zoualalian A. Comparison of two methods of measuring wood pyrolysis tar. *J Chromatogr A* 2007;1164: 240–7.
- [116] Horvat A, Kwapinska M, Xue G, Kwapinski W, Dooley S, Leahy JJ. Study of post sampling treatment of solid phase adsorption method on tar yields and comparison of two methods for volatile tar compounds. *European Biomass Conf Exhib Proc* 2016;2016:929–33.
- [117] Ghaffar S, Hashmi I, Awan MA, Nasir H, Amjad H. Determination of Volatile Organic Compounds (VOCs) in Potable Water Using Solid Phase Micro Extraction-Gas Chromatography (SPME-GC). *Arabian J Sci Eng* 2012;37:1255–62.
- [118] Parkinson DR, Warren JM, Pawliszyn J. Analysis of ergosterol for the detection of mold in soils by automated on-fiber derivatization headspace extraction-SPME-GC/MS. *Anal Chim Acta* 2010;661:181–7.
- [119] Pan J, Huang Y, Liu L, Hu Y, Li G. A novel fractionized sampling and stacking strategy for online hyphenation of solid-phase-based extraction to ultra-high performance liquid chromatography for ultrasensitive analysis. *J Chromatogr A* 2013;1316:29–36.
- [120] Zhang W, Zhang Z, Meng J, Zhou W, Chen Z. Adsorptive behavior and solid-phase microextraction of bare stainless steel sample loop in high performance liquid chromatography. *J Chromatogr A* 2014;1365:19–28.
- [121] Campíns-Falcó P, Herráez-Hernández R, Verdú-Andrés J, Cháfer-Pericás C. On-line determination of aliphatic amines in water using in-tube solid-phase microextraction-assisted derivatization in in-valve mode for processing large sample volumes in LC. *Anal Bioanal Chem* 2009;394:557–65.
- [122] Penalver R, Campillo N, López-García I, Hernández-Córdoba M. Solid-phase microextraction for the determination of iron organic compounds in seawaters and soils by gas chromatography coupled to microwave-induced plasma with atomic emission detection spectrometry. *Microchim J* 2020;154:104630.
- [123] Ruiz-Jimenez J, Lan H, Leleev Y, Hartonen K, Riekkola M. Comparison of multiple calibration approaches for the determination of volatile organic compounds in air

- samples by solid phase microextraction Arrow and in-tube extraction. *J Chromatogr A* 2020;1616:460825.
- [124] Ibragimova OP, Baimatova N, Kenessov B. Low-cost quantitation of multiple volatile organic compounds in air using solid-phase microextraction. *Separations* 2019;6:51.
- [125] Tursumbayeva M, Koziel JA, Maurer DL, Kenessov B, Rice S. Development of Time-Weighted Average Sampling of Odorous Volatile Organic Compounds in Air with Solid-Phase Microextraction Fiber Housed inside a GC Glass Liner: Proof of concept. *Molecules* 2019;24:406.
- [126] Ahmadi M, Elm Svensson E, Engvall K. Application of Solid-Phase Microextraction (SPME) as a Tar Sampling Method. *Energy Fuels* 2013;27:3853–60.
- [127] Duan C, Shen Z, Wu D, Guan Y. Recent developments in solid-phase microextraction for on-site sampling and sample preparation. *TrAC* 2011;30:1568–74.
- [128] Fernández-Amado M, Prieto-Blanco MC, López-Mahía P, Muniategui-Lorenzo S, Prada-Rodríguez D. Strengths and weaknesses of in-tube solid-phase microextraction: A scoping review. *Anal Chim Acta* 2016;906:41–57.
- [129] Bioenergy IEA. Gas analysis in gasification of biomass and waste. Guideline report 2018;2.
- [130] Borgmeyer J, Behrendt F. On-line tar monitoring using light-induced fluorescence: A setup for continuous operation in a biomass gasification plant environment. *Opt Laser Technol* 2020;123:105906.
- [131] Ahmadi M, Knoef H, Van de Beld B, Liliedahl T, Engvall K. Development of a PID based on-line tar measurement method – Proof of concept. *Fuel* 2013;113:113–21.
- [132] Patuzzi F, Roveda D, Mimmo T, Karl J, Baratieri M. A comparison between on-line and off-line tar analysis methods applied to common reed pyrolysis. *Fuel* 2013;111:689–95.
- [133] Carpenter DL, Deutch SP, French RJ. Quantitative measurement of biomass gasifier tars using a molecular-beam mass spectrometer: Comparison with traditional impinger sampling. *Energy Fuels* 2007;21:3036–43.
- [134] Israelsson M, Larsson A, Thunman H. Online measurement of elemental yields, oxygen transport, condensable compounds, and heating values in gasification systems. *Energy Fuels* 2014;28:5892–901.
- [135] Edinger P, Schneebeli J, Struis RPWJ, Biollaz SMA, Ludwig C. On-line liquid quench sampling and UV-Vis spectroscopy for tar measurements in wood gasification process gases. *Fuel* 2016;184:59–68.
- [136] Kaufman Rechulski MD, Schneebeli J, Geiger S, Schildhauer TJ, Biollaz SMA, Ludwig C. Liquid-Quench Sampling System for the Analysis of Gas Streams from Biomass Gasification Processes. Part 2: Sampling Condensable Compounds. *Energy Fuels* 2012;26:6358–65.
- [137] Gall D, Pushp M, Larsson A, Davidsson K, Pettersson JBC. Online Measurements of Alkali Metals during Start-up and Operation of an Industrial-Scale Biomass Gasification Plant. *Energy Fuels* 2018;32:532–41.
- [138] Ahmadi M, Brage C, Sjöström K, Engvall K, Knoef H, Van de Beld B. Development of an on-line tar measurement method based on photo ionization technique. *Catal Today* 2011;176:250–2.
- [139] Baumhagl C, Karellas S. Tar analysis from biomass gasification by means of online fluorescence spectroscopy. *Opt Lasers Eng* 2011;49:885–91.
- [140] Sun R, Zobel N, Neubauer Y, Cardenas Chavez C, Behrendt F. Analysis of gas-phase polycyclic aromatic hydrocarbon mixtures by laser-induced fluorescence. *Opt Lasers Eng* 2010;48:1231–7.
- [141] Mitsakis P, Mayerhofer M, Meng X, Spliethoff H, Gaderer M. Optical measurement of tars in a fluidized bed gasifier: influence of fuel type and gasification parameters on their formation. *Biomass Convers Biorefin* 2013;3:157–67.
- [142] Capper S, Khan Z, Kamble P, Sharp J, Watson I. Progression towards Online Tar Detection Systems. *Energy Procedia* 2017;142:892–7.
- [143] Borgmeyer J. Continuous On-Line Tar Monitoring in Hot Process Gases from Biomass Gasification by Means of Fluorescence Spectroscopy. Berlin: Technische Universität; 2019. PhD Thesis.
- [144] French R, Czernik S. Catalytic pyrolysis of biomass for biofuels production. *Fuel Process Technol* 2010;91:25–32.
- [145] Magrini K, Follett R, Kimble J, Davis M, Pruessner E. Using pyrolysis molecular beam mass spectrometry to characterize soil organic carbon in native prairie soils. *Soil Sci* 2007;172:9.
- [146] Sykes R, Yung M, Novaes E, Kirst M, Peter G, Davis M. High-Throughput Screening of Plant Cell-Wall Composition Using Pyrolysis Molecular Beam Mass Spectroscopy. *Methods Mol Biol* 2009;581:169–83.
- [147] Haddix ML, Magrini-Bair K, Evans RJ, Conant RT, Wallenstein MD, Morris SJ, et al. Progressing towards more quantitative analytical pyrolysis of soil organic matter using molecular beam mass spectroscopy of whole soils and added standards. *Geoderma* 2016;283:88–100.
- [148] Defoort F, Thiery S, Ravel S. A promising new on-line method of tar quantification by mass spectrometry during steam gasification of biomass. *Biomass Bioenergy* 2014;65:64–71.
- [149] Rapagnà S, Gallucci K, Foscolo PU. Olivine, dolomite and ceramic filters in one vessel to produce clean gas from biomass. *Waste Manage* 2018;71:792–800.
