1

Introduction

For the past several hundred years, most of our daily needs for transport fuels, chemicals, heat, and power have been met by using fossil carbon-rich sources (i.e., coal, crude oil, and natural gas). These fossil fuels are likely to continue forming the backbone of energy resources for the foreseeable future as well. According to the International Energy Agency, fossil fuels currently make up to 85% of total world primary energy consumption and are widely believed to be responsible for the increase of greenhouse gas concentrations (e.g., carbon dioxide, methane, and nitrous oxide) in the Earth's atmosphere. The atmospheric CO_2 concentrations have risen from 280 ppm before the Industrial Revolution to 424 ppm_v in the year 2024, and the Intergovernmental Panel on Climate Change (IPCC) forecasts that the atmospheric CO_2 could reach as high as 590 ppm_v by the end of this century. The policy response to CO_2 emissions was a United Nations agreement in 1997, the Kyoto Protocol, which was extended in 2015 by the Paris Agreement (COP 21). In the Paris Agreement, a long-term goal was set by the signatories to limit the increase in global temperature to no more than 2°C above pre-industrial levels, but aimed to keep it to 1.5°C.

There are many technical pathways for transitioning to a sustainable energy system, including optimal use of resources, improving the efficiency of thermal power and other industrial plants, phasing out coal-fired power generation, expanding power generation from renewable energy sources, and switching to electricity instead of fossil fuels in areas such as transportation, buildings, and industry. Increased efficiency is always desirable since it not only means better use of resources but also indirectly reduces the impact on the environment. From the point of view of limited resource availability and environmental impact, the use of fossil fuels is not sustainable in the long-term perspective. However, in the transition from fossil fuels to renewable energies, efficient and environmentally friendly use of fossil fuels must also be ensured. For example, the German government passed legislation in 2020 to phase out coal-fired power generation by 2038 at the latest, and preferably by 2035. While the phase-out is underway, the expansion of renewables is targeted. So, in 2024, the share of renewable energies (mainly wind and solar power) in the public electricity supply in Germany reaches a record level of more than 50%. Globally, wind and solar provided about 14% of the world's electricity demand in 2024

Sustainable Polygeneration based on Carbon Capture and Utilisation, First Edition. Falah Alobaid and Bernd Epple. Published 2026 by Wiley-VCH GmbH.

(according to Statista), and their share is expected to continue to rise while their costs continue to fall. Nevertheless, if power grids are to accommodate a greater share of renewables with variable feed-in, they will need the flexibility of supporting infrastructure such as energy storage systems. For some energy-intensive technologies (e.g., metallurgy and cargo ships) that are difficult to electrify, many experts describe a growing role for hydrogen or ammonia as a fuel produced from renewables or low-emission energy sources.

A promising concept for achieving a sustainable energy system is multigeneration (widely known as polygeneration). In this concept, several services are provided simultaneously, e.g., electricity, heat, cooling, and raw materials for the chemical industry, whereby the plant can be fired with fossil fuels (e.g., coal or natural gas), renewable energy sources such as biomass and solar energy or waste heat. Compared to single-generation units, polygeneration plants can significantly improve overall efficiency, minimise overall losses and emissions, and improve resource utilisation through appropriate fuel switching or blending. CO_2 capture and utilisation methods as part of polygeneration may offer several advantages for the synthesis of chemicals and fuels.

1.1 Carbon Dioxide

A large portion of atmospheric CO_2 over the last million years has been governed by the biogeochemical carbon cycle. Together with the nitrogen cycle and the hydrologic cycle, the carbon cycle involves a sequence of events that are critical to Earth's ability to sustain life. It describes the movement of carbon, how it is fixed and released throughout the Earth's biosphere, pedosphere, geosphere, hydrosphere, and atmosphere. Among the most important natural processes leading to the release of carbon dioxide from land and ocean into the atmosphere are animal and plant respiration, and the decay of vegetation that converts oxygen and nutrients into CO_2 and energy. The carbon taken up by vegetation (123 Gt per year) is stored in biomass, but 60 Gt of carbon produced by plant respiration processes is released back into the atmosphere per year. The release of CO_2 from currently decaying biomass and the respiration of animals in the ecosystem contribute to another 60 Gt of carbon per year (Dusenge et al., 2019). This results in a carbon fixation of 3 Gt of carbon per year in soils. In the oceans, photosynthetic organisms also take up 92 Gt of carbon per year, while respiration and decay lead to a release of 90 Gt of carbon per year. Overall, this leads to a carbon fixation of 2 Gt per year in ocean sediments. Volcanic emissions also release carbon from rocks deep in the Earth's crust, but the amount is relatively small on a global scale, at about 0.13 Gt of carbon per year. The estimated 9 Gt of carbon per year released by human activities, i.e., from the use of fossil fuels (e.g., coal, crude oil, and natural gas), but also the production of materials (e.g., concrete), deforestation and agriculture (including livestock), has created an imbalance in the global carbon cycle. As the rate of carbon release exceeds the rate of carbon fixation, the concentration of carbon in the atmosphere increases by 4.13 Gt per year. Looking at carbon dioxide instead of carbon, the CO_2 emissions hit a record of 36.7 Gt in 2019. The COVID-19 pandemic reduced global CO_2

emissions by 1.9 Gt to 34.8 Gt in 2020, but CO_2 emissions rose again when lockdown measures were relaxed, reaching 37.4 Gt in 2024 (Statista). In the annual report of the National Oceanic and Atmospheric Administration (NOAA), the average global atmospheric CO_2 concentration reached 423.64 ppm_v in November 2024, which is the highest level ever measured and about 50% higher than the CO_2 concentration at the beginning of industrialisation in the 18th century (see Figure 1.1).

