Biofuels Production by Biomass Gasification: A Review

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Abstract: The production of biofuels from renewable sources is a major challenge in research. Methanol, ethanol, dimethyl ether (DME), synthetic natural gas (SNG), and hydrogen can be produced from syngas which is the result of the gasification of biomasses. Syngas composition varies according to the gasification technology used (such as fixed bed reactors, fluidized bed reactors, entrained flow reactors), the feedstock characteristics, and the operating parameters. This paper presents a review of the predominant biomass gasification technologies and biofuels obtained from syngas by biomass gasification.

1. Introduction

Currently, there is a growing interest in renewable energy sources because of the cost and the environmental impact of crude oil. The use of renewable sources also is becoming increasingly important because of other environmental concerns such as greenhouse gas emissions (GHG) [1–3]. Biomass could be exploited to produce biofuels such as methanol, ethanol, dimethyl ether (DME), synthetic natural gas (SNG), hydrogen, etc. Several governments have launched programs to promote renewable sources, many with a specific focus on biofuels. The European Union has the goal of a 10% share of biofuels in the transport industry by 2020 [4]; however, in the US, biofuels production is expected to reach 36 billion gallons by 2022 [5]. Industrial plants are increasingly focusing their activities on biogas production for power generation or on biomethane upgrading for grid injection. Biogas production is a simple and consolidated technology with a low level of organic transformation into biogas, approximately 5–10 wt. %, dependent on the biomass type as well as on the operative conditions [6,7]. Biodiesel and bioethanol are other biofuels which could be produced with mature technologies, but in both cases, the biomasses used are in competition with the food chain (vegetable oils, cereals, beets, and sugar cane), arising several ethical and social issues [8]. A solution to avoid food/no-food competition is the use of lignocellulosic biomass, which is a residual or derivative from agro-industrial wastes. These second generation biofuels do not compete with food production [9–11]. The purpose of this review is to provide a critical overview of biofuels synthesized from syngas by biomass gasification [12]. The production of high value-added biofuels like methanol, bio-hydrogen, ethanol, DME, SNG and biofuels via Fischer-Tropsch (FT) [13–16] will be addressed in terms of thermodynamics and kinetics. Studies by E.U. International Energy Agency and U.S. Department of

Energy show that it is possible to obtain a 50% CO_2 reduction by 2050, bringing biofuel use to 26% [17]. Biofuels might represent a viable way for sustainable development and economic growth in the near future. In 2011, approximately 3.4 million workers were already employed in this industry [18,19].

2. Syngas Production via Gasification Technologies

Gasification is a key process for the thermo-chemical conversion of biomass. In the presence of a gasifying agent (GA), biomass is converted to a multifunctional gaseous mixture, usually called syngas or synthesis gas, which can be used for the production of energy (heat and/or electricity generation), chemicals (ammonia), and biofuels. Furthermore, a solid residue after biomass conversion (Char) is generally found [20–23]. Syngas consists of a mixture of CO, H_2, CO_2, CH_4 (primary components) and H_2O, H_2S, NH_3, tar, and other trace species (secondary components), with a composition dependent on feedstock type and characteristics, operating conditions (i.e., GA, gasifier temperature and pressure, type of bed materials), and gasification technology [24–27].

According to the International Energy Agency (IEA) Bioenergy Task 33E—Thermal Gasification of Biomass database [28], there are 114 operational biomass gasification plants globally, 14 idle/on hold biomass gasification plants, and 13 under construction/planned biomass gasification plants. This results in a total number of 141 plants, with the following end use of the syngas produced (Figure 1): 106 plants for power production, with global electric power produced from biomass-derived syngas $\cong$ 356 MW and global thermal power produced from biomass-derived syngas $\cong$ 185 MW; 24 plants for liquid fuel production (methanol, ethanol, DME, FTS, diesel, gasoline), with global production of liquid fuel from biomass-derived syngas $\cong$ 750,000 t/year; 8 plants for gaseous fuel production (SNG and H_2), with global production of gaseous fuel from biomass-derived syngas $\cong 3.2 \times 10^8$ Nm^3/year; 7 plants for chemical production (various), with global production of chemical from biomass-derived syngas $\cong$ 9000 t/year. It is worth highlighting that in four plants, syngas is used for both power production and fuel production.
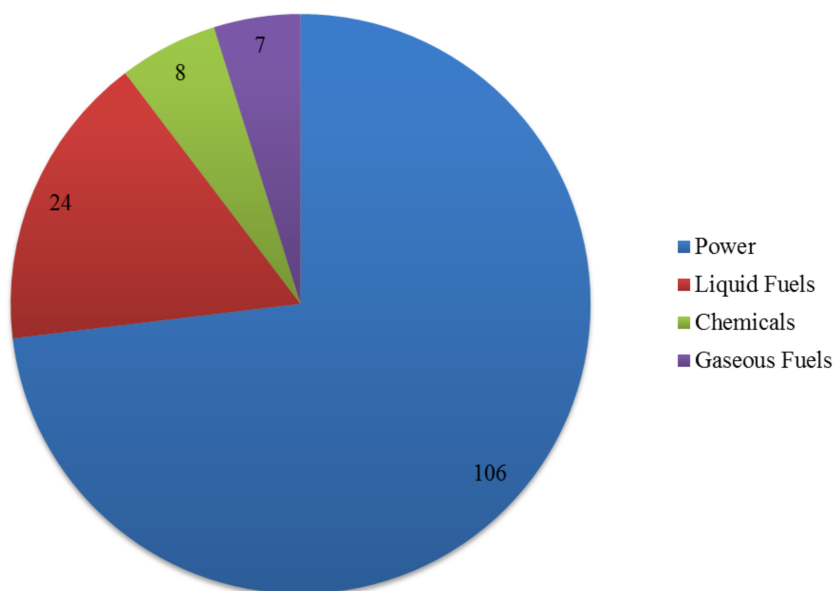

Figure 1. Number of biomass gasification plants (operational/idle/on hold/under construction/planned) as function of biomass-derived syngas end use (adapted from IEA T33 database [28]).

Through an analysis of the number of biomass gasification plants that are operational/idle/on hold/under construction/planned as a function of start-up year for each end use considered (Figure 2), it is possible to observe that the use of syngas for power production increased in the period 1985–2009, achieving a maximum number of plants (12). After this period, use decreased, with only four plants

opened in 2016 and two plants in 2017, with one new plant planned in 2018 and one planned in 2019. This trend may be due to the recent termination of public funds, which were allocated for energy production from renewable sources by national governments. However, an opposite trend can be observed for liquid fuels as an end use of syngas. Since 2007, the number of biomass gasification plants where the syngas produced is used for liquid fuel production has increased. Four new plants are planned as a result of the continuous improvement of the technological maturity of the processes. For both gaseous fuels and chemicals, the trend seems to be almost constant with time. Although no new plants are planned for 2018/2019 for chemical production, one new plant is planned in 2018 and one new plant is planned in 2019 for gaseous fuel production. A list of plants of biofuel production is reported in Section 3.
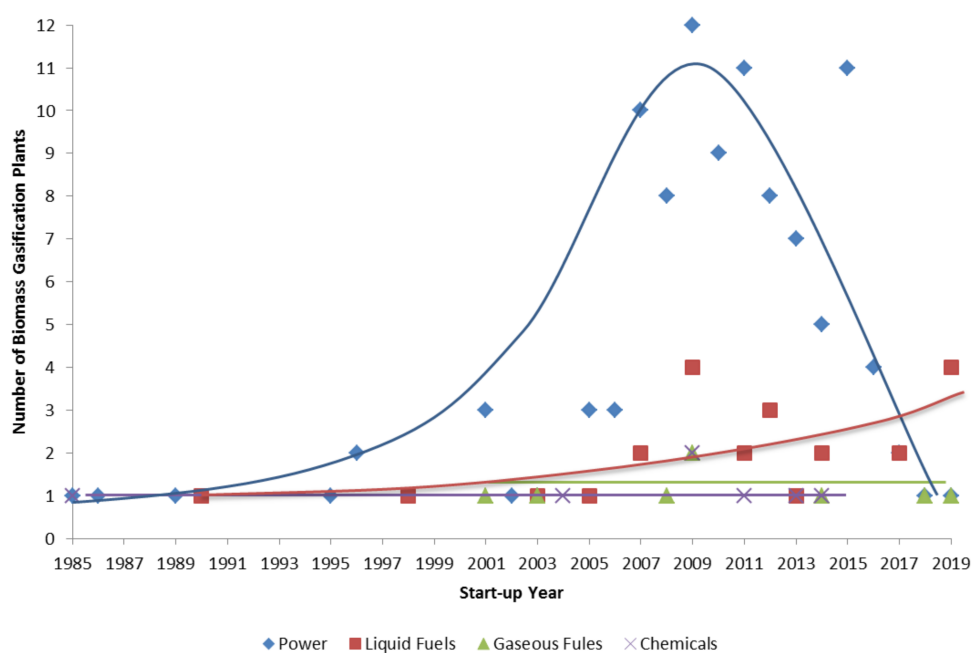

Figure 2. Trend of number of biomass gasification plants (operational/idle/on hold/under construction/planned) as a function of start-up time—trend lines are qualitative (self-processed data from IEA T33 database [28]).