- [150] Barisano D, Canneto G, Nanna F, Alvino E, Pinto G, Villone A, et al. Steam/oxygen biomass gasification at pilot scale in an internally circulating bubbling fluidized bed reactor. *Fuel Process Technol* 2016;141:74–81.
- [151] De Andrés JM, Narros A, Rodríguez ME. Behaviour of dolomite, olivine and alumina as primary catalysts in air-steam gasification of sewage sludge. *Fuel* 2011;90:521–7.
- [152] Benedikt F, Kuba M, Schmid JC, Müller S, Hofbauer H. Assessment of correlations between tar and product gas composition in dual fluidized bed steam gasification for online tar prediction. *Appl Energy* 2019;238:1138–49.
- [153] Mauerhofer AM, Schmid JC, Benedikt F, Fuchs J, Müller S, Hofbauer H. Dual fluidized bed steam gasification: Change of product gas quality along the reactor height. *Energy* 2019;173:1256–72.
- [154] Fuentes-Cano D, von Berg L, Diéguez-Alonso A, Scharler R, Gómez-Barea A, Anca-Couce A. Tar conversion of biomass syngas in a downstream char bed. *Fuel Process Technol* 2020;199:106271.
- [155] Gupta A, Thengane SK, Mahajani S. Kinetics of pyrolysis and gasification of cotton stalk in the central parts of India. *Fuel* 2020;263:116752.
- [156] Gil-Lalaguna N, Sánchez JL, Murillo MB, Rodríguez E, Gea G. Air-steam gasification of sewage sludge in a fluidized bed. Influence of some operating conditions. *Chem Eng J* 2014;248:373–82.
- [157] Meng J, Wang X, Zhao Z, Zheng A, Huang Z, Wei G, et al. Highly abrasion resistant thermally fused olivine as in-situ catalysts for tar reduction in a circulating fluidized bed biomass gasifier. *Bioresour Technol* 2018;268:212–20.
- [158] Göransson K, Söderlind U, Zhang W. Experimental test on a novel dual fluidised bed biomass gasifier for synthetic fuel production. *Fuel* 2011;90:1340–9.
- [159] Kirnbauer F, Wilk V, Hofbauer H. Performance improvement of dual fluidized bed gasifiers by temperature reduction: The behavior of tar species in the product gas. *Fuel* 2013;108:534–42.
- [160] Yahaya AZ, Rao Somalu M, Muchtar A, Anwar Sulaiman S, W. Ramli Wan Daud, Effects of temperature on the chemical composition of tars produced from the gasification of coconut and palm kernel shells using downdraft fixed-bed reactor. *Fuel* 2020;265:116910.
- [161] Cortazar M, Alvarez J, Lopez G, Amutio M, Santamaria L, Bilbao J, et al. Role of temperature on gasification performance and tar composition in a fountain enhanced conical spouted bed reactor. *Energy Convers Manage* 2018;171:1589–97.
- [162] Mahinpey N, Gomez A. Review of gasification fundamentals and new findings: Reactors, feedstock, and kinetic studies. *Chem Eng Sci* 2016;148:14–31.
- [163] Rapagnà S, Jand N, Kiennemann A, Foscolo PU. Steam-gasification of biomass in a fluidised-bed of olivine particles. *Biomass Bioenergy* 2000;19:187–97.
- [164] Fremaux S, Beheshti SM, Ghassemi H, Shahsavani-Markadeh R. An experimental study on hydrogen-rich gas production via steam gasification of biomass in a research-scale fluidized bed. *Energy Convers Manage* 2015;91:427–32.
- [165] Xiao Y, Xu S, Liu Y, Qiao C. Catalytic steam co-gasification of biomass and coal in a dual loop gasification system with olivine catalysts. *J Energy Inst* 2020;93:1074–82.
- [166] Guo S, Wei X, Li J, Che D, Liu H, Sun B, et al. Experimental Study on Product Gas and Tar Removal in Air-Steam Gasification of Corn Straw in a Bench-Scale Internally Circulating Fluidized Bed. *Energy Fuels* 2020;34:1908–17.
- [167] Narváez I, Orío A, Aznar MP, Corella J. Biomass gasification with air in an atmospheric bubbling fluidized bed. Effect of six operational variables on the quality of the produced raw gas. *Ind Eng Chem Res* 1996;35:2110–20.
- [168] Tian Y, Zhou X, Yang Y, Nie L. Experimental analysis of air-steam gasification of biomass with coal-bottom ash. *J Energy Inst* 2020;93:25–30.
- [169] Tian Y, Zhou X, Lin S, Ji X, Bai J, Xu M. Syngas production from air-steam gasification of biomass with natural catalysts. *Sci Total Environ* 2018;645:518–23.
- [170] Ren Q, Wang S. Catalytic Gasification of Biomass Over Fe-MgO Catalyst. *Rev Chim* 2018;69:2933–6.
- [171] Sui M, Li G, Guan Y, Li C, Zhou R, Zarnegar A. Hydrogen and syngas production from steam gasification of biomass using cement as catalyst. *Biomass Convers Biorefinery* 2020;10:119–24.
- [172] Cao Y, Bai Y, Du J. Study on gasification characteristics of pine sawdust using olivine as in-bed material for combustible gas production. *J Energy Inst* 2021;96:168–72.
- [173] Milne TA, Evans RJ, Abatzoglou N. Biomass Gasifier Tars: Their Nature, Formation, and Conversion 1998.
- [174] Mayerhofer M, Mitsakis P, Meng X, De Jong W, Spliethoff H, Gaderer M. Influence of pressure, temperature and steam on tar and gas in allothermal fluidized bed gasification. *Fuel* 2012;99:204–9.
- [175] Kuba M, Hofbauer H. Experimental parametric study on product gas and tar composition in dual fluid bed gasification of woody biomass. *Biomass Bioenergy* 2018;115:35–44.
- [176] Calvo LF, Gil MV, Otero M, Morán A, García AI. Gasification of rice straw in a fluidized-bed gasifier for syngas application in close-coupled boiler-gasifier systems. *Bioresour Technol* 2012;109:206–14.
- [177] Molino A, Larocca V, Chianese S, Musmarra D. Biofuels production by biomass gasification: A review. *Energies* 2018;11:4.
- [178] De Sales CAVB, Maya DMY, Lora EES, Jaén RL, Reyes AMM, González AM, et al. Experimental study on biomass (eucalyptus spp.) gasification in a two-stage downdraft reactor by using mixtures of air, saturated steam and oxygen as gasifying agents. *Energy Convers. Manage* 2017;145:314–23.
- [179] Campoy M, Gómez-Barea A, Vidal FB, Ollero P. Air-steam gasification of biomass in a fluidised bed: Process optimisation by enriched air. *Fuel Process Technol* 2009;90:677–85.
- [180] Pandey B, Sheth PN, Prajapati YK. Air-CO<sub>2</sub> and oxygen-enriched air-CO<sub>2</sub> biomass gasification in an autothermal downdraft gasifier: Experimental studies. *Energy Convers Manage* 2022;270:116216.
- [181] Gil J, Corella J, Aznar MP, Caballero MA. Biomass gasification in atmospheric and bubbling fluidized bed: Effect of the type of gasifying agent on the product distribution. *Biomass Bioenergy* 1999;17:389–403.



- [182] Jeremiáš M, Pohorelý M, Svoboda K, Skoblia S, Beno Z, Šyc M. CO<sub>2</sub> gasification of biomass: The effect of lime concentration in a fluidised bed. *Appl Energy* 2018; 217:361–8.
- [183] Pinto F, André R, Miranda M, Neves D, Varela F, Santos J. Effect of gasification agent on co-gasification of rice production wastes mixtures. *Fuel* 2016;180: 407–16.
- [184] Kitzler H, Pfeifer C, Hofbauer H. Pressurized gasification of woody biomass—Variation of parameter. *Fuel Process Technol* 2011;92:908–14.
- [185] Kihedu JH, Yoshiie R, Naruse I. Performance indicators for air and air–steam auto-thermal updraft gasification of biomass in packed bed reactor. *Fuel Process Technol* 2016;141:93–8.