Fossil fuels are, by nature, a limited resource with a total potential of about 580×10^3 EJ, where coal accounts for by far the largest share at around 88%. The current reserves of fossil fuels (in 2024), i.e., the deposits that can be economically and technically exploited, amount to about 40×10^3 EJ. With the current consumption of about 0.525×10^3 EJ per year, and given the increasing demand for coal, crude oil, and natural gas, known reserves will continue to account for the largest share of world primary energy consumption in the medium term, apart from possible shortages in the oil supply. This is since the expansion rate of renewable energy sources (e.g., biomass, wind, and solar) cannot keep up with the pace of increasing global energy demand (due to economic growth and the rapidly increasing global population). Biomass provides a stable feed into the power grid, but its use should not impact food availability and prices. By contrast, the availability of wind turbines and photovoltaic systems in the power grid is limited and difficult to predict. They typically provide a fluctuating feed to the power grid, requiring energy reserve solutions such as flexibly dispatchable power generation units (e.g., Combined Cycle Power Plant [CCPP]), or energy storage systems (e.g., high-temperature thermal energy storage or rechargeable batteries) to balance electricity supply and demand. These solutions differ in their potential impact, technological maturity, and economic viability, so the future electricity system could incorporate some of these concepts to varying degrees and integrate value-added processes beyond electricity, such as power-to-fuel technologies. The latter is known as carbon-neutral fuels or e-fuels (e.g., hydrogen, methane, methanol, or ammonia) and can be produced from renewable energy sources by the electrolysis of water to make hydrogen that can be used to hydrogenate the carbon dioxide captured from thermal power plants or air, or derived from carbonic acid in seawater (Haaf et al., 2018). In contrast to the power sector, where the share of renewable energies has risen sharply in recent

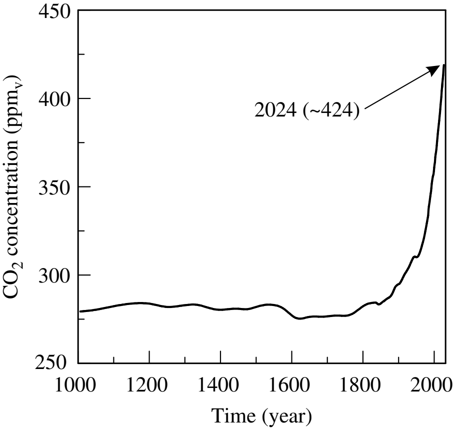

Figure 1.1 The development of the globally averaged carbon dioxide concentration over time.

years, the transport sector (e.g., cars, vans, buses, trucks, and aeroplanes) is heavily dependent on fossil fuels, especially gasoline, diesel, heavy fuel oil, and kerosene. Nevertheless, great progress was made in the introduction of electric cars and vans in the European Union in 2024, with around 14% of new registrations being electric vehicles. The world still relies on conventional energy resources for domestic needs such as heating, cooling, and water production. In addition, natural gas and crude oil are still important raw materials in the chemical and petrochemical industry for the manufacture of a wide range of products, from plastics to fertilisers and pharmaceuticals.

Currently, fossil fuels are used almost exclusively in a linear economy, in that they are consumed directly for energy services (e.g., electricity, heating, and cooling), freshwater production, and chemical synthesis (e.g., plastics or fertilisers). As a result, the carbon content of the used fossil resources is released into the atmosphere as CO_2 after use. For example, only 14% of plastic waste is recycled, and most of it is processed into low-quality products (Pilapitiya & Ratnayake, 2024; Syberg et al., 2021), while the remaining part incinerated or landfilled after material use. To keep climate change within 2°C or 1.5°C compared to the pre-industrial era, following the Paris Climate Agreement, only a limited amount of anthropogenically emitted CO_2, known as the 'Carbon Budget', can be released. There is a wide range of estimates for the remaining carbon budget, but they are essentially on the order of 580 Gt_{CO_2} for the 1.5 °C target or 1500 Gt_{CO_2} for the 2°C target (Damon Matthews et al., 2021; Friedlingstein et al., 2023). If no efforts are made to reduce CO_2 emissions, these carbon budgets will be depleted in about 15 and 40 years, respectively (the average global CO_2 emissions amount to 37.4 Gt_{CO_2} per year).

The IPCC regularly summarises the state of scientific research on climate change and, in this context, identifies possible measures to reduce CO_2 emissions to achieve a circular carbon economy (a replacement of the existing linear economy), in which carbon once used is made available for subsequent products through innovative processes. Figure 1.2 provides a simplified illustration of the circular carbon economy concept. In the outer cycle (electricity cycle), power can be generated from renewable sources (e.g., wind, solar, and hydropower) and in thermal power plants equipped with carbon capture technology. The power generated can be stored and/or used for domestic and industrial purposes, and in water electrolysis plants to produce hydrogen. The hydrogen is fed into the second cycle, where it can be used as a reducing gas in steel production and, if required, for environmentally friendly power generation (e.g., with a fuel cell or gas turbine). The hydrogen can also be fed into the inner cycle, where biomass and waste are processed through gasification or pyrolysis into important raw materials (chemicals and fuels). The synthesised fuels can be burned in thermal power plants with carbon capture technology to generate electricity, while the chemical products serve as the basis for a wide range of valuable products such as fertilisers and plastics manufacturing. After being used, the wastes (plastics) are returned to the gasification plant, ensuring a continuous and sustainable resource cycle.

The current potential to control and reduce CO_2 emissions is based on three main strategies, namely the growing share of renewable energy sources, the efficient

