Reforming processes for syngas production: A mini-review on the current status, challenges, and prospects for biomass conversion to fuels

José Juan Bolívar Caballero [*], Ilman Nuran Zaini [*], Weihong Yang

Department of Materials Science and Engineering, KTH Royal Institute of Technology, Brinellvägen 23, SE-114 28, Stockholm, Sweden

ARTICLE INFO

ABSTRACT

Dedicated bioenergy combined with carbon capture and storage are important elements for the mitigation scenarios to limit the global temperature rise within 1.5 °C. Thus, the productions of carbon-negative fuels and chemicals from biomass is a key for accelerating global decarbonisation. The conversion of biomass into syngas has a crucial role in the biomass-based decarbonisation routes. Syngas is an intermediate product for a variety of chemical syntheses to produce hydrogen, methanol, dimethyl ether, jet fuels, alkenes, etc. The use of biomass-derived syngas has also been seen as promising for the productions of carbon-negative metal products. This paper reviews several possible technologies for the production of syngas from biomass, especially related to the technological options and challenges of reforming processes. The scope of the review includes partial oxidation (POX), autothermal reforming (ATR), catalytic partial oxidation (CPO), catalytic steam reforming (CSR) and membrane reforming (MR). Special attention is given to the progress of CSR for biomass-derived vapours as it has gained significant interest in recent years. Heat demand and efficiency together with properties of the reformer catalyst were reviewed more deeply, in order to understand and propose solutions to the problems that arise by the reforming of biomass-derived vapours and that need to be addressed in order to implement the technology on a big scale.

1. Introduction

The reduction of global greenhouse gases (GHGs) emissions, particularly CO_2, remains the top priority of climate change mitigation. Unless it is restrained, global warming will lead to the utmost disruptions to the global economy. It is predicted that up to 18% of the worldwide GDP could be erased when the global temperature increases by 3.2 °C [1]. Hence, a significant amount of GHGs emissions should be cut to meet the Paris Agreement climate target of limiting the global temperature rise well within 2 °C, preferably to 1.5 °C [2]. Following the guideline from Intergovernmental Panel on Climate Change (IPCC), limiting global warming to 1.5 °C can only be achieved by reducing at least 45% of the global CO_2 emission from 2010 level by 2030; after that, a net-zero emission should be achieved by around 2050 [3].

In 2021, the global economy rebounded by 4.8%, which caused the total CO_2 emission to rise back to the level of 33 Gt, from 31.5 Gt in the previous year [4]. Industrial and transportation sectors are the main GHGs emitters, which are responsible for approximately 27 and 16% of the total emissions, respectively [5]. As the transition towards renewable energy has been well established in many energy sectors, the industrial sector has been trailing behind [6]. Thus, accelerating the decarbonisation of the energy-intensive industrial sectors is critical for

climate change mitigation. Industrial decarbonisation will take place variously in different regions depending on the local aspects, which is greatly determined by the cost and availability of biomass, renewable electricity, and carbon storage locations [6].

Biomass is a key for global decarbonisation as it facilitates the production of carbon-negative fuels and chemicals. Biomass typically refers to organic, non-fossilised and biodegradable materials that are derived from plants, animals and microorganisms. Products and waste from agriculture and forestry as well as biodegradable organic fractions of industrial and municipal waste are also included in the definition. Furthermore, gases and liquids recovered from the decomposition of non-fossilised and biodegradable materials are also considered biomass [7]. As emphasised by IPCC, dedicated bioenergy combined with carbon capture and storage (BECCS) are important elements of almost all mitigation scenarios that limit the global temperature rise within 1.5 °C [3]. For the transportation sector, these scenarios include the utilisation of biomass-based liquid fuels to initially cancel out the gasoline and diesel used for light-duty vehicles, as well as the hard-to-replace petroleum products used for aviation and long-haul transport fuels in the advanced stage [8]. Later, when carbon capture and storage (CCS) technologies are available, the captured biomass carbon is subsequently transferred
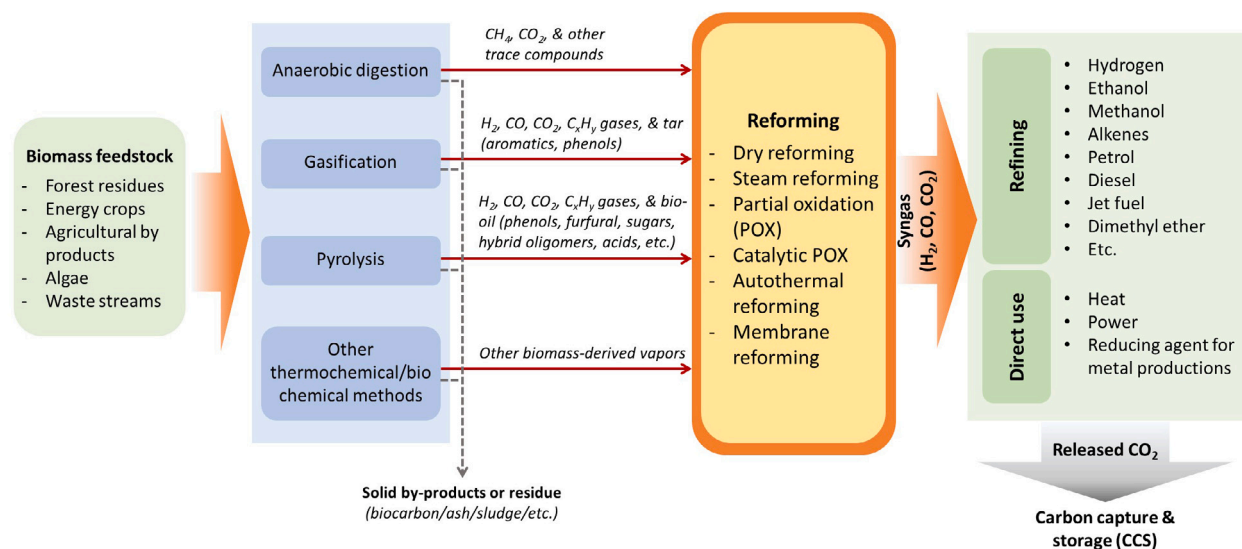
Fig. 1. Roles of reforming processes in the productions of carbon-negative fuels and chemicals from biomass.

as CO_2 to long-term geologic storage; completing the carbon-negative cycle [8]. Similarly, there have been various proposals regarding the use of biomass, with or without CCS, for the decarbonisation of the industrial sector. These mainly involve the energy-intensive industries such as steel, pulp and paper, refinery, cement, and mining sectors. Examples of those proposals are the substitution of natural gas by biomass syngas [9] or bio-oil [10] for the heating of industrial furnace; the use of biomass syngas for carbon-negative steel productions [11], and gasification of biomass residue from pulp and paper industries for biofuels productions [12].

The utilisation of biomass and conversion into syngas plays a crucial role in the biomass-based decarbonisation route, as illustrated in Fig. 1. Syngas is a mixture of mainly CO and H_2. It is the most important bridge between carbon resources and fuels/chemicals [13]. Syngas provides a flexible building block for a variety of chemical syntheses, including methanol (MeOH) and dimethyl ether (DME) production together with the production of higher hydrocarbons via Fischer–Tropsch (FT) synthesis [14]. The H_2/CO molar ratio is an important parameter that determines the downstream application of syngas. For example, MeOH synthesis requires a H_2/CO of 2:1, an efficient FT process requires a H_2/CO ratio of 0.3–4 [15]. Correspondingly, the development of reforming technologies, as the main processes of syngas productions, remain a primary concern in the field of biomass energy.

The reforming processes are considered mature technologies in the field of fossil fuels conversion as many of their applications have a Technology Readiness Level (TRL) of 8 to 9 [16]. The most common application of these technologies is the fossil-based H_2 production through the steam reforming processes of natural gas. Other fossil-based feedstocks for hydrogen production through steam reforming are methanol, propane, butane, naphtha, jet fuel, and diesel [17].

Different from the reforming of natural gas, reforming processes of biomass-derived vapours are more challenging due to the unique, wide range, and complication of different biomass types. Biomass usually needs to be pretreated, this means preparing the fuel for conversion and can be done chemically (steam and acid pretreatment) or physically (chipping, shredding, drying) [18,19]. The downstream gas usually contains dust and traces of sulphur that reduce conversion in catalytic processes and can cause clogging and high pressure drop [20,21]. The organic compounds in biomass-derived vapours require high temperature and active catalyst to be reformed. During the process, they can break down and cause coke formation, carbon deposition on the surface of the catalyst that reduces its surface area, reducing conversion and stability [22]. To summarise, biomass thermochemical conversion

processes typically requires a high amount of energy, and an active and stable catalyst if the processes are catalytic. In order to make the process profitable and commercial, energy efficiency and process stability represent the main challenges to be solved.

In the latest years, research has focused on how to solve these bottlenecks. Previous review papers have focused mainly on thermochemical conversion processes [23], reforming technologies [24–27] and catalyst properties (support, active site, design, stability and deactivation) [28,29]. Catalyst stability remains the biggest challenge for the commercialisation of the technology. In addition, there is an information gap concerning energy consumption and efficiency. Therefore, this mini-review provides a general overview of the progress of reforming processes for syngas production from biomass, especially related to their technological options and challenges. A special section is dedicated to the progress on catalytic steam reforming (CSR) due to the significant interest in this field. In addition, the last section of this review focuses on the progress of electrically heated reformers as a view on the energy question. The development of these reformers could have a significant impact on achieving the future global net-zero emission target. As for the electrification of the reforming systems, to the best of authors' knowledge, reviews on this subject have been rarely done so far.

2. Production of syngas from biomass

As depicted in Fig. 1, the syngas production routes from biomass typically start with a thermochemical or biochemical process that converts the solid biomass into vapours and solid residue (ash, char, other inorganics). The produced vapour contains non-condensable gases and condensable hydrocarbons (tar or bio-oil). The common and well-established methods of these processes mainly consist of gasification, pyrolysis, and anaerobic digestion [13]. Reforming processes are then required to convert the biomass-derived vapour into clean syngas consisting of mainly H_2 and CO. In the case of gasification, the high-temperature gasifiers produce raw syngas that often still has a significant amount of heavy hydrocarbon gases (C_2–C_4) and tar compounds (mostly are naphthalene, benzene, and toluene). In this case, the main role of reforming processes is to crack these hydrocarbon compounds in the raw syngas to produce a final cleaned syngas. Meanwhile, the vapour produced from biomass pyrolysis has a significantly high concentration of condensable fraction, which is commonly referred to as bio-oil. Bio-oil consists of more complex hydrocarbon compounds with larger carbon numbers than that tar from gasification. Similarly,

Table 1

Comparison of syngas composition between different gasifying agents.

Gasifying agent	H_2	CO	CH_4	CO_2	Reference
Air-steam	17–12 mol%	40–38 mol%	7.5–7 mol%	38–42 mol%	[32]
Air	7.5–7 mol%	30–25 mol%	4.5–5 mol%	60–62.5 mol%	[32]
Oxygen-steam	36.5–39 mol%	18–25 mol%	3–4.7 mol%	43–46 mol%	[33]

Table 2

Comparison of tar yield between different biomass gasifiers [34].

Reactor type	Operating conditions	Tar (g/N m³)
Fluidised bed	Feed particle size: < 20 mm Temperature: 750–900 °C	10 (average)
Updraft fixed bed	Feed particle size: 5–100 mm Gas exit temperature: 200–400 °C	30–150
Downdraft fixed bed	Feed particle size: 20–100 mm Gas exit temperature: 700 °C	0.015–3.0
Crossdraft fixed bed	Feed particle size: 5–20 mm Gas exit temperature: 1250 °C	0.01–0.1

the role of the reformer is to crack these compounds into final syngas, which is more challenging and energy-intensive due to the complexity of bio-oil. On the other hand, the production of syngas in the anaerobic digestion routes involve the reforming of CH_4 produced from digesters into H_2 and CO.

2.1. Gasification

Gasification is a thermochemical process in which reactions between a fuel (i.e. biomass, coal) and a gasifying agent (steam, air, etc.) take place at high temperatures. The fuel (coal or pretreated biomass) enters the gasifier unit together with the gasifying agent(s) where it undergoes thermochemical conversion to syngas (also called producer gas). Syngas is mainly composed of small chemical compounds (like CO, H_2, N_2, CO_2), light hydrocarbons (CH_4, C_2H_4, C_2H_6, etc.), tar, and ash/unreacted char [30]. Due to the high temperature, the yield of solids is low which leads to higher amounts of syngas generation than pyrolysis. Based on the gasification agent, biomass gasification can be divided into air gasification, oxygen gasification, steam gasification, etc. Table 1 presents the typical syngas compositions produced from different gasifying agents.

Gasifiers can be divided into fixed bed (updraft and downdraft), moving bed, fluidised bed (bubbling and circulating) and entrained flow gasifier. In a fixed bed the biomass bed is stationary while the reaction front passes through it, its two configurations (updraft and downdraft) refer to counter current and co-current flows respectively. Fluidised bed gasifiers are divided based on the modes of heat transfer and fluid dynamics. In general, fluidised bed gasifiers allow a high and uniform heat and mass transfer between the solid biomass and the gasifying medium, which allows good mixing and contact that increase the reaction rates and conversion efficiencies, minimising tar and char production (together with biomass particle size and temperature). Temperature is an important parameter for maximising the gas yield, high temperatures (>1000 °C) are favourable for tar and char cracking and for endothermic reactions. However, extremely high temperatures are energy demanding [31].

Tar formation is one of the biggest challenges of gasification. Tar leaves the gasifier in form of aerosol together with the syngas, it condenses and forms sticky deposits by quenching downstream. These deposits can develop into more complex tar structures via polymerisation, which increases the treatment difficulty. The presence of excessive tar compounds in the syngas can cause serious technical problems like fouling and blockage of the equipment [35]. In some cases, tar is also poisonous for catalysts as it can cause catalyst deactivation, which inhibits the conversion of syngas in the fuel cells, methanation, and Fischer–Tropsch synthesis processes [36].

Tar content in the syngas can be eliminated in two ways: by optimising the gasification operation conditions for in-situ tar removal, or via ex-situ/post-gasification treatments [37–39]. The in-situ options include the alteration of the operational conditions, such as optimising the operation conditions (e.g. temperature, residence time, or gasifying agents), the addition of bed additives, and adjustment of the gasifier design [37]. A lower gasification temperature results in a higher tar content, while pressure increase leads to almost a total elimination of phenols in tar. In a similar way, the tar content is also influenced by the gasifying agent, a higher amount of tar is produced in steam gasification and the lowest when air is supplied. Higher residence time leads to a decrease of oxygen compounds, which leads to longer contact between tar and the oxidising medium and achieves a maximum of 75% tar reduction. Downdraft gasifiers show lower tar content than updraft gasifiers. In a downdraft gasifier, both biomass and gas move downward, making the tar pass through the high-temperature combustion zone, cracking tar into noncondensable gases. When using a fluidised bed gasifier, the circulating variant allows a high level of mixing between the biomass and the bed material, causing partial oxidation and lower tar generation [38]. Table 2 shows a comparison of the tar generation between different gasifiers.

The ex-situ or post-gasification methods intend to remove tar in a post gasification step through mechanical/physical processes or reforming processes [38,39]. The former methods are used for separating particulated tar formed after syngas cooling using fabric filters, cyclonic separators, spray towers, scrubbers and wet cyclones. These methods typically have low tar removal efficiencies. For instance, fabric filters have removal efficiencies ranging between 0%–50%, cyclonic separators have 30%–70% removal efficiencies, and oil-based scrubbers typically provide an efficiency of 75%–98% [38]. These figures are usually not enough and further cleaning processes are required. On the other hand, the use of tar reforming processes could be more beneficial as it can convert the potential chemical energy stored in the tar into useful syngas, instead of just disposing of it. They also have relatively higher tar removal efficiencies. These methods include catalytic reforming (steam/dry), partial oxidation, thermal cracking, and plasma cracking [38,39]. The performance of these processes is significantly affected by the composition of the tar compounds, as they may differ from each other in terms of physical and chemical properties. In this review paper, the discussion on the tar elimination from the gasifier will be focused more on the use of high temperature reforming processes.

2.2. Biomass pyrolysis

Pyrolysis is a process in which organic matter thermochemically decomposes under anaerobic conditions [21]. The decomposition of biomass can take place at medium (300–800 °C) to high (800–1300 °C) temperatures [30] and it is the pre-step in a gasifier (devolatilisation) [34]. Pyrolysis results in three main products: biochar (solid), bio-oil (liquid, condensable gas) and gas (noncondensable gas):

Biochar is a valuable product of fast pyrolysis. It contains primarily carbon (≈85%) together with small amounts of oxygen, hydrogen and inorganic ash. Its heating value is between 25–32 MJ/kg dry basis, which is substantially higher than of the biomass (19.5–21 MJ/kg), the liquid and the gas product [34]. The carbon contained in the biomass is sequestered in a stable way in the biochar and it contributes to negative carbon emissions. Biochar can also displace carbon positive fossil fuels and be used as fertiliser [7].

