# Chapter 1
Introduction to Carbon Capture

The capture of CO_2 is motivated by the forecasted change in climate as a result of the world's dependence on fossil fuels for energy generation. Mitigation of CO_2 emissions is the challenge of the future for stabilizing global warming.The separation of CO_2 from gas mixtures is a commercial activity today in hydrogen, ammonia, and natural gas purification plants. Typically, the CO_2 is vented to the atmosphere, but in some cases, it is captured and used. The current primary uses of CO_2 include enhanced oil recovery (EOR) and the food industry (carbonated beverages). The traditional approach for CO_2 capture for these uses is solvent-based absorption. It is unclear whether this technology will be the optimal choice to tackle the scale of CO_2 emitted on an annual basis (~ 30 Gt worldwide). A new global interest in extending CO_2 capture to power plants is producing a dramatic expansion in R&D and many new concepts associated with clean energy conversion processes. The application of CO_2 capture technologies beyond concentrated sources is in view, but less tractable. The first and second laws of thermodynamics set boundaries on the minimum work required for CO_2 separation. Real separation processes will come with irreversibilities and subsequent inefficiencies taking us further from best-case scenarios. The inefficiency of a given process reveals itself in the form of operating and maintenance, and capital costs.

The interconnected nature of multiple fields of science and engineering is essential. Appreciating the physical and chemical properties of the various CO_2 emissions sources serves as a critical first step. Envisioning methods for its capture will occupy the next several decades of engineers, chemists, physicists, earth scientists, mathematicians, and social scientists. Where will the capture technology be applied? What might the technology involve? Will we one day place systems in the desert to capture dilute CO_2 directly from air? Will we install CO_2 separators on automobiles and airplanes so that consumers exchange CO_2 for fuel at refueling stations? CO_2 capture is often considered in the context of point sources such as coal-fired power plants or industrial processes, but breakthroughs in research must lead to applications of CO_2 capture to an even wider realization of its abatement potential.

Process engineering, materials science, catalysis and nanoscience will likely play key roles in hybridizing the known technologies toward an integrative approach to meet the challenge. Figure 1.1 illustrates the multiple scales that a particular

Fig. 1.1 Schematic of the overlap between the scales across the portfolio of solutions to CO_2 capture
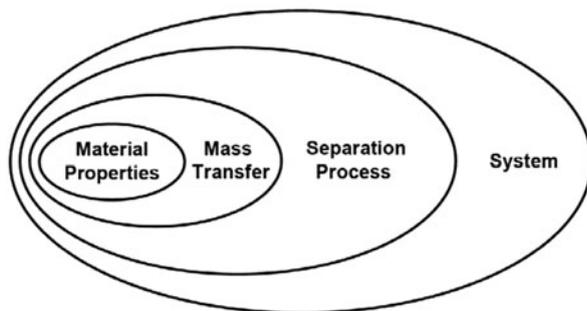
solution for CO_2 capture may entail. At the heart of any CO_2 capture technology is the material and its required properties for optimizing mass transfer from a gas mixture to a captured phase. The material may be a solvent, sorbent , membrane or catalyst. Mass transfer acts as the bridge and links the optimal material properties with the overall separation process, whether it is a combined absorber-stripper system, sorption apparatus, membrane module, or catalytic reactor. The material properties, mass transfer, and capture process must be considered as coupled and inherent to the system in total. In this case, the system is defined as the CO_2 capture environment and the local surroundings of the capture assembly.

A CO_2 capture technology may look quite different for the direct air capture of CO_2 (DAC) in which the concentration of CO_2 is quite dilute, *i.e.*, approximately 0.0390 mol% (390 ppm) versus its capture from the exhaust of a power plant, in which its concentration is on average 12 mol%. In addition to the concentration difference, CO_2 capture from a power plant must overcome the challenge associated with the timescale and throughput of emissions. For instance, a 500-MW power plant emits on average 11,000 tons[1] of CO_2 per day. Direct air capture is much less efficient. For example, assuming an air flow rate of 2 m/s, capturing 11,000 tons of CO_2 per day directly from the air requires a surface area of approximately 133,000 m^2 to process 2.31×10^{10} m^3 of air per day.[2]

This chapter provides a brief overview of CO_2 sources, as well as the physical and chemical nature of its environment. This overview motivates further discussion of fuel oxidation and combustion, the heart of CO_2 emissions. Knowledge of the chemical composition of a given exhaust mixture allows for the determination of the minimum work required for CO_2 separation from the mixture. The *2nd-law efficiency* is defined as the ratio between this ideal minimum work and the real work associated with the unit operations of the actual separation process. Known processes relying on absorption, adsorption, membrane, and hybrid processes can then be investigated. Chapter 2 focuses on Compression and Transport of CO_2. Knowledge of CO_2 phase behavior as a function of temperature and pressure throughout compression and transport processes is crucial to determine safe and cost-effective approaches to

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[1] Throughout the textbook, "ton" is in reference to a metric ton and is sometimes referred to as tonne, which is equal to 1000 kg.

[2] This assumes 100% capture of the CO_2 at a concentration in air of approximately 390 ppm.

handling CO_2 between the capture and potential-use stages. Once CO_2 is captured and compressed, the question becomes what to do with it. This will be addressed shortly. The phase behavior of CO_2 and fundamental equations associated with its compression also play a role in separations processes. Although compression and transport take place after CO_2 capture, presenting this material prior to the separation processes provides a foundation and set of equations referenced in future chapters.

Chapters 3–6 focus on Absorption, Adsorption, Membrane Technology, and Air Separation, respectively. These broad-reaching chapters are motivated by the operating, maintenance, and capital costs of a given separation process. Costs are bridged in step-wise fashion to the fundamental chemical and physical processes that underlie the mass transfer of CO_2 from a gas to its captured form. In particular, Chapter 6 discusses air separation (*i.e.*, the separation of air into N_2, O_2, and argon) as it may play a key role in CO_2 capture since N_2 is the primary inert gas diluting most CO_2-inclusive gas mixtures.

Chapters 7–9 examine nontraditional separation technologies that in the most ideal sense may be considered carbon-neutral. The topics covered in these chapters include the role that algae plays in CO_2 capture, CO_2 electrocatalysis and photocatalysis to fuel and chemicals, and mineral carbonation, respectively. These are interesting approaches to consider in the CO_2 capture portfolio since currently they are investigated primarily as post-capture processes. For instance, the conversion of CO_2 via algae, electrocatalytic, and photocatalytic processes to a chemical or fuel has mostly been investigated for the conversion of CO_2-rich gas streams as the input. However, with technological advancements it may be possible to use such approaches to combine CO_2 capture and conversion in a single process. Chapter 9 discusses mineral carbonation, focusing on the potential to form mineral carbonates from reacting CO_2 with an alkalinity source. Natural and industrial waste byproduct alkalinity sources are considered, with a particular focus on industrial waste alkalinity sources since the mineral carbonation process would be sequestering CO_2 in addition to other potentially hazardous components of the waste. The potential to reuse the mineral carbonates as aggregate for construction applications may serve as a driver to move this technology forward. These chapters review of each of these processes and their current challenges.

The separation processes considered in Chaps. 3–6 for CO_2 capture may be broken down into their fundamental unit operations with the work requirements determined for each stage of separation, such as blower power for gas compression or pumping power for solvent transport. The reader can work through the application of a capture technology from a gas mixture containing CO_2 and based upon the local environment and composition, determine the feasibility of capture with current separation tools or a hybrid thereof based upon its 2nd-law efficiency.

1.1 Relationship Between CO_2 and Climate

The combustion of fossil fuels, *i.e.*, coal, petroleum, and natural gas, is the major anthropogenic source of CO_2 emissions, with an estimated 30 gigatons (Gt) CO_2 (*e.g.*, 30 billion tons) generated per year as illustrated in Fig. 1.2 [1]. This figure shows the
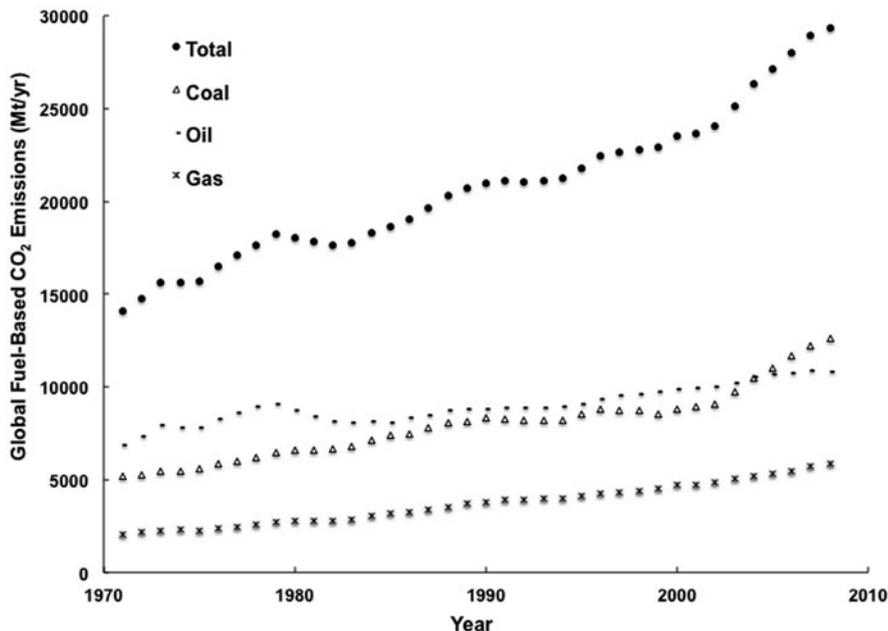
Fig. 1.2 Global fuel-based CO_2 emissions from the period of 1970–2008 (total and by fuel type) [2]

breakdown of CO_2 emissions by fuel type, with coal burning surpassing oil-sourced emissions around 2004. Figure 1.3 shows the breakdown in CO_2 emissions from the top-emitting countries, with China surpassing the U.S. around 2006 [2]. It is clear that human activities over the course of the 20th century, have led to increasing greenhouse gas (GHG) emissions. Studies indicate that increases in CO_2 concentration in the atmosphere leads to irreversible climate changes lasting up to 1,000 years, even after elimination of emissions [3]. Additionally, even if anthropogenic GHG emissions remained constant from today, the world would still experience continued warming for several centuries [4]. For global mean temperature stabilization, GHG emissions would have to cease today [3, 5], which is difficult due to our reliance on the existing fossil-based energy and transportation infrastructure, which is expected to contribute to GHG emissions for tens of years to come [6].