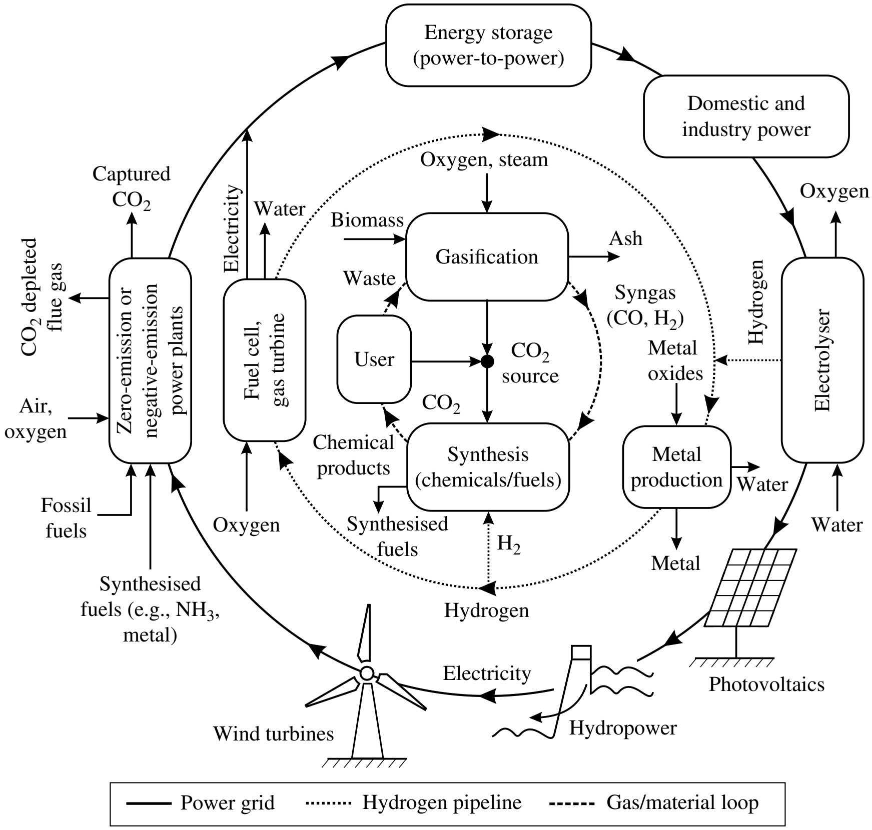

Figure 1.2 Circular carbon economy.

use of fossil fuels, and the deployment of carbon capture and storage technologies. The first strategy (electricity generation from renewables), which is in some cases weather-dependent, leads to a new discussion on the flexibility of power generation systems and especially the power grid (Alobaid et al., 2017; Hussain et al., 2023). In Germany, for example, fluctuating wind energy can lead to extreme situations, such as a sudden increase or decrease of several dozen GW_{el} within a few hours, resulting in negative prices on the spot market or dark doldrums, so-called blackout (a period in which no power or very little electricity can be generated from wind and solar). Energy reserves (e.g., conventional thermal power plants or energy storage systems) are necessary to achieve a balance between electricity supply and demand (Islam et al., 2024). Accordingly, the economic potential of cost-effective energy storage systems to efficiently integrate large renewable shares into the power grid is significant. Despite recent advances in rechargeable batteries, driven by the automobile industry, the specific costs of these storage systems still limit them to small-scale applications (e.g., light-duty electric vehicles and portable electronics). Currently, there is no economically viable energy storage technology capable of meeting the required capacity, which is on the scale of TWh rather than MWh. Thermal power plants are now the key factor in integrating larger shares of renewable energies into the power grid. Due to the massive expansion of renewable energies in some countries, however, the economic operation of thermal power plants should be achieved at 1,500–3,000 full-load hours per year, while these plants are traditionally designed for 6,000–8,000 full-load hours per year.

The second strategy aims at designing modern conversion systems with high efficiency, low emissions, and high flexibility in terms of load change rates and start-up/shutdown times, and with modern flue gas cleaning equipment. Currently, the average thermal efficiency of coal-fired power plants worldwide is between 30 and 38%. There is a broad consensus on the need to replace outdated, emission-intensive fleets with modern, highly efficient ones. The newly built coal-fired power plants can achieve a net efficiency of up to 46% for hard coal and 43% for lignite (Lee et al., 2023; Walter & Epple, 2017). In addition, modern Combined Heat and Power (CHP), or high-efficiency CCPPs, are among the most viable options for improving efficiency and reducing emissions. The nominal process efficiency of CCPPs can be as high as 60%. Large CCPPs with an efficiency of up to 62.2% are now operated in Germany (Irsching) (Scholz & Zimmermann, 2012), France (Bouchain) (Vandervort et al., 2016), Indonesia (Tambak Lorok) with a net electrical output of about 760 MW_{el} per unit (Alobaid et al., 2024; Vandervort et al., 2019). However, many scientists believe that these improvements may not be enough to reduce CO_2 emissions in the future, as demand for transportation, energy, and chemicals will likely increase.

The third strategy to reduce CO_2 emissions is related to CO_2 capture from the emission sources. Depending on where the CO_2 is captured (downstream or upstream of the process) and the method of fuel oxidation, three CO_2 capture methods are possible (pre-combustion, post-combustion, and oxyfuel) (Leung et al., 2014). In pre-combustion, the fuel is partly oxidised with air or oxygen and/or steam to form raw syngas consisting mainly of carbon monoxide, hydrogen, carbon dioxide, and other trace elements. After capturing the CO_2 and removing the trace elements, the cleaned syngas can be converted into value-added chemicals or combusted in an internal combustion engine, fuel cells, gas turbines, or combined cycles (Heinze, 2021). The post-combustion takes place just before the stack and is therefore also referred to as end-of-pipe technology, allowing for easy retrofitting into existing thermal power plants and industrial processes such as cement production. Both pre- and post-combustion involve the separation of CO_2 from a gas mixture, composed of CO_2, H_2, and CO in the first approach and CO_2 diluted in air and other combustion gases, such as sulphur dioxide or nitrogen oxides, in the second approach. CO_2 capture in pre- and post-combustion can be achieved by four different processes, namely absorption, adsorption, membrane separation, or cryogenic process (Soo et al., 2024; Yu et al., 2012). The adsorption processes separate gas mixtures by selective attachment of molecules to a solid surface (adsorbent). The absorption processes run on a similar principle, but a liquid solvent takes up the molecules. The membranes act like a filter that separates certain components from a stream of different gases based on different mechanisms. The feed stream is divided into two parts: the permeate stream, which consists of the gas molecules that could pass the membrane, and the retentate stream, which contains the gas molecules that could not pass the membrane. The cryogenic processes are based on the separation of gases by condensation (e.g., an air separation unit can separate oxygen from the air). Currently, absorption processes (scrubbing or carbonate-looping process) are considered the most mature technology for CO_2 capture from raw syngas obtained from a gasifier or flue gas from a combustion process (Hilz, 2019). In the third CO_2 capture method, the oxyfuel process, the fuel is burned with pure oxygen mixed with recirculated flue gas to achieve a lower adiabatic combustion temperature. After cleaning the flue gas of pollutants and separating the vapour by condensation, the flue gas consists of almost pure CO_2, which can be compressed effectively for transportation and storage. Providing pure oxygen via an energy-intensive air separation unit will result in a huge loss of overall efficiency, so the chemical-looping process, which is considered an energy-efficient oxyfuel method, has recently been used (Ohlemüller, 2019). Solid metal oxide particles are applied as oxygen carriers, and these particles circulate between two coupled circulating fluidized beds, namely the air and fuel reactors.

