Biomass Gasification as a Scalable, Green Route to Combined Heat and Power (CHP) and Synthesis Gas for Materials: A Review

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Abstract: The high externalized and still partly unknown costs of fossil fuels through air pollution from combustion, and their limited resources have caused mankind to (re)turn to renewable sources such as wind, solar, and biomass to meet its energy needs. Converting biomass to synthesis gas is advantageous since it can utilize a wide variety of (waste) feedstocks to obtain an energetic and versatile product at low cost in large quantities. Gasification is no new technology; yet in recent years, biomass gasification has attracted significant attention. Due to the non-depletable nature of agricultural waste and similar biomass side streams, which have little value and can bring environmental problems when mismanaged such as methane emissions, it is possible to obtain cheap electrical or thermal energy through the gas produced with high efficiencies. Combined heat and power (CHP) is the preferred use case, and recently the focus has moved to polygeneration, e.g., to make value-added products from the synthesis gas. Fischer–Tropsch synthesis from coal-derived syngas is now being complemented by the gas fermentation of biobased synthesis gas, where microorganisms yield materials from CO/H_2 (and CO_2) in an anaerobic process and from CH_4/O_2 in an aerobic process. Syngas methanation offers an alternative route to produce synthetic natural gas (SNG, or bio-SNG) as additional feedstock for gas fermentation. Materials made from syngas are decoupled from primary agricultural operations and do not compete with feed and food production. Due to the ample raw material base for gasification, which can basically be all kinds of mostly dry biomass, including waste such as municipal solid waste (MSW), syngas-derived products are highly scalable. Amongst them are bioplastics, biofuels, biobased building blocks, and single-cell protein (SCP) for feed and food. This article reviews the state-of-the-art in biomass gasification with a spotlight on gas fermentation for the sustainable production of high-volume materials.

Keywords: gasification; gasifier; biomass; environment; polygeneration; combined heat and power (CHP); gas fermentation; single cell protein (SCP); biopolymers; polyhydroxyalkanoates (PHA); hydrogen

1. Introduction

Humanity lived for tens of thousands of years with minimal impact on the planet. Even five centuries ago, during the Renaissance in Europe, the world was sparsely populated. However, rapid population growth due to the revolutions in agriculture, industry, and medicine has increased the global population by about 15 times. Of the eight billion people today, only a small fraction enjoys a very high standard of living; by contrast, approx. one-third of humans do not have access to electricity, and another third have a limited supply of it, and many people are also stuck in poverty, with all the associated problems, e.g., related to health. One in three people globally lack access to clean water, [1]. And

every day, 40,000 people, that is, 25 people every minute, die due to diseases [2] where the UN SDG (sustainable development goals) aims at global improvements.

In order to reduce human suffering, not only economic development is necessary, but it is also vital to create conditions to stabilize the world population and its consumption patterns. In the coming 50 years, when the global population will surpass 9 billion individuals and more, today's unfulfilled human needs will multiply drastically. The growing effort to meet these wants for meat, materials, energy, travel, and so forth in most of the developing countries of the world has created a huge demand for the use of energy such that by 2050 global energy consumption will double [3], and we are very well aware of the fact that already today we spend more resources than the globe can replenish, as the "Earth overshoot day" (August 1 in the current year [4]) or the "global boundaries" (where six of nine have been transgressed [5]) illustrate quite dramatically.

Since resources are limited, many efforts are made to tap into new, renewable energy sources and to use the existing ones optimally, and continuous progress is made in energy efficiency and clean energy, where energy storage is a critical, currently largely unresolved, issue. Amongst the forms of renewable energy, biomass is expected to have a pivotal role. Pressure for climate change mitigation by emission reductions has positioned biomass gasification as a critical technology in the global transition to renewable energy. As nations strive to meet their commitments under international agreements such as the Paris Agreement, there is a growing focus on scalable and sustainable energy solutions that can replace fossil fuels. Biomass gasification offers a pathway to not only generate renewable energy but also produce valuable chemicals and materials, thereby supporting the circular economy.

In this review article, the definitions related to biomass, biomass resources, and measures taken in the field of energy extraction from biomass in various countries are summarized and discussed, see also [2,6–8], with a focus on converting the biomass to synthesis gas for further processing to value-added products by gas fermentation next to heat and power production.

The global increase in energy use, especially through development, coupled with economic crises, leads to the reduction in sources of available fossil fuels and emerging renewable sources of energy, which places a huge burden on electricity distribution, increasing risks for blackouts. Energy storage at a large scale is still mostly impossible technologically and economically, despite several installations (e.g., pumped hydro) and novel concepts (like power-to-X, P2X, such as power-to-gas, where excess renewable energy is used to produce H_2 and/or CH_4 which is stored in the natural gas grid for later reconversion into electrical energy). Greenhouse gas emissions from the combustion of fossil fuels occur at a huge scale [2,9–12]), and have contributed strongly to anthropogenic CO_2 emissions and climate change [13].

Biomass is an abundant and ubiquitous resource. The amplest sources of biomass exist in the developing economies of Asia, South America, and Africa, which mainly include agricultural, wood, animal, and urban waste (municipal solid waste, MSW, although partly of fossil origin, is also considered a renewable resource by many researchers). Of course, in recent years, the energetic consumption of biomass has expanded in developed countries as well [2,14,15]. Sweden, for instance, has made a large investment in the biomass sector, and the GoBiGas project [16] marks a major milestone in the development of large-scale biomass gasification. Many Latin American countries such as Brazil provide more than 60% of their fuel needs from biomass sources, e.g., via sugar-cane-derived ethanol. In the US state of Michigan, the waste materials obtained from the cutting of forest trees provide about one percent of the state's electricity (300 megawatts) [9,17]. Biomass provides 35% of the energy in developing countries, and this share is only 3% in industrialized countries [18–20]. Traditional biomass burning requires low investments, but lacks efficiency. Figure 1 shows the power investments from 2019 to 2023 on a global level, where it can be seen that renewables and grid infrastructure dominate.
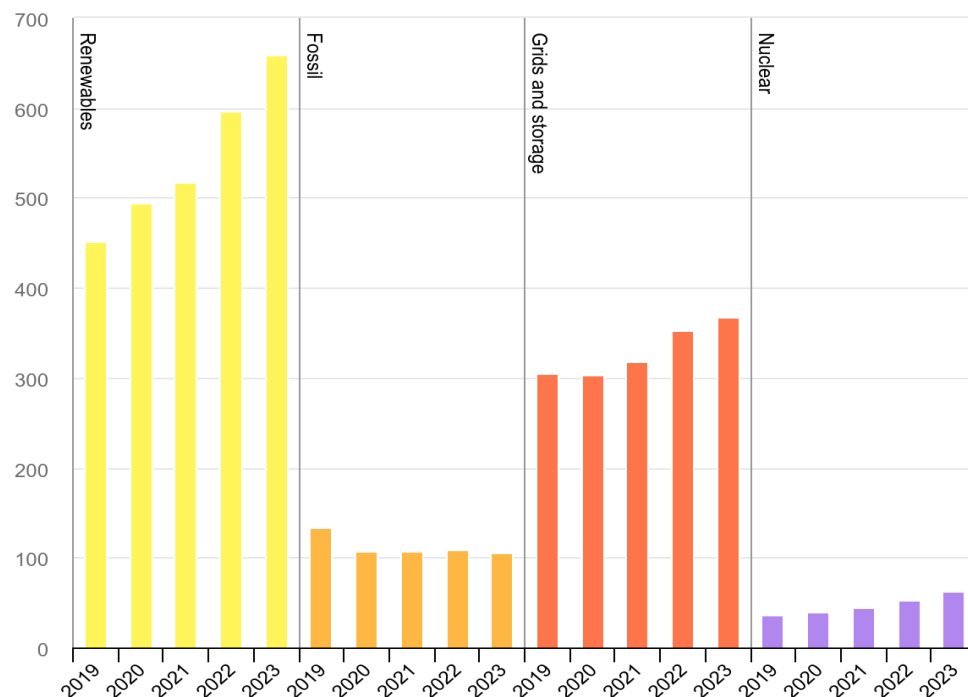
Figure 1. Power investments, 2019–2023, in billion USD (2022), by category. Source: [21].