Examples of irreversible climate changes include atmospheric warming, dry-season rainfall reductions in several regions comparable to those of the "dust bowl" era[3], more extreme weather events and inexorable sea level rise [3]. The carbon-climate response, which is defined as the ratio of temperature change to cumulative

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[3] The "dust bowl" era from 1930–1936 was a period of dust storms causing major ecological and agricultural damage to the prairie lands of the U.S. (panhandles of Texas and Oklahoma, and neighboring regions of New Mexico, Colorado, and Kansas) and Canada, causing severe drought followed by decades of extensive farming without crop rotation or other techniques to prevent wind erosion. Millions of acres of farmland became useless, with hundreds of thousands of people leaving their homes and migrating to California and other states.
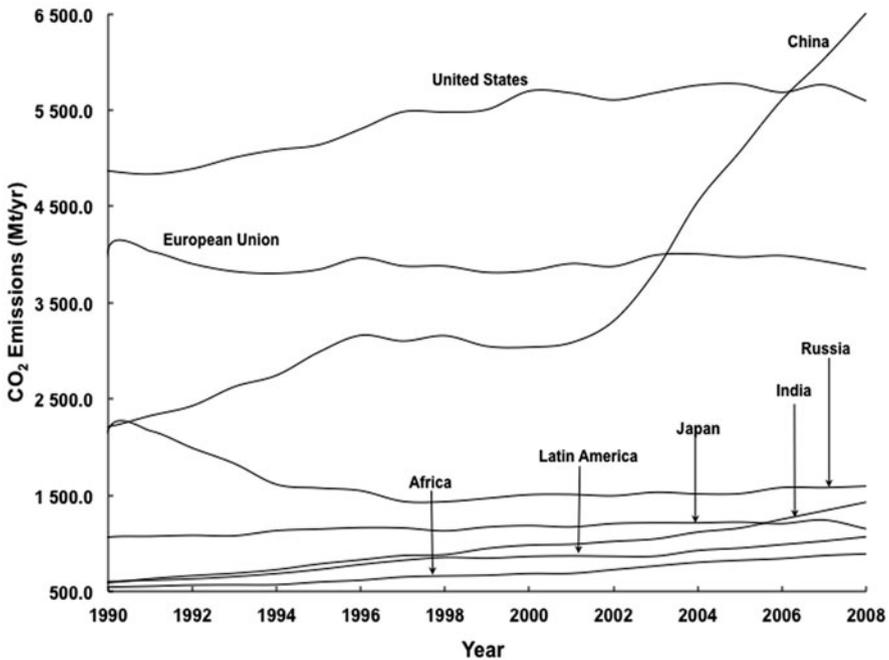
Fig. 1.3 Global fuel-based CO$_2$ emissions by top-emitting countries from 1990 to 2008 [2]

CO$_2$ emissions is estimated at approximately 1.0–2.1°C per 3600 Gt of CO$_2$ emitted into the atmosphere [7]. The natural carbon cycle is responsible for a portion of the removal of CO$_2$ from the atmosphere, some to the oceans and some to terrestrial vegetation. The natural carbon cycle includes exchange with the land biosphere (photosynthesis and deforestation), the surface layer of the ocean, and a much slower penetration into the depth of the ocean, which is dependent upon vertical transport and the buffering effect of the ocean's chemistry [3]. The carbon flows associated with global photosynthesis and respiration are generally an order of magnitude larger in scale than the extraction and combustion of fossil fuel, but are largely in balance. With updated estimates on CO$_2$ emissions from both deforestation and coal combustion, estimated emissions from deforestation and forest degradation represent approximately 12 to 13% of global anthropogenic CO$_2$ emissions [8], different from previous estimates of 20% [9]. In addition to CO$_2$, other GHGs include methane (CH$_4$), nitrous oxide (N$_2$O), hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF$_6$). Researchers predict that non-CO$_2$ GHG emissions will constitute approximately[4] one-third of total CO$_2$ equivalent emissions over the 2000–2049 period [10]. This textbook, however, focuses primarily on the separation of CO$_2$, which remains the primary anthropogenic contributor to climate change [11].

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[4] Based on 100-year global warming potentials.

Table 1.1 Estimated 2011 U.S. CO_2 exhaust emissions [2]

Source	Emissions sector (Mt CO_2/year)						Exhaust mixture
	Trans	Elec.	Comm.	Ind.	Res.	*Total*	
Petroleum	1952.68	102.30	54.93	416.83	100.91	2627.64	CO_2 (3–8 vol%) SO_2; NO_X; PM; CO
Natural gas	33.1	319.11	163.06	397.54	262.42	1175.24	CO_2 (3–5 vol%) NO_x; CO; PM
Coal	∼0	1983.81	9.28	187.99	0.81	2181.89	CO_2 (12–15 vol%) PM; SO_2; NO_X; CO; Hg
Total	1985.79	2405.22	227.26	1002.6	364.14	5984.77	

Table 1.2 Estimated 2008 U.S. and worldwide CO_2 process emissions [15]

Non-Fossil	Emissions (Mt CO_2/year)	CO_2 content (vol %)
Cement production	50 (world 2000)	14–33
Refineries	159 (world 850)	3–13
Iron and steel production	19 (world 1000)	15
Ethylene production	61 (world 260)	12
Ammonia processing	7 (world 150)	100
Natural gas production	30 (world 50)	5–70
Limestone consumption	19	50
Waste combustion	11 (electricity)	20
Soda ash manufacture	4	
Aluminum manufacture	4 (world 8)	

1.2 CO_2 Sources and Sinks

The combustion of fossil fuels produces an estimated 30 Gt of CO_2 per year. Deforestation of tropical regions accounts for an additional 4 Gt CO_2 per year [8]. Due to the natural carbon cycle and associated terrestrial and ocean CO_2 sinks, the annual increase in CO_2 emissions averages approximately 15 Gt CO_2 per year, which is equivalent to 2 ppm per year. Fossil fuel-based emissions of CO_2 may be sourced from both stationary (*e.g.*, power plant) and non-stationary systems (*e.g.*, automobile). There are approximately 13 Gt CO_2 per year on average from large stationary sources globally, and approximately 2.5 Gt in the U.S. as illustrated in Table 1.1 [2]. In addition to CO_2 emissions generation from the oxidation of fossil fuels, emissions may also be sourced as a result of a chemical process. Although these emissions sources represent a minor portion of total anthropogenic emissions, the chemical processing method currently used may be required for the formation of a useful product, such as cement or steel. Therefore, due to the difficulty of replacing CO_2-generating chemical processes with others that are absent of CO_2, it is crucial that these emissions sources are not disregarded.

Chemical Processes Although fossil-fuel oxidation processes produce the majority of emissions, there is a fraction of emissions generated from chemical processes. Examples presented in Table 1.2 [15] include cement manufacturing, iron and steel

production, gas processing, oil refining, and ethylene production. Mitigation associated with the capture of CO_2 from these industrial-based processes is small compared to that of the transportation and electricity sectors; however, there may not be alternatives to the materials created from these processes, such as cement, iron and steel production, etc. Several of these processes are discussed briefly.

Cement manufacturing results in CO_2 emissions sourced from *calcination* in addition to the fuel combustion emissions of the cement kilns. Estimated 2008 emissions worldwide from cement production were approximately 2 Gt of CO_2 with approximately 52 and 48% associated with the calcination process and cement kilns, respectively. Portland cement is a mixture of primarily di- and tricalcium silicates ($2CaO \cdot SiO_2$, $3CaO \cdot SiO_2$) with lesser amounts of other compounds including calcium sulfate ($CaSO_4$), magnesium, aluminum, and iron oxides, and tricalcium aluminate ($3CaO \cdot Al_2O_3$). The primary reaction that takes place in this process is the formation of calcium oxide and CO_2 from calcium carbonate, which is highly endothermic and requires 3.5–6.0 GJ per ton of cement produced.

Within the steel-making process a combination of emissions and the chemical processes comprise the estimated 1 Gt of CO_2 emitted worldwide. Steel-making, generates CO_2 as a result of carbon oxidation to carbon monoxide, which is required for the reduction of hematite ore (Fe_2O_3) to molten iron (pig iron). The CO_2 is also sourced from a combination of coal-burning and limestone calcination. In the second stage of the steel-making process, the carbon content of pig iron is reduced in an oxygen-fired furnace from approximately 4–5% down to 0.1–1%, and is known as the basic oxygen steelmaking (BOS) process. Both of these steps produce a steel-slag waste high in lime and iron content.

In 2008, roughly 630 refineries emitted on average 1.25 Mt each, resulting in approximately 850 Mt of CO_2 emitted in the atmosphere. In an oil refining process, crude oil, a mixture of various hydrocarbon components ranging broadly in molecular weight, is fractionated from lighter to heavier components. In a second stage, the heavier components are catalytically "cracked" to form shorter hydrocarbon chains. In addition to producing CO_2 as a byproduct of the distillation and catalytic cracking processes, the heat and electricity required for the methane reforming process used in H_2 production for hydrocracking and plant utilities produce additional CO_2.

Recovered natural gas from gas fields or other geologic sources often contains varying levels of nonhydrocarbon components such as CO_2, N_2, H_2S, and helium. Natural gas (primarily methane and ethane) and other light hydrocarbons such as propane and butane, to less extent, are the valuable products in these cases, and often the generated CO_2 is a near-pure stream. Concentrations of approximately 20% CO_2 are not uncommon in large natural gas fields. A unique case is Indonesia's Natuna field, which commercially produces natural gas containing approximately 70% CO_2 [12].