Long-term storage of the captured CO_2 is one way to reduce emissions, but it is questionable due to the environmental risk of leakage and the additional energy required to compress and transport the CO_2 to the storage site. As a viable option for carbon capture and storage, there has been increased research over the last decade into CO_2 utilisation, i.e., the artificial conversion of CO_2 captured from power plants and industrial plants into fuels or valuable chemicals using hydrogen produced by water electrolysis (powered by renewable energies). Such processes are referred to as carbon capture and utilisation. For many reasons, CO_2 can be seen as a beneficial C-resource to reduce or even replace fossil fuel consumption (Quadrelli & Centi, 2011; Valluri et al., 2022). These include, first, the growing socio-political pressure to reduce CO_2 emissions, and the introduction of CO_2 emission certificates in several countries has led to zero or even negative costs for CO_2. Second, using CO_2 instead of storing it eliminates the cost of CO_2 transport to the storage site, which can account for 35 to 40% of total CCS costs if the capture plant is more than 100–150 km from the storage site, as is the case in many European countries (Yi et al., 2015). Third, the CO_2 management strategies of a company can become a positive part of its public image. However, CO_2, as a product of combustion and other processes (cement and metallurgy), is an inert molecule, and its chemical reuse requires high-energy reactants and suitable catalysts. The synthesis of carbonaceous feedstock (chemicals or fuels) from the syngas (CO and H_2) is generally more favourable than the use of CO_2 due to its specific binding energy and oxidation number. It is easier to convert compounds with lower oxidation numbers (CO and H_2) into typical chemicals or fuels than compounds with negative oxidation numbers (CO_2 and H_2).

1.2 Conversion Processes

The conversion of fuels into useful products (e.g., power, heat, and chemicals) can take place based on various processes (thermal, biological, physical, and chemical processes) (Naik et al., 2010). Often, it is a combination of these processes, e.g., thermochemical, biochemical, and physicochemical.

The thermochemical conversion processes include pyrolysis (absence of air), gasification (reduced air), combustion (excess air), and in some cases, hydrothermal process (liquefaction) for feedstock with higher moisture content. The pyrolysis process has been used to produce charcoal for the past thousands of years, but it is only in the last 30 years that fast pyrolysis at moderate temperatures (about 500°C) and very short reaction times (up to 2 seconds) has become of great interest. The reason for this is that the process directly provides high yields of liquid fuel of up to 75 wt.%. The gasification has been in operation for many decades; the first gasifier (Winkler) was operated in Germany in 1922. Although there are many examples of demonstration and pre-commercial gasifiers, there are still relatively few plants operating successfully. The raw syngas produced by a gasifier can be used as a feedstock for chemical synthesis, e.g., methanol or Fischer-Tropsch products, after treatment (dust removal, gas scrubbing, and syngas conditioning). Clean syngas can also be used as a fuel gas to produce hydrogen, synthetic natural gas, a reducing gas in steel production, and for environmentally friendly electricity production in small to medium-sized plants (using internal combustion engines or fuel cells) or large plants (gas turbines) (Al-Sulaiman et al., 2011; Alobaid et al., 2018). The use of syngas (hydrogen-rich) instead of natural gas as a feedstock presents several challenges in the design and construction of gas turbines. Depending on the type of gasifier and the upstream syngas purification unit, the gas turbines must be configured for a wide range of possible syngas compositions and are typically still suitable for natural gas as an alternative fuel. The syngas has a higher flame velocity, a higher adiabatic combustion temperature, a wider ignition range, lower ignition energy, and a lower density than natural gas. This increases the risk of blowout and flashback (backfire), as well as the amount of NO_x formed (Taamallah et al., 2015). In natural gas-fired gas turbines, premixing the natural gas with a greatly increased proportion of air lowers the combustion temperature in the combustion chamber, leading to lower NO_x formation. This is hardly possible with hydrogen-fired gas turbines since hydrogen already reacts spontaneously with air at the compressor outlet, which means that no controlled combustion can take place in the combustion chamber. Accordingly, only diffusion flame design for the combustors is used when syngas (hydrogen-rich) or hydrogen is applied as fuel. To control the flame temperature, the fuel gas should be diluted with inert gases, i.e., nitrogen or steam (Chiesa et al., 2005; Funke et al., 2019).

The conversion of solid fuels (e.g., biomass or coal) into synthetic fuels or chemicals through gasification or pyrolysis is known as Indirect Liquefaction (IL) technology. The term ‘indirect’ here refers to the intermediate step (gasification or pyrolysis) in the generation of syngas for the subsequent production of liquid fuels or chemicals. In contrast, the hydrothermal process is referred to as the Direct Liquefaction (DL) technology, in which solid fuels are converted directly into a liquid phase with the aid of a catalyst at high temperatures (450–500°C) and pressures (150–300 bar) in the presence of a solvent (facilitates the process) and inert gases (e.g., He or N_2) or reducing gases (e.g., CO or H_2) (Shui et al., 2010). The addition of inert or reducing gases helps to break down the organic structure of the solid fuel into soluble products. The solute products, which include a wide range of hydrocarbons with a variety of molecular weights and forms (primarily of aromatic components), can then be upgraded by conventional petroleum refining techniques to meet the end-product requirements. The DL technology had already been demonstrated during World War II in Germany, but only at a high cost. Since then, continued development in the United States and other countries has focused on lowering costs with catalysts, enhanced reactor designs, and improvements in process efficiency. There have been many different processes developed, but most are similar in terms of their reaction chemistry and process concept. Shared features include dissolving the coal in a solvent and then hydrogenating the solid fuel with hydrogen over a catalyst (Vasireddy et al., 2011). The process can be efficient with overall thermal efficiency in the range of 65% (slightly below the IL technology). Few DL programs survived (e.g., the Hydrocarbon Technologies, Inc., today part of Headwater, Inc.), which was funded by the United States, Department of Energy (DOE). The DOE had been conducting a very active coal-to-liquids research program since 1970 in response to the 1973 Organisation of Petroleum Exporting Countries (OPEC) oil embargo. Shenhua Corporation obtained a license for this technology from DOE and built a DL plant fuelled by coal at Erdos in Inner Mongolia in 2002. Although the DL technology appears to be simpler and more efficient than the IL, it requires an external source of hydrogen, which can be provided by the gasification of additional feedstock or by water electrolysis. Nevertheless, many researchers believe that IL (based on a mature gasification or pyrolysis process) is more competitive than DL with current state-of-the-art technologies. Furthermore, the IL technology is better suited for CO_2 capture and has a long history of successful commercial use, as the Sasol company has been using IL since the 1950s.