- [186] Huynh CV, Kong S. Performance characteristics of a pilot-scale biomass gasifier using oxygen-enriched air and steam. *Fuel* 2013;103:987–96.
- [187] Jeremiáš M, Pohorelý M, Svoboda K, Manovic V, Anthony EJ, Skoblia S, et al. Gasification of biomass with CO<sub>2</sub> and H<sub>2</sub>O mixtures in a catalytic fluidised bed. *Fuel* 2017;210:605–10.
- [188] Corella J, Orío A, Toledo JM. Biomass gasification with air in a fluidized bed: Exhaustive tar elimination with commercial steam reforming catalysts. *Energy Fuels* 1999;13:702–9.
- [189] Mazumder J, de Lasa HI. Catalytic steam gasification of biomass surrogates: Thermodynamics and effect of operating conditions. *Chem Eng J* 2016;293: 232–42.
- [190] Luo S, Xiao B, Guo X, Hu Z, Liu S, He M. Hydrogen-rich gas from catalytic steam gasification of biomass in a fixed bed reactor: Influence of particle size on gasification performance. *Int J Hydrogen Energy* 2009;34:1260–4.
- [191] Cao Y, Bai Y, Du J. Air-gasification of pine sawdust using dolomite as in-bed material: Effects of gasification conditions on product characteristics. *J Energy Inst* 2021;95:187–92.
- [192] Kausshal P, Tyagi R. Steam assisted biomass gasification-an overview, Canadian. *J Chem Eng* 2012;90:1043–58.
- [193] Qin Y, Feng J, Li W. Formation of tar and its characterization during air–steam gasification of sawdust in a fluidized bed reactor. *Fuel* 2010;89:1344–7.
- [194] Guo F, Dong Y, Dong L, Guo C. Effect of design and operating parameters on the gasification process of biomass in a downdraft fixed bed: An experimental study. *Int J Hydrogen Energy* 2014;39:5625–33.
- [195] Kaewluan S, Pipatmanomai S. Potential of synthesis gas production from rubber wood chip gasification in a bubbling fluidised bed gasifier. *Energy Convers Manage* 2011;52:75–84.
- [196] Mallick D, Mahanta P, Moholkar VS. Co-gasification of biomass blends: Performance evaluation in circulating fluidized bed gasifier. *Energy* 2020;192: 116682.
- [197] Thamavithya M, Jarungthammachote S, Dutta A, Basu P. Experimental study on sawdust gasification in a spout–fluid bed reactor. *Int J Energy Res* 2012;36: 204–17.
- [198] Campoy M, Gómez-Barea A, Fuentes-Cano D, Ollero P. Tar Reduction by Primary Measures in an Autothermal Air-Blown Fluidized Bed Biomass Gasifier. *Ind Eng Chem Res* 2010;49:11294–301.
- [199] Couto N, Rouboa A, Silva V, Monteiro E, Bouziane K. Influence of the Biomass Gasification Processes on the Final Composition of Syngas. *Energy Procedia* 2013; 36:596–606.
- [200] Wolfesberger U, Aigner I, Hofbauer H. Tar content and composition in producer gas of fluidized bed gasification of wood-influence of temperature and pressure, *Environ. Prog. Sustainable Energy* 2009;28:372–9.
- [201] Berruoco C, Recari J, Güell BM, G.d. Alamo. Pressurized gasification of torrefied woody biomass in a lab scale fluidized bed. *Energy* 2014;70:68–78.
- [202] Szul M, Glód K, Iluk T. Influence of pressure and CO<sub>2</sub> in fluidized bed gasification of waste biomasses. *Biomass Convers Biorefinery* 2021;1:69–81.
- [203] Kurkela E, Kurkela M, Hiltunen I. The effects of wood particle size and different process variables on the performance of steam-oxygen blown circulating fluidized-bed gasifier, *Environ. Prog. Sustain Energy* 2014;33:681–7.
- [204] Berruoco C, Montané D, Matas Güell B, del Alamo G. Effect of temperature and dolomite on tar formation during gasification of torrefied biomass in a pressurized fluidized bed. *Energy* 2014;66:849–59.
- [205] Paasen SV, Kiel JHA. Tar formation in a fluidised-bed gasifier 2004.
- [206] Singh Siwal S, Zhang Q, Sun C, Thakur S, Kumar Gupta V, Kumar Thakur V. Energy production from steam gasification processes and parameters that contemplate in biomass gasifier – A review. *Bioresour Technol* 2020;297:122481.
- [207] Hoque M.E, Rashid F, Gasification Process Using Downdraft Fixed-Bed Gasifier for Different Feedstock, in: Valter Silva, Celso Eduardo Tuna (Eds.), Gasification, IntechOpen, Rijeka, 2021, Ch. 7.
- [208] Lopez G, Cortazar M, Alvarez J, Amutio M, Bilbao J, Olazar M. Assessment of a conical spouted with an enhanced fountain bed for biomass gasification. *Fuel* 2017;203:825–31.
- [209] Cortazar M, Lopez G, Alvarez J, Amutio M, Bilbao J, Olazar M. Advantages of confining the fountain in a conical spouted bed reactor for biomass steam gasification. *Energy* 2018;153:455–63.
- [210] Hernández JJ, Aranda-Almansa G, Bula A. Gasification of biomass wastes in an entrained flow gasifier: Effect of the particle size and the residence time. *Fuel Process Technol* 2010;91:681–92.
- [211] Agu CE, Pfeifer C, Eikeland M, Tokheim LA, Moldestad BME. Measurement and characterization of biomass mean residence time in an air-blown bubbling fluidized bed gasification reactor. *Fuel* 2019;253:1414–23.
- [212] Rupesh S, Muraleedharan C, Arun P. Influence of Residence Time on Syngas Composition in CaO Enhanced Air-Steam Gasification of Biomass. *Environ. Dev. Sustain.* 2021;24:8363–77.
- [213] Kinoshita CM, Wang Y, Zhou J. Tar formation under different biomass gasification conditions. *J Anal Appl Pyrolysis* 1994;29:169–81.
- [214] Lopez G, Alvarez J, Amutio M, Arregi A, Bilbao J, Olazar M. Assessment of steam gasification kinetics of the char from lignocellulosic biomass in a conical spouted bed reactor. *Energy* 2016;107:493–501.
- [215] Fryda LE, Panopoulos KD, Kakaras E. Agglomeration in fluidised bed gasification of biomass. *Powder Technol* 2008;181:307–20.
- [216] Schmid JC, Wolfesberger U, Koppatz S, Pfeifer C, Hofbauer H. Variation of feedstock in a dual fluidized bed steam gasifier-influence on product gas, tar content, and composition. *Environ Progress Sustainable Energy* 2012;31:205–15.
- [217] Herguido J, Corella J, Gonzalez-Saiz J. Steam gasification of lignocellulosic residues in a fluidized bed at a small pilot scale. Effect of the type of feedstock. *Ind Eng Chem Res* 1992;31:1274–82.
- [218] Schmid M, Beirrow M, Schweitzer D, Waizmann G, Spörl R, Scheffknecht G. Product gas composition for steam-oxygen fluidized bed gasification of dried sewage sludge, straw pellets and wood pellets and the influence of limestone as bed material. *Biomass Bioenergy* 2018;117:71–7.
- [219] Li J, Liu J, Liao S, Yan R. Hydrogen-rich gas production by air–steam gasification of rice husk using supported nano-NiO/γ-Al<sub>2</sub>O<sub>3</sub> catalyst. *Int J Hydrogen Energy* 2010;35:7399–404.
- [220] Susastriawan AAP, Saptoadi H, Purnomo. Comparison of the gasification performance in the downdraft fixed-bed gasifier fed by different feedstocks: Rice husk, sawdust, and their mixture. *Sustain Energy Technol Assess* 2019;34:27–34.
- [221] Park SJ, Son SH, Kook JW, Ra HW, Yoon SJ, Mun T, et al. Gasification operational characteristics of 20-tons-Per-Day rice husk fluidized-bed reactor. *Renew Energy* 2021;169:788–98.