Usually, gasification is divided into four steps: drying (endothermic step), pyrolysis (endothermic step), oxidation (exothermic stage), and reduction (endothermic stage). Tar-reforming can also be added as a step to produce light hydrocarbons from large tar molecules [20,21,23,29,30]. A simplified gasification reaction is reported below (Equation (1)) [21] and the main reactions are collected in Table 1 [20,21,23,29–31].

The heat required for the gasification process can be auto-thermally provided by exothermic combustion reactions or allo-thermally provided from external sources [32,33].
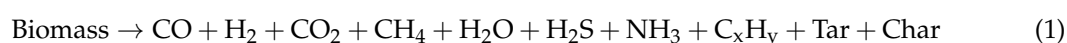
$$\text{Biomass} \rightarrow CO + H_2 + CO_2 + CH_4 + H_2O + H_2S + NH_3 + C_xH_y + \text{Tar} + \text{Char} \tag{1}$$

Table 1. Main reactions of the gasification process.

Gasification Step	Reaction
Pyrolysis	Biomass $\rightarrow$ CO + H$_2$+CO$_2$+CH$_4$+H$_2$O + Tar + Char
Oxidation	Char + O$_2$ $\rightarrow$ CO$_2$ Char + O$_2$ $\rightarrow$ CO$_2$ (*Char Oxidation*) C + $\frac{1}{2}$O$_2$ $\rightarrow$ CO (*Partial Oxidation*) H$_2$ + $\frac{1}{2}$O$_2$ $\rightarrow$ H$_2$O (*Hydrogen Oxidation*)
Reduction	C + CO$_2$ $\leftrightarrow$ 2CO (*Boudouard Reaction*) C + H$_2$O $\leftrightarrow$ CO + H$_2$ (*Reforming of Char*) CO + H$_2$O $\leftrightarrow$ CO$_2$ + H$_2$ (*Water Gas Shift (WGS) Reaction*) C + 2H$_2$ $\leftrightarrow$ CH$_4$ (*Methanation Reaction*) CH$_4$ + H$_2$O $\leftrightarrow$ CO + 3H$_2$ (*Steam Reforming of Methane*) CH$_4$ + CO$_2$ $\leftrightarrow$ 2CO + 2H$_2$ (*Dry Reforming of Methane*)
Tar Reforming	Tar + H$_2$O $\rightarrow$ H$_2$ + CO$_2$ + CO + C$_x$H$_y$ (*Steam Reforming of Tar*)

2.1. Gasification Parameters

Short overviews of the effects of the main types and characteristics of the biomass fed and the main gasification parameters on process performance is summarized in Tables 2 and 3, respectively [20, 21,24,25,32,34–37].

Table 2. Effect of feedstock characteristics on gasification process performance.

Feedstock Parameter	Observation
biomass type [32,34,38,39]	• Cellulose, hemicellulose and lignin are the principal components of *biomass* and their role during the gasification process is fundamental. • The syngas yield is related to the proportion between cellulose and hemicellulose, while the residue yield is determined by the lignin. • The higher the ratio of cellulose and hemicellulose to lignin, the higher the syngas yield. • Chemical and physical properties and the main components of several biomasses are reported in Tables 4 and 5, respectively. • Composition of syngas produced by several biomasses through different gasifiers and operative conditions is reported in Table 6.
moisture content [25,32,34,35,40,41]	○ By reducing *moisture content*, energy efficiency increases, syngas quality improves, syngas Higher Heating Value (HHV) increases, and conversion emissions decreases. ○ With moisture content higher than 30–40% w/w, an increase in tar content can be observed, to which corresponds a decrease in gasifier temperature and gas yield. ○ A moisture content in the range 10–20% w/w is generally required for conventional gasification technologies, keeping bed temperatures moderately stable. ○ Updraft fixed bed gasifiers can be operated with a moisture content up to 60% w/w, while downdraft fixed bed gasifiers can be operated with a maximum moisture content of 25% w/w. ○ Supercritical water gasification and plasma technologies can be used for the gasification of high-moisture-containing biomasses, although several drawbacks have to be considered, such as high installation costs and very significant energy requirements.
particle size [32,38,42–48]	■ By reducing particle size, surface area increases and diffusion resistance decreases. ■ Heat and mass transfer between particles improves, reaction rates increase and fuel conversion and gasification efficiencies enhance, resulting in total syngas yield increases, H$_2$ concentration increases and tar and char yields decrease and improving carbon conversion efficiency. ■ Particle size reduction may increase the pre-treatment cost of the feedstock. ■ Large-sized particles decrease the pre-treatment cost but feeding is complicated and devolatilization and overall gasification performance are reduced. ■ The effect of particle size on gasification performance may be reduced at higher temperatures. ■ For conventional gasifiers, particle size varies in the range 0.15–51 mm. ■ Particle size up to 51 mm can be tolerated by fixed bed reactors that are less sensitive to particle size due to longer residence times, if compared with entrained flow gasifiers. ■ Entrained flow gasifiers require a particle size not higher than 0.15 mm (pulverized). ■ Bubbling bed reactors can tolerate particle size up to 6 mm.

Table 2. *Cont.*

Feedstock Parameter	Observation
ash content [24,31,32,34,37]	➢ Biomass with *ash content* lower than 2% w/w can be used as feedstock material for fixed bed updraft gasifiers. ➢ Biomass with ash content higher than 10% w/w, such as residues of cereal crops, oil seed crops, root crops, grasses and flowers, causes high slag formation, particularly in downdraft gasification. ➢ Biomass with ash content higher than 20% w/w, such as rice husk, is the most difficult biomass for gasification. ➢ In order to decrease slagging, a gasifier should be preferably operated below ash flow temperature or above its melting point.

Table 3. Effect of operating conditions on the gasification process performance.

Gasification Parameter	Observation
bed material [32,36,49–53]	• *Bed material* plays a multifunctional role in the gasification process. • Bed material can be inert, acting as energy transfer medium for biomass conversion. • Bed material can show catalytic activity, improving syngas quality, capturing CO_2, promoting reaction reforming and favouring tar cracking. • Silica, dolomite, olivine, limestone, alkaline metal oxides and Ni and K-based catalysts are among the most used bed materials.
operating parameters [21,24,25,30,34,36,41,44,49, 54–59]	○ Gasification performance, syngas yield, and its composition strictly depend on the main *operating parameters*: partial pressure of gasifying agent (GA), heating rate and temperature, and pressure of gasification. ○ Reactivity of biomass char is influenced by the partial pressure of the GA. ○ An increase of syngas yield and a decrease of tar production can be obtained by increasing the heating rate. ○ High char conversion (conversion of carbon to char) and high CO and H_2 contents and low tar content can be achieved by operating gasification process at high temperature. ○ The typical temperature ranges for gasification of agricultural waste, RFD and woody biomass are 750–850 °C, 800–900 °C and 850–950 °C, respectively. ○ Temperature higher than 1000 °C presents two main drawbacks: ash melting and rigorous reactor specification requirement. ○ Gasification can be operated at atmospheric pressure or at higher pressures. ○ A decrease in light hydrocarbons and tar yield along with complete conversion of carbon can be obtained with pressurized regimes and larger equivalent ratios. ○ For some downstream applications of syngas, e.g., biofuels, fuel for turbines and engines etc., high-pressure syngas is required, therefore pressurized gasification processes are recommended although they are more technologically complex.
GAs [21,24,38,41,42,60–65]	■ *GAs* (air, oxygen, steam and CO_2) influence the quality of syngas, in terms of composition and heating value. ■ Air gasification leads to a syngas with a heating value in the range 4–7 MJ/Nm^3 and with lower concentrations of CO and H_2, as a result of the dilution by nitrogen; moreover, combustion of H_2 and CO takes place, resulting in CO_2 concentration increase. ■ O_2 gasification (expensive) leads to a syngas with a heating value up to 28 MJ/Nm^3, with higher concentrations of CO and H_2 and low concentration of tar. ■ Steam, as a GA, leads to a product gas with a heating value in the range 10–18 MJ/Nm^3 and with higher H_2 concentration, as a result of the WGS reaction, despite the energy required by the process increases due to endothermic step of gasification. ■ A combination of steam and oxygen can also be used, thus favouring biomass conversion and producing a syngas with an increase in CO_2 concentration and a decrease in CO and H_2 concentrations. ■ CO_2 gasification produces a CO rich syngas as a result of the slow reaction between CO_2 and carbon and with high heating value; however, an external heat supplier is required.
equivalence ratio (ER) [24,32,41,42,66–73]	➢ *Equivalence ratio (ER)* is the air to fuel ratio required for gasification and the stoichiometric air to fuel ratio required for combustion. ➢ ER values are lower than 1, with optimal value for biomass gasification in the range 0.2–0.3, both for fixed bed gasifiers and for fluidized bed gasifiers while entrained flow gasifiers usually require a 20% higher ER. ➢ At ER < 0.2, gasification is incomplete, while at ER > 0.4, gasification approaches combustion. ➢ By decreasing ER, H_2, and CO concentrations of the syngas increase. ➢ By increasing ER, H_2, and CO concentrations decrease while CO_2 concentration increases and a reduction of syngas heating value can be found. ➢ Tar cracking can be promoted by higher ERs, due to higher O_2 available for tar reforming reactions. ➢ Moisture and volatile contents influence ER which increases with a moisture content up to 15% while high concentration of volatiles leads to higher concentration tar.