The combustion process is an exothermic redox chemical reaction between hydrocarbon fuel and an oxidant. In various applications such as thermal power plants (e.g., CCPPs, coal-fired power plants, municipal waste incineration), the required heat is obtained from the combustion process of solid, liquid, or gaseous fuels (Spliethoff, 2010). The combustion process of solid fuels (e.g., coal or biomass) is more complex than liquid or gaseous fuels. It involves three major mechanisms (drying, pyrolysis, and oxidation of the volatiles and char). The flue gas formed in the combustion chamber of a steam generator, or a gas turbine, consists mainly of CO_2, H_2O, O_2, N_2, SO_2, and Ar. Usually, atmospheric air is used as an oxidant, but recently, the oxy-fuel process has been proposed to capture the CO_2 of the combustion process. Pure oxygen can be provided using an air separation unit (an energy-intensive process, leading to a high loss of overall efficiency) or chemical-looping combustion, which enables carbon capture with a low-energy input (Adánez et al., 2018). One spin-off from chemical-looping combustion is known as Oxygen-carrier-aided Combustion (OCAC) (Liu et al., 2023; Thunman et al., 2013). Here, the conventionally used silica-sand bed material is replaced with a metal oxide during combustion in the fluidized bed using air. The use of oxygen carriers as bed material leads to a more homogeneous distribution of oxygen and temperature in the bed since it improves the contact between fuel and air via redox sequence (i.e., the oxygen can be transported from oxygen-rich regions in the fluidized bed to oxygen-poor regions).

The thermochemical conversion processes (pyrolysis, gasification, and combustion), described above, exhibit higher temperatures and conversion rates but are suited to feedstock with lower moisture content and are generally less selective concerning products. For wet feedstock with a high content of organic substances, the biochemical processes are more appropriate. Here, the feedstock is converted, based on biological processes, into a secondary energy source, including gaseous fuels (e.g., hydrogen and methane), liquid fuels (e.g., ethanol, butanol, and diesel), or solid materials (e.g., polymers and carboxylic acids). The biochemical production of fuels is performed by microbial fermentation, anaerobic digestion, or enzymes (Calise et al., 2018). The biochemical processes mainly target the production of biogas from various types of biomass, followed by upgrading, including CO_2 capture, of the biogas to biomethane. By contrast, the physicochemical conversion processes are aimed at biodiesel production from biomass with high oil content (e.g., soybean and sunflower). They include the following stages, namely oil extraction, transesterification with methanol or ethanol, and biodiesel purification (Bonechi et al., 2017). In this book, emphasis is, however, placed on thermochemical conversion processes.

1.3 Polygeneration

Energy systems can only meet the multi-disciplinary requirements of this century if they are made more sustainable. Polygeneration is widely viewed as a potentially sustainable energy solution, which can use the same input and/or system to deliver multiple outputs simultaneously, resulting in higher fuel utilisation efficiency. The outputs of polygeneration plants include energy services (cooling, heating, and electricity), chemicals (e.g., hydrogen, fertilisers, polymers, and cosmetics), fuels (e.g., ethanol, diesel, methane, and methanol), and water (potable or for agricultural purposes). In this conte, existing Combined Heat, and Power (CHP) as well as Combined Cooling, Heat, and Power (CCHP) plants represent the simple form of polygeneration. Fuel use in a polygeneration plant is very diverse (fossil fuels, renewables, or hybrid). Decentralised polygeneration plants mainly use locally available energy sources (e.g., biomass, solar energy, or geothermal energy). Centralised plants are mainly based on coal and have a higher capacity than polygeneration plants based on renewable energies. Compared to conventional energy systems (single-generation plants), the concept of polygeneration offers several decisive advantages. This concept increases overall efficiency, reduces energy losses and emissions and enables the use of multiple fuels, improving resource utilisation through fuel switching or blending. The CO_2 capture and utilisation is also a viable option that offers several advantages in fossil fuel or biomass-based polygeneration for the synthesis of chemicals and fuels (the captured CO_2 is a carbon source). Also, the integration of CO_2 capture and utilisation systems in polygeneration plants allows useful heat to be provided from different sources at different temperatures. Optimal use of available heat between polygeneration and CO_2 capture and utilisation systems can reduce overall energy consumption (Heinze, 2021).

Polygeneration plants are sophisticated conversion systems that use different fuels (fossil, renewable, or hybrid) and produce different products (energy services, potable water, chemicals) based on different cycles (e.g., steam Rankine, organic Rankine, internal combustion engine, refrigeration, synthesis of chemicals, or desalination). Here, various thermal, chemical, and physical phenomena, as well as various flow patterns (e.g., single-phase flow and two-phase flows such as gas-liquid and gas-solid flows) are present. Experimental measurements, commonly on a laboratory scale, are considered the most fundamental basis for the development and design of commercial-scale plant components. Nevertheless, the availability of detailed experimental data is difficult for many reasons, such as the plant has not yet been constructed, access to the process is limited, and/or the process environment is harsh (high temperature, high pressure, or the presence of toxic gases). Therefore, most of the design, thermodynamic calculation and evaluation studies of polygeneration plants found in the literature are performed using one-dimensional and three-dimensional mathematical models (Alobaid et al., 2021; Calise et al., 2018; Martelli et al., 2021; Tabriz et al., 2023).