New developments in the sector of renewable energy lead to the creation of and improvements of technologies which enable the sustainable use of renewable energy. Renewable energy will be able to provide great opportunities and possibilities not only for developing countries and rural areas, but also for mature economies in the next years [2,7,22], as it is well in line with circular economy endeavors and targets.

Different technologies exist to convert (waste) biomass into energy. Electrical energy is more valuable than thermal one, and biomass is suitable to deliver both—and act as a storage medium beforehand.

In general, wet biomass can be transformed into biogas by anaerobic digestion, and dry biomass can be converted thermally, which can be achieved by classic combustion—or by gasification—into syngas (synthesis gas). While the processes of fixed-bed gasification, entrained-flow gasification, and fluidized-bed gasification can handle dry biomass, supercritical gasification is also applicable to wet biomass and wet waste streams [23].

The gasification process, which includes the thermochemical conversion of the raw materials to gas (the so-called synthesis gas, also known as syngas, a mix of mostly H_2 and CO, plus some CO_2 and CH_4), is an option that has received special attention in recent decades and has had significant development and spread of applications. The synthesis gas obtained from biomass in this technology can be used both for heat energy and electricity production, and many different devices are capable of using this gas after conditioning (mainly tar removal), e.g., a gas engine, which is most common, or a gas turbine. Compared to cogeneration (combined heat and power, CHP) by classic combustion, the alternative process of gasification can give a higher electrical efficiency (Lackner et al., 2013). Therefore, research in the gasification of biomass can help us transition to a non-dependence on fossil fuels and reduce the environmental pollution of greenhouse gasses, predominantly CO_2 [2,24,25].

As this review article will show, the gasification of biomass waste and side streams offers an immense potential of truly enabling a defossilized circular economy, in that not only energy, but also materials can be obtained from syngas. The latter aspect has vastly been overlooked by industry to date.

2. Materials and Methods

Biomass resources

According to the United Nations Climate Change Working Group (UNFCC), biomass is: "non-fossil and biodegradable organic materials that originate from plants, animals or microorganisms".

Biomass includes all substances in nature that were alive in the recent past or were made from living organisms, or are their wastes. Based on the globally accepted classification, the main sources of biomass are agricultural and forestry waste, livestock and animal waste, household (municipal) waste, and industrial waste as well as sewage sludge. It is organic matter that is either specifically grown (energy crops), harvested, or obtained as a side or waste stream. In another definition, it can be said that biomass is a composite material that is composed of a mixture of cellulose, hemicellulose, and lignin, and it also contains ash and moisture [26].

Biomass energy, which is also termed "bioenergy", includes energy produced from all types of waste, including that from living organisms, and has the highest potential after wind energy and particularly solar in the realm of renewables [27]. Bioenergy can be decentralized and implemented at different scales, as one of its advantages compare [28]. Smaller, regional units support local value creation and limit transportation, which makes smaller decentralized power advantageous over large centralized installations, as common with fossil fuels.

Based on data from IEA and IPCC, the capacity of using different sources of biomass until 2050 (Galimova et al., 2022) is presented in Tables 1 and 2 [29]. It is also stated in the studies of the IEA that the global energy demand will climb until 2050 to 600–1000 EJ.yr^{-1}, compare [30–32].

Therefore, a huge part of this demand can be met using the mentioned sources [33], and more and more countries commit to decarbonization and defossilization targets.

Table 1. The capacity to use renewable resources until 2050. Source: [34].

Renewable Energy Source	Utilization Capacity (Percentage)
Biomass	79.7
Hydropower	16.5
Geothermal	3.1
Solar	0.29
Wind	0.48
Ebb and flow and waves	Insignificant

As Table 1 shows, biomass is expected to have a dominant share amongst renewables on a global level, see also Table 2.

Table 2. The capacity of using different sources of biomass until 2050 is in terms of EJ.yr^{-1}. Source: [34].

Biomass Resources	Potential Capacity	Potential Capacity in Normal Mode
Organic waste and urban and industrial waste	50–150	100
Forestry residues	60–100	80
Agricultural residues in a normal state	100–140	120
Agricultural waste by using inefficient land	60–80	70
Agricultural residues using new technologies	130–150	140
Total	400–620	510

There are different categories for biomass resources [35]. A common classification is given by the US Department of Energy in the Biomass Energy Data Book, 4th edition (2024) [36]. In the mentioned book, biomass resources are grouped as primary, secondary, and tertiary materials, where primary materials are all land plants that are made by photosynthesis in land and water. Secondary materials include the waste streams and byproducts

of the food industry, forest wood residues, and animal waste [37–39]. Tertiary materials encompass all wastes: wastes after consumption such as fats, oils, urban (municipal) solid waste, urban woody biomass waste, packaging waste, but also sewage, and landfill gas [40]. Note that this definition includes fossil carbon that is contained in the waste.

Also, the American National Renewable Energy Laboratory (NREL) conducted a study in 2005 to quantify the potential of biomass resources [41]. It was carried out for the following categories:

- Agricultural waste including waste biomass from farming plus CH_4 from animal waste;
- Waste of wood (forest waste, wooden branches, and waste streams such as pallets and furniture);
- Municipal waste (municipal solid waste (MSW), landfill gas, and sewage sludge);
- Energetic plants (energy crops).

Figure 2 shows the share of the various primary energy sources in the production of electricity, in the European Union, in the recent past where bioenergy has a share of approx. 6% only [42], but it is growing.
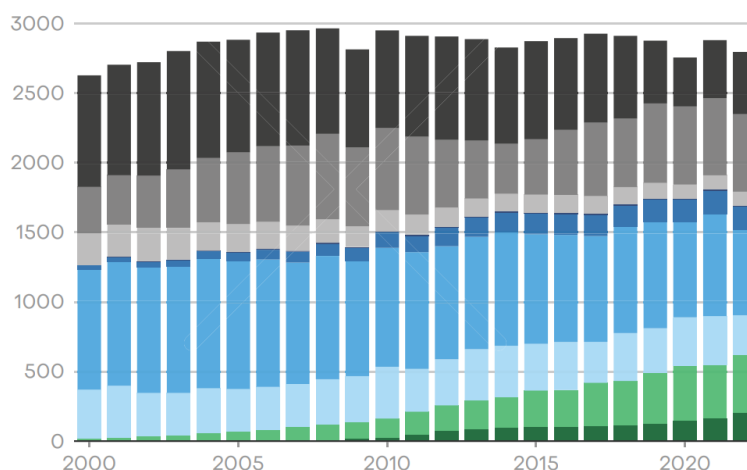

Figure 2. Electricity generation by source in Europe until 2022. Source: [43].

While the potential of hydropower has largely been exploited, there remains a huge unused potential for bioenergy, including energy crops and biomass waste and side streams.

Methods of hydrogen production from biomass:

Biomass constitutes, on a global level, one of the main fuels consumed by humans. Hydrogen can be considered an emerging fuel, and its production share from biomass is currently still low [6,44–46], yet one needs to state that the "hydrogen economy" is yet to truly get started, and making "green" hydrogen from biomass can be an environmentally benign way, next to H_2 from electrolysis using renewable electricity. Today, most hydrogen is obtained from natural gas, which sets free CO_2.

Considering that biomass consumes CO_2 in the growth stages, organic carbon can be considered circular, and the (net) CO_2 pollution caused by its combustion/gasification is much lower than the carbon footprint of fossil fuels [47], which reintroduce carbon into the atmosphere that had been sequestered for millions of years. Other pollutants can be higher from the energetic conversion of biomass, though, e.g., fine particles, where various life cycle assessment (LCA) approaches allow for comparative analyses. The discussion of hydrogen production from biomass dates back roughly 4 decades, when McDonald et al.,

(1981) produced hydrogen from grass from which the protein had been extracted [48]. Such multiple use is also pursued in second-generation biorefineries.

Hydrogen from biomass is termed "green" hydrogen, while H_2 from natural gas is dubbed "grey", with other colors being reserved for different feedstocks, e.g., "white" for naturally occurring molecular hydrogen. Cao et al. talk about "biorenewable hydrogen" [49].

For green hydrogen production from decarbonized biomass gasification (i.e., with CO_2 capturing), see, e.g. [50,51].

Hydrogen production from biomass follows two general routes: thermochemical conversion and biological conversion; see Table 3.

Table 3. Hydrogen production from biomass [52].