Table 3

Comparison between different pyrolysis types [30].

Pyrolysis type	Operating conditions	Yields
Slow	Temperature: 300–700 °C Vapour residence time: 10–100 min Heating rate: 0.1–1 °C/s	Bio-oil ≈ 30 wt% Biochar ≈ 35 wt% Gas ≈ 35 wt%
Fast	Temperature: 400–800 °C Vapour residence time 0.5–5 s Heating rate: 10–200 °C/s	Bio-oil ≈ 50 wt% Biochar ≈ 20 wt% Gas ≈ 30 wt%
Flash	Temperature: 800–1000 °C Vapour residence time < 0.5 s Heating rate: > 1000 °C/s	Bio-oil ≈ 75 wt% Biochar ≈ 12 wt% Gas ≈ 13 wt%

Table 4

Comparison of yield distribution between different pyrolyzers [24].

Reactor	Char (wt%)	Bio-oil (wt%)	Gas (wt%)
Fixed bed	31	50	18
Fluidised bed	10	59	28

Bio-oil is a combination of tars, heavier hydrocarbons and water. It is a black tarry fluid containing up to 20% water, consisting of mainly phenolic compounds [34]. It contains hundreds of organic compounds; acetic acid ($C_2H_4O_2$), propionic acid ($C_3H_6O_2$), propyl benzoate ($C_{10}H_{12}O_2$) and furfural ($C_5H_4O_2$) are some common compounds found in bio-oil [21]. The presence of water and oxygenated compounds create undesired properties like low heating value (13–18 MJ/kg [34]), incomplete volatility and acidity. Further treatment (i.e. upgrading) is thus required for future applications, like fuel and hydrogen production [40]. The long hydrocarbon chains in the pyrolysis gases can be cracked into smaller molecules (reformed), mainly CH_4, CO_2, CO_2, H_2 and H_2O via upgrading. Upgrading covers processes like thermal or catalytic reforming (decomposition into smaller molecules). These are explained more in detail in Section 3.1.

The gas fraction is composed of noncondensable, lower-molecular-weight gases like CO_2, CO, CH_4, ethane and ethylene. A typical heating value of the gas fraction is found in the range of 11–20 MJ/kg [34].

The pyrolysis conditions (temperature, heating rate, residence time) control the distribution between the different products (condensable gases, non-condensable gases and biochar). Therefore, it is of interest to increase the selectivity towards certain products. Slow pyrolysis favours char production, while fast (and flash) pyrolysis favours the liquid yield. For syngas production, it is of interest to increase the liquid content, which is achieved via fast pyrolysis. Four important features are to be considered: very high heating rate, reaction temperature between 425–600 °C, short residence time of vapour in the reactor and rapid quenching of the product gas [34]. Table 3 presents the comparisons of product yields for different pyrolysis processes.

The most common fast pyrolysis reactors used to optimise the bio-oil yield are rotating cone, ablative, conical spouted bed, bubbling fluidised bed and circulating bed. Fluidised beds are designed to provide an adequate gas–solid heat transfer (which is achieved if the biomass particles are very small), which makes fluidised beds optimal for maximising the bio-oil yield [24]. A comparison example of product distribution between different pyrolysis technologies is shown in Table 4.

2.3. Anaerobic digestion

Anaerobic digestion refers to the breakdown of organic matter in the absence of oxygen by microorganisms. A wide variety of biomass can be used as feedstock (food waste, organic fraction of municipal solid waste, sewage sludge, etc.) and this technology has the potential to provide 25% of the energy requirements of the world during the next 25 years. Organic matter is converted into biogas, which typically contains between 35%–75% CH_4 and 25%–55% CO_2 [27]. Depending

on the feedstock, biogas also typically contains minor amounts of other impurities compounds such as water vapour, hydrogen sulphide (H_2S), ammonia (NH_3), siloxanes, and aromatics [27]. The presence of these impurities may damage the fuel quality of the biogas. A comparison of the biogas composition produced from different feedstocks is shown in Table 5. Biogas can be used directly for combustion and electricity generation but requires purification (upgrading) for the production of chemicals and transportation fuels (>97% CH_4). Methanogenic microbes (methanogens) are responsible for the CH_4 production, they are viable at different temperatures and are classified accordingly into psychrophilic, mesophilic and thermophilic. Mesophilic systems are the most used due to their high robustness and stability, they require lower energy inputs (40 °C for maximum growth rate) and have satisfactory reaction rates [41]. Anaerobic digestion is commercially mature and a full-scale plant can have a production of 80 000–10 0000 N m³ per week [42].

A summary including process parameters and challenges for the different thermochemical conversion routes is shown in Table 6. In general, gasification technologies can be considered as proven and mature thermochemical conversion routes with their applications having already reached capacities of around 160 MW (e.g., Valmet's circulating fluidised bed plants [43]). Nevertheless, the current commercial applications of biomass gasifiers are mostly limited to combined heat and power productions. Despite the maturity of the technology, the productions of advanced biofuels through gasification are often considered not economically feasible with the current price of fossil fuels [44]. On the other hand, pyrolysis processes are gaining more interest due to the possibility of maximising biochar production to replace the fossil fuel-based carbon materials used in the process industries. Upgrading the pyrolysis vapour into valuable biofuels through reforming processes can improve the economic feasibility of the process. However, the more complex composition of pyrolysis vapour remains the main challenge of this process. The difficulty of scaling-up pyrolysis plants to several hundreds of MW is also a huge issue that needs to be addressed. Lastly, AD processes benefit from low operating temperature; hence, they are significantly less energy-intensive than gasification and pyrolysis. However, the main challenges of this conversion route are the limited capacity and feedstock selection.

3. Reforming technologies of biomass-derived vapours

The organic compounds in biomass vapours are thermally unstable at very high temperatures and can undergo thermal decomposition according to Reaction (1) [40]. During thermal and catalytic cracking, carbonaceous compounds are created. Char is referred to as the carbonaceous compound created by thermal decomposition, while coke is formed by polymerisation of small organic compounds inside the catalyst pores, leading to undesired catalyst deactivation [55]. Furthermore, soot is defined as elemental carbon produced by incomplete combustion of carbonaceous materials [22].

$$C_nH_mO_k \rightleftharpoons C_xH_yO_z + \text{gas}\,(H_2, CO, CO_2, CH_4) + \text{coke} \qquad (1)$$
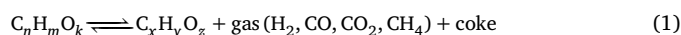
Some of the state-of-the-art reforming technologies are CSR, dry reforming (DR), membrane reforming (MR) and the autothermal reforming technologies: autothermal reforming (ATR), partial oxidation (POX) and catalytic partial oxidation (CPO). They can be used by themselves or in combination. Fig. 2 presents illustrations of the CSR, ATR, POX, and CPO as the common reformer technologies.

3.1. POX

POX refers to reforming in the presence of a sufficient amount of O_2 to allow partial oxidation of natural gas, hydrocarbons or biomass-derived vapours, according to Reaction (2) and (3). It is generally an exothermic reaction and it alleviates the heat load for the reaction.

Table 5

Comparison of the biogas composition obtained from anaerobic digestion with different feedstocks [27].

Biogas compositions	Sewage sludge digester	Agricultural waste digester	Landfills
CH_4 (%)	58–75	45–75	35–65
CO_2 (%)	20–40	25–55	15–40
N_2 (%)	0–8.1	0–5	1–25
O_2 (%)	<1	0.01–2	15–40
H_2 (%)	Traces	<0.5	0
H_2O (%)	n.a.	n.a.	0
CO (%)	<0.2	<0.2	1–5
H_2S (ppm)	0–62.9	10–180	0–427.5
Toluene (mg/N m^3)	2.8–11.8	0.2–7.0	1.7–287
Benzene (mg/N m^3)	0.1–0.3	0.1–1.1	0.6–35.6
Siloxanes (mg/N m^3)	0.1–5.0	Traces	0.1–5.0

Table 6

Comparison of different thermochemical conversion routes for biomass.

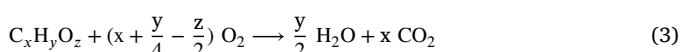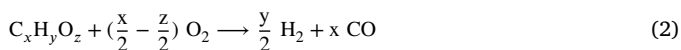|	Gasification [23,45–48]	Pyrolysis [30,49–51]	AD [41,52–54]
Common feedstocks	Lignocellulosic biomass, algae	Lignocellulosic biomass	Sewage sludge Agricultural waste
Products	Char = 0.6 - 2.5 wt% dry-ash-free fuel Producer gas[a] = up to 97 wt% Tar[a] = 1 - 5 wt%	Char = 12–35 wt% Bio-oil[a] = 30–75 wt% Gas[a] = 13–35 wt%	CH_4[a] = 45–72% CO_2 = 20%–55%
Temperature (°C)	700–1400	300–800	17–60
Pressure	Atmospheric to up to 70 atm.	Usually atmospheric, vacuum and high pressure pyrolysis may also be carried out	Commonly slightly above atmospheric pressure. High-pressure AD is in research
Plant capacity	Up to 160 MW	generally less than 25 MW	0.1–5 MW
Challenges	• Generation of problematic tar (can cause catalyst deactivation). • The need of high temperature. • High cost for reactor and apparatus. • Need an additional drying process for a high moisture content feedstock (e.g., forestry).	• Crude pyrolysis oil is not immediately useable, which requires upgrading • Catalyst development remains a key research frontier for creating high-value fuels and maximising profitability • Understanding of kinetics and reaction mechanisms are needed to optimise and design complex pyrolysis reactors. • Difficulties to scale up the process due to the need of external heating and uniform temperature.	• Slow rate of biogas generation • Limited capacity • Low energy content of the biogas • Biogas upgrading is expensive

[a]Reformable vapours.
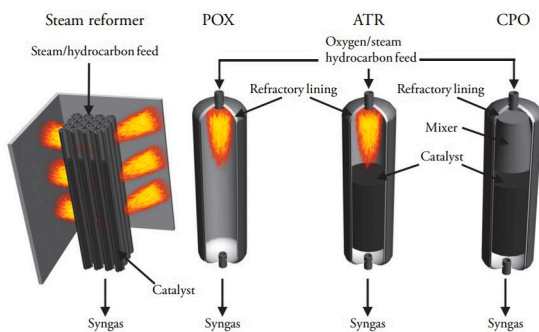
Fig. 2. Illustration of most common reformer types [56].

Reaction (2) can be endothermic or weakly exothermic depending on the x/z ratio, so some complete oxidation (Reaction (3)) is necessary so Reaction (2) can operate autothermally [57]. The provided heat is beneficial for coke removal as well as it improves the heat transfer rates and therefore the thermal efficiency. High conversion and equilibrium syngas production are also favoured [57]. There are three similar reforming processes that have the same principle of partial oxidation reactions: POX, ATR, and CPO.

$$C_xH_yO_z + \left(\frac{x}{2} - \frac{z}{2}\right) O_2 \longrightarrow \frac{y}{2} H_2 + x\, CO \tag{2}$$

$$C_xH_yO_z + \left(x + \frac{y}{4} - \frac{z}{2}\right) O_2 \longrightarrow \frac{y}{2} H_2O + x\, CO_2 \tag{3}$$

POX uses a feed with a high steam-to-carbon ratio in order to facilitate the steam reforming and water-gas shift reactions to increase the hydrogen content. Natural gas or liquid hydrocarbons are oxidised in a burner at high temperatures and high pressure. Catalysts are not required because the high temperature of the flame area of the reactor can drive the chemistry towards syngas production [58]. POX processes operate with non-stoichiometric fuel-to-air mixtures, at high temperatures and elevated pressures [59]. High temperatures are required to ensure complete conversion and minimise soot formation and a typical H_2/CO ratio is between 1.7–1.8 [58]. Large-scale reactors have a typical temperature range between 1150–1500 °C and pressures between 25–80 bar. The POX reactor is more compact than a steam reformer but less efficient due to the higher temperatures, which results in a higher amount of additional fuel to be burned and heat recycling [60].

3.1.1. Current status on the POX of biomass-derived vapours

The application of POX of biomass-derived vapours at commercial scales is relatively rare compared to that of natural gas reforming. In the past couple of years, IHI Corporation (Japan) has been intensively developing a dual fluidised bed gasifier of low-rank coal and biomass [61]. The company have successfully carried out a demonstration project of a 15 MW gasifier (up to 50 t/d of coal or biomass) in around 2016, despite the discontinuation of the project after thousands of operational hours. The gasifier generates a relatively high tar content which can reach 70 g/N m^3. Therefore, they have been developing a POX process intended to reform that tar-rich syngas. Tsuboi et al. [62] present the results from the developed POX process. In their study, a novel POX reactor utilising heat regeneration is developed and tested to clean the tar produced from a 4 t/d pilot woody biomass gasifier. The

Table 7
Selected cases of POX for the reforming of biomass-derived vapours.

Feedstock	Reactor	Operating parameters	Conversion (%)	H_2/CO	Notes	Ref.
Bio-oil & methanol	Quartz reactor	625–850 °C O/C = 0.7–1.6	85–95	–	CO yield = 50–70% H_2 yield ≈ 25%	[64]
Methane	Flow tube reactor	997–1494 °C CH_4/O_2 = 1–2	11–92	0.0–3.9	η_{CH_4} = 87% at 1494 °C with H_2/CO = 2.5	[66]
Methane	Flow tube reactor	1000–1592 °C CH_4/O_2 = 1.60–1.79	67–87	1.44–1.98	η_{CH_4} = 87% at 1580 °C with H_2/CO = 1.98	[63]
Glycerol	Quartz reactor	700–800 °C O_2 ratio = 0.3–0.45	>99	–	CO yield = 18–45% H_2 yield = 7–22% Complete conversion at 827 °C	[65]

results show that the reforming efficiency exceeds 99% at a reaction temperature of 1300 °C. In addition, the regenerative POX is claimed to consume 30% less oxygen than the conventional reformer. Nevertheless, there is no further information on the scaling up of this technology into commercial scales.

Other than the developed POX reactor above, there are several lab-scale studies have been reported. For example, Li et al. [63] presented a study of noncatalytic partial oxidation of undiluted CH_4 in a gas-flow reactor system incorporating indirect heating by induction. High reactive gas concentrations are more relevant to industrial applications in comparison with diluted flows, but the exothermic nature of the process, together with soot and coke formation represent common difficulties. In addition, the reaction mixture must be heated to ignition temperatures and rapidly quenched once ignition occurs, to avoid thermal runaway. Usually, conventional resistance heated furnaces withstand rapid thermal changes due to their thermal mass. Therefore, indirect heating by induction was investigated in a quartz reactor in both diluted and undiluted CH_4 flows [63]. On the other hand, Marda et al. [64] have investigated the noncatalytic POX of biomass-derived vapours (derived from poplar wood) mixed with methanol. The effects of both temperature (650–850 °C) and oxygen (O/C = 0.7–1.6) were investigated. Ayoobi et al. [65] have presented numerical methods with detailed chemistry for noncatalytic of glycerol to syngas at intermediate temperatures. Due to the lack of information on noncatalytic glycerol reforming in literature, qualitative comparisons are made with catalytic glycerol reformed (from literature). In addition, all approaches are validated by propane POX, where noncatalytic experimental results are available in literature [65]. An externally heated (in furnace) quartz reactor was presented as the study subject [65]. A resumed comparison of the different POX works is presented in Table 7.

3.1.2. Operating conditions

According to Marda et al. [64], POX of biomass-derived vapours at the temperature range of 650–850 °C could achieve high carbon conversions to syngas, which are between 85%–95% with high CO yields (50%–70%) and low H_2 yields (≈25%). It is also stated that higher selectivities for H_2 would be achieved and lower temperatures would be required in the presence of a catalyst [64]. Meanwhile, a simulation study was performed by Ayoobi et al. [65] showed that operating POX at a temperature between 600–1050 °C and an oxygen ratio between 0.3–1 (defined as the amount of oxygen that an oxygenated fuel has chemically bound into the molecule itself) cannot reach a complete conversion of glycerol into syngas. It was found that heavy hydrocarbons dominates the product mixture due to the incomplete conversion. The results show that a temperature of 900 °C with an oxygen ratio between 0.3–0.45 are favourable operating conditions for good syngas quality (85% of available LHV retained in syngas) [65].

Meanwhile, Li et al. [63] showed that in a diluted condition, very little conversion of CH_4 and O_2, was observed below 927 °C, but conversion increased rapidly above this temperature reaching 87% and 100% respectively at 1227 °C. Additionally, in undiluted conditions, it was difficult to achieve high CH_4 conversions, complete conversion of

O_2 was observed at all flow rates and the % conversion of CH_4 varied from 76% to 85% with no discernible trend. In addition, the required conditions (temperature, pressure, residence time) favour a high rate of carbon formation and subsequent deposition [63]. The high ignition temperature of CH_4 leads to inaccurate temperature measurement, reaction model development and understanding of reaction mechanisms. Therefore, the study by Li et al. [63] was enhanced using computational fluid dynamics (CFD) simulations to correct the temperature profiles from kinetic modelling. Induction heating was investigated in diluted CH_4, although temperature measurements represent a challenge, the combination of CFD and kinetic modelling allowed for the adjustment in temperature measurement, leading to better understanding of high temperature reactions [66].