Gasification Parameter	Observation
steam to biomass ratio (SB) [25,30,35,37,38,42,66,74,75]	✔ *SB* is defined as the ratio between the flow rate of the incoming steam and the flow rate of the biomass fed. ✔ SB optimal value for biomass gasification varies in the range 0.3–1.0. ✔ Higher H_2 and CO_2 concentrations were found for SB values in the range 1.35–4.04. ✔ In terms of SB capacity, fixed bed gasifiers outperform fluidized reactors that are in turn better than entrained flow gasifiers ✔ By increasing SB, H_2 and CO_2 concentrations and heating value of the syngas increase while CO and tar concentrations decrease, thanks to WGS, reforming and cracking reactions, which are promoted by steam. ✔ An excess of steam leads to a reduction of temperature, favouring tar formation; moreover, the higher the SB the higher the energy required by the gasification process.

Proximate analysis, elemental analysis and higher heating value of various biomass types/typologies are listed in Table 4.

Table 4. Chemical and physical properties of several biomass types/typologies [76–85].

Biomass Type/Typology	Proximate Analysis (% w/w)				Elemental Analysis (% w/w$_{dry}$)					HHV (MJ/kg$_{dry}$)
	Moisture	Ash	Volatile	Fixed Carbon	C	H	N	O	S	
Shells *	11–14	1–2	74–78	20–25	48–51	6	0.2–0.5	41–44	0.01–0.03	18–20
Pruning **	7–25	0.5–4	70–85	12–20	45–49	5–6	0.1–0.8	36–44	0.01–0.08	16–18
Straw ***	7–12	5–15	67–76	16–18	41–47	5–6	0.3–6	36–44	0.04–0.2	15–18
Dry Exhausted olive	9	4	77	19	51	6	0.3	38	0.02	20
Miscanthus	4	5	71	19	45	5	0.5	40	0.08	18
Pine	12.0	0.5	71.5	16.0	51.6	4.9	0.9	42.6	N.D.$^{\#}$	20.2
Holm-oak	9.5	2.4	70.2	17.8	51.1	5.3	0.9	42.7	N.D.$^{\#}$	19.4
Eucalyptus	10.6	0.7	74.8	13.9	52.8	6.4	0.4	40.4	N.D.$^{\#}$	21.2
Pine	10.0	0.4	73.6	15.7	52.1	6.36	0.07	41.0	0.05	17.8
Oak	7.3	3.7	12.7	83.6	49.9	5.98	0.21	42.6	0.05	19.1
Barley Straw	2.7	4.4	75.6	17.3	42.9	5.53	0.56	45.5	0.25	16.2
Hay	9.3	4.2	86.5	17.9	45.5	6.1	1.14	39.2	0.16	17.2
Miscanthus	9.0	1.7	73.5	18.5	47.5	6.2	0.73	40.7	0.15	19.4
Microalgae	5.1	19.9	64.5	10.4	52.7	7.22	8.01	28.9	0.49	16.6

* Shells of pine, hazel, walnuts and almonds. ** Pruning of beech, oak, spruce, poplar, willow, eucalyptus, grape, olives. *** Straws of wheat, corn, rye, barley, rice. $^{\#}$ Not Detected.

Cellulose, hemicellulose and lignin contents of several biomasses are listed in Table 5.

Table 5. Main components of several biomass types [86,87].

Biomass Type	Biomass Composition (% w/w)			
	Cellulose	Hemicellulose	Lignin	Others
Softwood	41	24	28	7
Hardwood	39	35	20	7
Wheat straw	40	28	17	15
Rice straw	30	25	12	33
Bagasse	38	39	20	3
Oak wood	34.5	18.6	28	-
Pine wood	42.1	17.7	25	-
Birch wood	35.7	25.1	19.3	-
Spruce wood	41.1	20.9	28	-
Sunflower seed hull	26.7	18.4	27	-
Coconut shell	24.2	24.7	34.9	-
Almond shell	24.7	27	27.2	-
Poultry litter	27	17.8	11.3	20
Deciduous plant	42	25	21.5	11.5
Coniferous plant	42	26	30	2
Willow plant	50	19	25	6
Larch plant	26	27	35	12

Composition and lower heating value of syngas, produced by several biomasses through different operative conditions (GA, equivalent ratio, steam to biomass ratio (SB), and temperature) and gasifiers (fluidized bed and fixed bed) are reported in Table 6.

Table 6. Composition of syngas from several biomass types [25,43,44,88–91].

Biomass Type	Syngas Composition (% v/v)				LHV (MJ/Nm³)	GA	ER	SB	T (°C)	GR
	CO	H₂	CH₄	CO₂						
Empty Fruit Bunch	21–36	10–38	5–14	10–65	7.5–15.5	air	0.15–0.35	-	700–1000	FlB
Pine sawdust	35–43	21–39	6–10	18–20	7.4–8.6	air-steam	0.22	2.7	700–900	FlB
Bamboo	23.5–30.6 % m/m	6.6–8.1 % m/m	4–5 % m/m	59–63 % m/m	1.6–1.9	air	0.4	-	400–600	FlB
α-cellulose	6.5–11.2	13.5–18.5	2.2–3.7	26.3–27.7	6.5–7.6	air-steam	0.27	0–1.5	800	FlB
Empty Fruit Bunch	32–45	18.3–27.4	12–15	16.6–36	12.3–15.3	air	0.15–0.35	-	850	FlB
Bamboo	23.5–30.6 % m/m (air); 36.1–40.3 % m/m (air-steam);	6.6–8.16 % m/m (air);10.9–16.5 % m/m (air-steam);	N.A.	N.A.	N.A.	air & air-steam	0.4	0:1; 1:1	400–600	FlB
Palm oil wastes	15–25	48–60	4–5	20–25	9.1–11.2	steam	-	1.3	750–900	FiB
Palm oil wastes	14–33	47–58	3–6	14–26	8.7–12	steam	-	0.67–2.67	800	FiB
Olive kernel	15–20% w/w	20–30% w/w	10–12% w/w	40–55% w/w	8.8–10.4	air	0.14–0.42	-	950	FiB

N.A. = not available; GA = gasifying agent; ER = equivalence ratio; SB = steam to biomass ratio; T = temperature; GR = gasification reactor; FlB = fluidized bed; FiB = fixed bed.

2.2. Gasification Reactors

Biomass gasification technologies can be classified into three types: fixed bed gasifiers, fluidized bed gasifiers, and entrained flow gasifiers [20].

Fixed bed gasifiers are considered the best choice for small-scale power generation plants of 10 MW [42]. They are classified as updraft and downdraft gasifiers [32]. In the former, biomass is supplied from the top, while the GA t is supplied from the bottom (counter-current). In the latter, the biomass and GA are introduced from the top (co-current) (Figure 3). The operating principle of updraft and downdraft gasifiers is shown in Figure 3 [24]. For updraft reactors, the sequence of the biomass is drying, pyrolysis, and reduction, finally arriving at the combustion zone, with syngas drawn out from the top. For downdraft reactors, both biomass and GA are supplied in the drying zone, going the through pyrolysis, combustion, and reduction, with syngas drawn out from the bottom. It is worth noting that in the downdraft configuration, gaseous products from pyrolysis are sent to the reduction zone, while in the updraft configuration, they are directly found in the syngas.
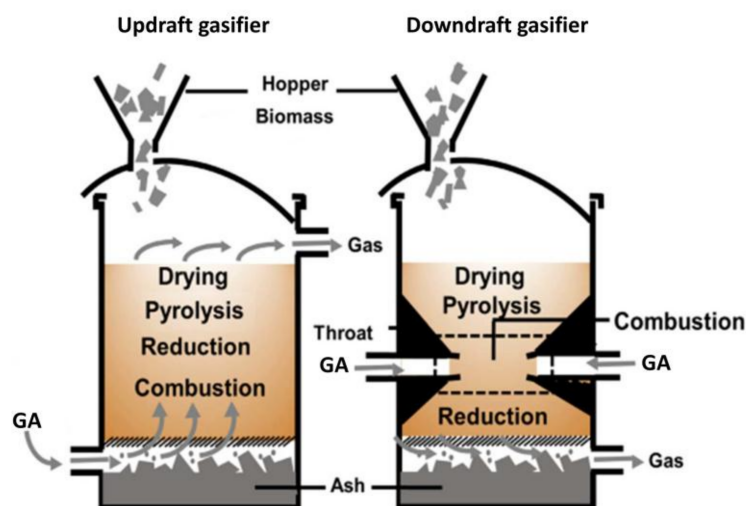

Figure 3. Fixed bed gasifier schematization (adapted from Sikarwar et al. [32]).