Thermochemical Conversion	Biological Conversion
Pyrolysis	Biological fermentation
Gasification	Biological photosynthesis
Supercritical Water treatment	Biological water gas shift (WGS)

The WGS reaction is $CO + H_2O \rightarrow CO_2 + H_2$. The biological conversion of biomass to hydrogen includes a type of transformation in which microorganisms such as archaea and bacteria [53] are used to perform enzymatic reactions and convert biomass into target products, which usually requires more time than a thermochemical process. A mix of methane and hydrogen "hythane" or "biohythane" obtained via microorganisms was described by O-Thong et al., (2016) [54].

Pyrolysis is not suited for hydrogen production [55].

Normal gasification:

Gasification is a partial oxidation of a carbonaceous raw material at high temperatures, which mainly yields carbon monoxide and hydrogen, along with carbon dioxide and methane, with a very small amount of water vapor and other compounds such as two- or three-carbon hydrocarbons [56,57]. The gasification agent can control the H_2/CO ratio; for instance, it can be increased by using steam instead of air; see below.

Conventional gasification requires a well-defined biomass with less than 35% (weight) water content, and often, even dryer feedstock is needed, down to 10% water content. In general, fuel for gasification needs to meet tighter specifications than fuel for combustion, and the quality requirements for the feedstock can pose a challenge for large-scale gasifiers. Using waste process heat to dry the input material can increase efficiency. Table 4 shows a number of experiments performed on different biomass sources by the gasification method.

Table 4. The results of some biomass gasification experiments.

Biomass	Type of Reactor	Catalyst	Hydrogen Yield (Volume %)	Temperature (°C)	Reference
Rice straw	fluidized bed	without catalyst	10	850	[58]
Rice straw	fixed bed	nickel	55.4	700	[59]
Rice husk	fluidized bed	without catalyst	6	600	[60]
Canola stalk	fixed bed	without catalyst	20	800	[61]
Almond shell	fluidized bed	lanthanum, nickel, or iron	62.8	800	[62]
Corn seed	Micro fixed bed	nickel	14.72	850	[63]

Gasification in supercritical water environment:

Supercritical water (i.e., water with a temperature of min. 374 °C and a pressure of min. 22 MPa = 220 bar) as a gasifying agent can also be used [64,65].

For the first time, Modell et al., (1978) investigated the effect of concentration and temperature on the gasification in water near its critical point, where glucose and maple

sawdust were tested [66]. These authors observed that no solid residue (biochar or tars) remained from the reaction and 18% hydrogen concentration was found in the syngas [66]. Tavasoli et al., (2009) tested the supercritical gasification of sugarcane bagasse in which using supercritical water in a continuous tube reactor shows that a concentration of 37% hydrogen could be achieved [63] (Table 5).

Table 5. The results of biomass gasification trials with supercritical water [63].

Biomass	Type of Reactor	Catalyst	Hydrogen Yield (Volume %)	Temperature (°C)	Reference
Corn stem	Discontinuous autoclave	without catalyst	19	500	[67]
Corn stem	Discontinuous autoclave	K_2CO_3	34	500	[67]
Corn stem	Continuous	without catalyst	12	650	[68]
Sunflower stem	Discontinuous autoclave	without catalyst	19	500	[67]
Sunflower stem	Discontinuous autoclave	K_2CO_3	48	500	[67]
Sugarcane bagasse	Tubular discontinuity	without catalyst	27	440	[69]

Gasification in a supercritical water environment leaves behind only low amounts of solid and liquid byproducts, and due to the high pressure of the process, the separation of CO_2 becomes easy [64,70,71], e.g., for a BECCS process setup (Bioenergy with Carbon Capture and Storage), see [72]. Supercritical gasification can also handle wet biomass feedstocks [23].

Prediction of the state of biomass energy until 2040

Based on the scenarios of advanced international policies and current policies published by the European Renewable Energy Council (EREC), in the best case, half of the world's energy in 2040 can be provided from renewable energies; this ratio will not be less than 24% in the most pessimistic case (Table 6). It follows from the evidence that renewable energy sources will play a significant role in the world's energy supply in the future, which is only logical given the finite nature of fossil resources and reserves. In the long term, renewable energy will take an even stronger part in the global energy provision. The reason for this is simple and definite—there is no other option for mankind. Humanity cannot limitlessly consume finite fossil resources, and the sun provides ~20,000 times mankind's energy demand. Solar energy is instant and needs energy storage installations. Biomass, by contrast, is already stored energy with a high energy density. In this section, the results of predictions for biomass are presented, based on the work in [73,74];

Table 6. Annual biomass utilization growth until 2050. Source: (European Renewable energy council (EREC) [34].

Year	2001–2010	2010–2020	2020–2030	2030–2040
Annual growth rate of biomass for energy according to the scenario	2.2%	3.1%	3.3%	2.8%

In the so-called advanced international policy scenario (API), biomass is the renewable energy source with the highest current use and a relatively low growth rate during the forecast period. But due to the various uses of heat, electricity, and fuel altogether, it will be the biggest source of energy supply in the future with strong likelihood. For this scenario, many applications in small decentralized systems have been assumed after 2010 [9,73,75].

In Table 7 below, based on the advanced international policy scenario, the projected growth of renewables can be seen. In particular, the share of biomass will be higher than that of other renewable sources within the coming 15 years [73].

Table 7. The share of new energies in the world's energy supply according to the AIP scenario, excerpt (source: European Renewable energy council (EREC) [34]. RES = renewable energy source; Mtoe = million tons of oil equivalent.

	2001	2010	2020	2030	2040
Total consumption in Mtoe	10,038.3	10,549	11,425	12,353	13,310
Biomass	1080	1313	1791	2483	3271
Total RES	1364.5	1745.5	2694.4	4289	6351
RES contribution	13.6%	16.6%	23.6%	34.7%	47.7%

In 2022, renewable energy sources summed up to 23% of the energy consumed in the EU, up from 21.9% in 2021. This increase was mainly due to a significant growth in solar power. The rise in the renewable energy share was also influenced by a decrease in non-renewable energy consumption in 2022, driven by high energy prices. However, the expectation is for renewable energy in Europe to continue expanding. Achieving the new 2030 target of 42.5% (Renewable Energy Directive, 2023) [76] will necessitate more than doubling the deployment rates of renewables observed over the last decade, requiring a substantial transformation of the European energy system. Other regions and countries face similar challenges. The US DoE (Department of Energy) has made, back in 2016, a study on their biomass potential, where the need for 1 billion tons of biomass per year was proclaimed [77] and that amount of biomass can be obtained at costs <50 USD/ton and from domestic production. This means that the USA could be self-sufficient as a full bioeconomy. A similar conclusion could be drawn for most other countries in the world; our usage patterns today are largely linear, and we could shift to a large extent to circularity based on organic carbon.

Figure 3 shows the global primary energy production, where traditional biomass has shown the most stable value, on the order of 10 PWh, over the last 200 years, now on the level of hydropower. For the most recent energy data, see World Energy Outlook (WEO) 2023 by IEA [78].
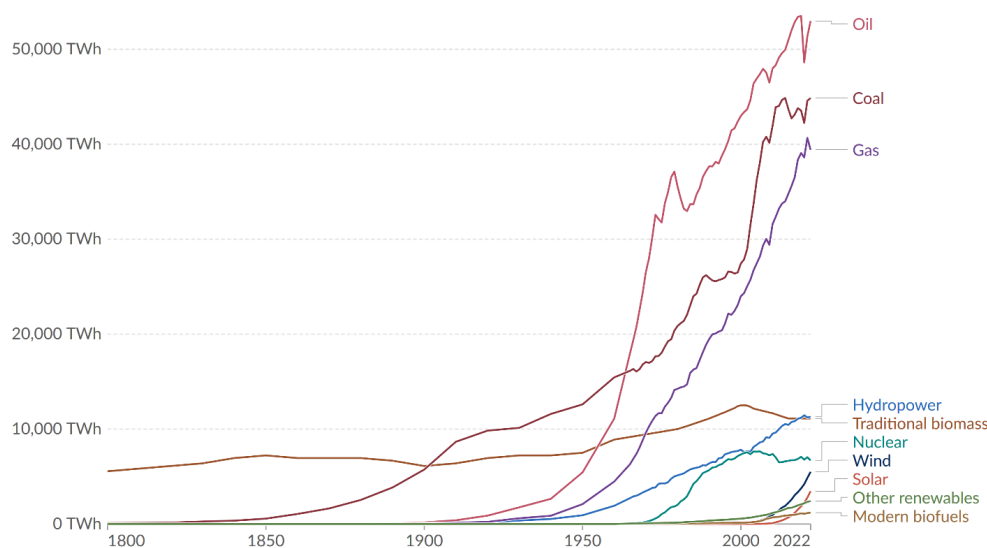

Figure 3. Sources of global primary energy consumption. Data source: Energy Institute—Statistical Review of World Energy (2023). [79]. License: Creative Commons BY license.