Typically, the design of a polygeneration plant starts with steady-state modelling. Here, it is assumed that the power plant operates continuously at its design base load. The steady-state models do not require control structures and are mathematically based on mass, momentum, species, and energy balances. Using steady-state simulation tools, analyses of the thermodynamic properties of the working fluid, mass, and energy flows, as well as process efficiency, can be conducted for a series of operating points. Steady-state simulation tools do not allow any information about transient operations. The relevant next step is therefore the process analysis with dynamic models during transients, load changes, and malfunction cases. Dynamic simulation is preferred for the proposal stage of a polygeneration plant project, e.g., to check whether the load changes according to specific customer requirements are feasible without unacceptable lifetime consumption in critical components. However, the investigation into the dynamic performance of polygeneration plants requires detailed information about the process and the related control structures. The inherent complexity of the governing differential conservation equations and the numerical solution methods make the dynamic simulation codes very sophisticated computer software with long development periods. The one-dimensional process simulation models (steady-state and dynamic) can be efficiently used to study the design and control of the entire polygeneration plant, considering the interaction with its subsystems. By contrast, three-dimensional simulation models known as Computational Fluid Dynamics (CFD) provide detailed insight into the flow patterns of individual components, such as heat exchangers or combustion chambers. Compared to experimental data, CFD results can provide qualitative and, in many cases, quantitative information about real systems. The obtained simulation results can be very useful for designing and understanding the process components and can provide detailed data on the velocity and temperature field, flow turbulence, heat and mass transfer, and chemical reaction rates. However, significant improvements are still needed in terms of accuracy (match between simulation and real process), performance (scale and resolution of simulation), and efficiency (computational effort). Ongoing developments could usher in a new era of virtual process engineering, where designers can engineer process components in real time without costly and time-consuming experimentation. It is not easy, however, to find the optimal design for a polygeneration plant that uses different

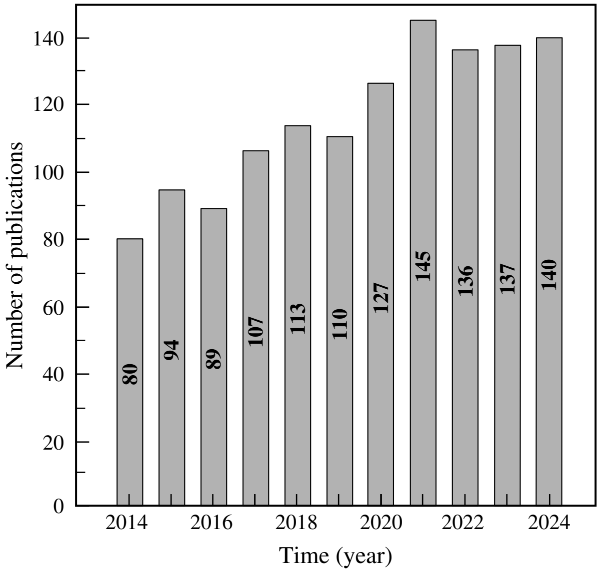

Figure 1.3 Number of publications per year from 2014 to 2024, found in Mendeley by using the keyword 'Polygeneration'.

input sources and produces different services. This is because the heat source may have a non-standard composite characteristic. In addition, different arrangements, sequences, or interconnections of the circuits used (e.g., steam Rankine, refrigeration, and desalination) are possible, and the optimal design solution is not obvious. Creating and simulating all possible configurations with simulation models can be extremely time-consuming. Here, key variables of the polygeneration plant circuits can be tuned by sensitivity analyses, which is why optimisation approaches such as mixed integer linear programming or particle swarm optimisation represent a great opportunity.

Figure 1.3 shows that a significant number of scientific works (approximately 1,200) have been published on the topic of polygeneration over the past decade (these include journal and conference proceedings papers, books, and book sections). Most literature studies are simulation works with an evaluation based on three types of metrics (social, economic, and environmental), including thermodynamic analysis (energetic and exegetic), techno-economic and socio-economic analysis, and environmental analysis. The storage/utilisation of carbon dioxide in polygeneration plants is relatively new in this research area, accounting for less than 5% of publications.

1.4 Structure

The book describes the technologies used for the conversion of solid fuels, in particular combustion, gasification, pyrolysis, and hydrothermal processes. All methods of CO_2 capture and utilisation are presented. The links between the conversion processes and CO_2 capture and utilisation are shown in terms of polygeneration.

The numerical simulation of polygeneration plants based on one-dimensional process simulation models (steady-state and dynamic) and three-dimensional CFD models is explained. To connect the theoretical part with practice, this book also presents experimental data, which were obtained from the 1 MW_{th} pilot plant at the Technical University of Darmstadt during the last 15 years.

The first part of this book presents the conversion process (prime mover) for fossil and renewable solid fuels (e.g., coal and biomass). The various conversion pathways, including thermochemical, biochemical, and physicochemical processes, for converting solid fuels into useful products such as electricity, heating, cooling, fuels, and valuable chemicals, are shown. Thermochemical conversion processes (combustion, gasification, pyrolysis, and hydrothermal process) are widely applied, compared to biochemical and physicochemical conversion processes and are therefore the focus of this book. Combustion technologies such as grate-firing, pulverised combustion, and solar- and geothermal-assisted power plants are explained in detail. The thermodynamic cycles used include the steam Rankine cycle, the organic Rankine cycle, the Kalina cycle, and the carbon dioxide Brayton cycle. Pollutant emissions from the combustion process, such as carbon monoxide, nitrogen oxides, sulphur oxides, particulate matter, and mercury, are presented. Also, the most popular gasification technologies, including fixed-bed, entrained-flow, fluidized-bed, plasma, solar-powered, and microwave-assisted gasifiers, are shown. The purification and conditioning of raw syngas (e.g., removal of particulates, halides and trace metals, tars and hydrocarbons, and acid gas) and the conversion technologies of cleaned syngas (either for the synthesis of fuels and chemicals or for the generation of electricity, heat, and refrigeration) are described. Pyrolysis, liquefaction, and steam reforming are also presented. For each conversion process, a comparative study of development status, capital and operational expenditures are provided. Finally, experimental measurements from the 1 MW_{th} test facility (one of the world's largest pilot plants for research purposes) at the Technical University of Darmstadt are presented. Here, the behaviour of combustion and co-combustion processes of difficult fuels (biomass and waste) during steady-state operation and load cycling is investigated, including hydrodynamics, temperatures, heat transfer, and flue gas composition. In addition, the high-temperature Winkler and novel chemical-looping gasification processes are shown. The goal is to demonstrate the entire process chain from biomass to biofuel, including fuel pre-treatment, gasification, raw syngas purification, and synthesis of chemicals and fuels for later commercialisation.