Exhaust Emissions Comparing the sectors (electricity, transportation, industrial, commercial, and residential), currently the electricity sector is the largest, representing 40% of total U.S. CO_2 emissions. Among all the sectors, comparing the different fossil fuel sources, *i.e.*, coal, petroleum, and natural gas, petroleum constitutes the

majority of the emissions at approximately 43%. Carbon capture technologies and the appropriateness of their application are highly dependent upon the following four factors: 1) the nature of the application, *i.e.*, a coal-fired power plant, an automobile, air, etc., 2) the concentration of CO_2 in the gas mixture, 3) the chemical environment of CO_2, *i.e.*, the presence of water vapor, acid species (SO_2, NO_x), particulate matter (PM), etc., and 4) the physical conditions of the CO_2 environment, *i.e.*, the temperature and pressure. A brief discussion of each of these factors highlights their importance.

The concentration of CO_2 plays a role in that the work required for separation decreases as the CO_2 concentration increases. The greater the CO_2 content in a given gas mixture, the easier it is to carry out the separation. This concept will be revisited toward the end of the chapter. If the CO_2 concentration in a gas mixture is too low then certain separation processes may be ruled out under their current design. For instance, in order for membrane technologies to be effective, a sufficient driving force is required. One of the many benefits of membrane technology is reduced capital cost. Membranes are a once-through technology in that the gas mixture enters the membrane in one stream and leaves the membrane as two streams, with one of the streams concentrated in CO_2. But since most of the sources of CO_2 are fairly dilute as shown in Table 1.1, this technology currently has limited application unless novel measures are taken. The chemical-process-based sources of CO_2 tend to have higher concentrations making these processes targets for membrane technology application. Examples include ammonia, hydrogen, and ethanol production facilities.

In addition, the chemical environment of CO_2 is important when considering the separation technology since some technologies may have a higher selectivity to other chemical species in the gas mixture. For instance, in coal-fired flue gas water vapor and acid gas species such as SO_2 and NO_x compounds may compete with CO_2 for binding in solution or on a material.

The final factor to consider is the temperature and pressure of the potential CO_2 application. If a process occurs at high temperature or pressure it may be possible to take advantage of the work stored at the given conditions for use in the separation process. For instance, a catalytic reaction involving CO_2 may be enhanced at high temperature. An example of a catalytic approach for flue gas scrubbing is the case of NO_x reduction to water vapor and N_2 from the catalytic reaction of NO_x with ammonia across vanadia-based catalysts. This approach to NO_x reduction in a power plant is referred to as selective catalytic reduction. Noncatalytic NO_x reduction, in which ammonia is injected directly into the boiler is also practiced, but is not as effective as the catalytic approach [13]. Membrane technology is another example, in that separation may be enhanced at high pressure.

Carrying out an exergy analysis [14] on a given CO_2 generation source and capture process is a useful exercise, which can aid in determining the potential irreversibilities associated with each step. Exergy is defined as the amount of energy in a process that is potentially available to do work. For instance, if one were to design a CO_2 separation process that effectively used the thermal energy available at the high temperature of the flue gas then this would be maximizing the exergy in the system. The flue gas temperature ranges from approximately 650°C at the exit of the boiler

Table 1.3 Current CO$_2$-EOR projects taking place in the U.S.[a] [17]

Location	CO$_2$ sources	CO$_2$ supply (MMcfd[b])	
		Natural	Anthropogenic
W. Texas/New Mexico/Arizona	Natural CO$_2$ (Colorado/New Mexico) Gas processing plants (W. Texas)	1670	105
Colorado/Wyoming	Gas processing plant (Wyoming)	–	230
Mississippi/Louisiana	Natural CO$_2$ (Mississippi)	680	–
Michigan	Ammonia plant (Michigan)	–	15
Oklahoma	Fertilizer plant (Oklahoma)	–	30
Saskatchewan	Coal gasification plant (North Dakota)	–	150
Total (MMcfd CO$_2$)		*2350*	*530*
Total (Mt CO$_2$)		*45*	*10*

[a]MIT EOR report estimates 65 Mt CO$_2$ for EOR annually [18]
[b]MMcfd stands for one million cubic feet per day of CO$_2$ and may be converted to Mt CO$_2$ per year by dividing by 18.9 Mcf per metric ton and multiplying by 365

down to approximately 40–65°C at the stack. Current technologies such as absorption and adsorption are exothermic processes that are enhanced at low temperatures and in a traditional sense are not effective strategies for taking direct advantage of the exergy of the high-temperature flue gas. For instance, the capture of CO$_2$ is most effective at low temperature for absorption and adsorption processes with the regeneration of the solvent or sorbent most effective at elevated temperatures. Membrane separation and catalytic-based technologies, may however, be enhanced at the elevated temperatures (and pressures) available at exit boiler or gasifier conditions, depending on the specific technology.

CO$_2$ Usage and Sinks   The primary use of CO$_2$ is for EOR, which has been taking place for several decades, beginning with the Permian Basin located in West Texas and neighboring area of southeastern New Mexico, underlying an area of approximately 190,000 km^2. The primary source of CO$_2$ for these activities include the natural CO$_2$ reservoirs in Sheep Mountain and the McElmo dome, both located in Colorado, and Bravo dome in New Mexico. The CO$_2$ gas is transported to the fields of the Permian Basin through pipeline networks. The existing networks of CO$_2$ pipeline in the U.S. are discussed in further detail in Chap. 2, Compression and Transport of CO$_2$. Currently, on average, CO$_2$-EOR provides the equivalent of 5% of the U.S. crude oil production at approximately 280,000 barrels of oil per day [16]. A limitation of reaching higher EOR production is the availability of CO$_2$. Natural CO$_2$ fields provide approximately 45 Mt CO$_2$ per year, with anthropogenic sources slowly increasing (currently 10 Mt CO$_2$ per year) as illustrated by the list of current activities in Table 1.3 [17].

Although the discussion of CO$_2$-EOR thus far has been centered on the usage of CO$_2$, EOR may also be a viable approach to potentially store CO$_2$. For instance, the CO$_2$ used for EOR is not completely recovered with the oil. In fact, only 20–40% of the CO$_2$ injected for EOR is produced with the oil, separated, and reinjected for additional production [18]. To date, EOR has not had any financial incentive to maximize

CO_2 left below ground. In fact, since the cost of oil recovery is closely coupled to the purchase cost of CO_2, extensive reservoir design efforts have gone into minimizing the CO_2 required for enhanced recovery. If, on the other hand, the objective of CO_2 injection is to increase the amount of CO_2 left underground while recovering maximum oil, then the approach to the design question changes. If there were such an incentive, likely an even larger fraction would stay below ground, via modifications of EOR. Researchers at Stanford University have investigated the co-optimization of CO_2 storage with enhanced oil recovery [19]. Their investigations conclude that traditional EOR techniques such as injecting CO_2 and water in a sequential fashion (*i.e.*, water-alternating-gas process) are not conducive to CO_2 storage. A suggested modified approach includes a well-control process, in which wells producing large volumes of gas are closed and only allowed to open as reservoir pressure increases. In addition to co-optimization of CO_2 storage with EOR, ongoing efforts exist for coupled CO_2 storage with enhanced coalbed methane recovery (ECBM) [20] and potentially enhanced natural gas recovery from gas shales [21].

As previously discussed, postcombustion capture of CO_2 has taken place commercially for decades, primarily for the purification of gas streams other than combustion products. Amine use for CO_2 capture was first patented in 1930 [22] and later in 1952 [23] for the purification of hydrocarbons. Since these times, its primary use has been to meet purity specification requirements for natural gas distribution and the food and beverage industry. Table 1.4 lists some selected power plant and industrial facilities that capture, transport, and store (temporarily in the case of the food industry) CO_2 in an integrated system. Comparing Tables 1.3 and 1.4, it is interesting to notice the difference in scale of CO_2 usage for EOR versus other industries. The Bellingham Cogeneration Facility located in Massachusetts generates electricity and uses a Fluor Econamine FG^{SM} regenerable solvent process and is capable of recovering 85–95% of the flue gas CO_2 for food-grade CO_2 at 95–99% purity. It is important to recognize that usage of CO_2 in the food industry is not a mitigation option as the CO_2 is subsequently reemitted into the atmosphere, yet the usage of CO_2 continues to drive the advancement of the separation technologies.

One might consider the option of converting CO_2 into additional useful products such as carbonates as previously discussed, but taking a look into the current scale of the worldwide chemical industry, one quickly recognizes that even if CO_2 was converted to useful products on the scale of every chemical produced worldwide, this would still constitute less than 5% of the current fossil-based CO_2 emissions. Consider the scale of CO_2 emissions associated with each of the primary energy resources. The annual emissions[5] generated from coal, petroleum, and gas are on the order of 13, 11, and 6 Gt CO_2, respectively [2]. Collectively, the emissions associated with the oxidation of fossil-based energy resources are on the order of 30 Gt CO_2 per year. Now, consider the top chemicals produced worldwide [24], which are shown in Table 1.5.

Lime, sulfuric acid, ammonia, and ethylene production are on the order of 283, 200, 154, and 113 million tons in 2009, respectively. If one could capture the CO_2

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[5] Data from 2008, IEA: Coal 12595 Gt CO_2; Oil 10821 Gt CO_2; Gas 5862 Gt CO_2.