One of the types of waste biomass that is available almost everywhere is municipal solid waste (MSW). Waste is defined as materials that are considered useless from the producer's point of view [80]. We talk about 2 billion tons of MSW that is produced globally every year, with projections pointing upwards. The landfilling of waste, particularly organic fractions, is not sustainable, and other end-of-life options should be deployed to achieve circularity. Landfilling not only demarcates the endpoint of a linear economy usage model, but it can also lead to detrimental environmental effects like water contamination through landfill leachate and climate burden as well as safety risks through landfill gas (CH_4), the spread of diseases, risk of fire with concurrent air pollution, etc. More and more countries are enacting bans on landfilling untreated waste, yet legacy landfills as well as unmanaged waste dumps will stay reactive for several more decades. While the initial purpose of waste incineration was to inert the input material and to reduce its volume, today's treatment plants focus on energy efficiency to reclaim the energy content of the non-recyclable fractions.
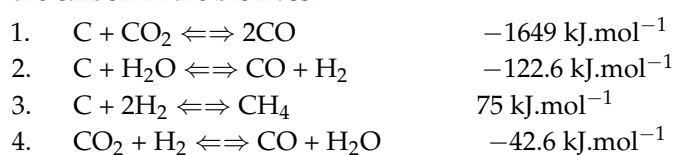
The first fuel used by man to meet his needs for energy was wood. Even today, this fuel is deployed by hundreds of millions of people around the world to prepare food and heat homes, and it is also utilized as charcoal in industrial processes. However, the reduction in wood fuel sources made the use of coal as fuel common. Coal production became popular in the 18th century, and had industrial use, e.g., in the iron smelting industry. At the end of the 18th century, gas production from coal became popular in a pyrolysis process in high capacities. Gas production was started in 1812 by the London Gas Company (Gas Light and Coke company) and after that, it became a commercial process [81,82], as "town gas".

Gasification has attracted renewed attention [83,84], with biomass at its core. Gasification yields a small quantity of liquid and solid byproducts when the reaction in the gasification reactor is not complete [57,85]. That char can be used for soil amelioration as biochar when the absence of toxic contaminants has been confirmed.

The ratio of CO/H_2 in syngas can be between 3:1 and 1:3 depending on the gasification medium (air or steam). Tar formation can be reduced and avoided by suitable oxygen and temperature control.

The heating value of synthesis gas is generally lower than the calorific value of natural gas [24]. It can be up to 8 MJ/kg [86], and typically lies in the range of 2–5 MJ/kg, while natural gas is around 50 MJ/kg.

The main gasification reactions are shown below, compare [87], where C stands for the carbon in the biomass:

1. $C + CO_2 \Longleftrightarrow 2CO$ -1649 kJ.mol^{-1}
2. $C + H_2O \Longleftrightarrow CO + H_2$ -122.6 kJ.mol^{-1}
3. $C + 2H_2 \Longleftrightarrow CH_4$ 75 kJ.mol^{-1}
4. $CO_2 + H_2 \Longleftrightarrow CO + H_2O$ -42.6 kJ.mol^{-1}

Gasification tries to optimize the yield in gas formation, while a combustion process continues until the maximum decomposition of the raw materials is achieved for the highest immediate energy release. In this process, an additional substance called the gasification agent also enters the reactor. This agent can be air, oxygen, steam, methane, or an inert gas such as, typically limited to the lab environment, helium [88,89].

The key difference between combustion and gasification is that gasification takes place in an environment that lacks oxygen [85,90]. Combustion is typically carried out in the lean (oxygen-rich) regime to allow for complete fuel formation and lower temperatures and thereby, lower thermal NOx emissions. In most gasification processes, partial combustion supplies the required heat energy.

Normally, there are 3 main motivations for choosing gasification over combustion [91]:

1. The calorific value of the product gas.
2. To reduce air pollution through the removal of sulfur and nitrogen before the end of the process. Here, different bed materials can be deployed.
3. The relative hydrogen content of the syngas, which can be controlled.

Combustion processes typically use steam generation to extract energy, while the syngas from gasification can be burnt in an engine in a second step, or be used otherwise.

Syngas can be deployed for processes that mainly require hydrogen (such as Fischer–Tropsch (FT) or ammonia synthesis). For a recent summary of the Fischer–Tropsch synthesis process, see, e.g., [92–95]. Biobased hydrogen can also be used to make useful products out of CO_2 in biological and chemical (catalytic) processes. It can be assumed that CO_2 recycling will become more important in the near future, and any CO_2 process will require energy, where hydrogen will be the carrier. Low-cost, sustainable hydrogen can be expected to be the critical element in using CO_2 from point sources, which can be considered a thermodynamically much better option than capturing CO_2 from very dilute sources such as the atmosphere.

Figure 4 reviews the history of gasification with its main milestones.
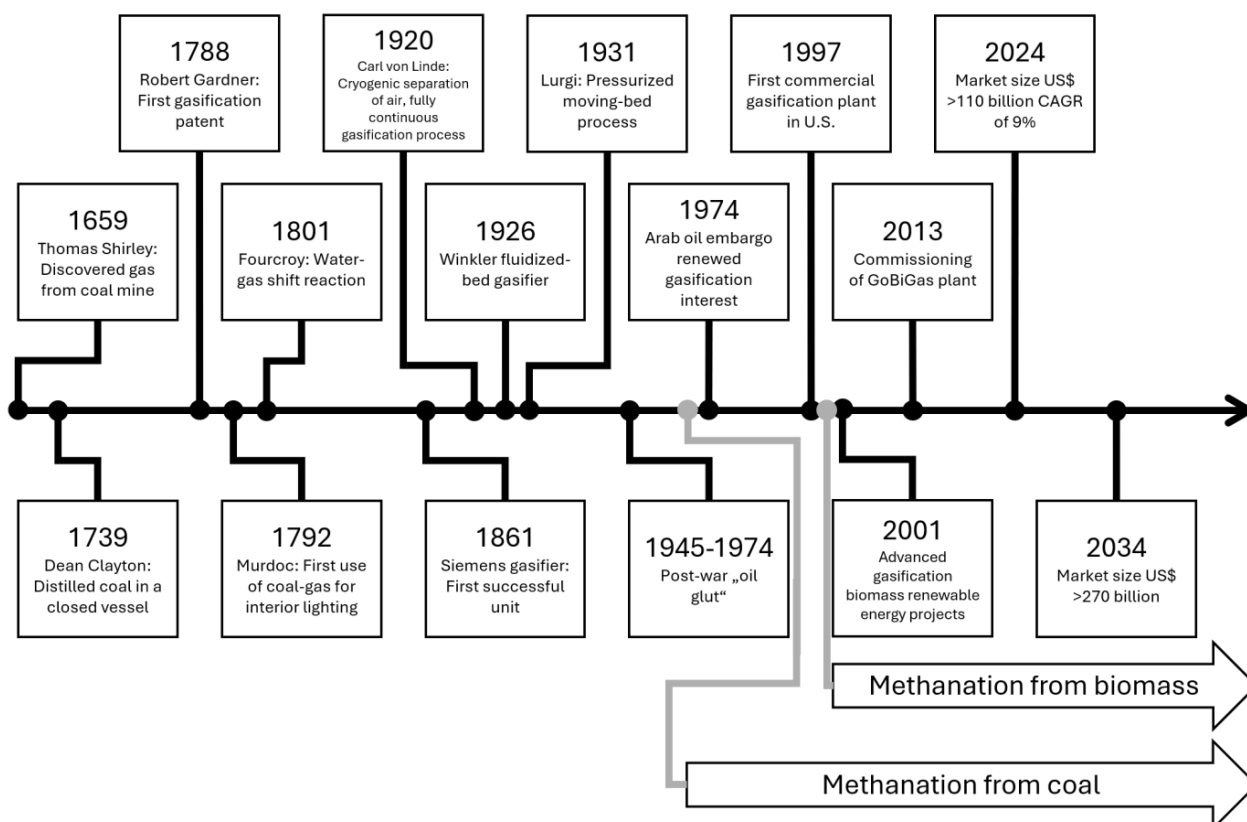

Figure 4. History of gasification, extended from [82]. Market data 2024 and 2034 from FMI [96]. One can see increased momentum.