- [222] Wang D, Liu YQ, Li WP, Wei MM, Ye YY, Li SR, et al. Study on the gasification of pine sawdust with dolomite catalyst in a pilot-scale fluidized bed gasifier, *Energy Sources A: Recovery Util. Environ Eff* 2020;42:1132–9.
- [223] Migliaccio R, Brachi P, Montagnaro F, Papa S, Tavano A, Montesarchio P, et al. Sewage Gasification in a Fluidized Bed: Experimental Investigation and Modeling. *Ind Eng Chem Res* 2021;60:5034–47.
- [224] Couto N, Monteiro E, Silva V, Rouboa A. Hydrogen-rich gas from gasification of Portuguese municipal solid wastes. *Int J Hydrogen Energy* 2016;41:10619–30.
- [225] Wang J, Cheng G, You Y, Xiao B, Liu S, He P, et al. Hydrogen-rich gas production by steam gasification of municipal solid waste (MSW) using NiO supported on modified dolomite. *Int J Hydrogen Energy* 2012;37:6503–10.
- [226] Zhang Z, Pang S. Experimental investigation of tar formation and producer gas composition in biomass steam gasification in a 100 kW dual fluidised bed gasifier. *Renew Energy* 2019;132:416–24.
- [227] Schmid M, Hafner S, Biollaz S, Schneebeli J, Waizmann G, Scheffknecht G. Steam-oxygen gasification of sewage sludge: Reduction of tar, H<sub>2</sub>S and COS with limestone as bed additive. *Biomass Bioenergy* 2021;150:106100.
- [228] Bronson B, Preto F, Mehrani P. Effect of pretreatment on the physical properties of biomass and its relation to fluidized bed gasification, *Environ. Prog. Sustainable Energy* 2012;31:335–9.
- [229] Bronson B, Gogolek P, Mehrani P, Preto F. Experimental investigation of the effect of physical pre-treatment on air-blown fluidized bed biomass gasification. *Biomass Bioenergy* 2016;88:77–88.
- [230] Kaewluan S, Pipatmanomai S. Gasification of high moisture rubber woodchip with rubber waste in a bubbling fluidized bed. *Fuel Process Technol* 2011;92: 671–7.
- [231] Barontini F, Frigo S, Gabbriellini R, Sica P. Co-gasification of woody biomass with organic and waste matrices in a down-draft gasifier: An experimental and modeling approach. *Energy Convers Manage* 2021;245:114566.
- [232] Ramos A, Monteiro E, Rouboa A. Biomass pre-treatment techniques for the production of biofuels using thermal conversion methods – A review. *Energy Convers Manage* 2022;270:116271.
- [233] Pecha MB, Arbelaez JIM, Garcia-Perez M, Chejne F, Ciesielski PN. Progress in understanding the four dominant intra-particle phenomena of lignocellulose pyrolysis: chemical reactions, heat transfer, mass transfer, and phase change. *Green Chem* 2019;21:2868–98.
- [234] Moiceanu G, Paraschiv G, Voicu G, Dinca M, Negoita O, Chitoiu M, et al. Energy consumption at size reduction of lignocellulose biomass for bioenergy. *Sustainability* 2019;11:2477.
- [235] Wargula Ł, Kukla M, Wiczorek B, Krawiec P. Energy consumption of the wood size reduction processes with employment of a low-power machines with various cutting mechanisms. *Renew Energy* 2022;181:630–9.
- [236] Lv PM, Xiong ZH, Chang J, Wu CZ, Chen Y, Zhu JX. An experimental study on biomass air-steam gasification in a fluidized bed. *Bioresour Technol* 2004;95: 95–101.
- [237] Jand N, Foscolo PU. Decomposition of wood particles in fluidized beds. *Ind Eng Chem Res* 2005;44:5079–89.
- [238] Rapagnà S, Mazziotti di Celso G. Devolatilization of wood particles in a hot fluidized bed: Product yields and conversion rates. *Biomass Bioenergy* 2008;32: 1123–9.
- [239] Li XT, Grace JR, Lim CJ, Watkinson AP, Chen HP, Kim JR. Biomass gasification in a circulating fluidized bed. *Biomass Bioenergy* 2004;26:171–93.
- [240] Wilk V, Hofbauer H. Influence of fuel particle size on gasification in a dual fluidized bed steam gasifier. *Fuel Process Technol* 2013;115:139–51.
- [241] Van Der Drift A, Van Doorn J. Effect of Fuel Size and Process Temperature on Fuel Gas Quality from CFB Gasification of Biomass. *Progress in Thermochemical Biomass Conversion* 2008:265–71.
- [242] Narnaware SL, Panwar NL. Catalysts and their role in biomass gasification and tar abatement: a review. *Biomass Convers. Biorefinery* 2021. In press.

- [243] Ruoppolo G, Miccio F, Miccio M, Brachi P, Chirone R. Sewage sludge ashes as a primary catalyst for the abatement of tar in biomass gasification: Bubbling versus spouted-fluidized bed configuration. *Can J Chem Eng* 2021;99:1706–14.
- [244] Serrano D, Kwapinska M, Horvat A, Sánchez-Delgado S, Leahy JJ. *Cynara cardunculus* L. gasification in a bubbling fluidized bed: The effect of magnesite and olivine on product gas, tar and gasification performance. *Fuel* 2016;173:247–59.
- [245] Tuomi S, Kaisalo N, Simell P, Kurkela E. Effect of pressure on tar decomposition activity of different bed materials in biomass gasification conditions. *Fuel* 2015;158:293–305.
- [246] Di Marcello M, Tsalidis GA, Spinelli G, de Jong W, Kiel JHA. Pilot scale steam-oxygen CFB gasification of commercial torrefied wood pellets. The effect of torrefaction on the gasification performance. *Biomass Bioenergy* 2017;105:411–20.
- [247] Pio DT, Gomes HGME, Tarelho LAC, Ruivo LCM, Matos MAA, Pinto RG, et al. Ilmenite as low-cost catalyst for producer gas quality improvement from a biomass pilot-scale gasifier. *Energy Rep* 2020;6:325–30.
- [248] Pushp M, Gall D, Davidsson K, Seemann M, Pettersson JBC. Influence of Bed Material, Additives, and Operational Conditions on Alkali Metal and Tar Concentrations in Fluidized Bed Gasification of Biomass. *Energy Fuels* 2018;32:6797–806.
- [249] Berdugo Vilches T, Marinkovic J, Seemann M, Thunman H. Comparing Active Bed Materials in a Dual Fluidized Bed Biomass Gasifier: Olivine, Bauxite, Quartz-Sand, and Ilmenite. *Energy Fuels* 2016;30:4848–57.
- [250] Larsson A, Israelsson M, Lind F, Seemann M, Thunman H. Using ilmenite to reduce the tar yield in a dual fluidized bed gasification system. *Energy Fuels* 2014;28:2632–44.
- [251] Niu Y, Han F, Chen Y, Lyu Y, Wang L. Experimental study on steam gasification of pine particles for hydrogen-rich gas. *J Energy Inst* 2017;90:715–24.
- [252] Hurley S, Xu C, Preto F, Shao Y, Li H, Wang J, et al. Catalytic gasification of woody biomass in an air-blown fluidized-bed reactor using Canadian limonite iron ore as the bed material. *Fuel* 2012;91:170–6.
- [253] Madadkhani S, Burhenne L, Bi X, Ellis N, Grace JR, Lewis T. Bauxite residue as an iron-based catalyst for catalytic cracking of naphthalene, a model compound for gasification tar. *Can J Chem Eng* 2021;99:1461–74.
- [254] Cheng L, Wu Z, Zhang Z, Guo C, Ellis N, Bi X, et al. Tar elimination from biomass gasification syngas with bauxite residue derived catalysts and gasification char. *Appl Energy* 2020;258:114088.
- [255] Pissot S, Faust R, Aonsamang P, Berdugo Vilches T, Maric J, Thunman H, et al. Development of Oxygen Transport Properties by Olivine and Feldspar in Industrial-Scale Dual Fluidized Bed Gasification of Woody Biomass. *Energy Fuels* 2021;35:9424–36.