It has been highlighted the importance of high temperatures in POX to assure the complete breakdown of heavy hydrocarbons and the subsequent intermediate lighter products, due to the catalyst absence [65]. More importantly, it has also been demonstrated that the O/C ratio has a higher effect on the conversion than the temperature and that a water-gas shift reactor would be required for maximising H_2 production [64]. The O/C ratio needs to be carefully calculated to provide the required heat without consuming valuable syngas. In general, the production efficiencies of desired products increases by increasing the oxygen ratio, decreasing at the same time the lower heating value (LHV) of the product mixture due to an increase of exothermic reactions [65].

3.2. ATR and CPO

ATR and CPO work in a similar way in comparison to POX. The main difference relies on the presence of the catalyst that allows for fuel conversion at a lower temperature, which is highly dependent on the fuel to be reformed and the catalyst. In ATR, air and oxygen can be used as oxidising agents, depending on the downstream purification processes. The fuel is partially oxidised in a burner, providing the energy for the endothermic SR. The catalysts are usually to-stage catalysts: the first stage consists of a combustion catalyst that provides heat to the second stage, which is optimised for the endothermic steam reforming (SR) reactions. ATR combines features of SR and partial (or full) oxidation, effective catalyst design can reduce the need for a robust burned and can reduce carbon and soot formation. The operating temperature is between 900–1150 °C with a pressure between 1–80 bar (based on natural gas). The ATR process produces a favourable H_2/CO ratio (≈2) and the ATR reactor is more compact in comparison to a steam reformer but larger than a POX unit [60].

CPO works in a similar way in comparison to ATR, with the main difference that CPO allows chemical conversion in a catalytic reactor without a burner. No flame is produced by combustion, instead, oxygen and the fuel are mixed in a mixer [60]. Catalytic reactions enhance reactions, therefore operating temperature and pressure can be decreased [59] providing the right H_2/CO ratio and selectivities and conversions close to equilibrium values [60]. The complete conversion of oxygen and near-complete conversion of the fuel is achieved within the catalyst bed located after the mixer. High temperatures (up to

Table 8
Examples of ATR and CPO for the reforming of biomass-derived vapours.

Feedstock	Reactor	Catalyst	Operating parameters	Conversion (%)	H_2/CO	Notes	Ref.
Bio-oil	Foam monolith	Rh-Ce/Al_2O_3	700–800 °C C/O = 0.71	85	≈35% CO ≈10% H_2	Carbon deposition at higher C/O	[57]
Bio-oil	Quartz reactor	Char	700–900 °C ER = 0.0–0.2	98.34–99.19	Gas composition CO ≈ H_2 ≈ 22.5 vol%	Optimal equivalence ratio (ER) = 0.05 ER = O_{real}/$O_{theoretical}$	[67]
AcidsL, alcohols, aldehydes, esters, polyols	Foam monolith	Pt– & Rh–Al_2O_3	400–700 °C C/O = 1.2–2.0	30–90	–	Rh yielded higher conversion than Pt Pt showed lower activity for oxygenate reforming	[68]

1000–1250 °C) are obtained close to the inlet of the catalyst bed, meaning that oxygen is consumed in the first millimetres of the catalyst bed. Afterwards, the endothermic reforming reactions take place, causing a temperature drop towards the end of the catalytic bed [60]. The main drawback is the use of oxygen, when using air in the process too much nitrogen is accumulated in the syngas, which results in large gas volumes that affects heat exchangers and compressors. Air separation to provide pure oxygen might be an alternative but costly [58].

3.2.1. Current status on the ATR and CPO of biomass-derived vapours

The developments of ATR and CPO for the treatment of biomass-derived vapours have been presented in mostly lab-scale studies. For instance, Rennard et al. [57] investigated the partial oxidation of biomass pyrolysis oil. Biomass-derived vapours derived from three different sources (poplar wood, pine and hardwood) mixed with methanol was reformed in a direct CPO system over α-Al_2O_3 foam monoliths coated with Rh(NO$_3$)$_3$ and Ce(NO$_3$)$_3$·6H_2O (1 wt% each of Ce and Rh). Yu et al. [67] studied the CPO reforming of pyrolysis tar over sewage sludge char. The reformer was a catalytic reactor (quartz tube) containing a char bed produced from sewage sludge pyrolysis [67]. Investigations using bio-oil model compounds have also been done. Kruger et al. [68] investigated the autothermal partial oxidation of two-carbon molecules containing the functional groups found in bio-oil (acids, alcohols, esters, polyols, etc.) over Pt– and Rh–Al_2O_3 catalysts. A resumed comparison of those studies on the different ATR and CPO works is presented in Table 8.

3.2.2. Catalyst developments

The oxidising environment of ATR or CPO during the reforming of heavy hydrocarbon compounds from biomass is challenging for transition metal catalysts [69]. In this process, transition metals are more prone to oxidation. Prompt reduction in the activity of the catalyst has been observed in long duration or high space velocity tests. In addition, the high operating temperature of the process contributes to the sintering of the active phase, which further reduces the activity of the catalyst. Thus, significant efforts in developing ATR/CPO have been suggested on finding new catalysts which are more resistant to oxidation, with the ability to maintain stable performance over a long duration [69].

Many studies have indicated that noble metal-based catalysts are good candidates for ATR/CPO. Specifically, Rh is considered to have the most promising results as active phase [69]. A study carried out by Kruger et al. [68] is one example that demonstrate the superior performance of Rh. Their study shows that Rh and Pt have linear or exponential increase of conversion between 400–700 °C with ethanol, acetaldehyde, ethylene glycol, acetic acid and dimethyl ether. In the case of methyl formate, Rh showed stable high conversion (95%–100%) between the entire temperature interval (400–700 °C) and Pt showed a quite stable conversion (95%–100%) in the interval (500–600 °C) [68].

According to latest research, noble-based catalysts are better candidates for ATR/CPO compared to transition metals. The use of non-noble metals has been investigated in other reforming technologies, presented in the following sections.

3.2.3. Operating conditions

The carbon conversion of bio-oil or biomass tar significantly depends on the operating temperature of ATR and CPO. In general, recent investigations on the ATR and CPO use a widely ranged operating temperature from 400 to 900 °C. Kruger et al. [68] reported the performance of ATR at low temperatures of 400–700 °C. The experiments were carried out using bio-oil model compounds and with C/O ratio between 1.2–2.0. It was found that the conversion ranged from 30%–90% for most investigated species using Rh as catalysts. Among the investigated compounds, esters were the most reactive species, while polyols, ethers and acids were the least reactive [68]. Other studies involving higher temperatures have demonstrated high conversion values. For example, the CPO of pure pine at 700–800 °C pyrolysis oil resulted in an average conversion of bio-oil carbon to CO and CO_2 of ≈97% [57]. The effects of the temperature and residence time were investigated by Yu et al. [67], at temperatures between 700–900 °C and residence times between 1.25–3.75 s. It was concluded that temperature plays a more significant role [67]. At 800 °C the tar concentration could not be decreased by increasing the residence time but tar conversion reached 99.19% at 900 °C [67]. It can be seen from the studies above that higher temperatures than 700 °C are still needed in ATR/CPO to ensure high conversion of biomass-derived vapours consisting of different organic compounds. Nevertheless, the choice of catalyst can lower the required temperature to a certain degree.

The amount of the oxidising agents is another important parameter that determines both carbon conversion and syngas composition. Rennard et al. [57] found that a maximum syngas production can be achieved at C/O = 0.71 during CPO of biomass pyrolysis oil. It was also observed that lower C/O ratios resulted in oxidation of syngas increasing water and CO_2 production, consuming valuable syngas. The CPO of a solution containing 80–20 wt% hardwood pyrolysis oil/methanol was performed at C/O = 0.9–1.1, the gas conversion was ≈90% and the gas yields were relatively constant under these conditions (H_2 ≈ 25% CO ≈ 65 %) [57]. Meanwhile, Yu et al. [67] varied the oxygen equivalence ratio (ER, defined as real O_2 volumetric flow divided by the theoretical O_2 volumetric flow needed for complete combustion) between 0–0.2 during the CPO of pine pyrolysis gases containing rich tar. They found that the optimal ER for the reforming process was ≈0.05, allowing for the highest contents of H_2 and CO and a tar conversion of 98.34%. It was observed that high ER would lead to consumption of combustible gases and sludge char, which affects its catalytic properties and can lead to an increase of the tar concentration [67].

The amount of oxidising agents also determines the coke formation on the surface of the catalysts. At higher C/O ratios coke formation and carbon deposition affect the reactor operation negatively, resulting in poor conversion [57]. Coke formation via polymerisation and char formation via dehydration of pyrolysis oils have been described as two major challenges [57]. Char formation can be avoided by introducing the fuel at ambient temperature and bringing it to gasification temperature (>700 °C) within a few milliseconds [57].

In a similar way as for POX, it has been shown the importance of temperatures in POX to assure the complete breakdown of heavy hydrocarbons. Temperatures between 700–900 °C (which are significantly

Table 9
Selected cases of DR of biomass-derived vapours.

Feedstock	Operating parameters	Catalysts	Conversions	H_2/CO	Ref.
Simulated biogas	600–850 °C; $CH_4:CO_2:N_2$ = 2:2:1	Ni/Al_2O_3 Ni/SiO_2 Ni/MgO Ni/CeO_2 Ni/ZnO	47%–95% (CH_4) 13%–82% (CH_4) 29%–91% (CH_4) 16%–78% (CH_4) 21%–74% (CH_4)	larger than 0.97 at 750 °C or higher larger than 0.90 at 750 °C or higher	[73]
Simulated biogas	650–900 °C	Ni/TiO_2 $Ni–Co/TiO_2$ Co/TiO_2	84% (CH_4) and 92% (CO_2) at 900 °C 87% (CH_4) and 93% (CO_2) at 900 °C 73% (CH_4) and 80% (CO_2) at 900 °C	0.75 at 900 °C 0.84 at 900 °C 0.74 at 900 °C	[74]
Simulated biogas	700–900 °C; $CH_4:CO_2$ = 1:1	$Ni/Mg/Al$ $Ni–Rh/Mg/Al$	86% (CH_4) and 91% (CO_2) at 900 °C 87% (CH_4) and 95% (CO_2) at 900 °C	0.87 at 900 °C 0.91 at 900 °C	[75]
Tar-rich syngas	900 °C; Tar 1.77 g/N m³	Ni/mayenite	93% tar conversion	Approx. 0.73	[72]

lower compared to POX) are required to achieve high conversions between 97%–99% [57,67]. The O/C ratio is to be carefully chosen, too high or too low O/C ratio has the same consequences as in POX with the addition of coke deposition on the catalyst surface at low O/C ratios. Since this is a catalytic process its stability will depend on the lifetime of the catalyst which means that the O/C ratio and the catalyst choice are the most important parameters to take into consideration. Transition metals are prone to oxidation and their oxidated variants will most likely affect the conversion in a negative way. Rh-based catalysts have shown promising results. Nevertheless, research should focus on more affordable, abundant and stable materials that can be used as catalysts.

3.3. DR

3.3.1. Current status on the DR of biomass-derived vapours

DR has gained popularity in recent years because it consumes two types of greenhouse gases (CH_4 and CO_2) and produces an appropriate H_2/CO ratio that is adequate for FT fuels and DME production. DR uses CO_2, which is usually available in large quantities and at low costs. This process is slightly more endothermic than SR and is favoured by high temperature and low pressure [29]. In the process, CO_2 replaces steam that is normally used in SR to produce syngas with a low H_2/CO ratio ($\approx$1) according to the main reaction expressed by Reaction (4).

$$CH_4 + CO_2 \longrightarrow 2CO + H_2 \qquad (4)$$

$$CO_2 + H_2 \longrightarrow CO + H_2O \qquad (5)$$
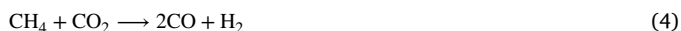
Another reaction that also governs the performance of DR is the reverse water-gas shift (RWGS), which can be written as Reaction (5). This reaction can drive a higher conversion of CO_2 than CH_4 [70]; however, it decreases the H_2/CO ratio of the produced syngas. More importantly, the RWGS reaction is helpful for suitable adjustment of the H_2/CO ratio for certain production of hydrocarbon fuels [71]. The developments of DR in the context of biomass fuels are particularly gaining more interest for the conversion of biogas from AD processes into syngas. This is due to the fact that biogas is already rich in CH_4 and CO_2. Until now, almost all research on DR typically are performed by using lab-scale facilities and modelled biogas as the feedstock, instead of using real biogas samples [27]. In addition, the application of DR for reforming tar produced from biomass gasification has also been proposed [72]. Table 9 presents the summary of some selected cases of the DR application for the reforming of biomass-derived vapours.

3.3.2. Catalyst developments

The main challenge of DR is the increased chance of coke deposition on the catalyst surface, which is more likely to take place in DR than SR or POX [25]. This is due to the fact that the tendency of coke formation depends on the carbon ratio to hydrogen and oxygen, in which the lower H/C and O/C ratios cause a higher coke formation. During reactions, the production of CO and consumption of H_2 via reverse water-gas shift together with the decomposition of CH_4, CO and hydrogenation of CO_2 and CO lead to this higher coke tendency [29,76]. In order to make this technology commercial, research should be directed toward the synthesis of highly active catalysts [76].

Non-noble metals catalysts (Ni, Co, Cu, and Fe) have gained major interest owing to their lower cost productions, as compared to other types of catalysts such as noble metals [27]. Ni has been the most studied material for the development of DR catalysts including the application on the industrial scale [71]. Gao et al. [73] investigated the effect of different support materials (Al_2O_3, SiO_2, MgO, CeO_2, and ZnO) for Ni catalysts on the conversion of simulated biogas sample ($CH_4/CO_2/N_2$ = 2:2:1) and the catalyst stability. They found that Ni/Al_2O_3 is the most active catalyst with the CH_4 conversion efficiency up to 95% at 850 °C, due to smaller particle size and stronger metal-support interaction. Manera et al. [72] developed Ni/mayenite catalysts and found that they are suitable for DR of tar produced from CO_2 gasification of elephant grass. At 900 °C, the DR of tar using the studied catalysts can reduce the gravimetric tar from 1.77 to 0.13 g/N m³, or correspond to about 93% of tar conversion. Mayenite ($Ca_{12}Al_{14}O_{33}$) is considered to have a superior performance for catalyst support for tar reforming due to its particular crystal structure and extra-framework oxygen [72].

Despite the benefit of the low cost and high activity, the use of Ni catalysts tends to generate a high coke deposition. This high coke formation leads to their deactivation in a short period; thus, causing a severe operational drawback. Therefore, recent research has focused on the development of Ni-based bimetallic catalysts for a better coke resistance performance. Noble metals (Rh, Ru, Pd, Pt, and Ir) are considered as a potential addition to improving the performance of Ni catalysts during DR processes, owing to their better coke resistance [27]. For example, Schiaroli et al. [75] added 0.03–1.4 wt% of Rh into Ni/Mg/Al catalysts and tested their performance during DR and combined SR/DR of modelled biogas with $CH_4:CO_2$ ratio of 1:1. It is concluded that the presence of low amount 0.5 wt% Rh is sufficient to preserve the catalyst structural properties after several catalytic tests, without strong evidence of deactivation. It is also proposed that the formation of a stable Ni–Rh alloy is favoured by the increased basicity of the support, that leads to a highly disperse active phase [75]. Other than the noble metals, transition metals such as Fe, Co, and Cu could have a significant impact when they are used as bimetallic catalysts, despite their low activity as monometallic catalysts [27]. Sharma et al. [74] synthesised bimetallic Ni–Co catalysts supported on titania (TiO_2), and found that the catalyst could withstand the catalytic performance during 15 h of continuous reforming without any significant decrease in the activity during the DR of biogas. The bimetallic catalysts allow higher resistance to coke formation and unwanted metal oxidation through regulated reactions between CH_4 and CO_2 [74]. It is also shown that the conversion rate of CH_4 rises with the increase of the Ni-to-Co ratio [74].

In conclusion, bimetallic catalysts can be used to tackle carbon deposition and show promising stability. From the economical perspective, Ni-based catalysts with Fe, Co and Cu show promising results as alternatives to noble metals.