Updraft gasifiers offer high thermal efficiency attributable to range of factors including good contact between the biomass and GA, small pressure drop, slight slag formation, as well as simple and robust design. Their main drawbacks include a high content of tar in syngas as well as limited flexibility in loading and process operation [20,21,41]. Operating temperature varies from a minimum of 650–700 °C to a maximum of 950–1150 °C [24,92–94]. Several research groups [24,92,94] have investigated syngas composition from several biomass updraft gasifiers with different gasification conditions, such as biomass type, gasification temperature, GA, and equivalence ratio (ER), highlighting that:

- H_2 composition varies from a minimum of 1.6–3% v/v (biomass type = mesquite wood; gasification temperature $\cong$ 1150 °C; GA = air; ER = 2.7) to a maximum of 30–50% v/v (biomass type = cedar wood; gasification temperature = 650–950 °C; GA = oxygen; ER = 0–0.3);
- CO composition varies from a minimum of 13–21% v/v (biomass type = mesquite wood; gasification temperature $\cong$ 1150 °C; GA = air; ER = 2.7) to a maximum of 22–25% v/v (biomass type = cedar wood; gasification temperature = 650–950 °C; GA = oxygen; ER = 0–0.3);
- CO_2 composition varies from a minimum of 9–12% v/v (biomass type = juniper wood; gasification temperature $\cong$ 1050 °C; GA = air; ER = 2.7) to a maximum of 25–30% v/v (biomass type = cedar wood; gasification temperature = 650–950 °C; GA = oxygen; ER = 0–0.3);

- CH$_4$ composition varies from a minimum of 1.5–1.8% v/v (biomass type = juniper wood; gasification temperature $\cong$ 1050 °C; GA = air; ER = 2.7) to a maximum of 8–10% v/v (biomass type = cedar wood; gasification temperature = 650–950 °C; GA = oxygen; ER = 0–0.3);
- Higher Heating Value varies from a minimum of 2.4–3.5 MJ/Nm^3 (biomass type = mesquite wood; gasification temperature $\cong$ 1150 °C; GA = air; ER = 2.7) to a maximum of 6.5–12.1% v/v (biomass type = cedar wood; gasification temperature = 650–950 °C; GA = oxygen; ER = 0–0.3).

Aljbour and Kawamoto investigated the effect of gasification conditions such as residence time, ER, S/C ratio, and gasification temperature on tar concentrations in the syngas, with cedar wood used as biomass feedstock to an updraft gasifier [93]. They found a variation of tar content from $\cong$30 g/Nm^3 to less than 1 g/Nm^3, highlighting that higher temperatures, along with sufficient contact time, can contribute to Polycyclic Aromatic Hydrocarbons reduction. Moreover, PAH conversion can be slightly increased by steam, while PAH contents can be greatly reduced by increasing the ERs.

Downdraft gasifiers produce low-tar and low-particulate syngas [95] but their main drawbacks include a difficult control of temperature [24], moreover biomass with low moisture content (<20–25% w/w) [21,96] and with low ash content [97,98] is required, as well as homogeneity of biomass input [20,41]. Operating temperature varies from a minimum of 900 °C to a maximum of 1000–1050 °C [99].

Several research groups [24,99–101] investigated syngas composition from several biomass downdraft gasifiers with different gasification conditions, such as biomass type, gasification temperature, GA, and equivalence ratio (ER), highlighting that:

- H$_2$ composition varies from a minimum of 8–12% v/v (biomass type = wood waste; gasification temperature = 900–1050 °C; GA = air; ER = 0.20–0.35) to a maximum of $\cong$21% v/v (biomass type = eucalyptus wood; gasification temperature = 950 °C; GA = air (two-stage air and premixed air/gas supply); ER = 0.27);
- CO composition varies from a minimum of $\cong$14% v/v (biomass type = eucalyptus wood; gasification temperature = 950 °C; GA = air; ER = 0.27) to a maximum of $\cong$23% v/v (biomass type = hazelnut shells; gasification temperature = 1000 °C; GA = air; ER = 0.35);
- CO$_2$ composition varies from a minimum of 5–8% v/v (biomass type = wood waste; gasification temperature = 900–1050 °C; GA = air; ER = 0.20–0.35) to a maximum of $\cong$11% v/v (biomass type = hazelnut shells; gasification temperature = 1000 °C; GA = air; ER = 0.35);
- CH$_4$ composition varies from a minimum of 1–3% v/v (biomass type = wood waste; gasification temperature = 900–1050 °C; GA = air; ER = 0.20–0.35) to a maximum of $\cong$4% v/v (biomass type = hazelnut shells; gasification temperature = 1000 °C; GA = air; ER = 0.35);
- Higher Heating Value varies from a minimum of 4.5 MJ/Nm^3 (biomass type = wood waste; gasification temperature = 900–1050 °C; GA = air; ER = 0.20–0.35) to a maximum of 6.5% v/v (biomass type = eucalyptus wood; gasification temperature = 950 °C; GA = air (two-stage air and premixed air/gas supply); ER = 0.27).

In terms of downdraft gasifiers, Jordan and Akay [102] and Jaojaruek et al. [101] investigatd syngas tar concentration. This research group observed a variation of tar content in the range 0.376–0.40 g/Nm^3 (biomass type = bagasse; gasification temperature = 1040 °C; GA = air; ER = 0.26). The latter research group found a variation of tar content from 0.0432 g/Nm^3 (biomass type = eucalyptus wood; gasification temperature = 950 °C; GA = air (two-stage air and premixed air/gas supply); ER = 0.27–1.27 g/Nm^3 (biomass type = eucalyptus wood; gasification temperature = 950 °C; GA = air; ER = 0.27).

Fluidized bed gasifiers are a popular choice for large scale power plants because they can be easily scaled up [21]. They are classified as bubbling fluidized bed gasifiers and dual bed gasifiers with separated chambers [21,103]. Both are based on the principle of fluidization of a solid bed. In bubbling fluidized bed gasifiers (fluidization/ GA speed = 2–3 m/s), the GA also acts as a fluidization agent and is supplied from the bottom; accordingly, gasification occurs within the bed (Figure 4). In dual bed gasifiers, gasification occurs in two steps [37,104]. Combustion is first carried out in a combustion

chamber, generating the heat required for gasification. Next, pyrolysis and gasification occur in the presence of high speed gas (5–10 m/s), which is carried out in a bubbling fluidized bed gasifier. Separation between syngas and bed material occurs via a cyclone separator at the outlet of the reactor [20,40] (Figure 4).

Fluidized bed gasifiers are characterized by high mass and heat transfer rate, which secures constant temperatures all over the gasifier and high tolerability to diverse biomass feedstock types. Moreover, catalysts can be used as part of the gasifier bed to enhance tar removal [21,105–108]. Operating temperature varies from a minimum of 700 °C to a maximum of 900 °C with syngas composition of 30–60% v/v H_2, 10–25% v/v CO, 15–20% v/v CO_2, and 8-12% v/v CH_4 for bubbling fluidized bed gasifiers [109,110] and of 22–27% v/v H_2, 27–40% v/v CO, 39–42% v/v CO_2, and 7–9% v/v CH_4 for circulating fluidized bed gasifiers [111].
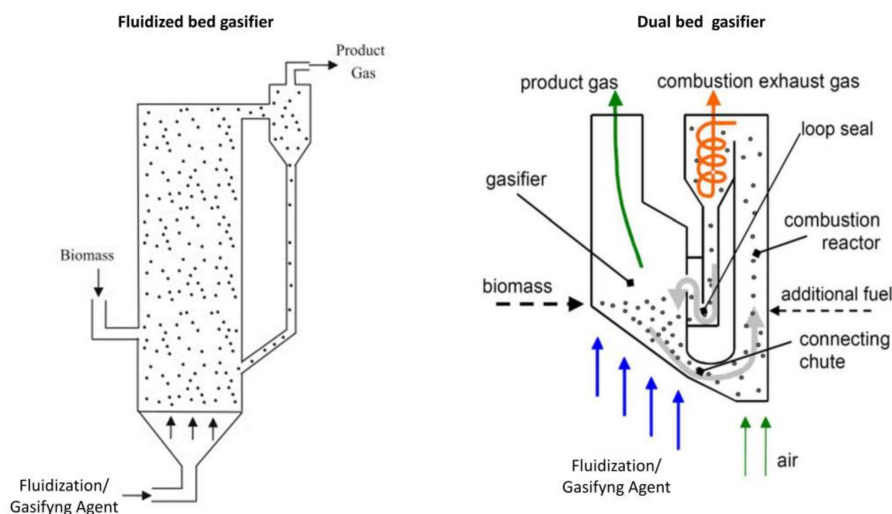

Figure 4. Fluidized bed gasifier schematization (adapted from Loha et al. [112]; Koppatz et al. [103]).

Entrained flow gasifiers are useful for large scale plants [113]. Thanks to the high operating temperature and the use of oxygen as GA, tar compounds are almost completely converted which is a great advantage for biomass gasification. However, when air is used as a GA, for example, in small-scale units, temperatures decrease which results in tar content growth [114]. As reported by Basu [42], a slurry prepared with mixing biomass and water may be used to facilitate feeding into the reactor.

On the other hand, entrained flow gasifiers require fine powder fuel (0.1–1 mm), despite the high energy cost for biomass size reduction is a great drawback for biomass gasification [20,37]. Therefore, a biomass pre-treatment via torrefaction is usually required for entrained flow gasifiers, allowing the aforementioned drawback to be overcome [115–117]. However, as reported by several authors, they are mainly operated as co-gasifiers, suppling both biomass and coal [118–120].

Entrained flow gasifiers are classified into two families: top-fed gasifiers and side-fed gasifiers [32]. A top-fed gasifier is a vertical cylinder reactor where fine particles (pulverized) and the GA are co-currently fed from the top in the form of a jet. Thermo-chemical conversion is performed by an inverted burner. Syngas is taken from the side of the lower section while slag is extracted from the bottom of the reactor (Figure 5). In a side-fed gasifier, the pulverized fed and the GA are co-currently fed by nozzles installed in the lower reactor, resulting in an appropriate mixing of biomass and GA. Syngas is extracted from the top and the slag from the bottom of the vessel (Figure 5).