- [256] Fürsatz K, Fuchs J, Benedikt F, Kuba M, Hofbauer H. Effect of biomass fuel ash and bed material on the product gas composition in DFB steam gasification. *Energy* 2021;219:119650.
- [257] Ruivo L, Oliveira H, Gomes H, Cruz N, Yaremchenko A, Tarelho LAC, et al. Siderite/Concrete catalysts for H<sub>2</sub>-enriched gas production from biomass steam gasification. *Energy Convers Manage* 2022;255:115280.
- [258] Ramadhani B, Kivevele T, Kihedu JH, Jande YAC. Catalytic tar conversion and the prospective use of iron-based catalyst in the future development of biomass gasification: a review. *Biomass Convers. Biorefinery* 2020;12:1369–92.
- [259] Sutton D, Kelleher B, Ross JRH. Review of literature on catalysts for biomass gasification. *Fuel Process Technol* 2001;73:155–73.
- [260] Shen Y, Yoshikawa K. Recent progresses in catalytic tar elimination during biomass gasification or pyrolysis - A review. *Renewable Sustainable Energy Rev* 2013;21:371–92.
- [261] Devi L, Craje M, Thüne P, Ptasinski KJ, Janssen FJJG. Olivine as tar removal catalyst for biomass gasifiers: Catalyst characterization. *Appl Catal, A* 2005;294:68–79.
- [262] Koppatz S, Pfeifer C, Hofbauer H. Comparison of the performance behaviour of silica sand and olivine in a dual fluidised bed reactor system for steam gasification of biomass at pilot plant scale. *Chem Eng J* 2011;175:468–83.
- [263] Kook JW, Choi HM, Kim BH, Ra HW, Yoon SJ, Mun TY, et al. Gasification and tar removal characteristics of rice husk in a bubbling fluidized bed reactor. *Fuel* 2016;181:942–50.
- [264] Kuba M, Kirnbauer F, Hofbauer H. Influence of coated olivine on the conversion of intermediate products from decomposition of biomass tars during gasification. *Biomass Convers Biorefin* 2017;7:11–21.
- [265] Mauerhofer AM, Benedikt F, Schmid JC, Fuchs J, Müller S, Hofbauer H. Influence of different bed material mixtures on dual fluidized bed steam gasification. *Energy* 2018;157:957–68.
- [266] Christodoulou C, Grimekis D, Panopoulos KD, Pachatouridou EP, Iliopoulou EF, Kakaras E. Comparing calcined and un-treated olivine as bed materials for tar reduction in fluidized bed gasification. *Fuel Process Technol* 2014;124:275–85.
- [267] Kirnbauer F, Wilk V, Kitzler H, Kern S, Hofbauer H. The positive effects of bed material coating on tar reduction in a dual fluidized bed gasifier. *Fuel* 2012;95:553–62.
- [268] Miccio F, Piriou B, Ruoppolo G, Chirone R. Biomass gasification in a catalytic fluidized reactor with beds of different materials. *Chem Eng J* 2009;154:369–74.
- [269] Ma X, Zhao X, Gu J, Shi J. Co-gasification of coal and biomass blends using dolomite and olivine as catalysts. *Renew Energy* 2019;132:509–14.
- [270] Roche E, de Andrés JM, Narros A, Rodríguez ME. Air and air-steam gasification of sewage sludge. The influence of dolomite and throughput in tar production and composition. *Fuel* 2014;115:54–61.
- [271] Pinto F, André RN, Carolino C, Miranda M, Abelha P, Direito D, et al. Effects of experimental conditions and of addition of natural minerals on syngas production from lignin by oxy-gasification: Comparison of bench- and pilot scale gasification. *Fuel* 2015;140:62–72.
- [272] Cortazar M, Lopez G, Alvarez J, Amutio M, Bilbao J, Olazar M. Behaviour of primary catalysts in the biomass steam gasification in a fountain confined spouted bed. *Fuel* 2019;253:1446–56.
- [273] Rauch R, Bosch K, Hofbauer H, Świerczyński D, Courson C, Kiennemann A. Comparison of different olivines for biomass steam gasification. Proceedings of the Conference for Science in Thermal and Chemical Biomass Conversion 2004.
- [274] Kuhn JN, Zhao Z, Felix LG, Slimane RB, Choi CW, Ozkan US. Olivine catalysts for methane- and tar-steam reforming. *Appl Catal, B* 2008;81:14–26.
- [275] Shahbaz M, Yusup S, Inayat A, Patrick DO, Ammar M. The influence of catalysts in biomass steam gasification and catalytic potential of coal bottom ash in biomass steam gasification: A review. *Renewable Sustainable Energy Rev* 2017;73:468–76.
- [276] Artetxe M, Alvarez J, Nahil MA, Olazar M, Williams PT. Steam reforming of different biomass tar model compounds over Ni/Al<sub>2</sub>O<sub>3</sub> catalysts. *Energy Convers Manage* 2017;136:119–26.
- [277] Tan RS, Tuan Abdullah TA, Abdul Jalil A, Md Isa K. Optimization of hydrogen production from steam reforming of biomass tar over Ni/dolomite/La<sub>2</sub>O<sub>3</sub> catalysts. *J Energy Inst* 2020;1177–86.
- [278] Savuto E, Navarro RM, Mota N, Di Carlo A, Bocci E, Carlini M, et al. Steam reforming of tar model compounds over Ni/Mayenite catalysts: effect of Ce addition. *Fuel* 2018;224:676–86.
- [279] Cao JP, Ren J, Zhao XY, Wei XY, Takarada T. Effect of atmosphere on carbon deposition of Ni/Al<sub>2</sub>O<sub>3</sub> and Ni-loaded on lignite char during reforming of toluene as a biomass tar model compound. *Fuel* 2018;217:515–21.
- [280] Wang G, Xu S, Wang C, Zhang J, Fang Z. Desulfurization and tar reforming of biogenous syngas over Ni/olivine in a decoupled dual loop gasifier. *Int J Hydrogen Energy* 2017;42:15471–8.
- [281] Xiao Y, Xu S, Tursun Y, Wang C, Wang G. Catalytic steam gasification of lignite for hydrogen-rich gas production in a decoupled triple bed reaction system. *Fuel* 2017;189:57–65.
- [282] Tang W, Cao J, Wang Z, He Z, Liu T, Wang Z, et al. Comparative evaluation of tar steam reforming over graphitic carbon supported Ni and Co catalysts at low temperature. *Energy Convers Manage* 2021;244:114454.
- [283] Sun H, Wang J, Zhao J, Shen B, Shi J, Huang J, et al. Dual functional catalytic materials of Ni over Ce-modified CaO sorbents for integrated CO<sub>2</sub> capture and conversion. *Appl Catal, B* 2019;244:63–75.
- [284] Kuhn JN, Zhao Z, Senefeld-Naber A, Felix LG, Slimane RB, Choi CW, et al. Ni-olivine catalysts prepared by thermal impregnation: Structure, steam reforming activity, and stability. *Appl Catal, A* 2008;341:43–9.
- [285] Świerczyński D, Libs S, Courson C, Kiennemann A. Steam reforming of tar from a biomass gasification process over Ni/olivine catalyst using toluene as a model compound. *Appl Catal, B* 2007;74:211–22.
- [286] Rapagnà S, Virginie M, Gallucci K, Courson C, Di Marcello M, Kiennemann A, et al. Fe/olivine catalyst for biomass steam gasification: Preparation, characterization and testing at real process conditions. *Catal Today* 2011;176:163–8.
- [287] Virginie M, Courson C, Niznansky D, Chaoui N, Kiennemann A. Characterization and reactivity in toluene reforming of a Fe/olivine catalyst designed for gas cleanup in biomass gasification. *Appl Catal, B* 2010;101:90–100.
- [288] Quan C, Xu S, Zhou C. Steam reforming of bio-oil from coconut shell pyrolysis over Fe/olivine catalyst. *Energy Convers Manage* 2017;141:40–7.
- [289] Nordgreen T, Liljedahl T, Sjöström K. Metallic iron as a tar breakdown catalyst related to atmospheric, fluidised bed gasification of biomass. *Fuel* 2006;85:689–94.