The second part of this book describes the processes for CO_2 capture and utilisation from emission sources (e.g., thermal power or industrial plants). Depending on where the CO_2 is captured (before, after, or during combustion), a distinction is made between three processes: pre-combustion, post-combustion, and oxyfuel combustion. The absorption, adsorption, membrane separation, and cryogenic processes used to capture CO_2 in pre-combustion and post-combustion capture are explained. Here, the carbonate-looping process (including directly heated carbonate-looping and indirectly heated carbonate-looping), which is an efficient post-combustion CO_2 capture process, is described in detail. The oxyfuel process and the method of providing pure oxygen via non-cryogenic and cryogenic processes are shown. The chemical-looping combustion, which is considered an energy-efficient oxyfuel process, is also presented. The costs of CO_2 capture, transport, and storage, as well as CO_2 capture used in the transportation sector (e.g., ships), are presented. The CO_2 utilisation technologies, such as direct use and indirect use (including chemical, biological, photochemical, and electrochemical), are explained in the second part of this chapter. Finally, semi-industrial scale tests from one of the world's largest pilot plants for research purposes at the Technical University of Darmstadt are presented for directly heated carbonate-looping process for coal, waste-derived fuels in a directly heated carbonate-looping process, indirectly heated carbonate-looping process and chemical-looping combustion for both gaseous and solid fuel. Furthermore, a comparative study of the development status and investment and operating costs is provided for the CO_2 capture and utilisation technologies.

The third part of this book provides a detailed description of sustainable polygeneration plants that are a promising concept for achieving a circular carbon economy. Here, the conversion devices (e.g., gas turbines, internal combustion engines, and fuel cells) and outputs (e.g., electricity, heating and cooling, raw materials for the chemical industry and fuel production, and potable water) are explained. Polygeneration is divided into fossil fuel-based polygeneration, renewable-based polygeneration, and renewable and fossil fuel-based polygeneration (hybrid polygeneration). For fossil fuels, coal-based, natural gas-based, and multiple fossil fuel-based polygeneration plants are presented. In addition, polygeneration plants based on other fossil fuels, such as oil shale and shale gas, are also explained. Renewable-based polygeneration plants that include biomass-based polygeneration, solar-based polygeneration, geothermal-based polygeneration, wind-based polygeneration, and multiple renewables-based polygeneration are presented. Hybrid polygeneration plants that are based on renewable energies and fossil fuels are also discussed. Furthermore, the CO_2 capture and utilisation in the context of polygeneration plants is shown. Given the complexity of polygeneration plants, the assessment methodology for single-generation plants cannot be applied directly. Here, a more comprehensive assessment is required, which is based on three types of metrics: social, economic, and environmental. The chapter includes tables summarising the status of developments, key findings, and the recent work in the literature on polygeneration plants.

The fourth part of this book introduces the mathematical models used for the simulation of polygeneration plants. The first section deals with the one-dimensional process simulation models (steady-state and dynamic), while the second section presents the three-dimensional CFD models. The background for process modelling, automation, and electrical components required for steady-state and dynamic simulation of polygeneration plants is described in detail. The different thermal-hydraulic models (mixture-flow model and the two-fluid flow models, including four-equation, five-equation, six-equation, and seven-equation flow models) are explained. In the second part, the CFD numerical methods for modelling single-phase flow and two-phase flow are described, including the mixture model, two-fluid model, and single-particle model. A table listing the most common simulation programmes for polygeneration plants by application is also shown.

The book concludes with relevant insights and conclusions for future research in the field of sustainable polygeneration plants with CO_2 capture and utilisation.

Bibliography

Adánez, J., Abad, A., Mendiara, T., Gayán, P., De Diego, L., & García-Labiano, F. (2018). Chemical looping combustion of solid fuels. *Progress in Energy and Combustion Science, 65*, 6–66.

Alobaid, F. (2018). *Numerical simulation for next generation thermal power plants*. Springer.

Alobaid, F., Almohammed, N., Farid, M. M., May, J., Rößger, P., Richter, A., & Epple, B. (2021). Progress in CFD simulations of fluidized beds for chemical and energy process engineering. *Progress in Energy and Combustion Science, 91*, 100930.

Alobaid, F., Mertens, N., Starkloff, R., Lanz, T., Heinze, C., & Epple, B. (2017). Progress in dynamic simulation of thermal power plants. *Progress in Energy and Combustion Science, 59*, 79–162.

Alobaid, F., Wieck, J., & Epple, B. (2024). Dynamic process simulation of a 780 MW combined cycle power plant during shutdown procedure. *Applied Thermal Engineering, 236*, 121852.

Al-Sulaiman, F. A., Hamdullahpur, F., & Dincer, I. (2011). Trigeneration: a comprehensive review based on prime movers. *International Journal of Energy Research, 35*(3), 233–258.

Bonechi, C., Consumi, M., Donati, A., Leone, G., Magnani, A., Tamasi, G., et al. (2017). Biomass: an overview. In *Bioenergy Systems for the Future Prospects for Biofuels and Biohydrogen* (pp. 3–42): Woodhead Publishing.

Calise, F., di Vastogirardi, G. d. N., d'Accadia, M. D., & Vicidomini, M. (2018). Simulation of polygeneration systems. *Energy, 163*, 290–337.

Chiesa, P., Lozza, G., & Mazzocchi, L. (2005). Using hydrogen as gas turbine fuel. *Journal of Engineering for Gas Turbines and Power, 127*(1), 73–80.

Damon Matthews, H., Tokarska, K. B., Rogelj, J., Smith, C. J., MacDougall, A. H., Haustein, K., et al. (2021). An integrated approach to quantifying uncertainties in the remaining carbon budget. *Communications Earth & Environment, 2*(1), 7.

Dusenge, M. E., Duarte, A. G., & Way, D. A. (2019). Plant carbon metabolism and climate change: elevated CO_2 and temperature impacts on photosynthesis, photorespiration and respiration. *New Phytologist, 221*(1), 32–49.

Friedlingstein, P., O'sullivan, M., Jones, M. W., Andrew, R. M., Bakker, D. C., Hauck, J., et al. (2023). Global carbon budget 2023. *Earth System Science Data, 15*(12), 5301–5369.