For both configurations, pressurized fuel into the gasifier is usually provided by a pneumatic feeding system [20,37]. They are highly efficient, with a standard operating temperature and pressure in the range 1300–1500 °C and 20–70 bar, respectively [40].
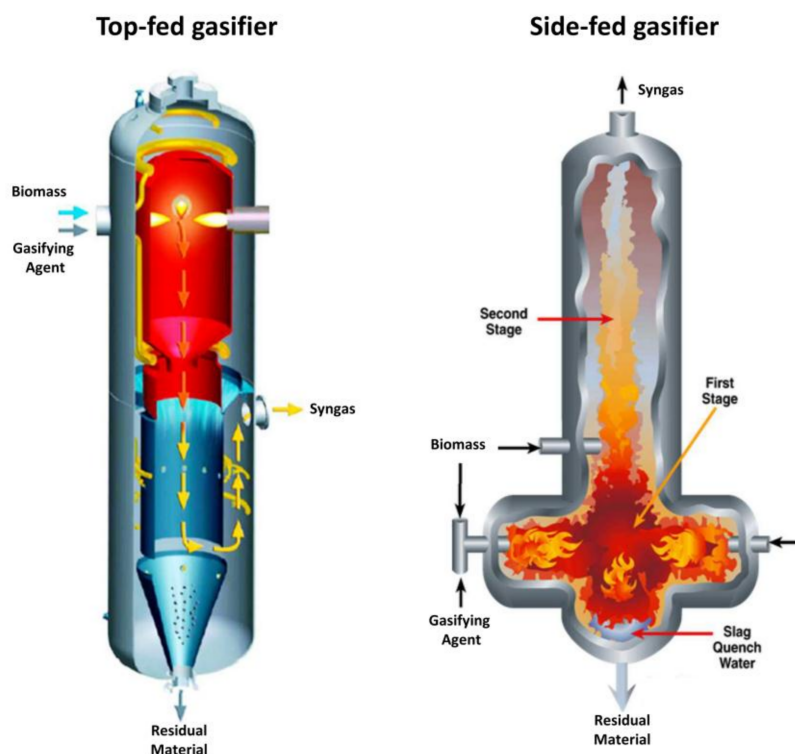
Figure 5. Entrained flow gasifier schematization (adapted from Basu [42] and NETL [121]).

Hernández and colleagues [45] investigated the effect of particle sizes in the range 0.5–8 mm on syngas composition by feeding a top-fed entrained flow gasifier with dealcoholised marc of grape. Experiments were carried out, using air as GA and at gasification temperature and pressure of 1050 °C and 3 bar, respectively. They observed that the lower the particle sizes, the higher the syngas quality. At a particle size of 0.5 mm, the best composition of syngas ($\cong$9% v/v H_2, $\cong$14% v/v CO, $\cong$16% v/v CO_2, 3% v/v CH_4, $\cong$58% v/v N_2) was found.

Briesemeister et al. [114] investigated the effects of operating temperature (900–1300 °C) and equivalence ratio of an air-blown entrained-flow gasifier on tar formation by using air as the GA. They observed tar -oading reduction to less than 0.2 g/Nm^3 at 1300 °C.

The main characteristics and performance of gasifiers are summarized below (Table 7).

Table 7. Characteristics and performance of gasification reactors (adapted from [35,40,45,95]).

Gasifier Type	Flows		Gasification Temperature [°C]	Cold Gas Efficiency [§] [%]	Char Conversion * [%]	Tar Content [g/Nm^3]
	Biomass	**GA**				
Updraft gasifier	downward	upward	950–1150 (max values) Syngas exit temperature: 150–400	20–60	40–85	1–150
Downdraft gasifier	downward	downward	900–1050 (max value) Syngas exit temperature: 700	30–60	<85	0.015–1.5
Fluidized bed gasifier	upward	upward	800–900	<70	<70	10–40
Circulating fluidized bed gasifier	upward	upward	750–850	50–70	70–95	5–12
Entrained flow gasifier	downward	downward	1300–1500	30–90	60–90	$\cong$0–0.2

§ Ratio between the flow of energy in the gas and the energy contained within the fuel [122]. * Conversion of residual carbon of the char [123].

3. Biofuels from Syngas

Biomass-derived syngas is used as a raw material in different thermochemical processes for the production of second-generation biofuels [124], both liquid, (such as methanol, ethanol, dimethylether (DME), and Fischer-Tropsch diesel) and gaseous (such as hydrogen and synthetic natural gas (SNG)) [125,126]. In particular, the type of biomass and its production process strongly influences their composition and heating value [127]. The production of liquid biofuel as an energy carrier could be very cost-effective because it would take the same infrastructure, storage system, and transportation used for Liquefied Petroleum Gas [128–130].

A list of worldwide second-generation biofuel plants, including Start-up Year, Technology Readiness Level (TRL) and Scale, Fed material, Output stream flow, Technology and Country, elaborated from the International Energy Agency (IEA) Bioenergy Task 33E - Thermal Gasification of Biomass database [28] is reported in Table 8. Notably in terms of TRL-Scale, 18 plants are characterized by a TRL higher than "4-5 Pilot". Specifically, 14 plants are characterized by TRL as "4-5 Pilot", 11 plants as "6-7 Demonstration", five plants as "8 First-of-a-kind commercial demo" and two plants as "9 Commercial".

Spath and Dayton [131] carried out a techno-economic screening for the production of fuels and chemicals from biomass-derived syngas, identifying several syngas conversion routes to methanol and its derivatives, such as DEM, ethanol, FT synthesis, hydrogen, and SNG, as described in Figure 6.
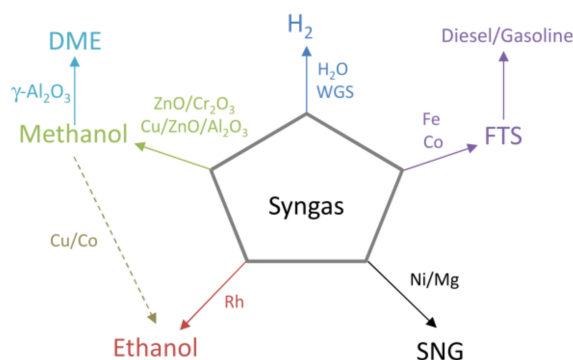

Figure 6. Syngas conversion routes to second-generation biofuels (adapted from Spath and Dayton [131]).

Syngas conversion condition (in terms of pressure, temperature, and catalyst) as well as its composition (in terms of H_2/CO and CO_2) in different biofuels are described in Table 9. Notably, in order to enhance the biofuel production process, the production of syngas has to be carried out in operative conditions which fit conditions required for its end use as much as possible.

Table 8. Worldwide second-generation biofuel plants (self-processed data from IEA T33 database [28]).

Company/Institute/University Name	Start-Up Year	TRL-Scale	Fed	Output (Stream Flow)	Technology	Country
Cutec	1990	TRL 4–5 pilot	straw, wood, dried silage, organic residues	FT liquids (0.02 t/year)	Atmospheric gasifier	Germany
Lahti Energia Oy	1998	TRL 9 commercial	wood waste	renewable diesel (HVO) (70 MWth)	Circulating Fluidized Bed gasifier	Finland
CHP Agnion Biomasse Heizkraftwerk Pfaffenhofen *	2001	TRL 4–5 pilot	wood waste (80,000 t/year)	SNG (32.5 MWth)	Agnion Heatpipe-Reformer	Germany
Enerkem	2003	TRL 4–5 pilot	wood chips, treated wood, sludge, municipal solid waste, petroleum coke, spent plastics and wheat straw	SNG, ethanol (375 t/year), methanol (475 m^3/year)	N.A	Canada
CHOREN Industries GmbH	2003	TRL 4–5 pilot	dry wood chips from recycled wood and residual forestry wood	FT liquids (53 t/year)	N.A.	Germany
Vienna University of Technology/BIOENERGY 2020+	2005	TRL 4–5 pilot	syngas from FICFB gasifier (5 m^3/h)	FT liquids (5 kg/day)	N.A.	Austria
Southern Research Institute **	2007	TRL 4–5 pilot	cellulosic, municipal wastes, syngas (4 t/day)	FT liquids (0.002 t/year), mixed alcohols	N.A.	United States
West Biofuels	2007	TRL 6–7 demonstration	clean wood, waste wood (5 t/day)	FT liquids	Dual fluidized bed thermal reforming	United States
Bio SNG Guessin	2008	TRL 6–7 demonstration	syngas from gasifier (350 m^3/year)	SNG (576 t/year)	N.A.	Austria
Enerkem	2009	TRL 6–7 demonstration	treated wood (i.e., decommissioned electricity poles, and railway ties), wood waste and MSW (48 t/day)	ethanol (4000 t/year), methanol (1000 t/year)	N.A	Canada
GTI Gas Technology Institute ***	2009	TRL 4–5 pilot	pellets, wood chips (24 t/day)	gasoline-type fuels (38 m^3/year)	N.A	United States
H2Herten GmbH ****	2009	TRL 6–7 demonstration	roadside greenery/syngas (13 MW)	H$_2$ (150 m^3/h)	Multi-stage reforming process	Germany
Virent, Inc.	2009	TRL 6–7 demonstration	cane sugar, beet sugar, corn syrup, hydrolysates from cellulosic biomass including pine residues, sugarcane bagasse and corn stover	diesel-type hydrocarbons (30 t/year)	N.A.	United States
BioMCN	2009	TRL 8 first-of-a-kind commercial demo	crude glycerine, others	methanol (200,000 t/year)	N.A.	Netherlands
TUBITAK MRC—ENERGY INSTITUTE—TURKEY	2009	TRL 4–5 pilot	biomass	SNG (0.2 MW)	Down draft fixed bed gasifier	Turkey