- [290] Cortazar M, Alvarez J, Olazar L, Santamaria L, Lopez G, Villafán-Vidales HI, et al. Activity and stability of different Fe loaded primary catalysts for tar elimination. *Fuel* 2022;317:123457.
- [291] Miccio F, Picarelli A, Ruoppolo G. Increasing tar and hydrocarbons conversion by catalysis in bubbling fluidized bed gasifiers. *Fuel Process Technol* 2016;141:31–7.
- [292] Asadullah M, Miyazawa T, Ito S, Kunimori K, Koyama S, Tomishige K. A comparison of Rh/CeO<sub>2</sub>/SiO<sub>2</sub> catalysts with steam reforming catalysts, dolomite and inert materials as bed materials in low throughput fluidized bed gasification systems. *Biomass Bioenergy* 2004;26:269–79.
- [293] Chairasert P, Vitidsant T. Effects of promoters on biomass gasification using nickel/dolomite catalyst. *Korean J Chem Eng* 2009;26:1545–9.
- [294] Cortazar M, Santamaria L, Lopez G, Alvarez J, Amutio M, Bilbao J, et al. Fe/olivine as primary catalyst in the biomass steam gasification in a fountain confined spouted bed reactor. *J Ind Eng Chem* 2021;99:364–79.
- [295] Barisano D, Freda C, Nanna F, Fanelli E, Villone A. Biomass gasification and in-bed contaminants removal: Performance of iron enriched olivine and bauxite in a process of steam/O<sub>2</sub> gasification. *Bioresour Technol* 2012;118:187–94.
- [296] Kuramoto K, Matsuoka K, Murakami T, Takagi H, Nanba T, Suzuki Y, et al. Cracking and coking behaviors of nascent volatiles derived from flash pyrolysis of woody biomass over mesoporous fluidized-bed material. *Ind Eng Chem Res* 2009;48:2851–60.
- [297] Matsuoka K, Kuramoto K, Murakami T, Suzuki Y. Steam gasification of woody biomass in a circulating dual bubbling fluidized bed system. *Energy Fuels* 2008;22:1980–5.
- [298] Abu El-Rub Z, Bramer EA, Brem G. Review of catalysts for tar elimination in biomass gasification processes. *Ind Eng Chem Res* 2004;43:6911–9.
- [299] Ferella F, Innocenzi V, Maggiore F. Oil refining spent catalysts: A review of possible recycling technologies. *Resour Conserv Recycl* 2016;108:10–20.
- [300] Nam H, Wang S, Sanjeev KC, Seo MW, Adhikari S, Shakya R, et al. Enriched hydrogen production over air and air-steam fluidized bed gasification in a

- bubbling fluidized bed reactor with CaO: Effects of biomass and bed material catalyst. *Energy Convers Manage* 2020;225:113408.
- [301] Gil J, Caballero MA, Martín JA, Aznar M, Corella J. Biomass gasification with air in a fluidized bed: Effect of the in-bed use of dolomite under different operation conditions. *Ind Eng Chem Res* 1999;38:4226–35.
- [302] Xie Y, Xiao J, Shen L, Wang J, Zhu J, Hao J. Effects of Ca-based catalysts on biomass gasification with steam in a circulating spout-fluid bed reactor. *Energy Fuels* 2010;24:3256–61.
- [303] Erkiaga A, Lopez G, Amutio M, Bilbao J, Olazar M. Steam gasification of biomass in a conical spouted bed reactor with olivine and  $\gamma$ -alumina as primary catalysts. *Fuel Process Technol* 2013;116:292–9.
- [304] De Andrés JM, Narros A, Rodríguez ME. Air-steam gasification of sewage sludge in a bubbling bed reactor: Effect of alumina as a primary catalyst. *Fuel Process Technol* 2011;92:433–40.
- [305] Pio DT, Ruivo LCM, Tarelho LAC, Frade JR, Kantarelis E, Engvall K. Tar formation during eucalyptus gasification in a bubbling fluidized bed reactor: Effect of feedstock and reactor bed composition. *Energy Convers Manage* 2021;229:113749.
- [306] Gómez-Barea A, Ollero P, Leckner B. Optimization of char and tar conversion in fluidized bed biomass gasifiers. *Fuel* 2013;103:42–52.
- [307] Bridgwater AV. The technical and economic feasibility of biomass gasification for power generation. *Fuel* 1995;74:631–53.
- [308] Chai Z, Zhu Z, Wang X, Wang K. Sulfur conversions during coal char gasification with a two-stage air supply in a pilot-scale circulating fluidized bed gasifier. *Energy Sources Part A* 2020;42:421–31.
- [309] Fan W, Lin Z, Kuang J, Li Y. Impact of air staging along furnace height on NO<sub>x</sub> emissions from pulverized coal combustion. *Fuel Process Technol* 2010;91:625–34.
- [310] Kang MS, Jeong HJ, Massoudi Farid M, Hwang J. Effect of staged combustion on low NO<sub>x</sub> emission from an industrial-scale fuel oil combustor in South Korea. *Fuel* 2017;210:282–9.
- [311] Cao Y, Wang Y, Riley JT, Pan W. A novel biomass air gasification process for producing tar-free higher heating value fuel gas. *Fuel Process Technol* 2006;87:343–53.
- [312] Robinson T, Bronson B, Gogolek P, Mehrani P. Comparison of the air-blown bubbling fluidized bed gasification of wood and wood–PET pellets. *Fuel* 2016;178:263–71.
- [313] Pan YG, Roca X, Velo E, Puigjaner L. Removal of tar by secondary air in fluidized bed gasification of residual biomass and coal. *Fuel* 1999;78:1703–9.
- [314] Wang X, Zhu Z, Wang K, Yu K, Lyu Q. Experimental study of pilot-scale CFB gasification: Effect of gasifying agent and coal feeding modes on the gasification performance. *Fuel* 2019;251:603–10.
- [315] Tsekos C, del Grosso M, de Jong W. Gasification of woody biomass in a novel indirectly heated bubbling fluidized bed steam reformer. *Fuel Process Technol* 2021;224:107003.
- [316] Heidenreich S, Foscolo PU. New concepts in biomass gasification. *Prog Energy Combust Sci* 2015;46:72–95.
- [317] Rapagnà S, Gallucci K, Marcellino MD, Foscolo PU, Nacken M, Heidenreich S. In situ catalytic ceramic candle filtration for tar reforming and particulate abatement in a fluidized-bed biomass gasifier. *Energy Fuels* 2009;23:3804–9.
- [318] Engelen K, Zhang Y, Draelants DJ, Baron GV. A novel catalytic filter for tar removal from biomass gasification gas: Improvement of the catalytic activity in presence of H<sub>2</sub>S. *Chem Eng Sci* 2003;58:665–70.
- [319] Ma L, Verelst H, Baron GV. Integrated high temperature gas cleaning: Tar removal in biomass gasification with a catalytic filter. *Catal Today* 2005;105:729–34.
- [320] Heidenreich S, Nacken M, Hackel M, Schaub G. Catalytic filter elements for combined particle separation and nitrogen oxides removal from gas streams. *Powder Technol* 2008;180:86–90.
- [321] Rapagnà S, Gallucci K, di Marcellino M, Matt M, Nacken M, Heidenreich S, et al. Gas cleaning, gas conditioning and tar abatement by means of a catalytic filter candle in a biomass fluidized-bed gasifier. *Bioresour Technol* 2010;101:7123–30.
- [322] Rapagnà S, Gallucci K, Di Marcellino M, Foscolo PU, Nacken M, Heidenreich S, et al. First Al<sub>2</sub>O<sub>3</sub> based catalytic filter candles operating in the fluidized bed gasifier freeboard. *Fuel* 2012;97:718–24.
- [323] Savuto E, Di Carlo A, Steele A, Heidenreich S, Gallucci K, Rapagnà S. Syngas conditioning by ceramic filter candles filled with catalyst pellets and placed inside the freeboard of a fluidized bed steam gasifier. *Fuel Process Technol* 2019;191:44–53.
- [324] Wang C, Zhang M, Han Z, Bai D, Duo W, Bi X, et al. Pilot verification of a two-stage fluidized bed gasifier with a downer pyrolyzer using oxygen-rich air. *Fuel* 2022;307:121816.