In 1792, coal-derived syngas was used to light the Soho foundry, and in 1802, that technology was introduced to the public. Frederick Albert Winsor (originally Friedrich Albrecht Winzer) also invented coal gas lamps in Germany in 1804. In general, until 1823, the use of gas for lighting was popular in a large number of English cities. At that time, the price of gas lamps was 75% lower than oil lamps and candles, and this accelerated the development and expansion of gas lamps. In 1859, gas lights spread throughout England, and in 1816, these lights became common in America as well [91].

The history of the gasification process can be divided into four stages: The first stage (1840–1940): Syngas from coal was mainly used to provide lighting for houses and streets as well as heating. With the invention of electric lamps, the demand for gas lamps decreased, but the demand for heating using city gas (town gas) remained. Then, natural gas started to replace city gas. The major embodiments of gasification technologies, such as Winkler

fluidized-bed gasifier, moving-bed gasifier under pressure (Lurgi), and entrained-flow gasifier started working in this period [91,97].

The second stage (1940–1975): During this period, gasification was used to obtain syngas for the chemical synthesis of hydrocarbons and other chemical processes. During World War II, the production of combined gas from coal and biomass gasification for consumption in cars increased, and in a few years, thousands of gasifiers were built to provide fuel for cars. Cars and trucks were equipped with on-board gasifiers. The discovery and extraction of a large amount of natural gas in the 1950s hindered the progress of syngas from coal and biomass, and instead, the manufacturing of a combination of natural gas and gasoline (naphtha) increased in the steam reforming process [91,98]. In South Africa, where apartheid shut off the country from international trade, domestic coal gasification to chemicals was developed, a route also deployed in China.

The third stage (1975–2000): This phase was entered after the 1973 oil crisis. In addition to the production of gas for heating, gasification became a common commercial process for the manufacturing of chemical raw materials. Integrated gasification combined cycle (IGCC) power plants [91,99] were developed. IGCC combines carbon capture and storage with combined cycle generation.

The fourth stage from 2000 onwards: In this stage, renewable energy has won in importance; fossil fuels are being depleted and becoming more expensive, in part due to an emerging legal framework (e.g., emissions trading). The gasification of biomass, as a means of environmentally friendly production of syngas for energy and materials, has gained significance [91,100]. For an overview of gasification plants, see the database of IEA (task 33): https://task33.ieabioenergy.com/database/ (accessed on 30 April 2024). [23]

Figure 4 also shows attempts to make methane from synthesis gas through methanation. For a review of the methanation of biomass-derived syngas, see, e.g., [101], and for modeling [102].

The most important gaseous fuel at the beginning of the industrial revolution was city gas, which was produced by two processes:

1. Pyrolysis, a continuous process of obtaining gas from coke with a relatively high calorific value;
2. Water gas process for syngas from coke [82].

A type of modeling using thermodynamic balancing for fluidized-bed gasification by steam was performed by Schuster and his colleagues [103] who predicted the synthesis gas composition of the fluidized-bed gasifier. In this research, wood waste is used as reactor feed. Jarungthammachote and Dutta (2007) developed a model for different types of gasification, which was able to predict the syngas composition [104]. Zainal et al., (2001) used the stoichiometric modeling method to predict the gas composition of different biomasses [105].

Pellegrini (2007) and his colleagues used a parametric approach to predict the effect of temperature and humidity on the product gas composition [106]. In this research, sugarcane bagasse was used as a gasifier feed. Due to the existence of rich forests and agricultural resources in developed countries, especially in the European area, where most research on gasification took place, a large number of the articles and measurements taken in the field of gasification are related to the wastes and side streams of these wood and agricultural industries, and not all possible biogenic waste and side streams have been fully studied.

Gasification process

As stated, gasification converts solid, carbonaceous materials into gaseous fuel with high calorific value and defined, simple composition, devoid of contaminants.

Abouemara et al., (2024) state the following maximum levels of contaminants for gas engines and gas turbines: <20 ppm of H_2S, <100 and <10–100 mg/Nm^3 of tars, <50 and 30 mg/Nm^3, respectively [107]. This technology includes partial oxidation (pyrolysis) and formation of hydrogen and carbon monoxide; Gasification is useful at different scales for electricity and heat (combined power and heat, CHP generation), but also syngas

as raw material for chemical synthesis, e.g., by the Fischer–Tropsch process, or to make hydrogen [82,85]. Interest has been taken in biofuels, amongst them methanol.

A number of gasification power plants are dedicated to the production of chemical raw materials from coal [24,82]), where one could envisage the next step, i.e., defossilization by switching to a renewable feedstock.

The advantages of gasification can be listed in a summarizing way as follows:

- Making more valuable materials than producing electricity ("polygeneration").
- Feedstock flexibility including heavy oil, coal, raw coke, sewage waste, hydrocarbon-polluted soil, and urban waste.
- The ability to remove contaminants from the feed and produce clean gaseous fuel.
- The ability to convert waste or low-value materials into valuable products.
- The ability to reduce or eliminate pollution and waste.
- The possibility of use in areas far from electricity production centers

The weaknesses and problems of using the gasification technology can be mentioned below:

- The need to prepare the biomass, as well as the limited possibility of some biomass sources (sustainable forest management practice is imperative, for instance).
- The need to refine the produced gas (removal of tars and dust).
- The need for relatively complex technical equipment compared to combustion.
- The need to employ specialized human resources ([82]), but this can be mitigated through automation.

Today, there are large-scale coal gasification plants (up to 5 $GW_{thermal}$), but only comparatively small biomass gasification plants, with the Swedish GoBioGas project aiming for scaling up from 20 $MW_{thermal}$ to 100 $MW_{thermal}$ being the largest one (the project now focusses on bio-CH_4).

The efficiency of electricity generation from syngas gas engines lies in the range of 20% to 35%, which is also typical for steam and gas turbines where up to 50% electrical efficiency is feasible. Integrated CHP systems can have an overall efficiency of as high as 90% [107]. The minimum efficiency for CHP in the state-of-the-art can be given as 60%. This threshold is also the limit to obtaining state support for biomass plants in Austria (Oekostrom, 2023). In a recent techno-economic optimization of a biomass gasification energy system, Soltani et al., (2023) estimated the exergy efficiency of the fuels MSW, wood, and paper biomass as 41.21%, 40.25%, and 39.33%, respectively, and the LCOE (levelized cost of energy) between 30.77 and 33.6 USD/MWh [108].

Different stages of the gasification process:

Gasification and combustion are two thermochemical processes that are relatively close to each other [85], but they have one important difference: gasification yields energetic compounds, while combustion aims at full energy release so that ideally only CO_2 and H_2O are released from the stack (a condensing boiler would recuperate the water vapor's latent heat, too, increasing efficiency by typically 10%). In gasification, hydrogen can be added to the gas product (e.g., via steam) to increase the ratio of H:C (i.e., H_2/CO) in the produced gas [91,109]. A gasification process is composed of several steps; see Figure 5 [91]:
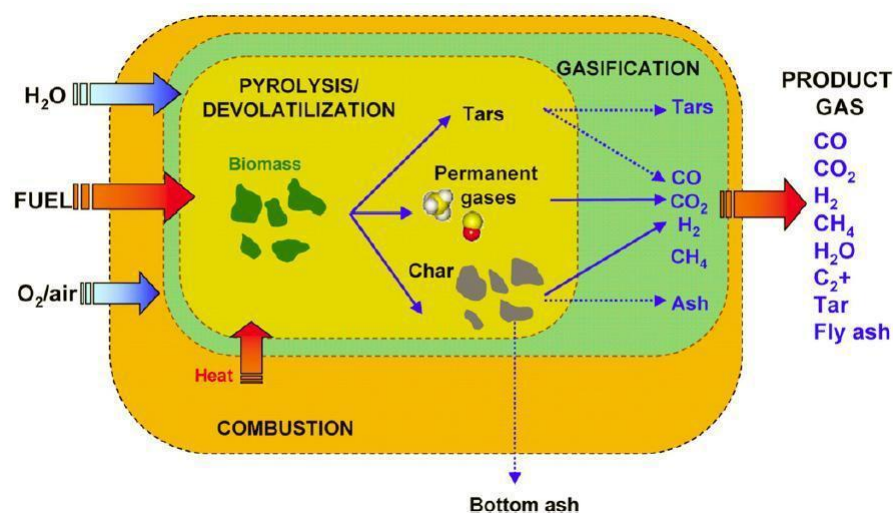
Figure 5. Gasification process. Source: [91].