Table 8. *Cont.*

Company/Institute/University Name	Start-Up Year	TRL-Scale	Fed	Output (Stream Flow)	Technology	Country
Greasoline GmbH	2011	TRL 4–5 pilot	bio-based oils and fats, residues of plant oil processing, free fatty acids, used bio-based oils and fats (3 t/year)	diesel-type hydrocarbons (2 t/year)	Catalytic cracking of bio-based oils + fats primarily produces diesel fuel-range hydrocarbons	Germany
LTU Green Fuels	2011	TRL 4–5 pilot	black liquor/pyrolysis oil (co-gasif. with black liquor)	methanol (4 t/day), DME (4 t/day)	N.A.	Sweden
BioTfueL-consortium	2012	TRL 4–5 pilot	forest waste, straw, green waste, dedicated crops	FT liquids (60 t/year), jet fuel component	N.A	France
Karlsruhe Institute of Technology (KIT)	2012	TRL 4–5 pilot	straw (0.5 t/h)	gasoline-type fuels (608 t/year)	Fast pyrolysis, high pressure entrained flow gasification, hot gas cleaning, DME- and gasoline synthesis	Germany
INEOS New Planet BioEnergy *****	2012	TRL 4–5 pilot	vegetative waste, MSW (300 t/day)	ethanol (3.469 m^3/h)	N.A.	United States
TUBITAK	2013	TRL 4–5 pilot	combination of hazelnut shell, olive cake, wood chip and lignite blends (0.2 t/h)	FT liquids (250 t/year)	Pressurised fluidized bed gasifier	Turkey
Enerkem Alberta Biofuels LP	2014	TRL 8 first-of-a-kind commercial demo	post-sorted municipal solid waste (MSW) (100,000 t/year)	ethanol (30,000 t/year), methanol	N.A	Canada
Goteborg Energi AB	2014	TRL 6–7 demonstration	forest residues, wood pellets, branches and tree tops	SNG (11,200 t/year)	Repotec indirect gasification technology and Haldor Topsoe fixed bed methanation	Sweden
Karlsruhe Institute of Technology (KIT)	2014	TRL 6–7 demonstration	straw (0.5 t/h)	DME (608 t/year), gasoline-type fuels (360 t/year)	Fast pyrolysis, high pressure entrained flow gasification, hot gas cleaning, DME- and gasoline synthesis	Germany
BioMCN	2017	TRL 8 first-of-a-kind commercial demo	wood chips	methanol (413,000 t/year)	N.A.	Netherlands
Total	2017	TRL 6–7 demonstration	straw, forest waste, dedicated energy crops	FT liquids (200,000 t/year)	N.A.	France
Go Green Fuels Ltd.	2018	TRL 8 first-of-a-kind commercial demo	refuse derived fuel and waste wood (7500 t/year)	SNG (1500 t/year)	N.A.	United Kingdom

Table 8. *Cont.*

Company/Institute/University Name	Start-Up Year	TRL-Scale	Fed	Output (Stream Flow)	Technology	Country
ECN	2019	TRL 6–7 demonstration	N.A.	SNG (300 MW)	N.A.	Netherlands
Fulcrum BioEnergy Sierra Biofuels Plant ******	2019	TRL 9 commercial	waste (20,000 t/year)	FT liquids (314,913 t/year)	N.A.	United States
Red Rock Biofuels	2019	TRL 8 first-of-a-kind commercial demo	N.A.	diesel-type hydrocarbons (1 t/year)	N.A.	United States
Vanerco (Enerkem & Greenfield Ethanol)	2019	TRL 6–7 demonstration	N.A.	ethanol (30,000 t/year)	N.A.	Canada

N.A. = not available; * Output 2 = 6.1 MWel; ** Output 3 = Power (electricity); *** Output 2 = 5 MWth; **** Output 2 = 4.2 MWth; ***** Output 2 = 6 MWel; ****** Output 2 = 6 MWel power (electricity).

Table 9. Syngas conversion condition and syngas composition (H_2/CO and CO_2) for different biofuels [21,22,36,131–142].

Biofuel	Pressure (bar)	Temperature (°C)	Catalyst	H_2/CO (mol/mol)	CO_2
methanol	250–300 50–100	350–450 200–300	ZnO/Cr_2O_3 $Cu/ZnO/Al_2O_3$	3 2	4–8% v/v
ethanol [+]	55–65 70–105	230–300	Rh catalysts MoS_2 or	2 $\cong$1–1.2	<1–5 mol % <5 mol %
DME	methanol synthesis	methanol synthesis	γ-Al_2O_3 catalysts; methanol synthesis with additives	$\cong$1	methanol synthesis; H_2/CO_2 = 3 §§,#
	30–70	200–300	Bifunctional catalysts (CuO–ZnO–MnO and zeolite)	$\cong$2; 3 §	$CO_2/(CO + CO_2)$ < 0.25 #
FTS	10–40 7–12	300–350 200–240	Fe catalyst Co catalyst	0.6–1.7; 2 * 2.0–2.15	H_2/CO_2 = 1 #; 3 #,* H_2/CO_2 = 3 #
hydrogen	1–30	200–1100	Ni, Fe, Mo catalysts	$\geq$2 †	-
SNG	1–25	200–450	Ni (mainly), Co, Fe, Ru catalysts	$\geq$3	H_2/CO_2 = 4 #

N.A. = Not Available; # Unit = mol/mol; † H_2O/CO; § $H_2/(CO + CO_2)$; §§ Methanol synthesis from CO_2 hydrogenation; + Direct conversion of syngas to ethanol; * Using potassium as promoter.

When biomass-derived syngas is used for biofuel production, the cleaning of the raw gas is needed strictly in order to remove contaminants and potential catalyst poisons as well as to achieve the qualitative composition required by the biofuel production process [36,143]. Several papers focused on biomass-derived syngas cleaning for end use applications were recently published [143–145]. Syngas contaminants are categorized as particulate matter (PM), condensable hydrocarbons (tars), alkaline metals (Na + K), nitrogen (NH_3 + HCN), sulphur (H_2S + COS + CS_2), and halides (HCl + HBr + HF) [143]. Syngas downstream process and cleaning levels required are reported in Table 10.

Table 10. Syngas purity as a function of the downstream process [36,131,139,143,146–152].

Contaminant	Syngas End Use				
	Methanol Synthesis (mg/m^3)	Ethanol [+] (ppmv)	FTS (ppmv)	hydrogen (ppmv)	SNG (ppmv)
PM	<0.02	0	0	0	0
Tars	<0.01	<0.5	<0.01 §	<1–2 ##; <2–5 ###	<2–5 ###
Alkali	<0.005 #	N.A.	<0.01	N.A.	N.A.
Nitrogen	<0.1	<1–10	<0.02–10	<1–10	<30
Sulphur	<0.5 #; <1	<1–50; 50–100 ++	<0.01–1	<1–50; 50–100 ++	<0.1 *
Halides	<0.001 #; <0.1	N.A.	<0.01	N.A.	<10

N.A. = not available; # Unit = ppmv; ## Unit = mg/Nm^3; ### Unit = g/Nm^3; § <1 ppmv for heteroatoms and BTX; + Direct conversion of syngas to ethanol; ++ A minimum content of sulphur (in the form of H_2S) of 50–100 ppmv is required by Mo catalysts to maintain sulfidity [147]; * For Ni Catalysts.

In addition to syngas cleaning, conditioning operations can be required to adjust syngas composition to meet the specifications of the downstream process in terms of H_2/CO ratio, H_2/CO_2 ratio, and CO_2 content, if necessary. In particular, the steam-reforming step and the WGS reaction are used to convert residual tar, light hydrocarbons, and methane to CO and H_2 as well as to achieve the targets H_2/CO and H_2/CO_2 required by the fuel production process, respectively. After H_2/CO and H_2/CO_2 adjustments, if necessary, the CO_2 removal step is carried out through physical or chemical steps [22,153].
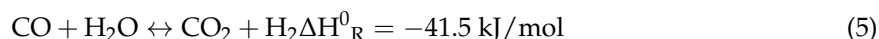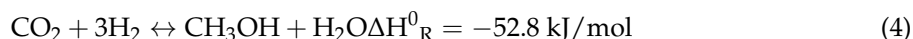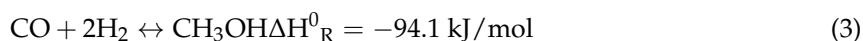
3.1. Methanol

Methanol is an alcohol predominantly used for the production of several chemical compounds such as olefins as well as for fuels such as gasoline over zeolite catalysts [131]. In the chemical industry, it is used for the production of formaldehyde and acetic acid that are intermediate for several products