- [325] Corella J, Herguido J, Alday FJ. Pyrolysis and Steam Gasification of Biomass in Fluidized Beds. Influence of the Type and Location of the Biomass Feeding Point on the Product Distribution. In: Bridgwater AV, Kuester JL, editors. *Research in Thermochemical Biomass Conversion*. Netherlands, Dordrecht: Springer; 1988. p. 384–98.
- [326] Kern S, Pfeifer C, Hofbauer H. Gasification of wood in a dual fluidized bed gasifier: Influence of fuel feeding on process performance. *Chem Eng Sci* 2013;90:284–98.
- [327] Wilk V, Schmid JC, Hofbauer H. Influence of fuel feeding positions on gasification in dual fluidized bed gasifiers. *Biomass Bioenergy* 2013;54:46–58.
- [328] Jaiswal R, Furuvi NCIS, Thapa RK, Moldestad BME. A CPFD model to investigate the influence of feeding positions in a gasification reactor. *Int J Energy Prod Manage* 2020;5:223–33.
- [329] Han Z, Geng S, Zeng X, Xu S, An P, Cheng J, et al. Reaction decoupling in thermochemical fuel conversion and technical progress based on decoupling using fluidized bed. *Carbon Resour Convers* 2018;1:109–25.
- [330] Kargo HO, Ng KS, Phan AN. Evaluation of the economic feasibility of a two-stage gasification system for hydrogen, liquid fuels and energy production from residues. *Energy Convers Manage* 2022;253:115126.
- [331] Spath P, Aden A, Eggeman T, Ringer M, Wallace B, Jechura J. Biomass to Hydrogen Production Detailed Design and Economics Utilizing the Battelle Columbus Laboratory Indirectly-Heated Gasifier. 2005.
- [332] Bui T, Loof R, Bhattacharya SC. Multi-stage reactor for thermal gasification of wood. *Energy* 1994;19:397–404.
- [333] Restrepo SYG, Rocha MH, Lora EES, Venturini OJ, Cobas VRM, Maya DM. Design and operation of a gas cleaning system for biomass gasification in a two-stage air-blown downdraft gasifier to meet quality requirements of solid oxide fuel cells. *Biomass Convers. Biorefinery* 2021. In press.
- [334] Sulc J, Stojil J, Richter M, Popelka J, Svoboda K, Smetana J, et al. Biomass waste gasification – Can be the two stage process suitable for tar reduction and power generation? *Waste Manage* 2012;32:692–700.
- [335] Brandt P, Larsen E, Henriksen U. High Tar Reduction in a Two-Stage Gasifier. *Energy Fuels* 2000;14:816–9.
- [336] Henriksen U, Ahrenfeldt J, Jensen TK, Gøbel B, Bentzen JD, Hindsgaul C, et al. The design, construction and operation of a 75kW two-stage gasifier. *Energy* 2006;31:1542–53.
- [337] Ahrenfeldt J, Thomsen TP, Henriksen U, Clausen LR. Biomass gasification cogeneration – A review of state of the art technology and near future perspectives. *Appl Therm Eng* 2013;50:1407–17.
- [338] Mun T, Seon P, Kim J. Production of a producer gas from woody waste via air gasification using activated carbon and a two-stage gasifier and characterization of tar. *Fuel* 2010;89:3226–34.
- [339] Choi Y, Cho M, Kim J. Steam/oxygen gasification of dried sewage sludge in a two-stage gasifier: Effects of the steam to fuel ratio and ash of the activated carbon on the production of hydrogen and tar removal. *Energy* 2015;91:160–7.
- [340] Pei H, Wang X, Dai X, Jin B, Huang Y. A novel two-stage biomass gasification concept: Design and operation of a 1.5 MWth demonstration plant. *Bioresour Technol* 2018;267:102–9.
- [341] Lopez G, Santamaria L, Lemonidou A, Zhang S, Wu C, Sipra AT, et al. Hydrogen generation from biomass by pyrolysis. *Nat Rev Methods Primers* 2022;2:20.
- [342] Park Y, Namioka T, Sakamoto S, Min T, Roh S, Yoshikawa K. Optimum operating conditions for a two-stage gasification process fueled by polypropylene by means of continuous reactor over ruthenium catalyst. *Fuel Process Technol* 2010;91:951–7.
- [343] Lopez G, Artetxe M, Amutio M, Alvarez J, Bilbao J, Olazar M. Recent advances in the gasification of waste plastics. A critical overview. *Renewable Sustainable Energy Rev* 2018;82:576–96.
- [344] Santamaria L, Lopez G, Fernandez E, Cortazar M, Arregi A, Olazar M, et al. Progress on Catalyst Development for the Steam Reforming of Biomass and Waste Plastics Pyrolysis Volatiles: A Review. *Energy Fuels* 2021;35:17051–84.
- [345] Lopez G, Garcia I, Arregi A, Santamaria L, Amutio M, Artetxe M, et al. Thermodynamic assessment of the oxidative steam reforming of biomass fast pyrolysis volatiles. *Energy Convers Manage* 2020;214:112889.
- [346] Cai W, Wang F, Zhan E, Van Venen AC, Mirodatos C, Shen W. Hydrogen production from ethanol over Ir/CeO<sub>2</sub> catalysts: A comparative study of steam reforming, partial oxidation and oxidative steam reforming. *J Catal* 2008;257:96–107.
- [347] Wu C, Williams PT. Hydrogen production by steam gasification of polypropylene with various nickel catalysts. *Appl Catal, B* 2009;87:152–61.
- [348] Akubo K, Nahil MA, Williams PT. Pyrolysis-catalytic steam reforming of agricultural biomass wastes and biomass components for production of hydrogen/syngas. *J Energy Inst* 2019;92:1987–96.
- [349] Xiao X, Meng X, Le DD, Takarada T. Two-stage steam gasification of waste biomass in fluidized bed at low temperature: Parametric investigations and performance optimization. *Bioresour Technol* 2011;102:1975–81.
- [350] Efika CE, Wu C, Williams PT. Syngas production from pyrolysis-catalytic steam reforming of waste biomass in a continuous screw kiln reactor. *J Anal Appl Pyrolysis* 2012;95:87–94.
- [351] Santamaria L, Lopez G, Arregi A, Amutio M, Artetxe M, Bilbao J, et al. Influence of the support on Ni catalysts performance in the in-line steam reforming of biomass fast pyrolysis derived volatiles. *Appl Catal, B* 2018;229:105–13.
- [352] Arregi A, Lopez G, Amutio M, Barbarias I, Bilbao J, Olazar M. Hydrogen production from biomass by continuous fast pyrolysis and in-line steam reforming. *RSC Adv* 2016;6:25975–85.
- [353] Fernandez E, Santamaria L, Artetxe M, Amutio M, Arregi A, Lopez G, et al. Conditioning the volatile stream from biomass fast pyrolysis for the attenuation of steam reforming catalyst deactivation. *Fuel* 2022;312:122910.
- [354] Chai Y, Gao N, Wang M, Wu C. H<sub>2</sub> production from co-pyrolysis/gasification of waste plastics and biomass under novel catalyst Ni-CaO-C. *Chem Eng J* 2020;382:122947.
- [355] Kumagai S, Yabuki R, Kameda T, Saito Y, Yoshioka T. Simultaneous recovery of H<sub>2</sub>-rich syngas and removal of HCN during pyrolytic recycling of polyurethane by Ni/Mg/Al catalysts. *Chem Eng J* 2019;361:408–15.
- [356] Czernik S, French RJ. Production of Hydrogen from Plastics by Pyrolysis and Catalytic Steam Reform. *Energy Fuels* 2006;20:754–8.
- [357] Arregi A, Seifali Abbas-Abadi M, Lopez G, Santamaria L, Artetxe M, Bilbao J, et al. CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> Promoters in the Steam Reforming of Polyolefinic Waste Plastic Pyrolysis Volatiles on Ni-Based Catalysts, ACS Sustainable. *Chem Eng* 2020;8:17307–21.