Figure 5 shows the supply of the fuel and gasifying agent from the left and the extraction of the product gas at the right. The processes of combustion, heat provision, pyrolysis/devolatilization, and gasification occur simultaneously. Ideally, tars are broken down. Depending on the gasification process, different bed materials can be used. Feedstock flexibility is a key advantage of the process.

The fuel is subjected to drying, after which thermal decomposition occurs. Pyrolysis and devolatilization take place. In the next phase, some of the syngas, and the remaining char, are burnt to provide energy for the process, since drying and gasification are endothermic. Although these stages occur one after the other, there is usually overlap [82,110,111]. Laboratory-scale units provide electrical heating.

Preheating and drying:

In general, each kilogram of moisture present in biomass needs 2260 kilojoules of energy in the gasifier to evaporate that water, so in general, a high amount of biomass moisture in gasification is not desirable. Therefore, a certain amount of drying/preheating is carried out before entering the feed into gasification. To produce gas with a higher calorific value, most commercial gasification systems require dry biomass as feedstock. The maximum permissible water content is between 10 and 20% by weight (Sikarwar et al., 2017; [82]). Note that this is a lower water content than that required for biomass combustion. Also, the particle size distribution of the fuel tends to be narrower for gasification than the typical combustion processes can tolerate. This can pose challenges for cheap feedstock provision.

The final drying of biomass happens after it enters the gasification unit, whose energy is supplied by the downstream gas currents in the hot area. This heat causes the feed to dry and the residual water is separated from it at a temperature of approx. 100 °C. As the temperature increases, compounds with low molecular weight begin to be emitted by devolatilization, and this process occurs up to roughly 200 °C [82,112].

Pyrolysis:

In the pyrolysis zone, no external mediators are added; pyrolysis occurs before (upstream of) the reduction zone and causes the thermal decomposition of large biomass molecules into smaller gaseous ones. One of the important products of this zone is tar, which is caused by the distillation of vapors produced in the process (Figure 6; [82,113,114]).
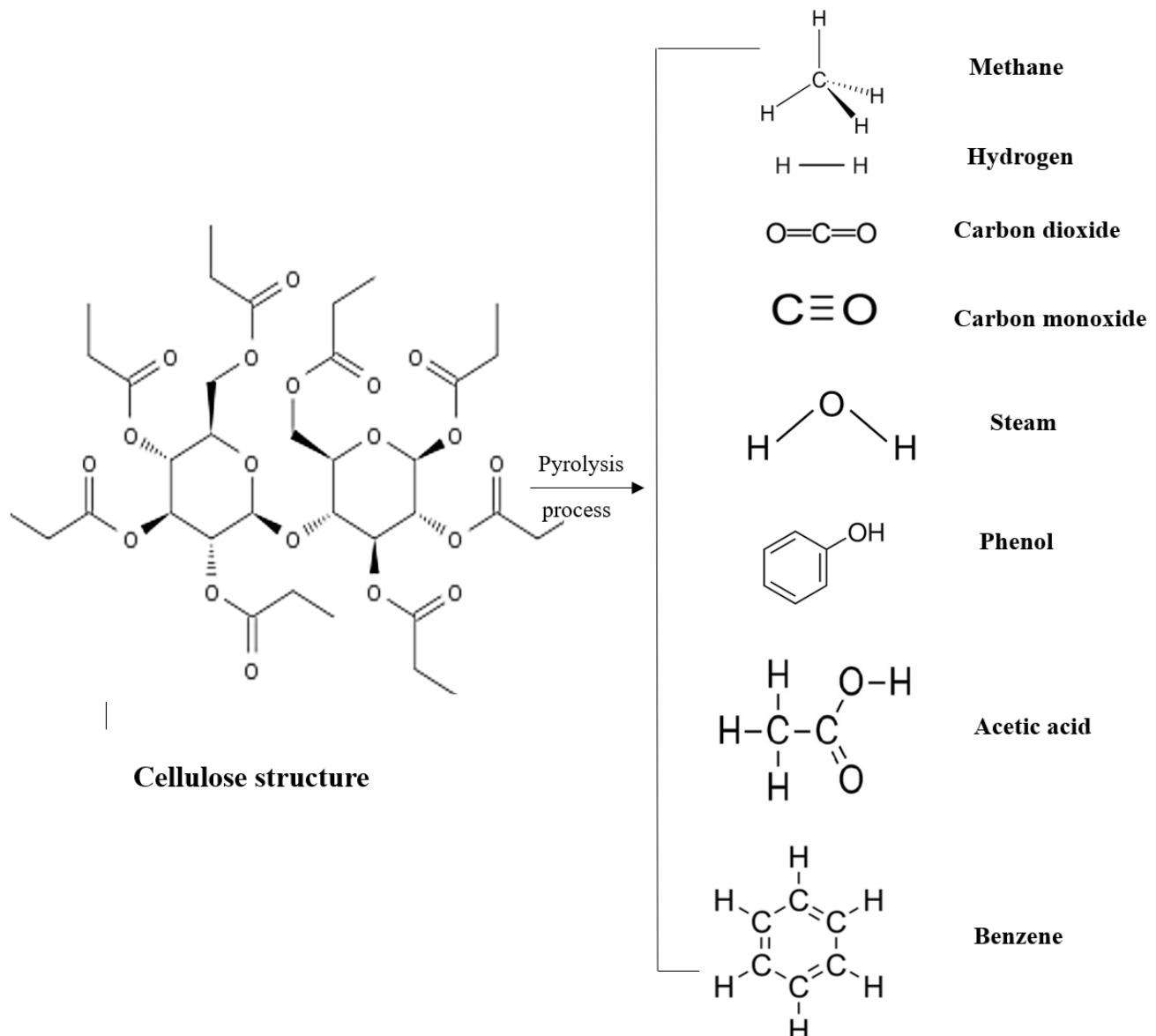
Figure 6. The conversion of organic macromolecules like cellulose into smaller molecules during pyrolysis. Redrawn based on the original illustration in [91].

The composition of pyrolysis products depends on the process temperature and heating rate [91,115]. Also, the reactor design and residence time are relevant. The primary product of pyrolysis consists of gasses (CH_4, CO_2, H_2, and CO) and solid char, and liquids. Part of these decompositions take place in the homogeneous reactions of the gas phase and part in the heterogeneous reactions of the gas–solid phase [91,115].

The pyrolysis process is characterized by a general reaction like the following equation [91,115].

$$C_n H_m O_p (biomass) \rightarrow \sum liquid\ C_x H_y O_z + \sum gas\ C_a H_b O_c + H_2O + C\ (char)$$
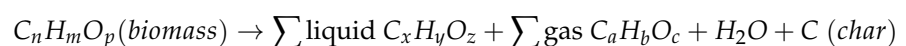
The production of tar and other products depends on the pressure of the gaseous compounds and the presence of mineral catalysts [91]

The pyrolysis temperature also determines the amount of syngas [91].