(such as plywood, foams, resins, and plastics). In the fuel sector, methanol is used to produce methyl tert-butyl ether (MTBE) which is used as an anti-knock instead of lead-based substances. Responsible for increasing the octane number of gasoline, MTBE also improves combustion by limiting the emission of harmful unburned products [154–156]. Methanol is a flammable substance, highly soluble in water as well as in several organics solvents such as ethers, alcohols, etc. Historically, methanol has been produced via a catalytic process using natural gas and steam as feeding. This is a two-step process; in the first step, methane is reformed by using steam at about 600–650 °C and nickel-based catalysts in order to increase the $CO + H_2$ yield. These catalysts are often doped with potassium [154,157] in order to avoid char formation which could reduce the active metal surface, reducing the catalytic effect on the reaction. The product of steam reforming reaction is syngas, which is composed of a mixture of hydrogen and carbon monoxide with a stoichiometric ratio of 3:1, as reported below:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H^0{}_R = -191.7 \text{ kJ/mol} \tag{2}$$
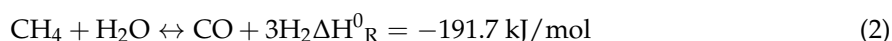
In the second step, syngas is converted to methanol by using predominantly copper-based on alumina support catalysts [158–160] through an exothermic equilibrium limited synthesis process at pressures in the range of 50–100 bar and temperatures in the range 200–300 °C, according to the following reactions [131,161–163]:

$$CO + 2H_2 \leftrightarrow CH_3OH \quad \Delta H^0{}_R = -94.1 \text{ kJ/mol} \tag{3}$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O \quad \Delta H^0{}_R = -52.8 \text{ kJ/mol} \tag{4}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H^0{}_R = -41.5 \text{ kJ/mol} \tag{5}$$

A ratio $(H_2 - CO_2)/(CO + CO_2)$ slightly above two is usually used in order to favour kinetics and to control by-products [131,164]. The main reaction for methanol production is the reaction based on CO and H_2 (Equation 3); however, Wender highlighted the effect of a methanol production promoter by carbon dioxide. Thus, in presence of CO_2, the rate of the reaction between CO and H_2 increased approximately by a factor of 100.

As a result of the exothermic nature of the reactions, a low temperature helps to increase the conversion. Furthermore, this is a reaction where there is a decreasing amount of mole numbers and by increasing the pressure, the reaction yield also increases. The choice of process temperature close to 250 °C is not attributable to the thermodynamics of reaction (preferred at lower temperature); it is a result of the higher performance of the catalysts in these operating conditions [165].
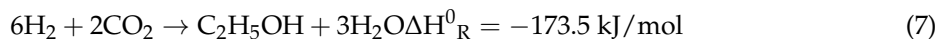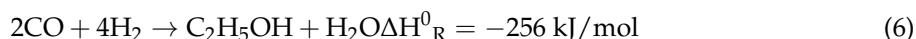
When syngas is used as feed stream, methanol production starts from the second step.
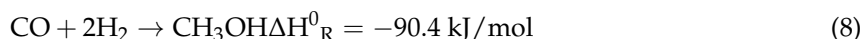
3.2. Ethanol

Similar to methanol, ethanol is an alcohol that has predominant use as a solvent, a reagent for chemical-pharmaceutical industry, or as a fuel. Nowadays, ethanol (like bioethanol) is often associated to the biofuel context; this a result of its use as a fuel in cars, especially in the US, or its use in place of MTBE or other anti-knock in combination with other fuels [13]. For several years, ethanol was produced through two predominant ways: alcoholic fermentation of sugars contained in the sugar cane or through the use of agricultural crops with high carbohydrate content, such as cereals [165,166]. However, this led to raise the issue regarding the competition between fuel production and human food [167,168]. To avoid this problem, several research centres and corporations have focused on lignocellulosic in bioethanol production for the past decade. This has led to an increase of cost production as a result of the required pre-treatment step before fermentation [169,170].

Another viable alternative for producing ethanol uses syngas derived from biomass gasification [171–173]. Ethanol from syngas is directly obtained by employing ad hoc catalysts such as Mo, Rh, K, Cu, Zn, and Fe [174–176] and this process is facilitated at pressure in the range of 1–100 bar and temperatures of about 230–300 °C [177]. The predominant reaction for ethanol production from

syngas consists in CO hydrogenation (Equation (6)); moreover, ethanol also can be produced by CO_2 hydrogenation (Equation (7)), which are both processes exothermic [139,178]:

$$2CO + 4H_2 \rightarrow C_2H_5OH + H_2O \, \Delta H^0{}_R = -256 \text{ kJ/mol} \tag{6}$$

$$6H_2 + 2CO_2 \rightarrow C_2H_5OH + 3H_2O \, \Delta H^0{}_R = -173.5 \text{ kJ/mol} \tag{7}$$

Beginning with syngas, ethanol production also can be carried out through methanol synthesis followed by methanol homologation, according to the following exothermic reactions catalysed by Cu/Co catalysts [21,139]:

$$CO + 2H_2 \rightarrow CH_3OH \, \Delta H^0{}_R = -90.4 \text{ kJ/mol} \tag{8}$$

$$CH_3OH + CO + 2H_2 \rightarrow C_2H_5OH + H_2 \, \Delta H^0{}_R = -90.4 \text{ kJ/mol} \tag{9}$$

Based on Equations (6), (8) and (9), one observees that for each mole of ethanol, 2 moles of carbon monoxide and 4 moles of hydrogen are required. At the same time, if the syngas also contains carbon dioxide, the stoichiometric ratio between hydrogen and carbon dioxide is three. For MoS_2 and Rh catalysts, which are the mainly used on industrial scale, the activity of both catalysts is inhibited by CO_2 in the syngas; however, the specific CO_2 concentration levels which allow this effect to be avoided are not clear [177]. Philips and colleagues [140] suggested a CO_2 concentration of 5% for MoS_2 catalyst, while van der Heijden and colleagues suggested <1 and <5 mol % of CO_2 for the Rh- and MoS_2-catalysts [139].

Clearly, the main issue of ethanol synthesis from syngas is the H_2/CO ratio. This ratio in the syngas may be closer to one, resulting from an occurrence of side reactions, such as WGS, which reduce the H_2/CO ratio from 2 to $\cong$1.0 [20,139].
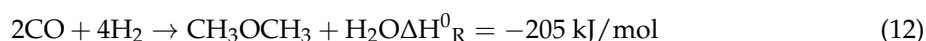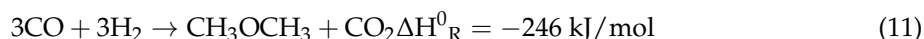
3.3. Dimethylether (DME)

Dimethylether (DME) is an ether used in several applications, e.g., spray propellant, paints, insecticides, glues, and adhesives [163]. Thanks to its chemical-physical properties, it is used as both anti-knock and automotive fuels [132,179–181].

DME is produced through a two-stage process: first one is the methanol synthesis followed by the methanol dehydration (Equation (10)). By means of acid catalysts, such as γ-Al_2O_3 [182–184], or the addition of additives such as ferrite or tungsten to Cu/ZnO/Al_2O_3 catalysts [185,186], the following methanol synthesis reaction occurs [21,187]:

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \, \Delta H_{298K} = -23.4 \text{ kJ/mol} \tag{10}$$
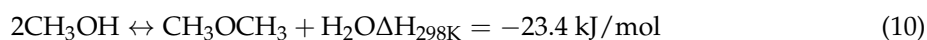
DME production also can be carried out in a single-step synthesis starting from syngas through the use of bifunctional catalysts (CuO–ZnO–MnO and zeolite) operated at 30–70 bar and 200–300°C, according to the following reactions [141,188]:
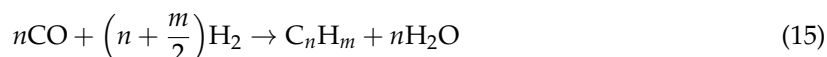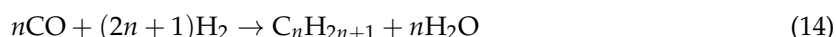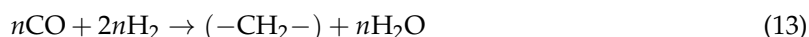
$$3CO + 3H_2 \rightarrow CH_3OCH_3 + CO_2 \, \Delta H^0{}_R = -246 \text{ kJ/mol} \tag{11}$$

$$2CO + 4H_2 \rightarrow CH_3OCH_3 + H_2O \, \Delta H^0{}_R = -205 \text{ kJ/mol} \tag{12}$$

Ateka and colleagues [141] pointed out that DME yield decreases with the increase of CO_2 concentration in the feed; however, for CO_2/(CO + CO_2) higher than 0.5, an asymptotic trend can be observed.

3.4. Fischer-Tropsch Synthesis (FTS)

In the last decades, Fischer-Tropsch Synthesis has been studied for the valorisation of syngas produced by agro-industrial gasification in order to have a biofuel with near zero carbon emission,

thanks to the potential use of biomass as feed [189–191]. FTS is used for the production of several biofuels such as gasoline, kerosene, and diesel fuel. Accordingly, it is possible to produce fuels with linear chains and with a high grade of purity [192] and simultaneously without sulphur, nitrogen, or aromatics [193,194]. At present, it is considered to be the most complete technology for transportation biofuel production [21]

FT Synthesis produces several hydrocarbons, paraffin, and olefins such as methane, ethane, ethylene, LPG (C3–C5), fuel (C5–C12), gasoline (C13–C22), and waxes (C23–C33). Their distribution depends on the type of the catalyst used as well as by the process parameters, such as temperature, pressure, feed gas composition, and residence time [195–198]. The set of reactions is described below [199,200]:

$$nCO + 2nH_2 \rightarrow (-CH_2-) + nH_2O \tag{13}$$

$$nCO + (2n+1)H_2 \rightarrow C_nH_{2n+1} + nH_2O \tag{14}$$

$$nCO + \left(n + \frac{m}{2}\right)H_2 \rightarrow C_nH_m + nH_2O \tag{15}$$

where n is the number of carbon atoms and m is the same for hydrogen atoms contained in the produced hydrocarbon.