3.3.3. Operating conditions

In general, DR processes are favoured at higher temperatures as they are endothermic. Higher operating temperatures promotes the conversion of both CH_4 and CO_2 into syngas. Chein et al. [77] investigated the thermodynamic equilibrium of CH_4 DR at different temperatures and pressures. The study demonstrated that the CH_4 conversion increasing with the increasing in reaction temperature, especially at temperatures between 400–800 °C. This trend is followed by the sharp increasing in the H_2 production within the same temperature range. The H_2/CO ratio can be larger than 1 at a temperature higher than 700 °C. Thereafter, at a temperature higher than 800 °C, the full conversion of CH_4 theoretically can be achieved. However, it should be noted that their study was conducted by using an equilibrium approach (Gibbs free energy minimisation). Thus, the simulated results tend to have a higher CH_4 conversion rate than the real catalytic CH_4 reforming processes. The study also indicated that high temperatures favour the carbon suppression, as no carbon was formed at a temperature higher than 750 °C [77]. In addition, the same study also demonstrated that DR is not favoured at elevated pressures. It is shown that higher pressures cause lower CH_4 and CO_2 conversions, while at the same time increase the carbon and H_2O formations.

Other than the aforementioned parameters above, the conversion of fuel during DR processes is influenced by the presence of impurities. For instance, the presence of H_2S could negatively affect fuel conversion owing to catalyst poisoning. The severity of the reduction in the conversion rate depends on the type of the catalyst and the concentration of H_2S [27]. Chein et al. [78] investigated the effect of H_2S on the activity of Ni-based catalysts (Ni/Al_2O_3 and $Ni–Pt/Al_2O_3$) at a temperature range between 600–800 °C. In the case of either Ni or Ni-noble metals catalysts, it was found that the conversion of CH_4 decreases significantly from 60 to about 25% when 100 ppm of H_2S is added in the biogas.

DR is strongly endothermic and requires higher temperatures compared to CSR to achieve high conversion (86%–95% at 900 °C [75]). The absence of steam and oxygen makes the catalyst highly prone to deactivation by coke deposition, making this the highest challenge. Recent research has shown that bimetalic catalysts (transition metals plus small amounts of noble metals) can increase the catalyst stability, maintaining stable production and lower deactivation for longer time [74,75]. Further research on bimetallic catalysts seems to be a promising solution for the commercialisation of the technology.

3.4. MR

Membrane reactors contain multi-component oxides that allow working temperatures above 1000 K and provide high oxygen flux and selectivity via ion transport. In the case of SMR, one possible way of their working principles consists of air being fed to one side of the membrane at 300 K and low pressure (0.03–0.20 bar), oxygen diffuses into the membrane to the other side where it reacts with CH_4 and steam at high pressure (3–20 bar) to produce syngas. MR is gaining interest mainly for the H_2 productions through SMR, owing to the enhancement of the hydrogen yield following the shift effect induced by the membrane permeation [79]. More importantly, membrane reactors allow direct production of a high purity grade of H_2 stream [79]. Thus, they may eliminate the need for additional gas separation processes after the reforming processes, which often can be energy-intensive.

The catalytic membrane reactor typically consists of two zones: the shell side zone that is packed with the catalyst (where the reactions take place) and the permeate zone where the sweep gas is introduced (see the upper part of Fig. 3). Membrane reactors consist of Pd–Pd alloy membranes that allow high hydrogen permeability and zirconia or perovskites membranes that are oxygen selective. Since the reforming reactions are reversible reactions, it is important to constantly remove the products from the shell zone to avoid the reverse reactions, thus

increasing conversion. This is achievable thanks to the selective membrane. This technology has several problems in industry applications: instability against acidic gases, high cost, decrease in hydrogen permeation due to adsorption of carbon monoxide, coke deposition during reforming reactions [29].

MR reactors are emerging technologies as their applications are still limited to the development phase. In the case of natural gas reforming, many reviews have focused on the modelling of membrane reactors and their scalability from laboratory to pilot/industrial scale [79]. Meanwhile, there are even more limited results have been reported on the applications of MR for the conversion of biomass-derived fuels into syngas. An example of the MR application to treat biomass tar is reported by Wang et al. [81]. In their study, a membrane reactor consisting of perovskite structure catalyst $La_{0.8}Sr_{0.2}Ni_{0.8}Fe_{0.2}O_{3-\delta}$ (LSNF) and ceramic $BaBi_{0.5}Co_{0.8}Nb_{0.15}O_{3-\delta}$ (BBCN) perovskite hollow fibre membrane was fabricated to perform oxidative steam reforming of toluene at 650–750 °C. It is shown that the membrane reactor can convert about 60% of toluene while maintaining a lower carbon formation. Moreover, the reactor also shows high selectivity, with H_2/CO ratio of the produced syngas equal to 2–3.

3.5. CSR

CSR is normally also referred to as steam methane reforming (SMR) in the field of natural gas reforming. SMR refers to the reaction between CH_4 and steam to produce syngas. Production of hydrogen by SMR is one of the largest endothermic processes and accounts for ≈50% of the global hydrogen supply. Natural gas reacts with steam according to the following Eqs. (6) and (7) [82]:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \tag{6}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{7}$$
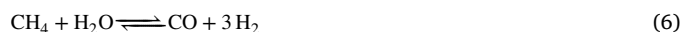
A mixture of natural gas and potential off-gases from the synthesis is typically combusted to supply the necessary heat to SMR [82]. CSR systems based on catalyst beds are mostly used, both fixed bed and fluidised bed have shown good yields and selectivity for hydrogen production [40]. Fixed bed reactors are simple reactors consisting of solid catalyst particles packed into the bed, their main drawbacks are low thermal conductivity and small catalyst surface areas inside the reactor [83]. Fluidised bed reactors consist of small catalyst particles loaded into a reactor that behaves like a fluid with the gas flow of the reactants. Solutions to the problems faced with fixed bed reactors are offered by this kind of technology: enhanced mass and heat transfer, minimising temperature gradients inside of the reactor. The reactant fluid and the catalyst are well mixed, which provides a higher surface area for the reaction [83]. Fluidised bed reactors offer good control over thermal decomposition. In a fixed bed reactor, thermal decomposition leads to coke deposition creating a char layer in the top and freeboard of the reactor. In a fluidised bed reactor, the circulation of the catalyst particles creates constant contact with the pyrolysis gas, making that carbon deposition small and increasing the gasification of char on the particles. However, conventional support materials used in SR are soft and not suitable for fluidisation due to attrition [84].

A reformer consists of a furnace containing more than 100 tubes, 10–14 m long, therefore reformers are quite bulky and can take up 1140 m^3 just to achieve 75% conversion [82]. The heat that is provided by burning fuel presents heat losses that can reach up to 50% [85].

Carbon deposition on the catalyst can become a problem in steam reformers, especially at lower S/C ratios (economically desirable) and with feedstocks containing higher hydrocarbons than CH_4. The carbon can cause sintering and can also deposit in the catalyst pores, which will reduce catalytic activity and eventually disintegrate the catalyst pellets to powder [56].

Even though SMR is a commercially mature technology, CSR of biomass-derived vapours is still under research due to rapid catalyst
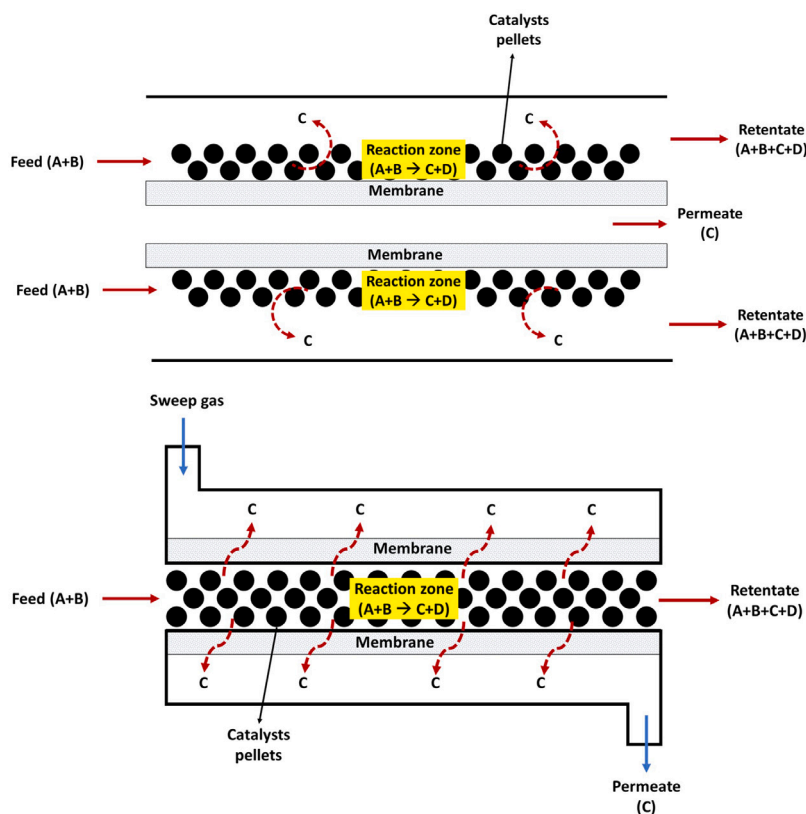
Fig. 3. Illustration of different configurations of tube-in-tube membrane reactor, with membrane layers coated on the outer surface of the inner tube (upper); and membrane layers coated on the internal surface of the inner tube (lower).
*Source:* Adapted from [79,80].

deactivation via carbon deposition. CSR refers to a series of catalytic reactions between biomass-derived vapours from pyrolysis or tar from gasification and steam to produce syngas with a high H_2/CO ratio [56]. CSR is an endothermic process; thus, hydrogen production is favoured by high temperatures. Hydrogen yield is typically obtained between 550–700 °C during CSR of heavy bio-hydrocarbon compounds, while higher temperatures could result in gradual decline due to coke forming and competition with cracking reactions of organic compounds [40].

The CSR of biomass-derived vapours can be presented in a general way as shown in Reaction (8) [40]:

$$C_nH_mO_k + (n-k)H_2O \rightleftharpoons n\,CO + (n + \frac{m}{2} - k)\,H_2 \tag{8}$$
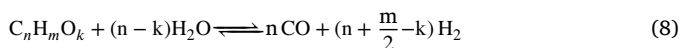
Deoxygenated hydrocarbons react also with steam, as shown in Reaction (9) [84]:

$$C_nH_m + (n-k)H_2O \rightleftharpoons n\,CO + (n + \frac{m}{2})\,H_2 \tag{9}$$
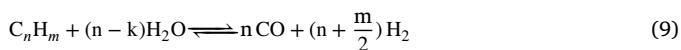
Excess steam oxidises carbon monoxide to carbon dioxide producing more hydrogen, as shown in Reaction (10) [40]:

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{10}$$

At high temperatures char formation takes place and carbon deposition can lead to catalyst inactivation, as shown in Reaction (11) [40]:

$$CO + H_2 \rightleftharpoons C + H_2O \tag{11}$$

Methanation and water-gas shift (WGS) could also take place. However, they are exothermic reactions and thus favoured by low temperatures [40,84].

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \tag{12}$$

In the case of CSR of biomass-derived compounds, the feeding gas needs to be treated. Solid particles are removed mostly by a cyclone

in the downstream process. However, a fraction of dust will continue in the feeding gas to the reformer, which is commonly referred to as "dusty" tar reforming. In this case, the reformer has to include a monolithic catalyst that can allow the dust flow through the channels without interfering with the reforming reactions. Dust can accumulate on the surface, blocking the pores and causing high pressure drop. Alternatively, a hot gas filter can be introduced, removing the majority of dust downstream the cyclone. In this case, the catalyst can be both monolithic or pelletised [20]. Gas cleaning is also needed to avoid sulphur poisoning of catalytic processes [21]. Sulphur compounds are strongly chemisorbed on the metal surface leading to catalyst deactivation, it is the most severe poison for Ni-based catalysts used in CSR of hydrocarbons [86].

Although catalyst deactivation via carbon deposition is a major challenge, heat transfer and wall temperature are also crucial issues. The wall of the reformer tubes needs to be as thin as possible to transfer as much heat as possible from the burners to the catalyst [56]. These represent the main challenges of biomass-derived vapours CSR. Since CSR provides the highest hydrogen yield in comparison to other reforming technologies, this technology has been chosen to be discussed in detail in this review paper.

4. CSR of biomass-derived vapours

4.1. Catalysts: developments and challenges

4.1.1. Active and support materials

The application of CSR for reforming of biomass gasification tar has been well established at large scales. As summarised by Andersson et al. [20], Haldor Topsoe A/S has developed a mega-monolith catalyst that has been used successfully to clean tar from a 10000 N m^3/h (20 MW) biomass gasifier plant in Skiive (Denmark), and a 1500 N m^3/h

demonstration plant (US DOE TIGAS project). The catalyst is basically a monolithic catalyst, that allows dust to pass through the monolithic channels while enabling the tar reforming reactions. The tar reformer is operated at 850–920 °C [87]. The operating temperature is raised by adding external air for three stages of combustion to compensate for the temperature drop due to the endothermic steam reforming reactions [87].

In contrast to the reforming of biomass gasification tar, applications of CSR for reforming of bio-oil from biomass pyrolysis are less mature technologies. This field has been recently gaining more interest as shown by the significant number of related studies. Similar to the other catalytic reforming processes (e.g. ATR, CPO, and DR), the current research on CSR of biomass pyrolysis vapour is mainly focused on the development of catalysts with high catalytic activity and coke resistance. Nobel metals (like Rh) have shown good reaction performances; however, as mentioned previously, Ni-based catalysts have attracted more attention due to their stability, cost-effectiveness, good thermal and chemical stability under reaction conditions and good catalytic activity in cleavage of C=C, C=O and C=H bonds [28]. The supports play an important role in heterogeneous catalysis, metal oxides have been reported to be good for SR of pyrolysis gas, for example, alumina (Al_2O_3) is the most studied support for this kind of application and is widely used due to its high surface area and mechanical strength. Complete conversion of pyrolysis gas has been observed using a Ni/Al_2O_3 catalyst at 800 °C and S/C ratio = 5, achieving a hydrogen selectivity of 90%. However, rapid catalyst deactivation is caused by coke deposition caused by the acidic nature of Al_2O_3, which sinters and reduces the surface area of the catalyst. Other supports for Ni-based catalysts, like ZrO_2 and MgO, have also been studied recently. ZrO_2 has good redox properties, while MgO provides a high oxygenate accessibility to Ni sites [28].

The use of bimetallic catalysts (secondary metal as a promoter) has also been reported. Catalysts like $Rh–Ni/CeO_2–Al_2O_3$ and $Ru–Ni/CeO_2–Al_2O_3$ have shown good H_2 production and also good resistance to carbon deposition by encouraging gasification of adsorbed carbon. The use of alkaline-earth elements (like Mg, Ca) as promoters have shown improvement in catalytic stability (by promoting the synergetic effect between metal and support), thus preventing coke formation from the acid sites of the catalyst [28].

Table 10 shows a summary of the catalytic performance of selected catalysts in SR. Monometallic catalysts show high conversion and high hydrogen selectivity, with the main drawback of catalyst activation after minutes (or hours in the case of Rh) due to coke deposition. Bimetallic catalysts show also good conversion and high hydrogen selectivity. Bimetallic catalysts with noble metals (Rh, Ru) show stable yields and no signs of catalyst deactivation after at least 12 h. Ni-based bimetallic catalysts have still problems with catalysts deactivation but the addition of potassium as promoter have shown stable conversion under 25 h, which suggests that promoter addition should to be further investigated to increase catalyst activity.

4.1.2. Catalyst deactivation

Catalysts used for CSR are prone to be deactivated during reaction processes. Loss of catalytic surface and support area are caused by degradation (typically referred to as sintering). Sintering takes place at high temperatures (>500 °C) and is favoured by the presence of steam in reducing environments [93]. Sintering is produced by agglomeration or migration of small crystallites into larger ones, which causes the collapse of the pore structure and loss of internal surface area of the catalyst [94]. Two major mechanisms for metal particle growth have been proposed [93]:

- Particle migration, caused by crystallite migration over the support after coalescence.
- Ostwald ripening (vapour transport), where metal species from crystallites migrate over the support via gas phase and are captured by another crystallite
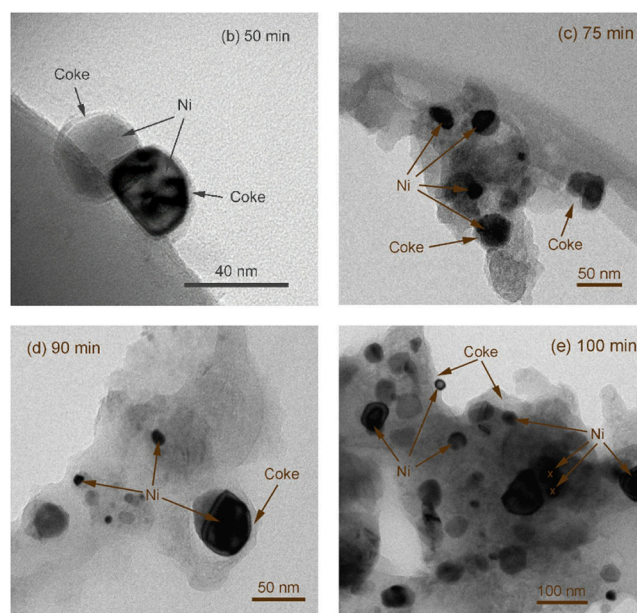

Fig. 4. TEM images of a fresh Ni-based catalyst used in steam reforming of biomass pyrolysis volatiles, showing coke encapsulation development over time.
Source: Reprinted with permission from [91].