Table 1.4 Selected commercial postcombustion capture processes at power plants and industrial facilities [16]

Project name and location	Plant type	Startup year	Capacity (MW)	Solvent	CO$_2$ captured (Mt/yr)
Projects located in the U.S.					
IMC Global Inc. Soda Ash Plant (Trona, CA)[a]	Coal and petroleum coke-fired boilers	1978	43	Amine (Lummus)	0.29
Bellingham Cogeneration Facility (Bellingham, MA)	Natural gas-fired power plant	1991	17	Amine (Fluor)	0.11
Projects located outside the U.S.					
Soda Ash Botswana Sua Pan Plant (Botswana)	Coal-fired power plant	1991	17	Amine (Lummus)	0.11
Statoil Sleipner West Gas Field (North Sea, Norway)	Natural gas separation	1996	NA	Amine (Aker)	1.0
BP Gas Processing Plant (In Salah, Algeria)	Natural gas separation	2004	NA	Amine (multiple)	1.0
Mitsubishi Chemical Kurosaki Plant (Kurosaki, Japan)	Natural gas-fired power plant	2005	18	Amine (MHI)	0.12
Snøhvit Field LNG and CO$_2$ Storage Project (North Sea, Norway)	Natural gas separation	2008	NA	Amine (Aker)	0.7

[a] CO$_2$ is captured from boiler flue gases and is used to carbonate brine for soda ash (sodium carbonate) production; soda ash is primarily used as a water softener, but has other uses associated with pH regulation

Table 1.5 Approximate production of top 10 chemicals produced U.S. and worldwide in 2009 [24]

Chemical	U.S. (Mt)	World (Mt)
1. Sulfuric acid	38.7	199.9
2. Nitrogen[a]	32.5	139.6
3. Ethylene	25.0	112.6
4. Oxygen[a]	23.3	100.0
5. Lime	19.4	283.0
6. Polyethylene	17.0	60.0
7. Propylene	15.3	53.0
8. Ammonia	13.9	153.9
9. Chlorine	12.0	61.2
10. Phosphoric acid	11.4	22.0

[a]N_2 and O_2 are both sourced from air and each have unique markets

Table 1.6 World CO_2 storage capacity estimates for several geologic formations [15b, 26]

Geologic formation	Worldwide (Gt CO_2)
Deep saline aquifers	1,000–10,000[a]
Depleted oil and gas fields	200–900
Unmineable coalbeds	100–300

[a]Source: IPCC (2007), deep saline aquifer capacity is noted as uncertain

at scale and turn it into useable chemicals equating to the current market of these top chemicals produced, this would mitigate a mere 2.5% of the CO_2 generated worldwide annually. This provides insight into the staggering scale of the fossil-based CO_2 emissions.

Although this book is focused solely on CO_2 capture, it is important to recognize the uses of CO_2 that might aid in advancing capture technologies. Additionally, if CO_2 is captured on the scale that is anticipated required for minimizing negative climate change impacts, the amount of CO_2 captured will be far greater than the current market usage. Carbon dioxide capture and storage (CCS) is expected to be a primary component of the portfolio of options for mitigating CO_2 emissions at the required scale [15b, 25].

Storage possibilities include the geologic formations: deep saline aquifers, depleted oil and gas fields, and unmineable coalbeds. Table 1.6 lists the CO_2 storage capacity estimates for these primary types of geologic formations considered. The accurate determination of the storage estimates presented in Table 1.6 is difficult, which is why the estimates range so broadly [27]. The geological nature of a storage site can be quite complex and each site can vary considerably.

The market for CO_2 use and the storage potential for CO_2 exist. The key is to determine the most effective portfolio of solutions [28] for the variety of emissions scenarios that exist to capture CO_2 for the existing markets. Steam-based electricity generation was not invented with the anticipation of capturing CO_2; therefore, it is reasonable to return to the beginning and to understand the formation pathway of CO_2 from the oxidation of fossil fuel and to possibly consider alternative approaches

to energy generation that could result in higher plant efficiencies with the inclusion of CO$_2$ capture.

1.3 Formation Pathways of CO$_2$

As discussed previously, the primary sources of CO$_2$ release into the atmosphere are listed in Table 1.1, with the majority of the CO$_2$ produced from the oxidation of fossil fuels. Understanding CO$_2$ capture technologies and envisioning solutions to this challenge requires knowledge of how the CO$_2$ is originally generated. This involves some background on fuel oxidation mechanisms, combustion science, and in general fuel-to-energy conversion processes. A more detailed description of the basic fundamentals of combustion processes is available in Appendix A.

Coal Oxidation Coal is a sedimentary rock formed of fossilized vegetation of different types. Coal may be sourced deep underground (average depths of approximately 600 ft) or close to the surface, having taken up to 400 million years to form under varying temperature and pressure conditions. The four major classes of coal, also known as *rank*, are lignite, subbituminous, bituminous, and anthracite, in order of youngest to oldest. The lowest ranked coal (lignite) has the lowest carbon content ($\sim$60 mass%) and is highest in volatiles and moisture content, compared to the highest rank coal, anthracite (carbon content $\sim$90 mass%) [29]. Coal is a complex amorphous mixture of carbon, hydrogen, oxygen, sulfur, nitrogen, moisture, ash, and trace metals. The ideal chemical composition of coal's three principal elements can be written as CH_mO_n. Usually, $m < 1$ and $m < n$. Coal primarily consists of carbon, hydrogen, and oxygen, but may also consist of nitrogen and sulfur, which lead to the formation of NO$_x$ and SO$_x$, respectively. Additionally, coal contains volatile trace metals that evolve from the coal at the high temperature conditions of the boiler. The trace metals, mercury, selenium, and arsenic are present at ppb levels in most flue gases [30]. However, it is important to note that depending on the type of coal and source from which the coal was mined, the chemical constituents may vary significantly. The chemical composition of coal varies greatly depending upon its rank and origin. Although coal combustion is a complex process since all coal is unique, in general it is consistent in that initially moisture and volatiles are driven off, followed by direct carbon oxidation.

Coal combustion is a heterogeneous reaction involving the oxidation of coal through the transport to and subsequent reactivity of O$_2$ with its surface. Heterogeneous implies that two phases are taking part in the reaction, *i.e.*, the solid coal surface and oxygen in the gas phase. The coal is comprised of pulverized porous particles ranging in size from 75–300 μm depending upon the boiler type. Gas-phase species reacting with the coal surface must diffuse through the intricate pore network within the coal particles as depicted by the scanning electron microscopy image in Fig. 1.4. In reality, the coal surface may be oxidized by a combination of species present in the gas phase, that is, O$_2$, CO$_2$, and H$_2$O proceeding by the following
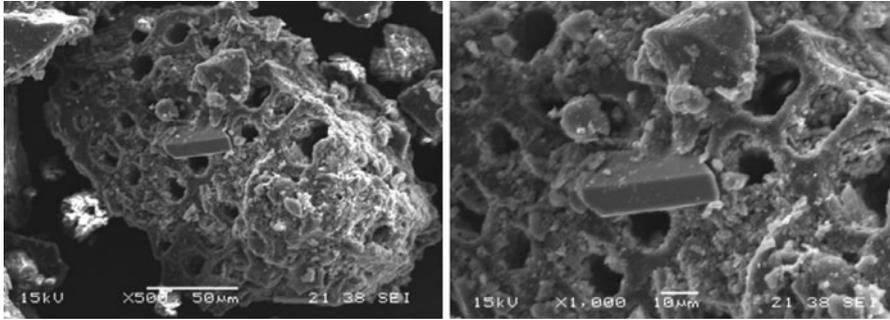
Fig. 1.4 Scanning electron microscopy images of subbituminous coal. The image on the right is a magnification of the particle on the left, both on the micron scale. (Courtesy of [1])

global reactions:

$$C + O_2 \rightarrow CO_2 \tag{1.1}$$

$$2C + O_2 \rightarrow 2CO \tag{1.2}$$

$$C + CO_2 \rightarrow 2CO \tag{1.3}$$

$$C + H_2O \rightarrow CO + H_2 \tag{1.4}$$

A global reaction is one that is comprised of a series of *elementary reactions*, which are reactions that proceed as they are written. For instance, Reaction (1.1) is not elementary since the formation of gas-phase CO_2 in this case would involve a series of elementary steps such as O_2 adsorption, O_2 bond stretching, CO bond forming, etc. At the high temperatures of coal combustion, a dominating reaction is heterogeneous carbon oxidation to the formation of CO, followed by homogeneous CO oxidation by O_2 to CO_2.

Coal-to-Electricity Conversion Just under 50% of the electricity generated in the U.S. is powered by coal-fired steam power plants. Figure 1.5 is a simplified version of a power plant with the basic components responsible for generating power. Understanding the coal-to-electricity conversion process allows one to appreciate the life cycle of CO_2 from the oxidation of the coal's carbon surface to the exit of the stack. Figure 1.5 also shows how other scrubbing technologies have been arranged downstream of the boiler exit. For instance, NO_x reduction (*i.e.*, mitigation) is taking place here using a high-temperature catalyst so its placement is at the boiler exit to maximize the thermal energy required for enhanced conversion. The removal of SO_x with an absorption set-up is placed at the lowest temperature available since absorption is an exothermic process. For CO_2 capture, an additional scrubbing unit would be placed in this plant configuration, with its exact location dependent upon the type of separation process used (*e.g.*, absorption, adsorption, membrane, or catalytic).