- [358] Pandey B, Prajapati YK, Sheth PN. Recent progress in thermochemical techniques to produce hydrogen gas from biomass: A state of the art review. *Int J Hydrogen Energy* 2019;44:25384–415.
- [359] Xiao X, Cao J, Meng X, Le DD, Li L, Ogawa Y, et al. Synthesis gas production from catalytic gasification of waste biomass using nickel-loaded brown coal char. *Fuel* 2013;103:135–40.
- [360] Yu H, Liu Y, Liu J, Chen D. High catalytic performance of an innovative Ni/magnesium slag catalyst for the syngas production and tar removal from biomass pyrolysis. *Fuel* 2019;254:115622.
- [361] Santamaria L, Lopez G, Arregi A, Artetxe M, Amutio M, Bilbao J, et al. Catalytic steam reforming of biomass fast pyrolysis volatiles over Ni-Co bimetallic catalysts. *J Ind Eng Chem* 2020;91:167–81.
- [362] Santamaria L, Arregi A, Lopez G, Artetxe M, Amutio M, Bilbao J, et al. Effect of La<sub>2</sub>O<sub>3</sub> promotion on a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst for H<sub>2</sub> production in the in-line biomass pyrolysis-reforming. *Fuel* 2020;262:116593.
- [363] Angeli SD, Pilitsis FG, Lemonidou AA. Methane steam reforming at low temperature: Effect of light alkanes' presence on coke formation. *Catal Today* 2015;242:119–28.
- [364] Melo F, Morlanés N. Naphtha steam reforming for hydrogen production. *Catal Today* 2005;107–108:458–66.
- [365] Remiro A, Valle B, Aguayo AT, Bilbao J, Gayubo AG. Operating conditions for attenuating Ni/La<sub>2</sub>O<sub>3</sub>-αAl<sub>2</sub>O<sub>3</sub> catalyst deactivation in the steam reforming of bio-oil aqueous fraction. *Fuel Process Technol* 2013;115:222–32.
- [366] Arregi A, Amutio M, Lopez G, Artetxe M, Alvarez J, Bilbao J, et al. Hydrogen-rich gas production by continuous pyrolysis and in-line catalytic reforming of pine wood waste and HDPE mixtures. *Energy Convers Manage* 2017;136:192–201.
- [367] Seyedejn-Azad F, Abedi J, Sampouri S. Catalytic Steam Reforming of Aqueous Phase of Bio-Oil over Ni-Based Alumina-Supported Catalysts. *Ind Eng Chem Res* 2014;53:17937–44.
- [368] González-Gil R, Chamorro-Burgos I, Herrera C, Larrubia MA, Laborde M, Mariño F, et al. Production of hydrogen by catalytic steam reforming of oxygenated model compounds on Ni-modified supported catalysts. Simulation and experimental study. *Int J Hydrogen Energy* 2015;40:11217–27.
- [369] Richardson JT. Principles of catalyst development. New York: Plenum Press; 1989.
- [370] Kimura T, Miyazawa T, Nishikawa J, Kado S, Okumura K, Miyao T, et al. Development of Ni catalysts for tar removal by steam gasification of biomass. *Appl Catal, B* 2006;68:160–70.
- [371] Sánchez-Sánchez MC, Navarro RM, Fierro JLG. Ethanol steam reforming over Ni/La-Al<sub>2</sub>O<sub>3</sub> catalysts: Influence of lanthanum loading. *Catal Today* 2007;129:336–45.
- [372] Arregi A, Lopez G, Amutio M, Barbarias I, Santamaria L, Bilbao J, et al. Regenerability of a Ni catalyst in the catalytic steam reforming of biomass pyrolysis volatiles. *J Ind Eng Chem* 2018;68:69–78.
- [373] Gómez-Barea A, Leckner B, Villanueva Perales A, Nilsson S, Fuentes Cano D. Improving the performance of fluidized bed biomass/waste gasifiers for distributed electricity: A new three-stage gasification system. *Appl Therm Eng* 2013;50:1453–62.
- [374] Choi Y, Mun T, Cho M, Kim J. Gasification of dried sewage sludge in a newly developed three-stage gasifier: Effect of each reactor temperature on the producer gas composition and impurity removal. *Energy* 2016;114:121–8.
- [375] Pan Y, Abulizi A, Talifu D, Tursun Y, Xu S. Catalytic gasification of biomass and coal blend with Fe<sub>2</sub>O<sub>3</sub>/olivine in a decoupled triple bed. *Fuel Process Technol* 2019;194:106121.
- [376] Burhenne L, Rochlitz L, Lintner C, Aicher T. Technical demonstration of the novel Fraunhofer ISE biomass gasification process for the production of a tar-free synthesis gas. *Fuel Process Technol* 2013;106:751–60.
- [377] Benedikt F, Fuchs J, Schmid JC, Müller S, Hofbauer H. Advanced dual fluidized bed steam gasification of wood and lignite with calcite as bed material. *Korean J Chem Eng* 2017;34:2548–58.
- [378] Benedikt F, Schmid JC, Fuchs J, Mauerhofer AM, Müller S, Hofbauer H. Fuel flexible gasification with an advanced 100 kW dual fluidized bed steam gasification pilot plant. *Energy* 2018;164:329–43.
- [379] Schmid JC, Benedikt F, Fuchs J, Mauerhofer AM, Müller S, Hofbauer H. Syngas for biorefineries from thermochemical gasification of lignocellulosic fuels and residues—5 years' experience with an advanced dual fluidized bed gasifier design. *Biomass Convers Biorefinery* 2021;11:2405–42.
- [380] Di Carlo A, Moroni M, Savuto E, Pallozzi V, Bocci E, Di Lillo P. Cold model testing of an innovative dual bubbling fluidized bed steam gasifier. *Chem Eng J* 2019;377:119689.
- [381] Kuba M, Kraft S, Kirnbauer F, Maierhans F, Hofbauer H. Influence of controlled handling of solid inorganic materials and design changes on the product gas quality in dual fluid bed gasification of woody biomass. *Appl Energy* 2018;210:230–40.
- [382] Azizi K, Keshavarz Moraveji M, Arregi A, Amutio M, Lopez G, Olazar M. On the pyrolysis of different microalgae species in a conical spouted bed reactor: Bio-fuel yields and characterization. *Bioresour Technol* 2020;311:123561.
- [383] Amutio M, Lopez G, Alvarez J, Olazar M, Bilbao J. Fast pyrolysis of eucalyptus waste in a conical spouted bed reactor. *Bioresour Technol* 2015;194:225–32.
- [384] Amutio M, Lopez G, Artetxe M, Elordi G, Olazar M, Bilbao J. Influence of temperature on biomass pyrolysis in a conical spouted bed reactor. *Resour Conserv Recycl* 2012;59:23–31.
- [385] Pablos A, Aguado R, Tellabide M, Altzibar H, Freire FB, Bilbao J, et al. A new fountain confinement device for fluidizing fine and ultrafine sands in conical spouted beds. *Powder Technol* 2018;328:38–46.
- [386] Altzibar H, Estiati I, Lopez G, Saldarriaga JF, Aguado R, Bilbao J, et al. Fountain confined conical spouted beds. *Powder Technol* 2017;312:334–46.
- [387] Machin EB, Pedroso DT, Proenza N, Silveira JL, Conti L, Braga LB, et al. Tar reduction in downdraft biomass gasifier using a primary method. *Renew Energy* 2015;78:478–83.
- [388] Rahman MM, Aravindakshan S, Matin MA. Design and performance evaluation of an inclined nozzle and combustor of a downdraft moving bed gasifier for tar reduction. *Renew Energy* 2021;172:239–50.
- [389] Susanto H, Beenackers AACM. A moving-bed gasifier with internal recycle of pyrolysis gas. *Fuel* 1996;75:1339–47.
- [390] Rahman MM, Henriksen UB, Ahrenfeldt J, Arnavat MP. Design, construction and operation of a low-tar biomass (LTB) gasifier for power applications. *Energy* 2020;204:117944.
- [391] Kurkela E, Kurkela M, Hiltunen I. Pilot-scale development of pressurized fixed-bed gasification for synthesis gas production from biomass residues. *Biomass Convers. Biorefinery* 2021. In press.