Together with sintering, the thermal degradation or ageing of the catalyst support contributes to the loss of active sites favouring metal sintering, changing the metal-support interaction and collapse of the porous structure. Hence, thermally stable supports in oxidising atmospheres are required for reforming processes (like Al_2O_3, MgO, $MgAl_2O_4$, SiO_2, and TiO_2, among others) [33].

The metal particles in the catalyst surface are prone to oxidation in reforming conditions, which leads to a decrease in catalytic activity. Although noble and transition metals are prone to oxidation, Ni catalysts are the most susceptible. Therefore, an increase in the calcination temperature of Ni catalysts may allow higher resistance to oxidation up to 700 °C [33].

Coke deposition refers to the deposition of unwanted carbonaceous species onto the catalyst surface, blocking active sites and pores and thus leading to activity loss. This phenomenon is unavoidable in catalytic processes with hydrocarbons and oxygenates. Coke deposition can take place via different mechanisms: coke can be chemisorbed on the metal surface, producing a monolayer of metal carbide that blocks the active site (total encapsulation). Different metal carbide layers can bond via physisorption, creating multilayers that hinder access to active sites. The plugging of micro and mesopores blocks access to the inner pores and the disintegration of the catalyst structure can take place in advanced growth stages [33]. Coke deposition is the most destructive deactivation factor. It can also crush the catalyst pellets and increase the pressure drop in the reactor [93].

Three types of carbon have been observed in a reformer: encapsulating, filamentous (whisker) and pyrolytic carbon [33]:

- Encapsulating coke is formed at relatively low temperatures (< 500 °C) and is deposited on the metal particles. The oxygenated compounds to be reformed are adsorbed on the metal sites, followed by the subsequent condensation or polymerisation on the metal particle surface, resulting in covering or encapsulation of the metal particle. An example of TEM image of encapsulating coke is shown in Fig. 4.
- Filamentous (whisker) coke is formed at higher temperatures (>450 °C), it concerns the formation of carbon nanotubes and/or nanofibers. It is caused by the decomposition of CH_4, light hydrocarbons and CO by the Boudouard reaction (reversible reactions

Table 10

Catalytic performance of selected monometallic and bimetallic catalysts.

| Type	Feedstock	Catalyst	T (°C)	Conversion (%)	η_{H_2} (%)	S/C	Notes	Ref.
Monometallic catalyst	Pine wood derived pyrogas	10% Ni/Al$_2$O$_3$	600	>98	92.4	7.7	H$_2$ conv. decrease from ≈90% to ≈65% after 100 min Coke: 2.84 wt%	[88]
	Pine wood derived pyrogas	10% Ni/SiO$_2$	600	23	1.32	7.7	Coke: 0.6 wt%	[88]
	Pine wood derived pyrogas	10% Ni/MgO	600	>98	87.0	7.7	H$_2$ conv. decrease from ≈88% to ≈55% after 90 min Coke: 0.89 wt%	[88]
	Acids, polyols, cycloalkanes & phenols	5% Rh/MgAl$_2$O$_4$	500	100	74	3.5	Feed conv. decrease from 86% to 73% after 64 h Coke: 0.01 wt% C/h	[89]
Bimetallic catalyst	Glycerol, syringol, n-butanol, m-xylene, m-cresol & furfural	1% Rh-14 Ni/CeO$_2$–Al$_2$O$_3$	800	100	77.6	5	Coke: 6.69 mmol/g cat. Stable yields and no deactivation after 12 h	[90]
	Glycerol, syringol, n-butanol, m-xylene, m-cresol & furfural	1% Ru-14 Ni/CeO$_2$–Al$_2$O$_3$	800	100	71.9	5	Coke: 9.90 mmol/g cat. Stable yields and no deactivation after 12 h	[90]
	Pine wood derived pyrogas	14% Ni–Ca/Al$_2$O$_3$	600	100	93.5	7.7	Coke: 9.9 wt% H$_2$ conv decrease from ≈95% to ≈45% after ≈110 min	[91]
	Meat and bone meal derived bio-oil	20% Ni/1% K/γ-Al$_2$O$_3$	750	97.9–99	58.3	5	Addition of K resulted in minimal coke deposition showing good stability Carbon conv. ≈98% under 25 h (stable)	[92]
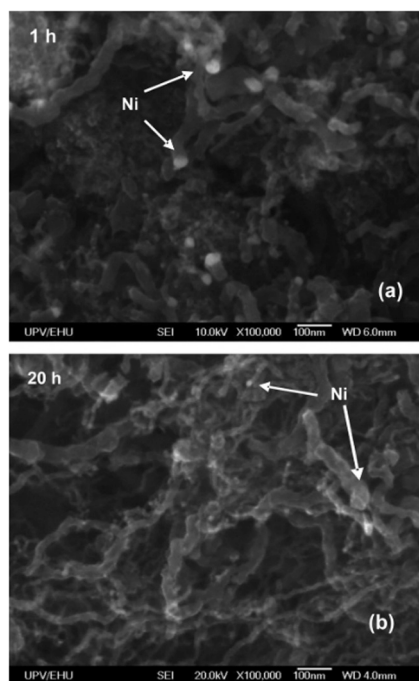
Fig. 5. SEM images of a 10Ni/Si catalyst (150–300 μm size) used in ethanol steam reforming for 1 h (a) and for 20 h (b) (reprinted with permission from [95]). The figures evidence the filamentous structure of the coke deposited with Ni particles on the top [95].

that require gasification conditions for coke removal). It is formed by adsorption of coke precursors on metal sites and consequent dissociation to atomic carbon, diffusion, nucleation and precipitation on the basis of the metal particle separates the metal crystal from the surface (from the catalyst support), lifting it as the carbon filament grows with the metal particle on its top. Filamentous coke is common for Ni, Co and Fe, since carbon dissolves into transition metals. Fig. 5 presents an SEM image of filamentous coke.

• Pyrolytic coke is formed at higher temperatures (>600 °C) by thermal cracking of hydrocarbons or oxygenates and it occurs mainly when reforming reactions are fully disfavoured at severe deactivation stages. Coke precursors are deposited all over the catalyst surface, leading to total encapsulation and void filling (even the voids caused by filamentous coke). Pyrolytic coke is usually avoided in reforming, due to highly active catalysts and catalyst regeneration before reaching severe deactivation stages. An example of pyrolytic coke is shown in Fig. 6

For the long-term performance of reforming systems, it is necessary to prevent carbon deposition. The addition of promoters and changing the active phase have been studied as methods for improving resistance against carbon formation. CeO$_2$ has been studied as promoter added to Al$_2$O$_3$ and has been proven to work effectively in catalysis. CeO$_2$ stores and releases oxygen reversibly, which increases carbon oxidation and improves the dispersion of the active phase physically. While high carbon oxidation activity prevents whisker carbon formation, the addition of CeO$_2$ has shown low activity in catalysis, which demands control over the optimum content of CeO$_2$ [93].

Since carbon deposition is favoured by acidic surfaces, alkali-doped alumina supports (such as CaO–Al$_2$O$_3$ and K$_2$Al$_2$O$_4$) can be used to reduce acidic sites by forming hydroxide, thus increasing the rate of carbon gasification reaction. The use of alkali promoters together with an optimum steam ratio (S/C) can reduce the whisker carbon formation, which is the most destructive form of carbon in nickel catalysts [93]. An overview of the different types of carbon deposition on Ni-based catalysts is found in Table 11.

4.1.3. Shaping and heat transfer inside the catalytic structure

Raw catalyst powder is usually shaped into specific structures depending on the desired function. Catalyst shape affects the structure of the catalyst bed, affecting pressure drop and heat removal or supply. In fixed bed reactors, a good rule of thumb is that the diameter of the catalyst particles should not be smaller than 1–2 mm to avoid high pressure drops. Catalyst size and shape are also decisive for the avoidance of both external and internal mass transfer limitations [98].

Pelleting is a high-pressure agglomeration technique. Catalyst powder is compressed in a die with a punching tool, producing particles (usually short cylinders) with high shape accuracy. Pelletising may however cause crushing of crystals and other problems related

Table 11
Carbon deposition on nickel-based catalysts during SR [93].

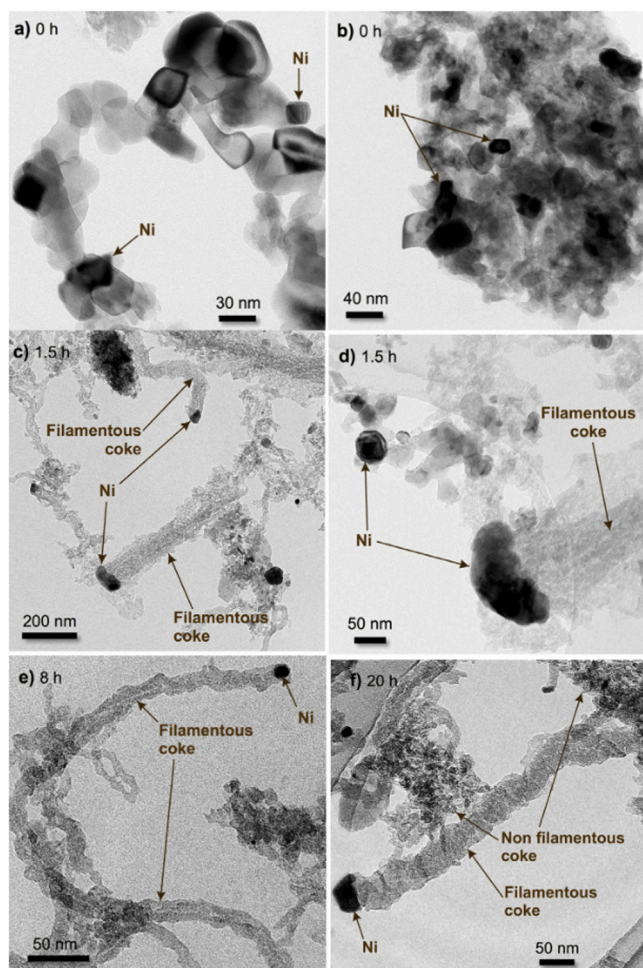|	Encapsulating film	Whisker	Pyrolytic carbon
Formation	Slow polymerisation of C_nH_m radicals on a Ni surface into an encapsulating film	Diffusion of C through Ni crystal, nucleation, and whisker growth with Ni crystal at top	Thermal cracking hydrocarbons: deposition of C precursors on the catalyst
Effects	Progressive deactivation	No deactivation of Ni surface: breakdown of catalyst and increasing pressure drop	Encapsulation of catalyst particles: deactivation and increasing pressure drop
Temperature range	<500°C	>450°C	>600°C
Critical parameters	Low temperature Low S/C Low H_2/C Aromatic feed	High temperature Low S/C Aromatic feed Low activity	High temperature Low S/C High pressure Acidic catalyst

Fig. 6. TEM images of the fresh (a and b) and deactivated Ni/La$_2$O$_3$–αAl$_2$O$_3$ catalysts during ethanol steam reforming after 1.5 h (c and d), 8 h (e), and 20 h (f) (reprinted with permission from [96]). Filamentous coke collapses forming non-filamentous coke, which is deposited in multi-layers both on Ni particles and on support (plugging pores and filling the voids between coke filaments in multilayers) [97].

to high mechanical stress, including changes in porosity and pore structure [98]. Pellets may have an internal porous structure with a randomly distributed catalytic area surface [99]. Pellets require a small size to achieve a high surface area, which enhances the diffusion of the gas through the catalyst pores to the active sites, therefore avoiding diffusion limitations. However, small pellets result in high pressure drop in the reformer. This can be avoided by increasing the macroporosity

of the bed by designing pellet shapes with one or two holes, with the trade-off of mechanical strength jeopardy of the pellets [100].

Heat transfer relies on convection within the pelletised system. The heat coming from combustion in a furnace is transferred to the tube wall, the pellets located close to the tube wall receive the heat effectively but the heat transfer to the pellets located in the tube centre relies solely on convection from the pellets located close to the tube wall. Bad heat transfer can cause local hot spots that cause sintering and catalyst deactivation [101]. Over time, catalyst pellets have a tendency to crush and break into powder. Accumulation of powder and fragments lead to clogging and creates a flow restriction [100].

Another type of common catalyst shape is the honeycomb design, monoliths with a multiplicity of parallel, straight channels. The shape of the channel cross-section may present different forms, like triangular, square, hexagonal or sinusoidal. They are characterised by their cell density (cells per square inch, cpsi) and wall thickness (mm). Honeycombs were initially developed for the catalytic treatment of exhaust gases since they are exposed to high volumetric gas flows and at low inlet pressure, so low pressure drop is required [98]. After being treated for catalytic activity (impregnation, calcination) a catalyst washcoat is formed on the walls of the cells. In comparison to packed beds, honeycombs show very little resistance to flow, hence lower pressure drop and lower energy losses are present [102]. In conventional honeycombs, the flow along the walls of the channels is laminar and diffusion is the governing mechanism of mass transport to the active site. This could lead to bad mixing of reactants, affecting the conversion negatively. High specific surface area is therefore important to ensure high conversion, it can be achieved by increasing the cell densities [98]. Ceramic and metal honeycombs are common honeycomb types. Ceramic honeycombs have high melting temperatures, are resistant to oxidation and can have excellent thermal shock resistance. Metallic honeycombs offer even lower pressure drop due to thinner walls and lower weight. Metals have however a much greater expansion coefficient than ceramics, especial bonding techniques are required to produce an adherent washcoat [102].

The great disadvantage of the parallel channel honeycomb is that it is an adiabatic reactor. This property limits the temperature control, which does not make it ideal for endothermic and exothermic reactions [102]. This is mainly true for ceramic honeycombs, metal honeycombs are non-adiabatic and can readily transfer hear. However, proper research to investigate heat transfer properties between ceramic and metal honeycombs has not been performed yet [100]. Monolithic supports provide better heat transfer in comparison to randomly packed beds of pelletised catalysts. Heat transfer via radial convection is non-existing but heat transfer via conduction through the solid phase structure to the active site is significant. Therefore, high thermal conductivity materials as monolith substrate will improve heat flux and reduce the thermal resistance of the structure [100]. As stated previously, high average heat flux would lead to fewer tubes, smaller furnaces volume and reduced cost [58].

In an experimental study by Roh et al. the heat transfer performance between a packed bed of Ru/Al_2O_3 pellets and a Ru/Al_2O_3 catalyst-coated FeCr honeycomb were compared while performing SMR. The heat flux was calculated as a function of the temperature difference between the furnace wall and the catalyst bed equilibrium temperature. The results show readily that the honeycomb (monolith bed) always has higher heat flux at the same temperature [100].

When integrating a honeycomb with the reformer, heat needs to be transported across the gap between the inner surface of the reformer and the outer surface of the honeycomb. Heat transfer performance is improved by reducing the gap clearance but too much tightness would require pressure that could affect the structure of the honeycomb [100]. Honeycombs have also shown good performance in CSR of pyrolysis gas. In a study conducted by Goyal et al. [103] SR of model bio-oil was investigated and compared using Ni/Al_2O_3 pellets and monolith, achieving the highest steady-state H_2 yield using the monolithic catalyst.

4.2. Heat transfer from source to reformer

In the conventional technology, the catalyst is loaded into a number of tubes placed inside a furnace. A large-scale industrial SMR consists of more than 100 tubular tubes with a length of 10 to 14 m, the combustion must occur at a higher temperature than the reaction temperature to generate the necessary inward heat flux into the reformer [82]. The reformer design can be optimised by the number and geometry of single reformers, heat transfer from the burners to the reforming tubes and catalyst design [85].

Nevertheless, limited thermal conductivity from the heat source to the reformer walls and across the catalytic surface represents a natural limitation, combined with a strongly endothermic reaction such as SR which leads to steep temperature gradients across the catalyst [82]. In conventional fired reactors, about 50% of the heat produced by combustion is transferred to the reformer tube walls and absorbed by the process, the resting 50% is available in the hot flue gas and can be recovered in the waste heat section for preheating duties and steam production [85]. High average heat flux would lead to fewer tubes, smaller furnaces volume and reduced cost [58], offering a possibility for improvement.

Yu el al. proposed a mathematical model validated with experimental results for SMR in a heat exchanger type steam reformer [104]. The reaction gas mixture is introduced in the reformer from the top through a catalytic tube, while hot flue gases flow from the bottom of the reformer to the top in a counter-flow configuration. The process consists of 168 reformer tubes with an effective tube length of 12.3 m. The feed temperature of the reaction mixture is 439 °C while the inlet and outlet temperature of the hot flue gas is 955 °C respectively 515 °C [104]. Therefore, a steep temperature profile between the heat source, the tube and the reaction gas is present, which demands extremely high combustion temperatures to heat up the reaction mixture to the operating temperature.