The steps of coal conversion to electricity are complex in reality, but are simplified here for a general understanding of the process:
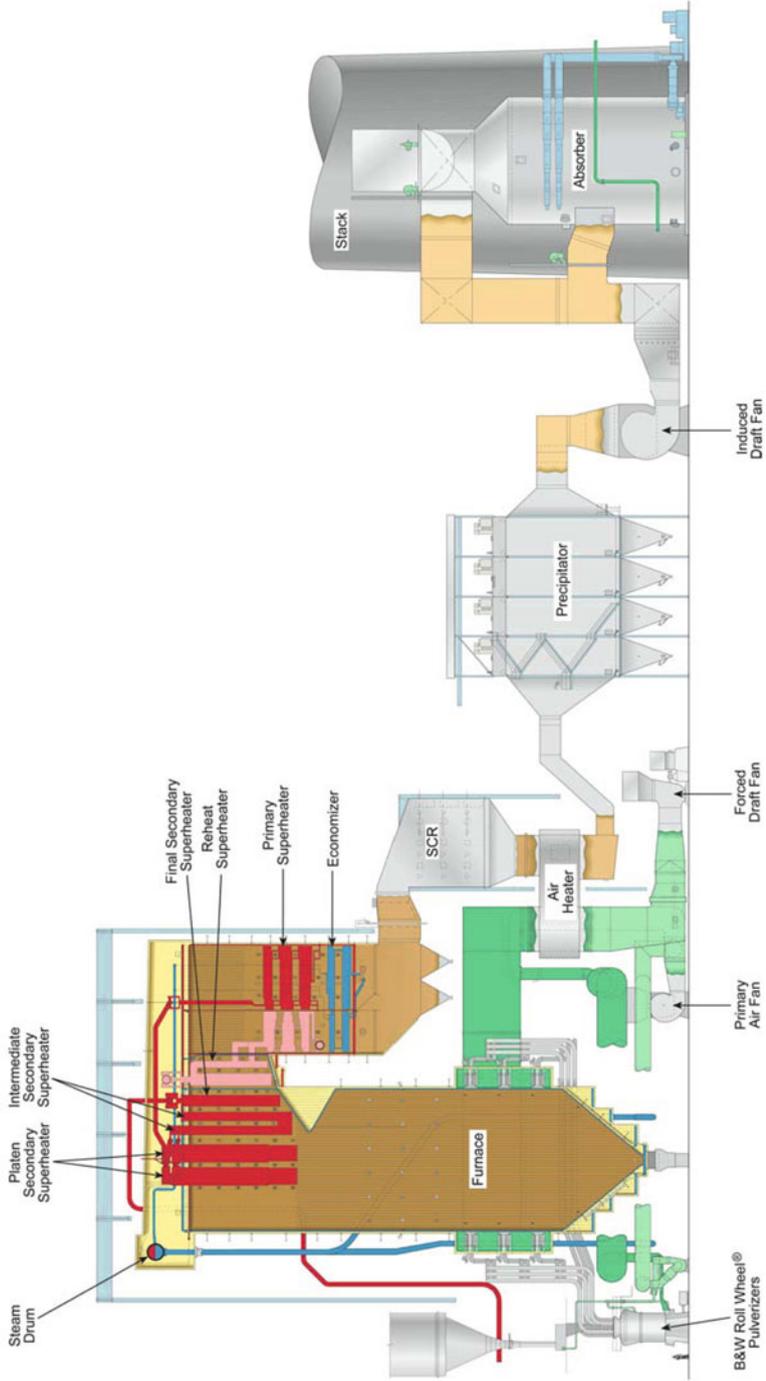
Fig. 1.5 Coal-fired power plant (Courtesy of The Babcock & Wilcox Company)

1. During startup, the furnace is pre-heated by combustion of auxiliary fuel such as natural gas or oil;
2. Pulverized coal powder is blown with air into a combustion chamber (boiler or furnace) through a series of nozzles; combustion of the coal particles creates hot combustion products;
3. Heat is transferred from the hot combustion products to water circulating in tubes along the boiler walls; this produces superheated steam, which is the working fluid for the steam turbines;
4. Pumps are used to increase the pressure of the working fluid;
5. Energy from the hot and pressurized steam is extracted in steam turbines that then transmit the energy to electric generators;
6. The electric generators convert the shaft work of the turbines into alternating current electricity;
7. Heat exchangers are used to condense the energy-drained steam from the turbines;
8. Pumps are used to return the condensed water to the boiler, where the cycle is then repeated; and
9. Pollution control devices are used to scrub the flue gas of NO_x (selective catalytic reduction), particulate matter (electrostatic precipitators and/or fabric filters), and SO_2 (calcium-based flue gas desulfurization units or lime spray dryers). Some power utilities are also equipped with activated carbon injection processes to capture mercury emissions; currently there are no full-scale CO_2 capture methods in place.

Liquid Fuel and Natural Gas Oxidation Converting petroleum to power requires evaporation and burning of a liquid fuel. Applications include diesel, rocket, and gas-turbine engines, oil-fired boilers and furnaces. In liquid fuel oxidation, the fuel is first vaporized and then combusted. Gas combustion may occur with or without flame, and flames are usually characterized as premixed or diffusion flames. In flame combustion, a reaction zone (flame) propagates through an air-fuel mixture where the hot combustion products are left behind the flame with temperature and pressure rising in the unburned fuel. In flameless combustion, rapid oxidation reactions occur throughout the fuel leading to very rapid combustion. The volumetric exothermicity that takes place in an engine is called autoignition. Premixed versus diffusion flames are characterized by the level of mixing that takes place between the fuel and oxidizing agent. A spark-ignition engine is an example in which the fuel and oxidizing agent are mixed prior to any combustion activity. On the other hand, within a diffusion flame the fuel is initially isolated from the oxidizing agent and the combustion reaction takes place simultaneous to mixing with flame propagation at the interface of the fuel and oxidant.

There are clear distinctions between the oxidation processes of coal, petroleum, and gas and subsequent differences between the mechanisms of CO_2 generation in each case. Understanding more thoroughly the nature by which CO_2 is formed may lead to advancements in fuel-to-energy conversion processes that minimize its generation. The capture of CO_2 in a traditional pulverized coal combustion process is termed *postcombustion capture* (PCC), since capture is taking place after the

Table 1.7 Approximate efficiencies of various plants with and without CO_2 capture (CC) [31]

Plant type	Plant efficiency w/out CC (%)[a]	Plant efficiency w/CC (%)
Coal, subcritical	33–39	23–25
Coal, supercritical	38–44	29–31
Coal, ultrasupercritical	43–47	34–37
NGCC[b]	45–51	38–43
IGCC[c]	37–44	32–39

[a]Plant efficiency is based upon the high heating value (HHV) of the fuel
[b]NGCC refers to a natural gas combined cycle power plant
[c]IGCC refers to an integrated gasification combined cycle power plant

combustion process. Another possibility is to modify the fuel-to-energy conversion process to maximize the concentration of CO_2 as to minimize the work associated with its separation.

1.4 Advanced Coal Conversion Processes

When fuel oxidation was first carried out for energy generation there was no intention to capture the CO_2 generated from the process. Air being the primary source of fuel oxidation is approximately 78% N_2, 21% O_2, and 0.95% Ar by volume on a dry basis, *i.e.*, excluding moisture content (plus trace amounts of CO_2, Ne, He, Kr, and Xe) [30]. The N_2 is predominantly an inert gas throughout the combustion process, thereby diluting the CO_2 generated in the flue gas stream and increasing the work required for CO_2 separation. Table 1.7 shows the difference in the efficiency with and without CO_2 capture for various plants.

Advanced coal conversion processes[6] are currently under development that reduce the work required for separation by creating CO_2-concentrated gas outlet streams. These include coal gasification, oxycombustion, and chemical looping combustion. These processes in fact, could be carried out on any fossil-based energy resource. Coal is primarily discussed since this is the most common energy resource available worldwide. Figure 1.6 shows the pathway of each advanced energy conversion process with the energy resource options as coal, biomass, waste, petroleum coke/residue or natural gas.

Gasification Coal gasification is a process in which the oxidation of coal is kept at a minimum, with just enough exothermicity to provide the required energy for driving the gasification reactions. The heat is controlled through the control of air

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[6] Although not discussed specifically, another energy conversion option is electrochemical conversion in a direct carbon fuel cell. Challenges are associated with the accessibility of the oxidizer to the electrochemical reaction sites, but progress continues to be made in this field. [51, 52] Electrochemical conversion processes are described in more detail in Chapter 8, but are focused on CO_2 reduction toward fuel synthesis, in which energy (renewable) is required as an input, rather than direct carbon (*e.g.*, coal, biomass, etc.) oxidation toward energy production.
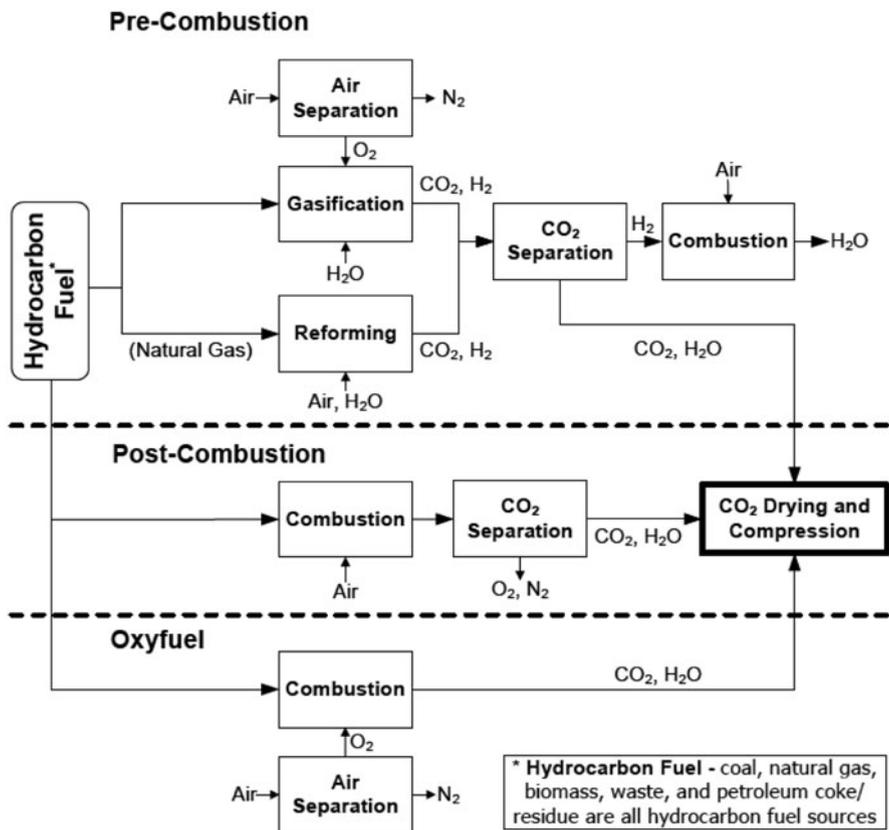
Pre-Combustion

Fig. 1.6 Schematic of primary options for CO_2 capture from various hydrocarbon-based energy conversion processes

or more often, oxygen input into the gasifier. A limitation of gasification is the need for an air separation unit (ASU) for the generation of high-purity O_2 as a feed gas to the gasifier. The gasification process suppresses the formation of water and instead produces primarily CO and hydrogen gas (H_2). IGCC systems operate at high pressures (*e.g.*, 500–700 psia) and require the oxidant stream to also be pressurized. Gasification takes place rapidly at temperatures above 1260°C, which is greater than the ash fusion temperature, allowing ash to become molten and separating easily from the gas. In addition to H_2 and CO, CH_4 is generated in small amounts and H_2S is also generated depending upon the extent of sulfur present in the energy resource. The hot and pressurized synthesis gas exits the gasifier and a particulate control device then removes particulate matter, after which steam is added to the fuel gas (also known as synthesis or syngas) to promote the conversion of H_2 and CO_2, which is called the water gas shift reaction, *i.e.*,