Co and Fe catalysts are often used for these reactions in the range of temperatures between 475 K and 625 K at pressure in the range 15–40 bar. In particular, cobalt catalysts improve performance in terms of conversion when compared with iron catalysts; however, iron catalysts guarantee a higher production in terms of olefin and alcohols than Co catalysts which give more paraffinic molecules [201].
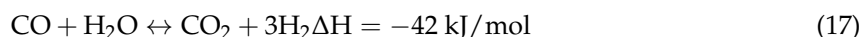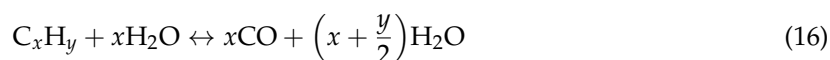
C_{20+} linear HCs, C_{5+} paraffins and medium weight olefins, which are further processed to generate usable liquid transportation fuels, are the most desired products obtained via FTS [21].

3.5. Hydrogen

At present, hydrogen is predominantly used in chemical and oil industries: $\cong$61% of H_2 produced worldwide is used for ammonia synthesis process, $\cong$23% for oil refining, and $\cong$10 for methanol synthesis. Moreover, $\cong$4% of global H_2 produced is used for merchant users and $\cong$3% for other application [202]. In particular, H_2 is considered a valuable and clean alternative to fossil fuel that feeds low temperature fuel cells, such as proton exchange membrane (PEM), and allows electric energy conversion, avoiding pollutant and greenhouse gas emissions [38,203]. Notably, H_2 for fuel cells is considered a near-term technology [121]. For example, H_2 purity higher than 98–99.9% v/v for application in ammonia synthesis (N_2:H_2 = 1:3 mol/mol) is required [204]; H_2 use in PEM technology requires high purity grade (99.99% v/v—ISO 14687) with gas compositions such as: <0.5–4.5 ppmv CO, <20 ppm CO_2; <0.25 ppmv H_2S; <1–10 ppmv NH_3 [148].

Currently, the predominant feedstock for H_2 production consists in steam reforming of hydrocarbons ($\cong$95%) which has the significant drawback of greenhouse gas emissions [38]. In order to make the production of H_2 more sustainable, a renewable eco-friendly alternative to fossil fuel is required. A potential hydrogen source of the future is believed to be biomass [203].

As reported in the previous section, hydrogen is a component of syngas, from a minimum of $\cong$5–10% v/v to a maximum of $\cong$40–50% v/v, depending on gasifier type, biomass feed, and operating conditions. Biomass gasification using steam as a GA results in syngas with H_2 content higher than 40% v/v, reducing tar production [205,206]. In order to increase H_2 concentration, syngas is reformed via catalysed reactions such as the steam reforming of methane and higher hydrocarbons as well as the WGS reaction [125,207,208], using several catalysts, such as Ni, Fe, and Mo catalysts at temperature in the range 200–1100 °C and pressure between 1 and 30 bar [207,209–211]:

$$C_xH_y + xH_2O \leftrightarrow xCO + \left(x + \frac{y}{2}\right)H_2O \tag{16}$$

$$CO + H_2O \leftrightarrow CO_2 + 3H_2 \Delta H = -42 \text{ kJ/mol} \tag{17}$$

There are several technologies for hydrogen/CO_2 separation in the syngas both in bed and out bed, such as polymeric membranes, chemical and physical adsorption of carbon dioxide, temperature swing adsorption (TSA), and pressure swing adsorption (PSA); however, pressure swing adsorption has been considered the most economical technology in several cases [201].

Soukup et al. [212] reported a product gas with a H_2 content of 70% v/v using a dual fluidized bed gasification system with CO_2 adsorption along with suitable catalysts.
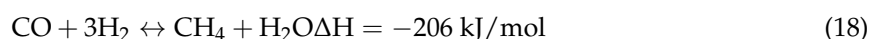
An example of platform of hydrogen from biomass is the project "Hydrogen from biomass for Industry" [208], according to which the production of hydrogen was carried out by several steps, beginning with syngas produced via steam gasification of biomass; this was followed by steam gasification, CO-shift stage, CO_2-separation with a pressurized water scrubber, a PSA system, a steam reformer, and advanced gas cleaning components [22] with H_2 purity > 98–99% v/v.

Fail and colleagues [148] investigated hydrogen production by using a pilot plant fed with syngas produced by steam gasification of biomass. The pilot plant consisted of several units for syngas conditioning (WGS reactor, wet scrubber operated with rapeseed oil methyl ester, pressure swing adsorption (PSA) for hydrogen purification), resulting in H_2 purity > 99.97% v/v.

Gasification via water in supercritical condition (SWC = 22.1 MPa and 374 °C) is a valuable way to process wet biomass, producing hydrogen-rich syngas [213,214]. Demirbas [215] investigated the effect of operating temperatures (650–700 K) on hydrogen production from biomass gasification in supercritical water condition, observing an increase of hydrogen content from 6.6% to 9.4% with the temperature increasing from 650 to 700 K.
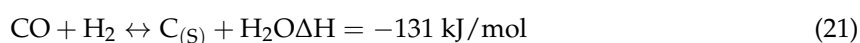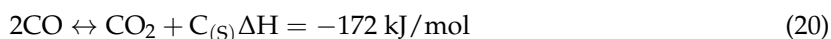
3.6. Synthetic Natural Gas (SNG)

SNG production by syngas represents an interesting way for biofuels production; this is a result of the infrastructures, distribution, and sales, which are identical to those used for methane [216–219]. A review of SNG production was recently carried out by Rönsch et al. [220], in which a comparison among several catalysts was performed, highlighting the main metal for methanation catalysts. Synthesis of methane by syngas could be achieved by using the same catalysts used in the steam reforming reactions, mainly Ni on alumina; however, other catalysts, such as Ru, Co, and Fe, can be used [221]. The reactions involved in the SNG production by syngas are showed below:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \Delta H = -206 \text{ kJ/mol} \tag{18}$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \Delta H = -165 \text{ kJ/mol} \tag{19}$$
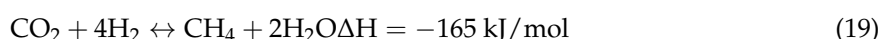
Both carbon monoxide hydrogenation and carbon dioxide hydrogenation are exothermic reactions; therefore, continuous cooling of the reactor is necessary to guarantee a temperature of 250–300 °C, i.e., the activation temperature of the catalysts. In order to increase the performance of these reactions, the operative pressure must be in the range between 15 and 25 bars [222]. The Achilles' heel for these reactions is the low hydrogen content in the syngas, which is lower than the stoichiometric value [218]. Moreover, CO_2 conversion is inhibited when CO content increases over a certain value. [223]; for example, Weatherbee and Bartholomew reported a strong inhibition of methane production at CO concentration higher than 0.012%, using Ni-based catalysts. [224].

Another issue for SNG production is char formation, in particular because of the low process temperature:

$$2CO \leftrightarrow CO_2 + C_{(S)} \quad \Delta H = -172 \text{ kJ/mol} \tag{20}$$

$$CO + H_2 \leftrightarrow C_{(S)} + H_2O \quad \Delta H = -131 \text{ kJ/mol} \tag{21}$$

Char formation could cause deactivation of Ni-based catalysts, thus decreasing the performance of methane production [225].

After the dewatering step, the gas produced by SNG process consists of methane and carbon dioxide, usually in equimolar composition. In these operative conditions, thanks to the high pressure

of SNG, CO_2 separation is considered economically feasible for the production of SNG with a high grade of methane purity [226].

4. Conclusions

In this manuscript, a critical overview is presented of gasification technologies and second-generation biofuels synthesized from syngas by biomass gasification, such as methanol, ethanol, dimethyl ether, Fischer-Tropsch Synthesis, hydrogen, and synthetic natural gas. Synthesis of biofuels from syngas is a feasible and effective way for confronting worldwide energy requirements and GHG emission at the same time.

The main parameters affecting syngas production and composition, such as gasification technologies (fixed bed reactors, fluidized bed reactors, entrained flow reactors), feedstock characteristics (biomass type, moisture content, particle size, ash content), and operating gasification conditions (bed material, temperature, pressure, GA, equivalence ratio, SB) are explored. As shown, syngas composition strictly depends on feedstock, technology, and operating parameters.

Purity of syngas in order to produce second-generation biofuels is highlighted, in terms of particulate matter, condensable hydrocarbons, alkaline metals, nitrogen, sulphur, and halides. Syngas cleaning requirements depend on downstream processes, operating conditions, catalysts, and main reaction mechanisms.

Synthesis of second-generation biofuels from biomass-derived syngas requires the optimization of the gasification process, specifically fed biomass, gasifier type and operating conditions, as well as syngas cleaning and conditioning. In order to define the concept of a whole synthesis chain, gasification process optimization, in terms of proper ratio of syngas components and of contaminant removal, has to be related to the type of the biofuel production process, in terms of catalyst and operating conditions. Notably, parameters has to be identified and defined according to end use, such as operating pressure of gasifiers in order to have syngas at proper downstream pressure, specified composition (such as H_2/CO and CO_2), and required syngas purity.

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