4.3. Electrically heated reformer

The external heating used in conventional CSR requires plenty of energy and time to provide the right temperature to the catalytic bed, this results inevitably in high-temperature gradients in the bed and represents one of the biggest challenges for commercial operations. While structured catalysts in metallic supports are used to improve heat transfer, electrical heating, electrical heating results in an overall process improvement [105]. Electrical heating has also been investigated in other reforming technologies, like partial oxidation via indirect induction [63].

Earlier attempts for electrification of CSR were performed via electrochemical catalytic reforming (ECR). In this technology, the catalyst is embedded around an electrified annular Ni–Cr wire connected to
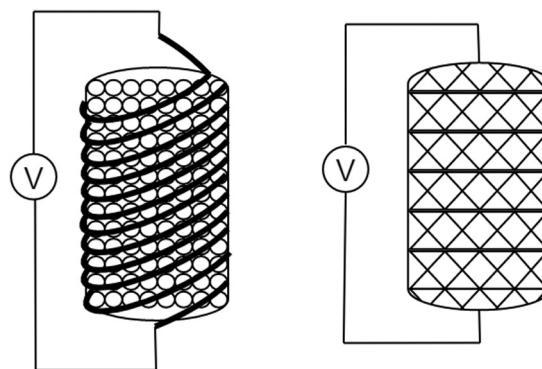

Fig. 7. Electrical heating reforming technologies. Left: Induction heating (ECR) in a packed bed reactor. Right: Resistive heating (EHC) in a fixed bed reactor.

AC, that heats up the catalyst bed by induction, as illustrated by 7. Electrically heated furnaces are also used in order to keep constant temperature and investigate the effect of the current on the conversion [106,107]. Electrochemical catalytic reforming (ECR) of bio-oil with steam has been studied for hydrogen production [107]. It has been shown that the presence of electric current promotes reforming remarkably, the temperature of the catalyst around the wire increases, hence the catalytic activity is enhanced to so extent. However, the electrified wire only heats a very small part of the catalyst directly [106]. Tao et al. have studied ECR of tar using compound models like benzene and toluene, an electric current of 4 A and a temperature of 800 °C resulted in a toluene conversion of 99.9% with a low carbon content (0.15 wt%) [106]. Yuan et al. [107] have studied ECR of fast pyrolysis bio-oil. They have concluded that ECR shows overall better conversion performance than regular SR at the same temperature and high current, as well as better energy performance. Catalyst deactivation due to carbon deposition took place, leading to a hydrogen yield decrease of 10% after 18 h and 50% after 36 h [107]. Table 12 presents the performance comparisons of different electrically heated reformers with different hydrocarbon feedstocks.

The latest development research has focused on the direct electrification of the catalyst support by resistive heating (Joule heating). Electrically heated catalysts (EHC) have been considered promising in the vehicular systems, they can be used for dealing with the cold start emission of diesel and gasoline engines by instantaneously heating the three-way catalytic convertor for reduction of CO, HC and NO_x [105]. Direct internal heating can give the reformer a good temperature distribution and increase the overall heat transfer coefficient to 10 times that of external heating, reducing, therefore, the heating start up time [108]. EHC can therefore reduce the heating area and the heating time, decreasing the overall energy demand for the reaction system [105]. In addition, the electrification of the reformer substitutes the reformer furnace with several tubes with one single electrically heated tube reformer, improving heat transfer properties and reducing the reformer's total volume. This technology promises a better heat transfer efficiency and uniform heating across the catalytic material [82].

EHC has been used for SMR and CSR of tar. Earlier research made by Zhang et al. [108] shows experimental analysis on the development of a co-axial cylindrical CH_4 steam reformer using an electrically heated alumite catalyst (Ni/Al_2O_3/Alloy catalyst). Direct internal electrical and external heating were compared, internal heating showed an increased overall heat transfer coefficient, resulting in a better transverse gas temperature distribution, higher reaction performance and shorter start-up time to reaction temperature [108]. Wismann et al. [82] constructed an electrically heated reformer for SMR with a FeCrAl-alloy tube, due to its temperature-independent electrical resistance. The reformer tube is 50 cm long with a 28 cm long, 128 μm wide nickel-impregnated washcoat. The experimental results were validated with a

Table 12
Comparison between electrically heated reformers.

Technology	Feedstock	Operating parameters	Yield (%)	Notes	Ref.
ECR	Toluene	S/C = 3 24 h 4 A 800 °C	99.9	Carbon content = 0.15 wt%	[106]
	Benzene	S/C = 3 24 h 4 A 800 °C	–	Carbon content = 0.17 wt%	[106]
	Bio-oil	S/C = 5.8 5 h 4 A 600 °C	≈95	–	[107]
EHC	Benzene	S/C = 3 40 min 80 A 750 °C	80.4	–	[105]
	Methane	S/C = 3 80 h 12 A ≈ 700°C	80–99	–	[108]
	Methane	S/C = 3 240 V 800 °C	≈85	–	[109]

computational model to further understand the process and extrapolate results. A feed mixture of CH_4, H_2O and H_2 preheated to 100 °C is the reaction mixture, it is introduced into the reformer at 1.7 NL/min. CH_4 conversion reaches ≈87 % towards the end of the reformer. The inward heat flux along the reformer was also measured. The results show a stable, almost constant heat flux along the coated zone. These results show good heating control, providing uniform heating.

Renda et al. [109] have presented a study on the direct electrification of the surface of the structured catalyst. SiC heating elements were used as catalyst support with a 5 wt% Ni washcoat for performing both SR and DR of CH_4. The system could be heated up to 800 °C and CH_4 conversion reached over 85% for both SR and DR. The energy consumption in terms of kWh Nm^{-3} H_2 was also investigated and it was concluded that it is comparable to the energy consumption of modern electrolysers (≈59.7 kWh kg^{-1} H_2).

Choi et al. [105] have previously investigated the catalytic steam reforming of tars using an EHC. A thermally treated Fe–Cr alloy monolith with a washcoat of NiO/MgO/γ-Al_2O_3 (0.0252 g per g monolith) was electrically heated by supplying 200–300 W (70–80 A) to reach the desired reaction temperature (700–750 °C) within 20 s. The reformer was tested for benzene steam reforming, 80.4% of benzene could be converted into syngas with a CO & H_2 fraction of 90.0% at 750 °C in the EHC system. In addition, the EHC system was proven to be an effective way for controlling coke formation, compared to BSR results in conventional fixed-bed systems [105].

4.4. 3D Printed catalysts

As described in the previous section, the advancement of the electrically heated catalysts highly depends on the development of the main monolith catalyst structure. Hence, significant attention should be given to the optimisation of the performance of such catalysts. The emerging 3D printed material techniques allow manufacturing tailored shapes that can allow new operating windows for catalytic processes, it can be used to optimise flow patterns and maximise heat and mass transfer [110,111], solving in this way the drawbacks of classical honeycombs: bad mixing due to laminar flow and diffusion-governed mass transport. 3D printing techniques have been known for more than 30 years, but recently this technology has started being used for investigating the design and production of novel catalysts [110,112–116]. 3D catalyst design can be used for satisfying multiple criteria, different materials can be used for catalyst manufacturing, allowing for
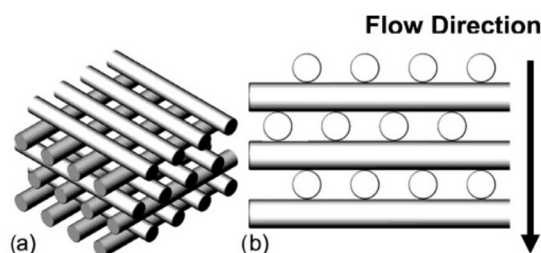

Fig. 8. Schematic of the lattice structure of 3D printed honeycomb: (a) isometric and (b) side views [117].
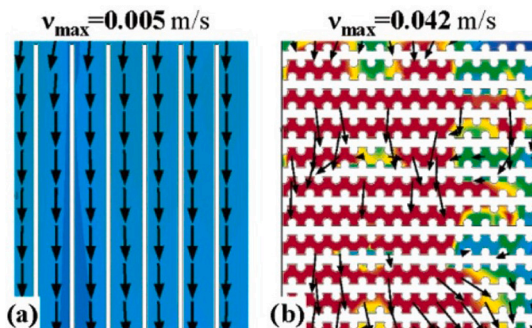

Fig. 9. Cross-sectional views of flow velocities for (a) conventional honeycomb and (b) 3D honeycomb lattice supports [117].

a combination of metallic structure and ceramic porous material. The porosity of the ceramic tan be tailored to enhance the mass transfer and the heat transfer is benefited by the fast conduction through the metal support. In addition, the support can be designed in a so-called lattice structure, which means that the channels are interconnected, resulting in low pressure drop and enhanced flow and radial mixing, which also contributes to faster heat transfer from or to the surroundings [110], as shown in Figs. 8 and 9.

In a study by Stuecker et al. [117], the catalytic activity of hexaaluminate on CH_4 combustion was investigated on traditional and 3D printed honeycomb, with the same amount of active catalytic phase. The 3D printed honeycomb (see Fig. 8) had a lattice support

Table 13

Advantages and challenges of different reformer technologies for the biomass conversions to fuels and chemicals [23,25,29,69,79].

Technology	Advantages	Challenges
POX	– Desulphurisation is not required	– High operating temperature – Low H_2/CO ratio – Requires oxygen plant leading to high cost – Syngas is diluted with high CO_2 concentration
ATR/CPO	– Lowest operating temperature than POX – CH_4 content can be tailored by temperature adjustment	– Limited commercial experience – Reduction of catalyst activity due to the highly oxidative atmosphere and temperature – Requires oxygen plant
DR	– Suitable for the biogas reforming due to the readily available feed CO_2	– Low H_2/CO ratio – Limited applications – High tendency for coke formation due to low H/C and O/C ratios
CSR	– Technologically mature – Possibility for low operating temperatures – High H_2 yields – Best H_2/CO ratio for liquid fuels production	– High CO_2 emissions – Requirement for catalyst regeneration – High energy demand – More costly than POX & ATR
MR	– Oxygen separation from air via membrane permeability – Constant product removal – Direct separation of products which can eliminate further need of gas separation processes – High selectivity to allow higher H_2/CO ratio	– High cost for the membrane materials – The least mature technology – Sensitive to acidic gases

structure that promotes turbulence, which enhances mass transfer of reactants to the catalyst surface. The 3D printed honeycomb showed approximately 6 times more CH_4 conversion at 600 °C in comparison to the conventional honeycomb [117]. Metallic 3D honeycombs have also been studied. Danaci et al. conducted a study about CO_2 methanation over Ni/Al_2O_3 coated 3D structured catalysts and compared them to conventional catalyst powder. Good results were obtained with the 3D honeycombs (CO_2 conversion of 91% CH_4 selectivity of 98% at 400 °C) and high stability over time. The high stability is attributed to the catalyst structure, which permits uniform temperature distribution and avoids local hot spots that cause sintering and catalyst deactivation [101].

5. Summaries and perspectives

This work has reviewed thermochemical conversion processes (gasification, pyrolysis and AD) for the production of reformable gases (CH_4 and biomass-derived vapours) and different reforming technologies for syngas production. The main drawbacks and challenges of those reformer technologies have been presented focusing on biomass conversion. Table 13 shows a summary of the advantages and challenges of the different reforming technologies. Despite the issues in energy efficiency and the need of process improvement, the conventional reforming processes (SR, POX, ATR) of fossil-based feedstocks are technologically mature. The transition towards reforming processes using biomass requires solving improving already existing drawbacks and solving new issues that appear with the new fuels. This applies specifically to biomass-derived vapours. As stated previously, hydrocarbons larger than CH_4 are prone to cause carbon deposition, which leads to catalyst deactivation. This is especially problematic in CSR, since the absence of oxygen does not allow coke gasification.

In general, CSR of biomass-derived vapours provides great benefits over other reforming technologies, due to the possibility of high H_2 yields and relatively mature technology. This is especially relevant with the current strong trend on the production of H_2 for the decarbonisation of industrial and transportation sectors [6]. Combining the H_2 production from biomass with CCS, would enable a great extent of flexibility for various decarbonisation routes. Nevertheless, CSR is a highly endothermic process and therefore requires a high heat duty. The main challenges of CSR that need to be addressed in order to implement the technology on a big scale are mainly related to

Table 14

Specific energy demand for H_2 production and H_2/CO ratio of different reforming technologies obtained from numerical simulations.

	Energy demand (kWh kg^{-1} H_2)	H_2/CO
ATR	5.76 [118]	1.1–2 [60,119]
DR	16.28 [118]	≈1 [73]
CSR	10.84 [118]	⩾3 [120]
Electrified CSR	≈4 [121]	⩾3 [120]

heat loss and nonuniform heating (inherited from conventional SMR), and catalyst deactivation (especially challenging for biomass-derived vapours). The required heat for CSR is usually provided by combustion and it needs to be carried at a higher temperature than the reforming temperature to ensure that the heat flux is high enough so the heat transfer is efficient [104]. The use of combustion at high temperatures to compensate for the heat losses, together with the need for a large volume of tubes and furnaces are costly [82]. Moreover, the use of external combustion to supply the heat for CSR generates an additional CO_2 streams emission, which would increase the cost of carbon capture in a full BECCS process. To solve these challenges, alternative ways to heat CSR processes should be one of the main priorities for future research and developments.

As discussed in this mini-review, direct electrification of CSR is a promising way to address the aforementioned issues. The direct electrification results in increased overall heat transfer coefficient (decreasing the overall heating demand and the heating start up time) and reduces the reformer's total volume [82,105]. The electrification of the reformer has the possibility to decrease the specific energy demand (kWh$_{el}$ kg^{-1} H_2) and provide high H_2 production when combined with CSR, as described in Table 14. As discussed previously, the use of an electrically heated reformer in the form of a fixed bed reactor with honeycomb-supported Ni/Al_2O_3 looks promising reforming process, offering good mass and heat transfer properties, low pressure drop, reducing reactor volumes in comparison to conventional technology, good biomass-derived vapours conversion, and hydrogen selectivity.

The energy demand of CSR is strongly connected to the energy efficiency of the process, which is mainly affected by the heat flux and temperature profile inside of the reformer [59,104]. Reformers with packed beds with pellets present poor heat transfer by convection between the catalyst pellets, together with eventual great pressure
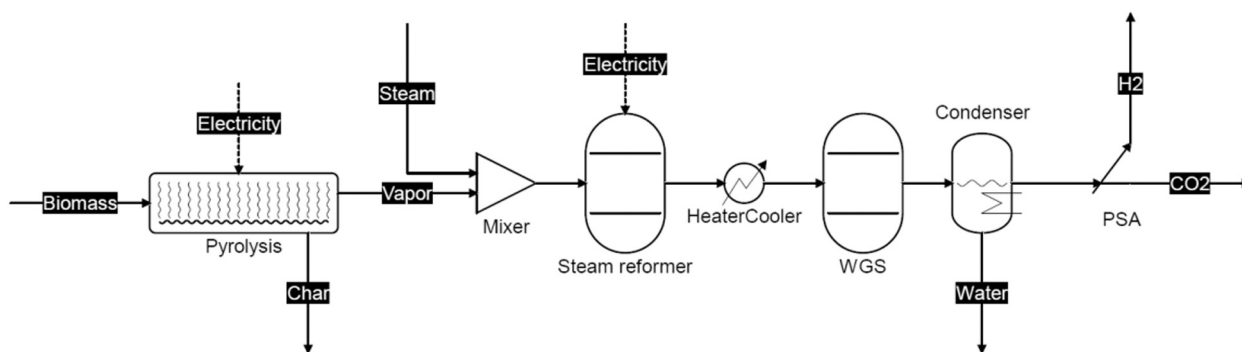
Fig. 10. Co-production of biochar and H_2 via electrified pyrolysis and CSR of biomass [122].

drop [98,100]. Meanwhile, conventional honeycombs show low pressure drop and better heat transfer properties but the flow along the walls of the cells is laminar and governed mainly by diffusion, which means no proper mixing and strong dependence on high specific surface area to ensure high conversion [98,102]. In contrast, 3D printing technology for manufacturing catalysts allows turbulent flow and uniform heating, which improve the conversion yield and reduce deactivation by sintering [101,111]. Thus, 3D printing catalysts should be developed to support the advancement of the electrified reformer.

Replacing conventional combustion with electrical heat could also simplify the carbon capture process in a BECCS process. At the same time, it may also allow maximum use of biomass, as there is no biomass fuel being combusted to supply the required heat. However, this scenario will mostly depend on the availability of low-cost renewable electricity. An example of this scenario is recently proposed by Zaini et al. [122], which combine a fully electrified biomass pyrolysis process and a subsequent electrified reformer (see the schematic diagram in Fig. 10) for the co-production of biocarbon and H_2. Similarly, Wang et al. [123] recently proposed electrified reformers to be used for the production of carbon-negative bio-methane from the organic fraction of municipal solid waste.