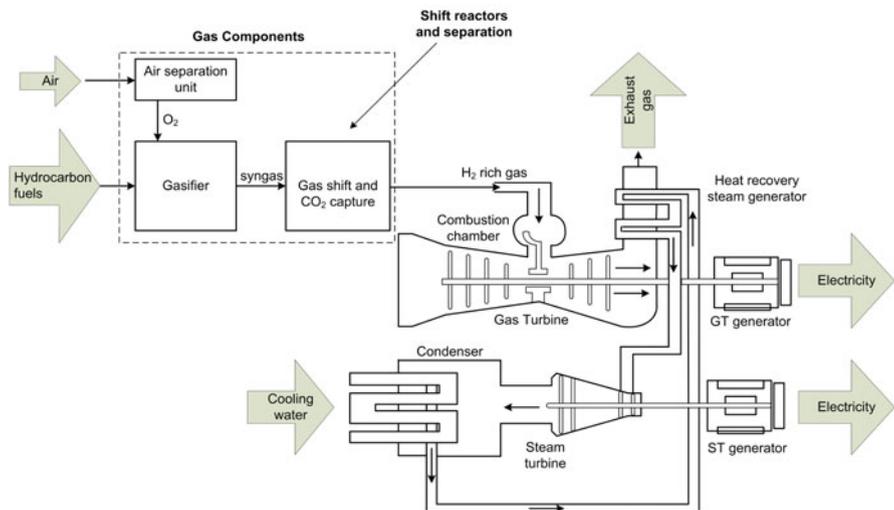$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{1.5}$$

Fig. 1.7 Detailed schematic of an integrated gasification combined cycle (IGCC) plant

and is exothermic by approximately 41 kJ/mol CO_2 generated. The reaction is equilibrium-limited, leading to an increase in conversion as temperature decreases. The current industrial approach is to cool and clean the fuel stream before entering a high-temperature shift reactor at approximately 315–445°C. This step is sometimes followed by a low-temperature shift reactor that operates at approximately 200–250°C. The equilibrium can be shifted using a catalytic metallic membrane reactor selective to the removal of H_2 on the right hand side of Reaction (1.5). These types of reactors will be discussed in more detail in Chap. 5 on Membrane Technology. Shifting the equilibrium to optimize conversion is preferred, since this limits the cooling required of the gas stream.

The concentration of CO_2 in this process is substantially greater than in coal combustion making its separation from the fuel gas mixture easier. The capture of CO_2 in an IGCC process is termed *precombustion capture* since the fuel combustion takes place after the capture process as demonstrated in Fig. 1.7. For electricity generation, the synthesis gas (largely hydrogen) is burned directly and then passed through a gas turbine for electricity generation. The heat recovered from this process is used to generate steam, which is passed through a steam turbine for additional electricity generation, resulting in a combined cycle. The efficiency of an IGCC plant is on the order of 37–44%, compared to a newer existing ultrasupercritical pulverized coal-fired power plant, which is on the order of 43–47%. It is important to recognize the competition that will likely exist between steam and gas processes as technologies are advanced (*i.e.*, turbine technology) toward the handling of gas. Although the cost of electricity of a traditional coal combustion power plant is lower than that of an IGCC plant, with the inclusion of CO_2 capture, the efficiency is higher (see Table 1.7) and hence the cost is less in the gasification case [33].
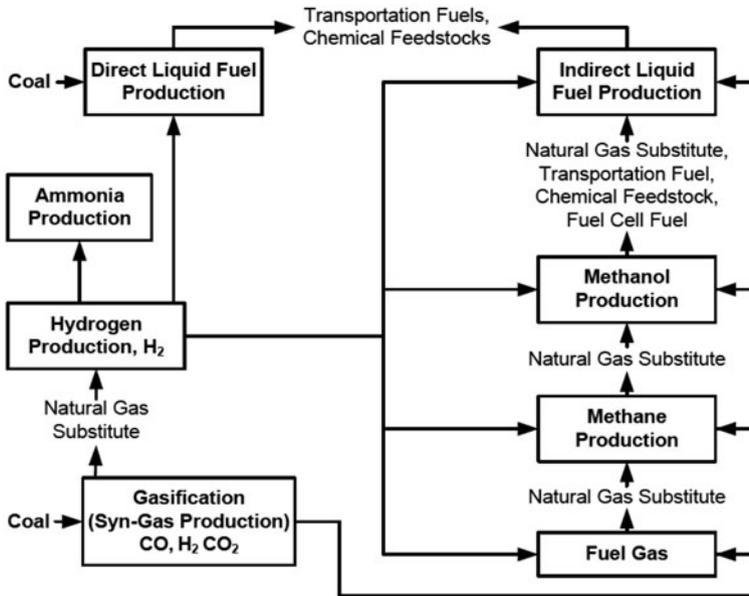
Fig. 1.8 Schematic of fuel and chemical products produced from a synthesis gas via the Fischer-Tropsch (FT) process

Fischer-Tropsch Process   Rather than directly combusting the synthesis gas in an IGCC process, the syngas may also be converted to fuel and/or chemicals via Fischer-Tropsch (FT) synthesis. The original inventors of the process were Franz Fischer and Hans Tropsch, who worked at the Kaiser Wilhem Institute during the 1920s. The first commercialization took place in 1934, with the first industrial plant in operation in Germany in 1936, with annual production of over 1 million tons of FT liquid fuel at that time. The largest scale FT operation, based on a coal-to-liquid (CTL) conversion process, is operated by Sasol in South Africa, which is high in coal reserves and low in petroleum [34]. Due to oil embargos in opposition to Apartheid, South Africa advanced their CTL process in an attempt to gain independence from petroleum [35]. Figure 1.8 demonstrates the flexibility of the FT process in terms of the variety of petroleum-based products that can result.

An important parameter for controlling the FT conversion and selectivity is the hydrogen-carbon ratio (H/C). The required H/C ratio for commercial production of hydrocarbon fuels, *i.e.*, Diesel and gasoline is approximately 2 on a molar basis, while the ratio ranges from 1.3–1.9 for petroleum crude oil and 0.8 for typical bituminous coals [36]. A critical challenge for FT conversion is increasing the H/C ratio or the H_2/CO ratio. The hydrogen content in the syngas enhances the conversion efficiency toward the production of hydrocarbon products, with the additional hydrogen sourced from steam during the gasification step. Steam reacts with CO resulting in the water-gas shift reaction (*i.e.*, $CO + H_2O \leftrightarrow CO_2 + H_2$). The effect of the water-gas shift reaction can be varied depending on the type of FT catalyst, with the direction of the

water-gas shift equilibrium dependent on the syngas composition [37]. Though the H/C or the H_2/CO ratio for the FT process is increased through the addition of steam, there is a subsequent efficiency penalty associated with the use of steam generated from the gasifier, in addition to the condensation of unused steam after the FT reactor. The future of coal-to-liquid processes may be limited due to: 1) its competition with existing "alternative liquid fuels," such as biofuels, as well as 2) its inevitable result of net CO_2 emissions since the H:C ratio is higher in liquids than in coal.

Oxyfuel Combustion   Sometimes referred to as oxycombustion, oxyfuel combustion involves an ASU to allow coal to be burned in an oxygen-enriched environment, which leads to minimal dilution of CO_2 in the flue gas stream. The flue gas stream in an oxyfuel combustion process includes primarily CO_2 and water vapor, which can be condensed out fairly easily. To prevent the temperatures in the boiler from getting too large, up to 70% of the flue gas stream is recycled back to dilute the oxygen-enriched environment and maintain temperatures similar to conventional air-blown designs. Major challenges associated with the application or retrofit of oxyfuel combustion on an existing power plant is the cost of the ASU and potential leakage of air into the flue gas stream. It is important to keep in mind, however, that a typical stream from an ASU may contain approximately 3% N_2 and 2% Ar depending upon the method used for separation. In general, major oxyfuel developers now see the primary application in new plants, or at existing plants that are "repowered" with modern and more efficient boilers. The following demonstration plants are currently in place: Vattenfall in Sweden [38], IHI in Japan [39], and Alstom Power in the U.S. [40], with 2 × 900, 1000, and 450-MW capacities, respectively. Although the cost of electricity is greater from an oxyfuel combustion plant compared to a coal-fired plant with air, it has been shown that the cost may be lower with the inclusion of CO_2 capture [41].