Funke, H.-W., Beckmann, N., & Abanteriba, S. (2019). An overview on dry low NO_x micromix combustor development for hydrogen-rich gas turbine applications. *International Journal of Hydrogen Energy, 44*(13), 6978–6990.

Haaf, M., Unger, A., Ströhle, J., Epple, B., & Hilz, J. (2018). *Methanol production via the utilization of electricity and CO_2 provided by a waste incineration plant*. Paper presented at the 14th Greenhouse Gas Control Technologies Conference Melbourne.

Heinze, C. (2021). *Konzeption einer Pilotanlage auf Grundlage einer technoökonomischen Bewertung von flexiblen Polygenerationsprozessketten*. Technical University of Darmstadt.

Hilz, J. B. L. (2019). *Experimental investigation of a semi-industrial carbonate looping process for scale-up*. Cuvillier Verlag.

Hussain, S., Lai, C., & Eicker, U. (2023). Flexibility: literature review on concepts, modeling, and provision method in smart grid. *Sustainable Energy, Grids and Networks, 35*, 101113.

Islam, M. M., Yu, T., Giannoccaro, G., Mi, Y., La Scala, M., Rajabi, M. N., & Wang, J. (2024). Improving reliability and stability of the power systems: a comprehensive review on the role of energy storage systems to enhance flexibility. *IEEE Access, 12*, 152738–152765.

Lee, S., Kim, J., Tahmasebi, A., Jeon, C.-H., Liu, Y., & Yu, J. (2023). Comprehensive technical review of the high-efficiency low-emission technology in advanced coal-fired power plants. *Reviews in Chemical Engineering, 39*(3), 363–386.

Leung, D. Y., Caramanna, G., & Maroto-Valer, M. M. (2014). An overview of current status of carbon dioxide capture and storage technologies. *Renewable and Sustainable Energy Reviews, 39*, 426–443.

Liu, X., Duan, L., Duan, Y., Li, L., Sun, Z., & Sun, G. (2023). Improved fuel conversion through oxygen carrier aided combustion during incineration of biomass-based solid waste in a rotary kiln. *Fuel, 331*, 125714.

Martelli, E., Alobaid, F., & Elsido, C. (2021). Design optimization and dynamic simulation of steam cycle power plants: a review. *Frontiers in Energy Research, 9*, 1–31.

Naik, S. N., Goud, V. V., Rout, P. K., & Dalai, A. K. (2010). Production of first and second generation biofuels: a comprehensive review. *Renewable and Sustainable Energy Reviews, 14*(2), 578–597.

Ohlemüller, P. G. (2019). *Untersuchung von chemical-looping-combustion im megawatt-Maßstab*. Cuvillier Verlag.

Pilapitiya, P. N. T., & Ratnayake, A. S. (2024). The world of plastic waste: a review. *Cleaner Materials, 11*, 100220.

Quadrelli, E. A., & Centi, G. (2011). Green carbon dioxide. *ChemSusChem, 4*, 1179–1181.

Scholz, C. & Zimmermann, H. (2012). *First long-term experience with the operational flexibility of the SGT5-8000H*.

Shui, H., Cai, Z., & Xu, C. (2010). Recent advances in direct coal liquefaction. *Energies, 3*(2), 155–170.

Soo, X. Y. D., Lee, J. J. C., Wu, W.-Y., Tao, L., Wang, C., Zhu, Q., & Bu, J. (2024). Advancements in CO_2 capture by absorption and adsorption: a comprehensive review. *Journal of CO_2 Utilization, 81*, 102727.

Spliethoff, H. (2010). *Power generation from solid fuels*. Springer Science & Business Media.

Syberg, K., Nielsen, M. B., Clausen, L. P. W., van Calster, G., van Wezel, A., Rochman, C., et al. (2021). Regulation of plastic from a circular economy perspective. *Current Opinion in Green and Sustainable Chemistry, 29*, 100462.

Taamallah, S., Vogiatzaki, K., Alzahrani, F. M., Mokheimer, E. M., Habib, M., & Ghoniem, A. F. (2015). Fuel flexibility, stability and emissions in premixed hydrogen-rich gas turbine combustion: technology, fundamentals, and numerical simulations. *Applied Energy, 154*, 1020–1047.

Tabriz, Z. H., Khani, L., Mohammadpourfard, M., & Akkurt, G. G. (2023). Biomass driven polygeneration systems: a review of recent progress and future prospects. *Process Safety and Environmental Protection, 169*, 363–397.

Thunman, H., Lind, F., Breitholtz, C., Berguerand, N., & Seemann, M. (2013). Using an oxygen-carrier as bed material for combustion of biomass in a 12-MWth circulating fluidized-bed boiler. *Fuel, 113*, 300–309.

Valluri, S., Claremboux, V., & Kawatra, S. (2022). Opportunities and challenges in CO_2 utilization. *Journal of Environmental Sciences, 113*, 322–344.

Vandervort, C., Leach, D., & Scholz, M. (2016). *Advancements in H class gas turbines for combined cycle power plants for high efficiency, enhanced operational capability and broad fuel flexibility. the future of gas turbine technology*. Paper presented at the Proceedings of the 8th International Gas Turbine Congress, Brussels, Belgium.

Vandervort, C., Leach, D., Walker, D., & Sasser, J. (2019). *Commercialization and fleet experience of the 7/9HA gas turbine combined cycle*. Paper presented at the Turbo Expo: Power for Land, Sea, and Air.

Vasireddy, S., Morreale, B., Cugini, A., Song, C., & Spivey, J. J. (2011). Clean liquid fuels from direct coal liquefaction: chemistry, catalysis, technological status and challenges. *Energy & Environmental Science, 4*(2), 311–345.

Walter, H., & Epple, B. (2017). *Numerical simulation of power plants and firing systems*. Springer.

Yi, Q., Li, W., Feng, J., & Xie, K. (2015). Carbon cycle in advanced coal chemical engineering. *Chemical Society Reviews, 44*(15), 5409–5445.

Yu, C.-H., Huang, C.-H., & Tan, C.-S. (2012). A review of CO_2 capture by absorption and adsorption. *Aerosol and Air Quality Research, 12*(5), 745–769.