Together with the energy challenges, catalyst stability represents a big bottleneck for big-scale production. Carbon deposition is a significant problem in reforming processes, it leads to gradual catalytic oxidation which leads to an increase of oxygenates that produce even more coke. Carbon deposition blocks the surface of the catalyst reducing its catalytic activity, it can be minimised by using bimetallic catalysts [28] or/and applying optimum S/C ratio and temperature [40] and reduced by co-feeding O_2 into the system. Using alkaline-earth elements (Mg, Ca, K) as promoters seems to be a promising alternative to avoid coke deposition [28,92], which increases the stability of the catalyst and assures good production performance in continuous processes. The addition of O_2 allows gasification or combustion of the deposited carbon, this also provides energy for the endothermic reforming reactions. The trade-off is a decrease in H_2 yield and increase in CO_2 yield [84] together with additional gas cleaning if air is used for combustion [58] and eventual catalyst active metal oxidation.

The beyond state-of-the-art reforming process would therefore present the following characteristics:

- Good energy efficiency (heat transfer, uniform heating)
- High biomass-derived vapours to syngas conversion
- Long-life catalyst with high surface area and low pressure drop
- Less CO_2 emissions
- Compact size reformer.

Fig. 11 contains a graphic summary of the reviewed reforming processes, challenges, aims and development routes presented in this paper.

Reforming technologies are not only important for syngas production, effective reformers are also used for energy production in fuel cells. Solid oxide fuel cells (SOFCs) and molten carbonate fuel cells (MCFCs) are high-temperature fuel cells with fuel flexibility, which means that they can use other fuels than hydrogen. Lower hydrocarbons and hydrogen-rich liquids can be are used as fuels by reforming processes in a thermally integrated reformed inside of the fuel cell. Low-temperature fuel cells (like PAFC and PEMFC) do not possess this special feature and syngas needs to be reformed prior use in the fuel cell [93]. Therefore, achievements in the development of advanced reforming processes as suggested in this section could be implemented in other fields.

6. Conclusion

The development of reforming technologies for syngas production from biomass has been the main concern in the field of bio-energy. As an intermediate product, biomass-derived syngas is a key for global decarbonisation as it allows the production of carbon-negative fuels and chemicals. This decarbonisation route is essential for addressing climate change. Nevertheless, reforming processes of biomass-derived vapours are more challenging due to the high energy demands and the unique biomass properties. Therefore, this study evaluated the progress of reforming technologies (POX, ATR, CPO, DR, MR and CSR) for biomass conversion to syngas. Some reforming methods are considered mature and ready for commercialisation, such as the POX, ATR, and CSR of tar-rich syngas from gasification. In contrast, the reforming of heavy biomass-derived hydrocarbons (e.g., biomass pyrolysis vapours) is mostly still under research at lab or pilot scales. Considering the current trend of H_2 decarbonisation pathways, CSR processes of biomass is promising due to the high H_2 yield. However, compared to the fossil-based feedstocks, catalyst deactivation due to the coke formation has been identified as the biggest challenge for scaling-up. Coke deposition can be limited to a certain degree by having a high steam-to-carbon ratio and temperature, but the catalyst shape and design are also decisive. The development of bimetallic catalysts with promoters (e.g., alkali and alkaline earth metals) in the emerging 3D printed monolithic support show promising features to tackle carbon deposition. In addition, the direct electrification of the catalyst is a promising approach to lower the energy demand for H_2 production. Therefore, incremental improvements on these emerging topics could significantly assist in implementing the reforming processes.

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.
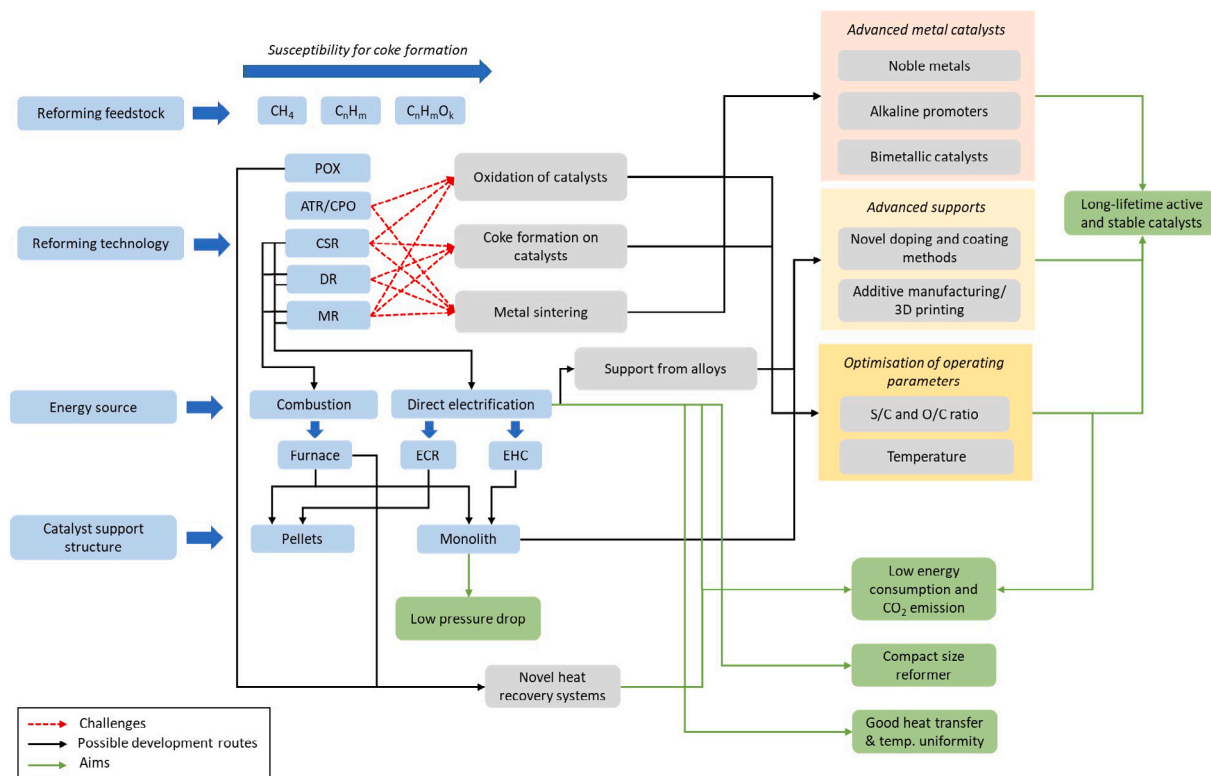
Acknowledgement

Fig. 11. Challenges and possible routes for reformer development based on the reviewed progress and status of different reformer technologies in this study.

References

[1] Swiss Re Institute. The economics of climate change. Technical report, 2021.

[2] United Nations/Framework Convention on Climate Change (UNFCCC). The Paris agreement. 2015.

[3] IPCC, 2018. Summary for policymakers. In: Global warming of 1.5°C. An IPCC Special Report on the impacts of global warming of 1.5°C above pre-industrial levels and related global greenhouse gas emission pathways, in the context of strengthening the global. Technical report, World Meteorological Organization, Geneva, Switzerland: World Meteorological Organization; p. 32.

[4] IEA. Global Energy Review 2021.

[5] World Resources Institute. World greenhouse gas emissions: 2016. 2020.

[6] Nurdiawati Anissa, Urban Frauke. Towards deep decarbonisation of energy-intensive industries: A review of current status, technologies and policies. Energies 2021;14(9):2408.

[7] Basu Prabir. Biomass characteristics. In: Biomass gasification, pyrolysis and torrefaction. Elsevier; 2013, p. 47–86.

[8] Gelfand Ilya, Hamilton Stephen K, Kravchenko Alexandra N, Jackson Randall D, Thelen Kurt D, Robertson G Philip. Empirical evidence for the potential climate benefits of decarbonizing light vehicle transport in the U.S. with bioenergy from purpose-grown biomass with and without BECCS. Environ Sci Technol 2020;54(5):2961–74.

[9] Jóźwiak Piotr, Hercog Jarosław, Kiedrzyńska Aleksandra, Badyda Krzysztof. CFD analysis of natural gas substitution with syngas in the industrial furnaces. Energy 2019;179:593–602.

[10] LKAB. The world's first fossil-free pellet plant. 2020.

[11] Pissot Sébastien, Thunman Henrik, Samuelsson Peter, Seemann Martin. Production of negative-emissions steel using a reducing gas derived from DFB gasification. Energies 2021;14(16):4835.

[12] Dahlquist Erik, Naqvi Muhammad, Thorin Eva, Yan Jinyue, Kyprianidis Konstantinos, Hartwell Philip. Experimental and numerical investigation of pellet and black liquor gasification for polygeneration plant. Appl Energy 2017;204:1055–64.

[13] Cheng Kang, Kang Jincan, King David L, Subramanian Vijayanand, Zhou Cheng, Zhang Qinghong, et al. Chapter three - advances in catalysis for syngas conversion to hydrocarbons. In: Song Chunshan, editor. Advances in catalysis, vol. 60. Academic Press; 2017, p. 125–208.

[14] Bernardi Andrea, Graciano Jose EA, Chachuat Benoît. Production of chemicals from syngas: an enviro-economic model-based investigation. In: Kiss Anton A, Zondervan Edwin, Lakerveld Richard, Özkan Leyla, editors. Computer aided chemical engineering, vol. 46. Elsevier; 2019, p. 367–72.

[15] Lu Shanshan, Shi Yanmei, Meng Nannan, Lu Siyu, Yu Yifu, Zhang Bin. Electrosynthesis of syngas via the co-reduction of CO2 and H2O. Cell Rep Phys Sci 2020;1(11):100237.

[16] Jarvis Sean M, Samsatli Sheila. Technologies and infrastructures underpinning future CO 2 value chains: A comprehensive review and comparative analysis. Renew Sustain Energy Rev 2018;85:46–68.

[17] García L. Hydrogen production by steam reforming of natural gas and other nonrenewable feedstocks. In: Compendium of hydrogen energy. Elsevier; 2015, p. 83–107.

[18] Agbor Valery B, Cicek Nazim, Sparling Richard, Berlin Alex, Levin David B. Biomass pretreatment: Fundamentals toward application. Biotechnol Adv 2011;29(6):675–85.

[19] Isaksson Johan, Åsblad Anders, Berntsson Thore. Influence of different pretreatment methods on biomass gasification and production of fischer-tropsch crude integrated with a pulp and paper mill. Chem eng trans 2013;35.

[20] Andersson Klas J, Skov-Skjøth Rasmussen Martin, Højlund Nielsen Poul Erik. Industrial-scale gas conditioning including topsoe tar reforming and purification downstream biomass gasifiers: An overview and recent examples. Fuel 2017;203:1026–30.

[21] Görling Martin, Larsson Mårten, Alvfors Per. Bio-methane via fast pyrolysis of biomass. Appl Energy 2013;112:440–7.

[22] Chylek P, Jennings SG, Pinnick R. SOOT. In: Holton James R, editor. Encyclopedia of atmospheric sciences. Oxford: Academic Press; 2003, p. 2093–9.

[23] Aziz Muhammad, Darmawan Arif, Juangsa Firman Bagja. Hydrogen production from biomasses and wastes: A technological review. Int J Hydrogen Energy 2021;46(68):33756–81.

[24] Garcia-Nunez JA, Pelaez-Samaniego MR, Garcia-Perez ME, Fonts I, Abrego J, Westerhof RJM, et al. Historical developments of pyrolysis reactors: A review. Energy Fuels 2017;31(6).

[25] Usman Muhammad, Wan Daud WMA, Abbas Hazzim F. Dry reforming of methane: Influence of process parameters—A review. Renew Sustain Energy Rev 2015;45:710–44.

[26] Pinsky Roxanne, Sabharwall Piyush, Hartvigsen Jeremy, O'Brien James. Comparative review of hydrogen production technologies for nuclear hybrid energy systems. Prog Nucl Energy 2020;123.

[27] Gao Yuchen, Jiang Jianguo, Meng Yuan, Yan Feng, Aihemaiti Aikelaimu. A review of recent developments in hydrogen production via biogas dry reforming. Energy Convers Manage 2018;171:133–55.

[28] Setiabudi HD, Aziz MAA, Abdullah Sureena, Teh LP, Jusoh R. Hydrogen production from catalytic steam reforming of biomass pyrolysis oil or bio-oil derivatives: A review. Int J Hydrogen Energy 2020;45(36):18376–97.

[29] Ghoneim Salwa A, El-Salamony Radwa A, El-Temtamy Seham A. Review on innovative catalytic reforming of natural gas to syngas. World J Eng Technol 2016;04(01).

[30] Zhang Yaning, Cui Yunlei, Chen Paul, Liu Shiyu, Zhou Nan, Ding Kuan, et al. Chapter 14 - gasification technologies and their energy potentials. In: Taherzadeh Mohammad J, Bolton Kim, Wong Jonathan, Pandey Ashok, editors. Sustainable resource recovery and zero waste approaches. Elsevier; 2019, p. 193–206.

[31] Ahmad Anis Atikah, Zawawi Norfadhila Abdullah, Kasim Farizul Hafiz, Inayat Abrar, Khasri Azduwin. Assessing the gasification performance of biomass: A review on biomass gasification process conditions, optimization and economic evaluation. Renew Sustain Energy Rev 2016;53.

[32] Wongsiriamnuay Thanasit, Kannang Nattakarn, Tippayawong Nakorn. Effect of operating conditions on catalytic gasification of bamboo in a fluidized bed. Int J Chem Eng 2013;2013.

[33] Bonilla Javier, Gordillo Gerardo, Cantor Carlos. Experimental gasification of coffee husk using pure oxygen-steam blends. Front Energy Res 2019;7.

[34] Basu Prabir. Biomass Gasification, Pyrolysis and Torrefaction: Practical Design and Theory. 2018.

[35] Salem Ahmed M, Zaini Ilman Nuran, Paul Manosh C, Yang Weihong. The evolution and formation of tar species in a downdraft gasifier: Numerical modelling and experimental validation. Biomass Bioenergy 2019;130:105377.

[36] Zaini Ilman Nuran, Gomez-Rueda Yamid, García López Cristina, Ratnasari Devy Kartika, Helsen Lieve, Pretz Thomas, et al. Production of H2-rich syngas from excavated landfill waste through steam co-gasification with biochar. Energy 2020;207:118208.

[37] Saleem Faisal, Harris Jack, Zhang Kui, Harvey Adam. Non-thermal plasma as a promising route for the removal of tar from the product gas of biomass gasification – A critical review. Chem Eng J 2020;382(September 2019):122761.

[38] Valderrama Rios Martha Lucia, González Aldemar Martínez, Lora Electo Eduardo Silva, Almazán del Olmo Oscar Agustin. Reduction of tar generated during biomass gasification: A review. Biomass Bioenergy 2018;108.

[39] Anis Samsudin, Zainal ZA. Tar reduction in biomass producer gas via mechanical, catalytic and thermal methods: A review. Renew Sustain Energy Rev 2011;15(5):2355–77.

[40] Adeniyi Adewale George, Otoikhian Kevin Shegun, Ighalo Joshua O. Steam reforming of biomass pyrolysis oil: A review. Int J Chem React Eng 2019;17(4).

[41] Xu F, Li Y. Biomass digestion. In: Encyclopedia of sustainable technologies. Elsevier; 2017, p. 197–204.

[42] Holliger Christof, Fruteau de Laclos Hélène, Hack Gabrielle. Methane production of full-scale anaerobic digestion plants calculated from substrate's biomethane potentials compares well with the one measured on-site. Front Energy Res 2017;5.

[43] Valmet. Valmet Gasifier for biomass and waste.

[44] Larsson Anton, Gunnarsson Ingemar, Tengberg Freddy. The GoBiGas project: Demonstration of the production of biomethane from biomass via gasification. Technical report, Göteborg Energi; 2018.

[45] 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.

[46] Alamia Alberto, Larsson Anton, Breitholtz Claes, Thunman Henrik. Performance of large-scale biomass gasifiers in a biorefinery, a state-of-the-art reference. Int J Energy Res 2017;41(14):2001–19.

[47] Hannula Ilkka, Kurkela Esa. A parametric modelling study for pressurised steam/O2-blown fluidised-bed gasification of wood with catalytic reforming. Biomass Bioenergy 2012;38:58–67.

[48] Lundberg Louise, Tchoffor Placid A, Pallarès David, Johansson Robert, Thunman Henrik, Davidsson Kent. Influence of surrounding conditions and fuel size on the gasification rate of biomass char in a fluidized bed. Fuel Process Technol 2016;144:323–33.

[49] Sharifzadeh Mahdi, Sadeqzadeh Majid, Guo Miao, Borhani Tohid N, Murthy Konda NVSN, Garcia Marti Cortada, et al. The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: Review of the state of art and future research directions. Prog Energy Combust Sci 2019;71:1–80.

[50] Al-Haj Ibrahim Hassan. Introductory chapter: Pyrolysis. In: Recent advances in pyrolysis. IntechOpen; 2020.