Chemical Looping Combustion   The chemical looping combustion process involves the injection of metal oxides into the boiler that act as oxygen transporters (rather than air) for coal of natural gas oxidation, similar to the other processes previously discussed, minimizing the dilution of CO_2 in the flue gas stream [42]. Within the chemical looping process, the solid oxygen carrier circulates between two fluidized bed reactors to transport oxygen from the combustion air to the fuel. Typical metal oxides include iron and nickel. Iron is low cost and nonhazardous making it an optimal choice. The metal oxide is reduced in a fuel reactor (*i.e.*, reduction reactor) while oxidizing the fuel and is then transported into an air reactor (*i.e.*, oxidation reactor) where it is reoxidized by air. The carrier particles are then transported back into the fuel reactor after passing through a cyclone for separation from the hot N_2 and O_2 gases. Benefits of this process are similar to those of oxyfuel combustion, *i.e.*, the flue gas is not diluted with N_2 and this process leads to lower NO_x formation. However, it is important to note that the majority (∼70%) of the NO_x formed is not from the N_2 in the combustion air, but rather, from the surface functional groups on the coal itself. A simple schematic demonstrating the principle of chemical looping combustion is shown in Fig. 1.9. Additional details regarding these advanced coal conversion processes are available in the literature [43].
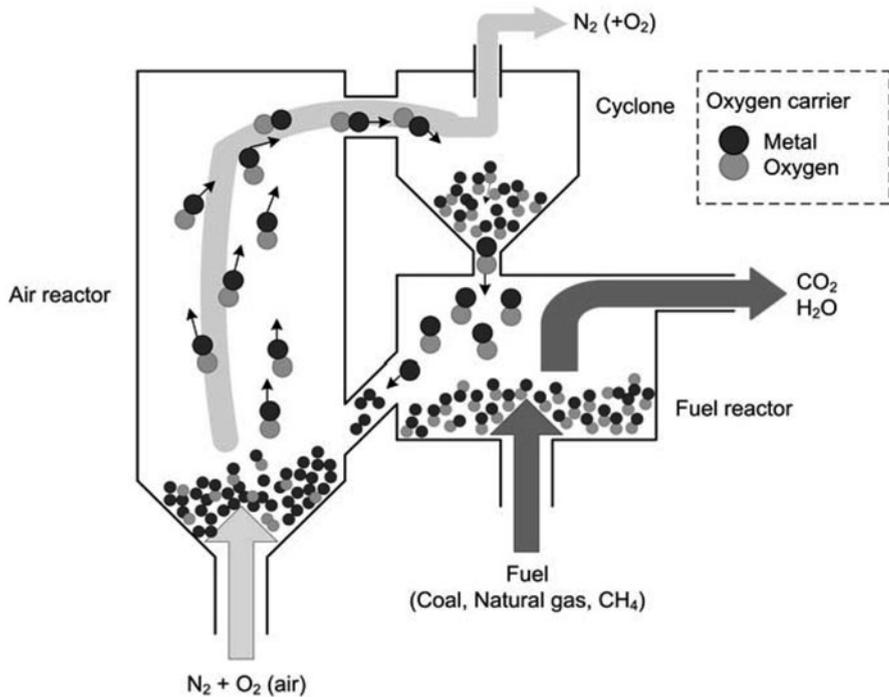
**Fig. 1.9** Schematic demonstrating the principle of chemical looping combustion

1.5   Minimum Thermodynamic Work for CO_2 Separation

The first law of thermodynamics is concerned with the conservation of energy. The change in total energy of the system going from state 1 to state 2 is equal to the heat added to the system minus the work done, and can be expressed as,

$$Q - W = \Delta E_{1\rightarrow 2}, \tag{1.6}$$

in which Q and W may be positive or negative with the sign indicating the direction of energy flow. Examples of energies include internal energy, kinetic energy, and potential energy. The internal energy is comprised of the molecular energies within a given system, more specifically these include the energy contributions from the translational, vibrational, and rotational degrees of freedom within a molecule. Kinetic energy can be expressed as $\frac{1}{2}mv^2$, where m is the mass of a moving object and v is its velocity. Potential energy can be expressed as mgz, where m is the mass of a stationary object, g is the acceleration due to gravity, and z is elevation. Additional energies exist such as nuclear, electromagnetic, etc., but are not necessary for discussion in the context of CO_2 capture.

The second law of thermodynamics is concerned with entropy, which is generated during irreversible processes. Examples that include such irreversibilities are heat transfer across a temperature gradient, friction, mixing or stirring processes, and

Fig. 1.10 Schematic of
carbon capture
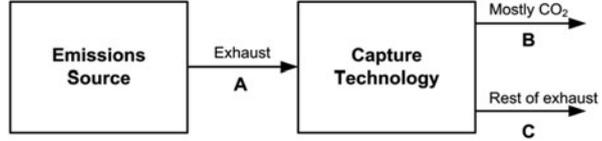
many chemical reactions. Irreversible processes prevent a system from returning to its original state and additionally, they reduce the available work (*i.e.*, exergy) of a given system.

The minimum work required to separate CO_2 from a gas mixture can be calculated based upon the combined first and second laws of thermodynamics. Figure 1.10 is a representation of the a generic CO_2 separation process along with the general emissions source and capture technology with corresponding gas streams. Stream A represents a CO_2-inclusive gas stream mixture (not limited to a combustion exhaust) while stream B contains mostly CO_2 depending upon the process purity, and stream C contains primarily the remainder of gas stream A. Ideally, stream B would be mostly (or all) CO_2 and stream C would be very low (or zero) in CO_2.

The minimum work required for separating CO_2 from a gas mixture for an *isothermal* (constant temperature) and *isobaric* (constant pressure) process is equal to the negative of the difference in Gibbs free energy of the separated final states (streams B and C in Fig. 1.10) from the mixed initial state (stream A in Fig. 1.10). For an *ideal gas* (minimal gas species interactions), the Gibbs free energy change between stream A to streams B and C is:

$$W_{min} = \Delta G_{sep} = \Delta G_B + \Delta G_C - \Delta G_A \tag{1.7}$$

For an ideal mixture, the partial molar Gibbs free energy for each gas is [44, 45]:

$$\frac{\partial G}{\partial n_i} = G_i^\circ + RT \ln\left(\frac{p_i}{p}\right) \tag{1.8}$$

such that p_i is the partial pressure of the ith gas and p is total pressure. Therefore, the total Gibbs free energy of an ideal gas mixture is:

$$G_{TOTAL} = \sum_i n_i \frac{\partial G}{\partial n_i} \tag{1.9}$$

The minimum work required to go from state 1 to states 2 and 3 is associated with the free energy difference between the product and reactant states, which can be calculated by combining Eqs. (1.8) and (1.9) as:

$$G_A = n_A^{CO_2} G_{CO_2}^\circ + n_A^{A-CO_2} G_{A-CO_2}^\circ + RT\left(n_A^{CO_2} \ln\left(y_A^{CO_2}\right) + n_A^{A-CO_2} \ln\left(y_A^{A-CO_2}\right)\right)$$

$$G_B = n_B^{CO_2} G_{CO_2}^\circ + n_B^{B-CO_2} G_{B-CO_2}^\circ + RT\left(n_B^{CO_2} \ln\left(y_B^{CO_2}\right) + n_B^{B-CO_2} \ln\left(y_B^{B-CO_2}\right)\right)$$

$$G_C = n_C^{CO_2} G_{CO_2}^\circ + n_C^{C-CO_2} G_{C-CO_2}^\circ + RT\left(n_C^{CO_2} \ln\left(y_C^{CO_2}\right) + n_C^{C-CO_2} \ln\left(y_C^{C-CO_2}\right)\right),$$
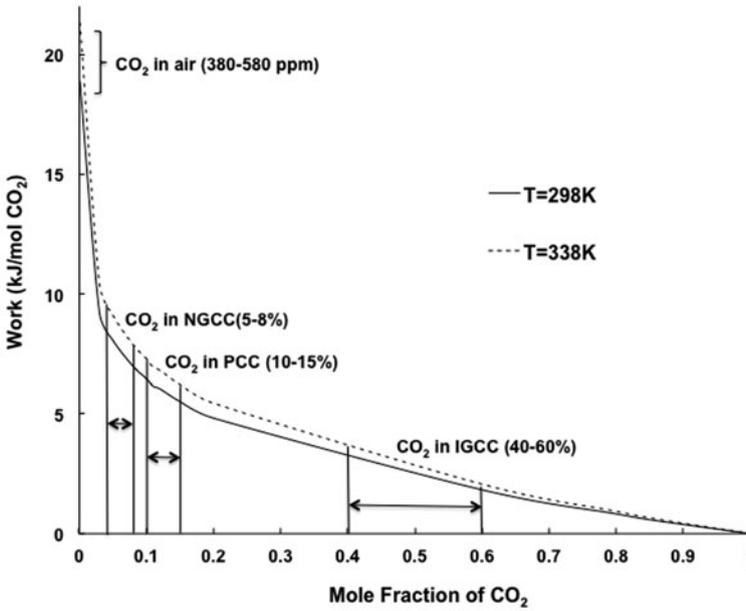
$$\tag{1.10}$$

Fig. 1.11 Minimum thermodynamic work for various coal or gas-to-electricity conversions

And thus the minimum work is:

$$W_{\min} = RT \left[n_B^{CO_2} \ln \left(y_B^{CO_2} \right) + n_B^{B-CO_2} \ln \left(y_B^{B-CO_2} \right) \right]$$

$$+ RT \left[n_C^{CO_2} \ln \left(y_C^{CO_2} \right) + n_C^{C-CO_2} \ln \left(y_C^{C-CO_2} \right) \right]$$

$$- RT \left[n_A^{CO_2} \ln \left(y_A^{CO_2} \right) + n_A^{A-CO_2} \ln \left(y_A^{A-CO_2} \right) \right] \qquad (1.11)$$

where R is the ideal gas constant (8.314 J/mol K), T is the absolute temperature, $y_i^{CO_2}$ is the mole fraction of CO_2 in the gas mixture, i, such that i can represent either stream A, B, or C in Fig. 1.10, and $y_i^{i-CO_2}$ represents the remainder of a given gas stream A, B, or C. The quantity of greatest interest is the minimum work per mole of CO_2 removed, that is, $W_{min}/(n_{CO_2})$. For $T = 25°C$ (298 K), the minimum work when beginning with coal flue gas at 12% CO_2, is 172 kJ/kg CO_2; when beginning with air at 0.04% CO_2, is 497 kJ/kgCO_2, which is approximately a factor of three greater. The minimum work required for separation is highly dependent upon the starting concentration of CO_2 in a given gas mixture.

Figure 1.11 is a plot of the minimum work, W_{min} at varying temperatures for CO_2 separation as a function of the molar concentration of CO_2 in the initial gas mixture. As the concentration of CO_2 decreases, the minimum work required for separation increases. Additionally, an increase in temperature leads to an increase in the thermodynamic minimum work required for separation.

Example 1.1   Assume a 500-MW coal-fired power plant emits a flue gas containing 4 kmol CO$_2$/s, 5 kmol H$_2$O/s, 1 kmol O$_2$/s and 20 kmol N$_2$/s. What is the minimum work for the isothermal and isobaric separation of CO$_2$ from the flue gas mixture for 90% capture and 98% purity at 45°C?