The heating rate of the biomass particles (and their size) influences the composition of the pyrolysis products. A fast heating rate up to medium temperature (400–600 °C) causes volatile substances to be released and the production of fuel liquids, while a slow

heating rate up to that temperature causes gasification to gaseous products and more char production (Figure 7, [91]).
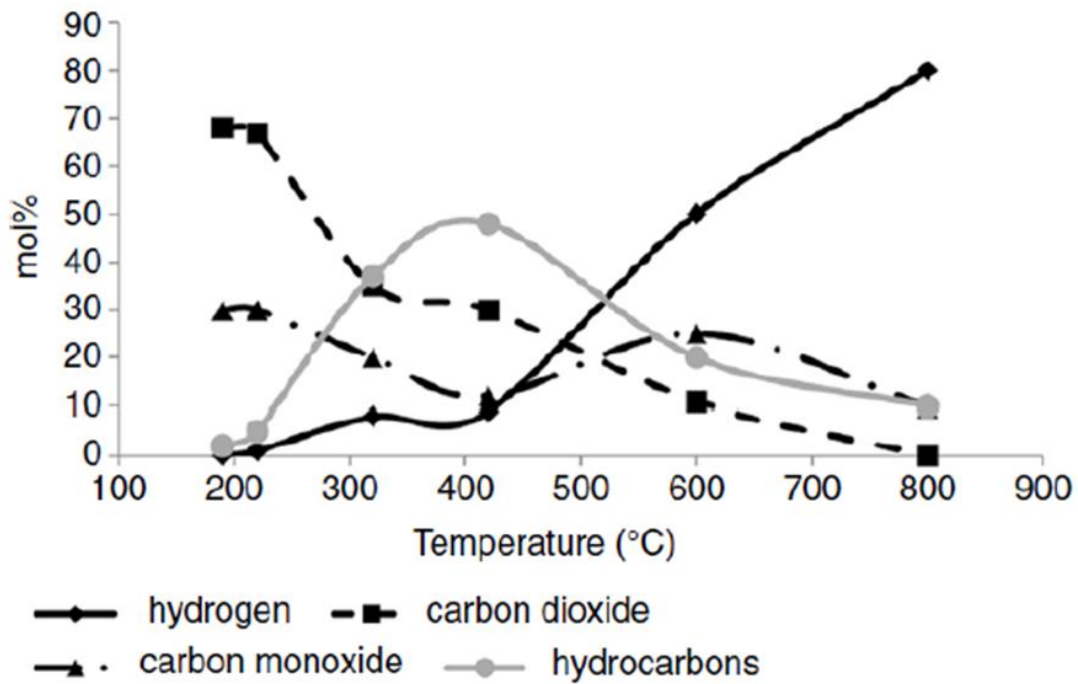

Figure 7. How pyrolysis temperatures influence the production of different gasses [91].

If the heating rate is low, first the formation of vapors occurs quickly and then the gasification process is complete. If the heating rate is high, the gasification and pyrolysis process will occur simultaneously (Figure 8, [82,116]).
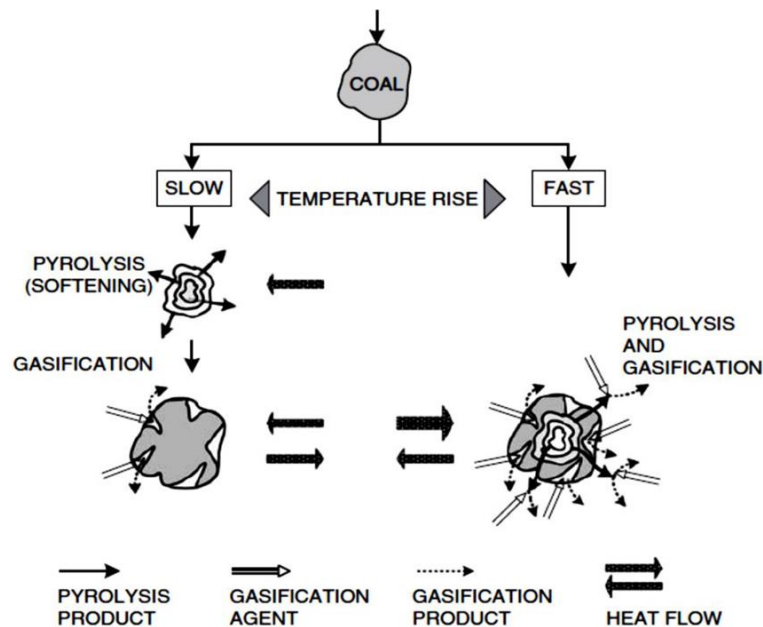

Figure 8. Effect of heating rate on a fuel particle, here coal ([82]). The model can also be applied to biomass.

Dwelling time also has an important effect on production. When the heating rate is low and the residence time is long, the slow and gradual release of volatiles in the reactor

allows secondary reactions between char components and volatiles to occur, leading to the production of secondary char [91,117].

In order to achieve the desired products, the following experimental results should be considered in the reactor:

In order to increase the fraction of char product ("biochar"), a long residence time in conjunction with a low heating rate and low temperature should be applied. Such a product, when free from heavy metals, can be used for soil amelioration.

In order to increase the fraction of liquid products, a high heating rate, intermediate final temperature (400–600 °C), and short residence time should be applied.

In order to increase the yield of gaseous products, a low heating rate, high final temperature (700–900 °C), and long residence time should be applied [91]

Regeneration:

The regeneration stage after pyrolysis includes chemical reactions between reaction educts, products, and steam inside the reactor. Char gasification is one of the most important parts of the process. Char produced in pyrolysis, which is obtained from biomass, is not necessarily pure carbon and may contain adsorbed hydrocarbons. The porosity of biomass char is about 40 to 50%, while coal char has a porosity of only about 2 to 18%. The pore size of biomass char typically 20-30 micrometers exceeds that of coal char [118,119].

The main reactions that occur in this step are as follows:

(1) Boudouard reaction $CO_2 + C \rightarrow 2CO$ -172.6 (kJ/mol)
(2) Water–gas reaction $C + H_2O \rightarrow CO + H_2$ -134.4 (kJ/mol)
(3) Methane production reaction $C + 2H_2O \rightarrow CH_4$ $+75$ (kJ/mol)

By subtracting Equations (1) and (2), one obtains the water–gas displacement equation [105,120].

Water–gas displacement reaction $CO_2 + H_2 \rightarrow CO + H_2O$ $+41.2$ (kJ/mol)

Note: by contrast, the so-called water–gas shift reaction (WGSR) describes the reaction of carbon monoxide and water vapor to carbon dioxide and hydrogen: $CO + H_2O \rightleftharpoons CO_2 + H_2$

Gasifier design:

The embodiments of gasification reactors are very similar and are divided into two main types: fixed beds and fluidized beds. Since the reaction between the gasification agent air (or oxygen or steam) and fuel (biomass) takes place in the gasifier, they are classified according to the entry ways of air (oxygen) and fuel into the gasifier [121,122].

Fixed beds:

Fixed-bed reactors are considered to be one of the most widely used gasification reactors due to their simplicity in design. They are designed on medium and small scales. And, they are mainly divided into two types—updraft and downdraft [84,121].

Reactor with updraft gas producer:

The reactor has specific areas for the regeneration and pyrolysis combustion section. In this reactor, air enters from below and interacts with the flow of materials (fuel). This reactor reaches high efficiency because the hot gas is directed through the fuel bed and exits the reactor at a low temperature [121,123].

The heat content of the gas can be used for preheating and drying the input material (biomass). A high amount of soot and tar in the final gas and the limited ability for partial load operation are disadvantages of a reactor with updraft gas producer. For this reason, in line with the goals of reducing greenhouse gas production, this system is less used [121].

Downdraft gas producer reactor:

In this reactor, the incoming air flows downward, that is, on the fixed bed of solid feed and gas, it is drawn downward. Low overall efficiency and operational problems regarding steam and high ash content are the general problems of small downflow gas-producing reactors [123]. The time to start up the device and reach the appropriate temperature for gas production is shorter than that of upflow reactors, hence these reactors are preferred over upflow reactors for use in various systems [121].

Twin-fire gas producer reactor:

The advantages of reflow and counterflow reactors are combined to create a reactor with two combustion chambers. This reactor includes a specific area for reaction. Induction drying takes place at a low temperature and gas decomposition occurs at a higher temperature. This reactor produces clean and suitable gas [84,121].

Gas production reactor with cross draft (cross draft producer)

Although this reactor has some advantages over other reactors, it does not seem like an ideal reactor. Among its disadvantages, we can point out the high exit temperature of the gas and a low H_2/CO ratio, which is the result of its design. The characteristic of this design is exclusively for fuels that have little ash content, such as wood and coking coal. One of the main features of this reactor is the ability to load well, and the start-up time is very fast [121,124].