[51] B.V. BTG Bioliquids. BTG Bioliquids pyrolysis.

[52] Shen Yanwen, Linville Jessica L, Urgun-Demirtas Meltem, Mintz Marianne M, Snyder Seth W. An overview of biogas production and utilization at full-scale wastewater treatment plants (WWTPs) in the United States: Challenges and opportunities towards energy-neutral WWTPs. Renew Sustain Energy Rev 2015;50:346–62.

[53] Chen Yuling, Rößler Benjamin, Zielonka Simon, Lemmer Andreas, Wonneberger Anna-Maria, Jungbluth Thomas. The pressure effects on two-phase anaerobic digestion. Appl Energy 2014;116:409–15.

[54] Szymańska Daniela, Lewandowska Aleksandra. Biogas power plants in Poland—Structure, capacity, and spatial distribution. Sustainability 2015;7(12):16801–19.

[55] Du Shoucheng, Valla Julia A, Bollas George M. Characteristics and origin of char and coke from fast and slow, catalytic and thermal pyrolysis of biomass and relevant model compounds. Green Chem 2013;15(11):3214–29.

[56] Tunå Per. Generation of synthesis gas for fuels and chemicals production [Ph.D. thesis], Lund: Lund university; 2013, p. 253.

[57] Rennard David, French Rick, Czernik Stefan, Josephson Tyler, Schmidt Lanny. Production of synthesis gas by partial oxidation and steam reforming of biomass pyrolysis oils. Int J Hydrogen Energy 2010;35(9).

[58] Aasberg-Petersen K, Bak Hansen JH, Christensen TS, Dybkjaer I, Christensen P Seier, Stub Nielsen C, et al. Technologies for large-scale gas conversion. Appl Catal A 2001;221(1–2):379–87.

[59] Keiski RL, Ojala S, Huuhtanen M, Kolli T, Leiviskä K. Partial oxidation (POX) processes and technology for clean fuel and chemical production. In: Advances in clean hydrocarbon fuel processing. Elsevier; 2011.

[60] Liu Ke, Deluga Gregg D, Bitsch-Larsen Anders, Schmidt Lanny D, Zhang Lingzhi. Catalytic partial oxidation and autothermal reforming. In: Hydrogen and syngas production and purification technologies. Hoboken, NJ, USA: John Wiley & Sons, Inc.; 2009.

[61] Corporation IHI. Making effective use of unused energy: Utilization of the twin IHI gasifer. IHI Eng Rev 2017;50.

[62] Tsuboi Yosuke, Ito Shintaro, Takafuji Makoto, Ohara Hiroaki, Fujimori Toshiro. Development of a regenerative reformer for tar-free syngas production in a steam gasification process. Appl Energy 2017;185:1217–24.

[63] Li Chao'en, Burke Nick, Gerdes Karl, Patel Jim. The undiluted, non-catalytic partial oxidation of methane in a flow tube reactor – An experimental study using indirect induction heating. Fuel 2013;109.

[64] Marda Jonathan R, DiBenedetto Joelle, McKibben Shannon, Evans Robert J, Czernik Stefan, French Richard J, et al. Non-catalytic partial oxidation of bio-oil to synthesis gas for distributed hydrogen production. Int J Hydrogen Energy 2009;34(20).

[65] Ayoobi Mohsen, Schoegl Ingmar. Non-catalytic conversion of glycerol to syngas at intermediate temperatures: Numerical methods with detailed chemistry. Fuel 2017;195.

[66] Li Chao'en, Kuan Benny, Lee Woo Jin, Burke Nick, Patel Jim. The non-catalytic partial oxidation of methane in a flow tube reactor using indirect induction heating – An experimental and kinetic modelling study. Chem Eng Sci 2018;187.

[67] Yu Haimiao, Xu Yangyang, Chen Geng, Chen Dezhen. Experimental study on partial oxidation reforming of pyrolysis tar over sewage sludge char. Energy Fuels 2016;30(11).

[68] Kruger Jacob S, Rennard David C, Josephson Tyler R, Schmidt Lanny D. Effect of functional groups on autothermal partial oxidation of bio-oil. Part 1: Role of catalyst surface and molecular oxygen. Energy Fuels 2011;25(7).

[69] Moreira Rui, Bimbela Fernando, Gandía Luis M, Ferreira Abel, Sánchez Jose Luis, Portugal António. Oxidative steam reforming of glycerol. A review. Renew Sustain Energy Rev 2021;148:111299.

[70] Kathiraser Yasotha, Oemar Usman, Saw Eng Toon, Li Ziwei, Kawi Sibudjing. Kinetic and mechanistic aspects for CO2 reforming of methane over Ni based catalysts. Chem Eng J 2015;278:62–78.

[71] Abdullah Bawadi, Abd Ghani Nur Azeanni, Vo Dai-Viet N. Recent advances in dry reforming of methane over Ni-based catalysts. J Cleaner Prod 2017;162:170–85.

[72] Manera Christian, Perondi Daniele, Barcellos Thiago, Godinho Marcelo. CO2 gasification of elephant grass: Effect of Ni/mayenite catalyst on dry reforming of tar. Biomass Bioenergy 2020;143:105829.

[73] Gao Yuchen, Aihemaiti Aikelaimu, Jiang Jianguo, Meng Yuan, Ju Tongyao, Han Siyu, et al. Inspection over carbon deposition features of various nickel catalysts during simulated biogas dry reforming. J Cleaner Prod 2020;260:120944.

[74] Sharma Himanshu, Dhir Amit. Hydrogen augmentation of biogas through dry reforming over bimetallic nickel-cobalt catalysts supported on titania. Fuel 2020;279:118389.

[75] Schiaroli N, Lucarelli C, Sanghez de Luna G, Fornasari G, Vaccari A. Ni-based catalysts to produce synthesis gas by combined reforming of clean biogas. Appl Catal A 2019;582:117087.

[76] Szima Szabolcs, Cormos Calin-Cristian. Exergoeconomic analysis for a flexible dry reforming power plant with carbon capture for improved energy efficiency. 2019, p. 1681–6. http://dx.doi.org/10.1016/B978-0-12-818634-3.50281-2.

[77] Chein RY, Chen YC, Yu CT, Chung JN. Thermodynamic analysis of dry reforming of CH4 with CO2 at high pressures. J Nat Gas Sci Eng 2015;26:617–29.

[78] Chein Reiyu, Yang Zeng-Wei. H2S effect on dry reforming of biogas for syngas production. Int J Energy Res 2019;43(8):3330–45.

[79] Amiri Taher Yousefi, Ghasemzageh Kamran, Iulianelli Adolfo. Membrane reactors for sustainable hydrogen production through steam reforming of hydrocarbons: A review. Chem Eng Process Process Intensif 2020;157:108148.

[80] Kim Chang-Hyun, Han Jae-Yun, Lim Hankwon, Lee Kwan-Young, Ryi Shin-Kun. Methane steam reforming using a membrane reactor equipped with a pd-based composite membrane for effective hydrogen production. Int J Hydrogen Energy 2018;43(11):5863–72.

[81] Wang Zhigang, Oemar Usman, Ang Ming Li, Kawi Sibudjing. Oxidative steam reforming of biomass tar model compound via catalytic babi0.05co0.8nb0.15o3-hollow fiber membrane reactor. J Membr Sci 2016;510:417–25.

[82] Wismann Sebastian T, Engbæ k Jakob S, Vendelbo Søren B, Bendixen Flemming B, Eriksen Winnie L, Aasberg-Petersen Kim, et al. Electrified methane reforming: A compact approach to greener industrial hydrogen production. Science 2019;364(6442):756–9.

[83] Hafeez Sanaa, Pallari Elena, Manos George, Constantinou Achilleas. Catalytic conversion and chemical recovery. In: Plastics to energy: Fuel, chemicals, and sustainability implications. Elsevier; 2018, p. 147–72.

[84] Trane R, Dahl S, Skjøth-Rasmussen MS, Jensen AD. Catalytic steam reforming of bio-oil. Int J Hydrogen Energy 2012;37(8):6447–72.

[85] Ferreira-Aparicio Paloma, Benito MJ, Sanz JL. New trends in reforming technologies: From hydrogen industrial plants to multifuel microreformers. Catal Rev - Sci Eng 2005;47(4):491–588.

[86] Rostrup-Nielsen JR. In: Figueiredo José Luís, editor. Sulfur poisoning BT - Progress in catalyst deactivation. Dordrecht: Springer Netherlands; 1982, p. 209–27.

[87] Voss Bodil, Madsen Jørgen, Hansen John B, Andersson Klas J. Topsøe tar reforming in skive - the tough get going. Catal Rev 2016;(May).

[88] Santamaria Laura, Lopez Gartzen, Arregi Aitor, Amutio Maider, Artetxe Maite, Bilbao Javier, et al. Stability of different Ni supported catalysts in the in-line steam reforming of biomass fast pyrolysis volatiles. Appl Catal B 2019;242.

[89] Xing Rong, Dagle Vanessa Lebarbier, Flake Matthew, Kovarik Libor, Albrecht Karl O, Deshmane Chinmay, et al. Steam reforming of fast pyrolysis-derived aqueous phase oxygenates over Co, Ni, and Rh metals supported on MgAl2O4. Catal Today 2016;269.

[90] Italiano C, Bizkarra K, Barrio VL, Cambra JF, Pino L, Vita A. Renewable hydrogen production via steam reforming of simulated bio-oil over Ni-based catalysts. Int J Hydrogen Energy 2019;44(29).

[91] Ochoa Aitor, Arregi Aitor, Amutio Maider, Gayubo Ana G, Olazar Martin, Bilbao Javier, et al. Coking and sintering progress of a Ni supported catalyst in the steam reforming of biomass pyrolysis volatiles. Appl Catal B 2018;233:289–300.

[92] Lónyi Ferenc, Valyon József, Someus Edward, Hancsók Jenő. Steam reforming of bio-oil from pyrolysis of MBM over particulate and monolith supported Ni/γ-Al2O3 catalysts. Fuel 2013;112.

[93] Bartholomew CH. Mechanisms of catalyst deactivation. Appl. Catalysis A: General 2001;212(1–2):17–60.

[94] Nasrallah M Deraz. Sintering process and catalysis. Int J Nanomater Nanotechnol Nanomed 2018.

[95] Vicente Jorge, Montero Carolina, Ereña Javier, Azkoiti Miren J, Bilbao Javier, Gayubo Ana G. Coke deactivation of Ni and co catalysts in ethanol steam reforming at mild temperatures in a fluidized bed reactor. Int J Hydrogen Energy 2014;39(24):12586–96.

[96] Montero Carolina, Ochoa Aitor, Castaño Pedro, Bilbao Javier, Gayubo Ana G. Monitoring Ni 0 and coke evolution during the deactivation of a Ni/La 2 O 3 –αAl 2 O 3 catalyst in ethanol steam reforming in a fluidized bed. J Catal 2015;331:181–92.

[97] Ochoa Aitor, Bilbao Javier, Gayubo Ana G, Castaño Pedro. Coke formation and deactivation during catalytic reforming of biomass and waste pyrolysis products: A review. Renew Sustain Energy Rev 2020;119.

[98] de Jong Krijn Pieter. Synthesis of solid catalysts. Wiley; 2009,

[99] Arce Pedro, Oyanader Mario, Whitaker Stephen. The catalytic pellet: A rich prototype for engineering up-scaling. Chem Eng Edu 2007;41:185–94.

[100] Baharudin Luqmanulhakim, Watson Matthew. Monolithic substrate support catalyst design considerations for steam methane reforming operation. Rev Chem Eng 2017;Ahead of Print:481–501.

[101] Danaci Simge, Protasova Lidia, Lefevere Jasper, Bedel Laurent, Guilet Richard, Marty Philippe. Efficient CO2 methanation over Ni/Al2O3 coated structured catalysts. Catal Today 2016;273:234–43.

[102] Heck Ronald M, Gulati Suresh, Farrauto Robert J. The application of monoliths for gas phase catalytic reactions. Chem Eng J 2001;82(1–3):149–56.

[103] Goyal Nikhil, Pant KK, Gupta Rohit. Hydrogen production by steam reforming of model bio-oil using structured Ni/Al2O3 catalysts. Int J Hydrogen Energy 2013;38(2):921–33.

[104] Yu Yong Ho, Sosna Mihail H. Modeling for industrial heat exchanger type steam reformer. Korean J Chem Eng 2001;18(1):127–32.

[105] Choi Il-Ho, Seo Myung Won, Ra Ho Won, Lee Kwan-Young, Hwang Kyung-Ran. Advanced approach for catalytic decomposition of tar: Electrically heated catalyst system. Chem Eng Process - Process Intensif 2021;165.

[106] Tao Jun, Lu Qiang, Dong Changqing, Du Xiaoze, Dahlquist Erik. Effects of electric current upon catalytic steam reforming of biomass gasification tar model compounds to syngas. Energy Convers Manage 2015;100:56–63.

[107] Yuan Lixia, Chen Yaqiong, Song Chongfu, Ye Tongqi, Guo Qingxiang, Zhu Qingshi, et al. Electrochemical catalytic reforming of oxygenated-organic compounds: A highly efficient method for production of hydrogen from bio-oil. Chem Commun 2008;(41):5215–7.

[108] Zhang Q, Nakaya M, Ootani T, Takahashi H, Sakurai M, Kameyama H. Simulation and experimental analysis on the development of a co-axial cylindrical methane steam reformer using an electrically heated alumite catalyst. Int J Hydrogen Energy 2007;32(16).

[109] Renda Simona, Cortese Marta, Iervolino Giuseppina, Martino Marco, Meloni Eugenio, Palma Vincenzo. Electrically driven SiC-based structured catalysts for intensified reforming processes. Catal Today 2020.

[110] Lind Anna, Vistad Ørnulv, Sunding Martin Fleissner, Andreassen Kari Anne, Cavka Jasmina Hafizovic, Grande Carlos A. Multi-purpose structured catalysts designed and manufactured by 3D printing. Mater Des 2020;187.

[111] Bogdan Elżbieta, Michorczyk Piotr. 3D printing in heterogeneous catalysis—The state of the art. Materials 2020;13(20).

[112] Manzano J Sebastián, Weinstein Zachary B, Sadow Aaron D, Slowing Igor I. Direct 3D printing of catalytically active structures. ACS Catal 2017;7(11).

[113] Konarova Muxina, Aslam Waqas, Ge Lei, Ma Qing, Tang Fengqiu, Rudolph Victor, et al. Enabling process intensification by 3 D printing of catalytic structures. ChemCatChem 2017;9(21).

[114] Díaz-Marta Antonio S, Tubío Carmen R, Carbajales Carlos, Fernández Carmen, Escalante Luz, Sotelo Eddy, et al. Three-dimensional printing in catalysis: Combining 3D heterogeneous copper and palladium catalysts for multicatalytic multicomponent reactions. ACS Catal 2018;8(1).

[115] Azuaje Jhonny, Tubío Carmen R, Escalante Luz, Gómez Mónica, Guitián Francisco, Coelho Alberto, et al. An efficient and recyclable 3D printed α-Al 2 O 3 catalyst for the multicomponent assembly of bioactive heterocycles. Appl Catal A 2017;530.

[116] Li Xin, Li Wenbin, Rezaei Fateme, Rownaghi Ali. Catalytic cracking of n-hexane for producing light olefins on 3D-printed monoliths of MFI and FAU zeolites. Chem Eng J 2018;333.

[117] Stuecker John N, Miller James E, Ferrizz Robert E, Mudd Jason E, Cesarano Joseph. Advanced support structures for enhanced catalytic activity. Ind Eng Chem Res 2004;43(1):51–5.

[118] Martínez-Rodríguez Angel, Abánades Alberto. Comparative analysis of energy and exergy performance of hydrogen production methods. Entropy 2020;22(11).

[119] Wang Tiejun, Yang Yong, Ding Mingyue, Liu Qiying, Ma Longlong. Autothermal reforming of biomass raw fuel gas to syngas in a novel reformer: Promotion of hot-electron. Appl Energy 2013;112.

[120] Gao Ningbo, Liu Shuang, Han Ying, Xing Chen, Li Aimin. Steam reforming of biomass tar for hydrogen production over nio/ceramic foam catalyst. Int J Hydrogen Energy 2015;40(25).

[121] Ambrosetti Matteo, Beretta Alessandra, Groppo Gianpiero, Tronconi Enrico. A numerical investigation of electrically-heated methane steam reforming over structured catalysts. Front Chem Eng 2021;3.

[122] Zaini Ilman Nuran, Sophonrat Nanta, Sjöblom Kurt, Yang Weihong. Creating values from biomass pyrolysis in Sweden: Co-production of H2, biocarbon and bio-oil. Processes 2021;9(3).

[123] Wang Shule, Wen Yuming, Shi Ziyi, Nuran Zaini Ilman, Göran Jönsson Pär, Yang Weihong. Novel carbon-negative methane production via integrating anaerobic digestion and pyrolysis of organic fraction of municipal solid waste. Energy Convers Manage 2021;115042.