Currently, there are about 64 manufacturers of large gasification equipment around the world [112,125].

Kumar et al., (2009) investigated the effects of furnace temperature, steam–biomass ratio, and equivalence ratio in a fluid-bed gasifier [25]. Due to the low temperature in a part of the gasifier bed, the formation of CH_4 was higher than in the other experiments [104] (13 to 24%) and H_2 was low (4 to 15%). At a sufficiently high temperature (850 degrees Celsius), the amount of H_2 starts to deviate from the conventional behavior and decreases with the increase in the equilibrium ratio. Campoy et al., (2009) investigated the effect of oxygen concentration in the enriched air of biomass gasification steam in a fluidized bed [126].

Gasification and fuel cells:

Abouemara et al., (2024) studied the combination of biomass gasification and solid oxide fuel cells (SOFCs) [107]. They found a remarkable electrical efficiency of the fuel cells running on syngas of 30–60%. Fuel cells require cleaner syngas than gas engines and gas turbines, and their electrical efficiency on pure hydrogen was reported to be up to 90%, yet one can see the potential of this new technology, where the TRL (technology readiness level) is currently at 1–3. As the share of electrical energy is expected to increase in the future, the syngas from biomass coupled with fuel cells could play a dominant role in carbon-neutral power.

Polygeneration—the future of biomass gasification:

Polygeneration follows more than 2 objectives, e.g., electricity, heat, cooling, or materials [127], starting with trigeneration [128].

Producing value-added materials from gasification gives the operators additional revenue and independence from energy prices. The conversion of syngas into bioplastics and protein for feed and food has been proposed [129,130].

For a recent review on polygeneration, see [131].

Gas fermentation:

While classic fermentation with bacteria and yeasts uses sugars as feedstock, gas fermentation deploys gaseous raw materials and chemoautotrophic microbes. There are aerobic processes, which utilize methane, and anaerobic processes that work on CO or $CO_2 + H_2$ with various biocatalysts. A major advantage over carbohydrates is that there is no competition over feed and food resources, as feed gas can be produced by a wide variety of (waste) feedstocks. Gas fermentation is typically carried out in plug flow reactors instead of stirred tanks to increase the raw material utilization, and different strategies are applied to increase mixing and mass transfer, overcoming the low solubility of CH_4 and H_2, respectively, in the aqueous growth medium [132]. The target products of gas fermentation are commodities such as fuels, protein for feed and food (single-cell protein, SCP), and bioplastics, amongst them polyhydroxyalkanoates (PHA). Perret et al., (2024) demonstrated ethanol production from syngas using *C. ljungdahlii* continuously over 3000 h [133]. Flüchter et al., (2019) [134] made PHB using *Clostridium coskatii*. Redl et al., (2017) used *Moorella thermoacetica* to obtain acetone from syngas [135]. One strategy to increase the number of possible target products is a two-stage fermentation, where syngas is converted into acetate using, e.g., acetogenic bacteria, and then the acetate is fermented aerobically using different bacteria or fungi. In that way, for instance, single-cell protein (SCP), PHB,

lipids, butanol, hexanol, and octanol could be obtained [136]. For a discussion of fermenter types for gas fermentation, see [137]. Table 8 lists possible target products from syngas fermentation, with acetate and ethanol being the most straightforward ones.

Table 8. Products accessible through syngas fermentation (selection).

Feedstock	Strain(s)	Product	Optimum Conditions	System	Performance Data	Source
Syngas (H_2, CO)	Mixed	Acetate	T = 20 °C, pH = 4.5	2 L, bottled pure gasses	Theoretical acetate production of 83%	[138]
CO or CO_2 + H_2	*Clostridium carboxidivorans*	Hexanol, Butanol, and Ethanol (H-B-E fermentation)	pH = 5.6	0.25 L CSTR	Highest productivity 60 mg/L*h of total solvent on syngas	[139]
Syngas	*Eubacterium callanderi* KIST612 (formerly *E. limosum*)	Acetate (*)	T = 37 °C, pH = 7	0.5 L bubble column		[140]
Syngas	*Clostridium ljungdahlii*	Ethanol			Techno-economic analysis	[141]
Syngas	*Clostridium autoethanogenum*	Ethanol		Scale-up to large systems	7–8.5 g/(L*h)	[142]
Syngas	Mixed	Caproate, caprylate		Biofilm-based reactor systems		[143]
Syngas	*Rhodopseudomonas palustris PT*	Hydrogen (**) (Biohydrogen, water–gas shift (WGS) reaction)	Ambient (30 °C, pH = 7)	Serum bottles (125 mL)		[144]
Syngas	Anaerobic culture from a 3000 m^3 municipal solid waste digester	Methane (biomethanation)	T = 55 °C	Reverse membrane bioreactor (RMBR)		[145]

(*) other strains for syngas to acetate are *Acetobacterium woodii*, *Clostridium aceticum*, *C. ljungdhalii*, and *C. autoethanogenum* [140]. (**) dark fermentation is an alternative route for biomass to H_2, see [146].

Robles-Iglesias et al., (2023) demonstrated that syngas can be converted into oils and beta carotene by 2-stage fermentation, where first acetate and butyrate (2 VFA, Volatile Fatty Acids) were made and then a yeast, an engineered *Yarrowia lipolytica*, converted this compound into the target products in a second fermenter [147]. For downstream processing (ethanol), see, e.g., [148]. For a discussion of medium and mineral recycling in syngas fermentation with an electrodialysis system, see [140]. A recent review on syngas fermentation was prepared by Sun et al., (2019) [149] and Calvo et al., (2022) [150], who concluded the following:

After a period of low interest from 1984 to 2008, there is now strong interest in syngas fermentation, with 3 emerging topics (metabolic engineering, chain elongation, and biorefineries); there is little collaboration, which can be an opportunity for advancement in the near future.

By the methanation of syngas [101,102], CH_4 for aerobic gas fermentation can be obtained from waste biomass streams, enabling methanotrophic gas fermentation. The microorganisms in gas fermentation can tolerate impurities in feed gasses better than conventional catalysts, and they allow for specific end-product manufacturing. Additional potential can be seen in the side stream valorization of fermentation processes, as well as in energy recovery, e.g., through heat pumps [151].

3. Conclusions

Many stakeholders have an extensive program to research, develop, and maximize the potential of gasification with a renewed interest in biomass as fuel. Gasification is a reliable way to produce low-cost, environmentally friendly energy, i.e., power and heat, preferably in combined mode (CHP), as well as hydrogen and synthesis gas. A wide range of high-value products and chemicals, including fuels for transportation, proteins for feed and food, biopolymers as well as biobased building blocks can be produced from synthesis gas through gas fermentation. As such, making materials from syngas is a way to "escape" volatile oil prices and economic and environmental concerns by providing commodity materials from a new, broad, and previously underutilized feedstock base, one of a renewable nature. The ample availability of waste biomass, and the flexibility of the gasification process, are particularly attractive. It is expected that the most important users of large-scale gasification in the future will be found among the following industries: metallurgy, ceramics, cement, lime, and pulp and paper, mainly for energy provision. In these industrial branches, converting furnaces, boilers, and dryers from oil fuel to biobased syngas is basically a simple operation.

Reducing the consumption of energy from oil and gas in energy-intensive industries through the conversion of waste materials into syngas for energy provision is a safe and justified way from an environmental and economic perspective.

For materials, the gas fermentation of syngas offers a viable route, which is decoupled from primary agricultural production. The waste and side streams of various biomass resources can be utilized to make biofuels, bioplastics, and protein for feed and food as well as biobased building blocks for the chemical industry, defossilizing multiple branches. It is particularly the aspect of scalability which has to be borne in mind. Syngas can be made from virtually all carbonaceous raw materials, and it can be a key enabling technology to make the bioeconomy happen, where biocatalysts allow for the selective production of a wide array of materials. In the future, the integration of biomass gasification with carbon capture and storage (CCS) technologies could further mitigate carbon emissions, positioning biomass as a cornerstone of the bioeconomy. This synergistic approach not only supports energy security but also promotes environmental sustainability by reducing reliance on fossil fuels and minimizing waste through the valorization of agricultural and urban residues, and gas fermentation can be used to make bulk materials from the syngas.

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