Solution

Given: $\dot{n}_{CO_2} = 4$ kmol CO$_2$/s $\dot{n}_{H_2O} = 5$ kmol H$_2$O/s

$\dot{n}_{O_2} = 1$ kmol O$_2$/s $\dot{n}_{N_2} = 20$ kmol N$_2$/s

Capture $= 0.90$ Purity $= 0.98$

Using Eq. (1.11),

$$W_{\min} = RT \left[n_B^{CO_2} \ln \left(y_B^{CO_2} \right) + n_B^{B-CO_2} \ln \left(y_B^{B-CO_2} \right) \right]$$
$$+ RT \left[n_C^{CO_2} \ln \left(y_C^{CO_2} \right) + n_C^{C-CO_2} \ln \left(y_C^{C-CO_2} \right) \right],$$
$$- RT \left[n_A^{CO_2} \ln \left(y_A^{CO_2} \right) + n_A^{A-CO_2} \ln \left(y_A^{A-CO_2} \right) \right]$$

where stream A is the flue gas mixture entering the separator, stream B at 98% purity contains 90% of the CO$_2$ contained in stream A, and stream C contains the remaining 10% of the CO$_2$ contained in stream A. Performing a mole balance on the separator yields:

Stream A: $\dot{n}_A^{CO_2} = 4$ kmol CO$_2$/s $\dot{n}_A^{A-CO_2} = 26$ kmol A $-$ CO$_2$/s

$\dot{n}_A = 30$ kmol A gas/s

$y_A^{CO_2} = 0.13$ $y_A^{A-CO_2} = 0.87$

Stream B: $\dot{n}_B^{CO_2} = (4$ kmol CO$_2$/s$)(0.90) = 3.6$ kmol CO$_2$/s

$\dot{n}_B = (3.6$ kmol CO$_2$/s$)/(0.98)$

$= 3.67$ kmol B gas/s to ensure 98% purity

$\dot{n}_B^{B-CO_2} = 3.67$ kmol B gas/s $-$ 3.6 kmol CO$_2$ gas/s

$= 0.07$ kmol B $-$ CO$_2$/s

$y_B^{CO_2} = 0.98$ $y_B^{B-CO_2} = 0.02$

Stream C: $\dot{n}_C^{CO_2} = (4$ kmol CO$_2$/s$)(0.1) = 0.4$ kmol CO$_2$/s

$\dot{n}_C = \dot{n}_A - \dot{n}_B$

$= 26.33$ kmol C gas/s from the system (separator) molar

balance

$$\dot{n}_C^{C-CO_2} = 26.33 \text{ kmol C gas/s} - 0.4 \text{ kmol } CO_2 \text{ gas/s}$$

$$= 25.93 \text{ kmol C} - CO_2/\text{s}$$

$$y_C^{CO_2} = 0.015 \qquad\qquad\qquad y_C^{C-CO_2} = 0.985$$

The flue gas is entering the separator at 45°C or 318 K. Substituting these values into Eq. (1.11) yields a thermodynamic minimum work of 24,756 kJ/s or 6.88 kJ/mol CO_2 captured, with a CO_2 capture rate of 3.6 kmol CO_2/s.

2nd-Law Efficiency Real systems will always use more energy than the thermodynamic minimum since the minimum is derived for a reversible isothermal process. The capture of CO_2 or more specifically, separating CO_2 from a gas mixture, takes significant work for dilute mixtures of CO_2 and additional work for increased capture and purity. The separation process may depend upon current technologies such as absorption, adsorption, membranes, or some hybrid approach that has yet to be developed. Take for example absorption, which is outlined in Chap. 3; within this process blowers are used to drive a flue gas upward through a packed bed or spray tower, in which a liquid solvent is driven downward countercurrently using pump work. Additional work is required through the addition of heat for the solvent regeneration process, which drives the CO_2 off in a pure stream for compression, which also takes work. Each of these processes have associated efficiencies based upon irreversibilities, such as friction, heat transfer, gas expansion, gas mixing, etc.; therefore, the actual work required for CO_2 separation from a gas mixture deviates from the thermodynamic minimum work based upon the unit operations of the process and the extent of their individual inefficiencies. The ratio of the reversible or thermodynamic minimum work to the real work is termed the 2nd-Law efficiency [46] and is defined as:

$$\eta_{2nd} = \frac{W_{min}}{W_{real}} \tag{1.12}$$

The chemistry and physics of the underlying mechanisms of the various unit operations are discussed in the following chapters and analyzed in addition to the design and process in which the underlying chemistry and physical principles exist. Through the investigation of each of the steps in the given separation process there will be the opportunity to question and probe the actual work required of a given process and to assess the sensitivity of potentially tuning the related parameters to maximize the process's 2nd-law efficiency.

The 2nd-law efficiency has been investigated for a variety of gas scrubbing processes that span a wide range of concentrations. In Fig. 1.12, the 2nd-law efficiency is plotted as a function of decreasing concentration for 90% CO_2 capture from coal-fired power and NGCC plants, as well as for varying levels of NO_x, SO_x and mercury (Hg) scrubbing. For all "actual" work calculations, the Integrated Environmental Control Module developed by Rubin et al. [47] from Carnegie Mellon University was used. In the case of the postcombustion capture of CO_2, SO_x, NO_x, and Hg it was assumed
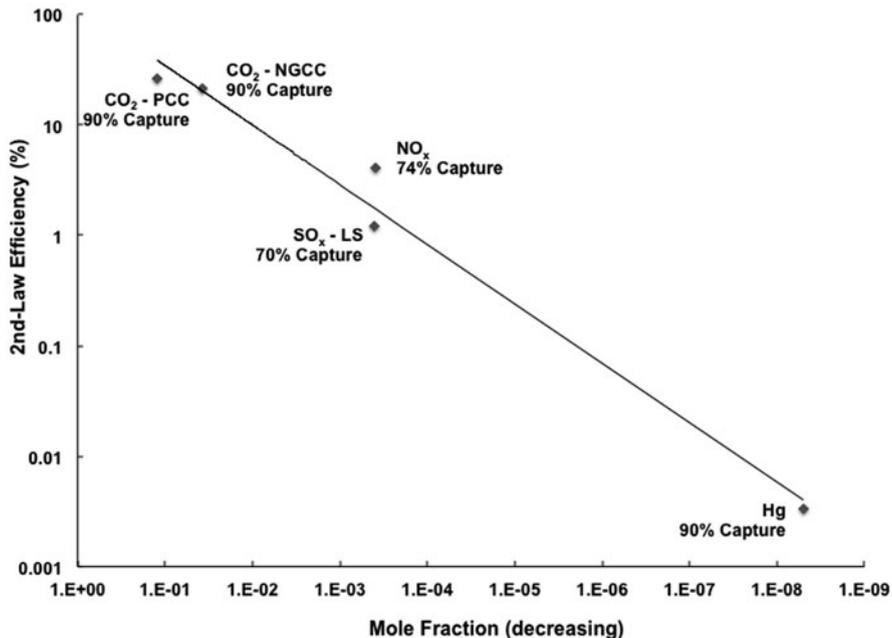
Fig. 1.12 Plot showing the relationship between the 2nd-law efficiency and concentration of initial gas mixture

that low-sulfur Appalachian bituminous coal was burned in a 500-MW utility boiler. The capture technologies assumed for CO_2, SO_x, NO_x, and Hg consisted of amine scrubbing, wet flue gas desulfurization, selective catalytic reduction, and activated carbon injection, respectively. In the case of NGCC, precombustion separation based upon amine scrubbing is assumed for a 477-MW plant. It is interesting to note that the 2nd-law efficiency decreases with decreasing CO_2 concentration [48]. This implies that there are still efficiencies to gain in SO_x, NO_x, and Hg capture since these processes do not include regeneration, yet they still follow the trend.

1.6   Cost of CO$_2$ Capture

Costs of separation may be divided into technical versus non-technical costs. Examples of non-technical costs may include account depreciation and return on investment, interest rate, labor, etc. Costs associated with the technology include the cost of the equipment, chemicals used, power consumption to operate the separation process, power cost, etc. Additional factors that may affect the cost of CO_2 capture include the choice of power plant and capture technology. For instance, will an existing plant be retrofitted or will the capture technology be applied to a new plant? The process design and variables associated with plant operation, such as plant
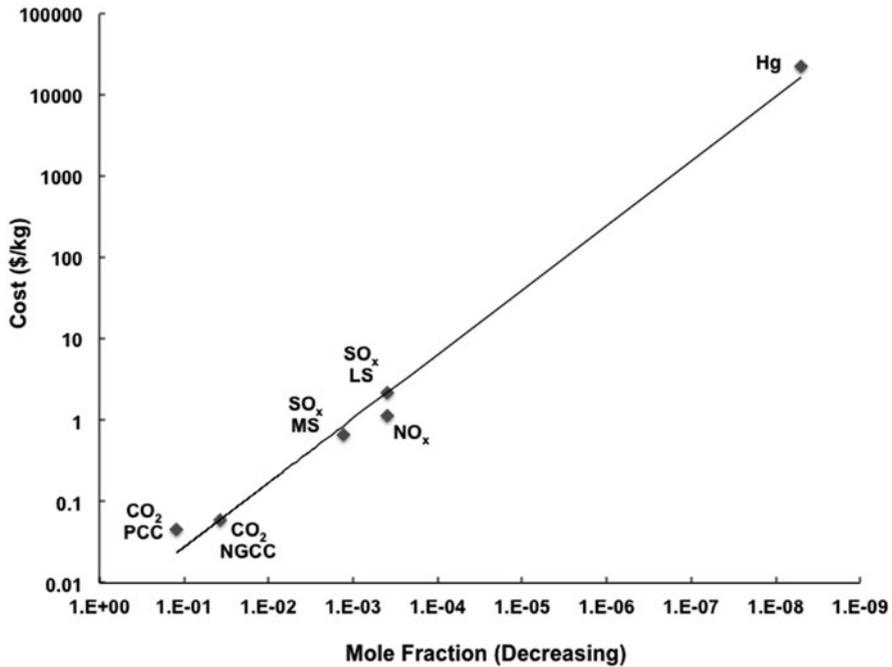
Fig. 1.13 Sherwood plot of various gas scrubbing processes demonstrating the cost increase with decreasing concentration

capacity, capture rate, and CO_2 concentration in and out will also influence costs. The system boundaries may influence the cost, for instance whether the capture technology is implemented on one facility or multiple plants or whether there will be energy resource integration to power the capture process, such as the implementation of natural gas, nuclear, wind, or solar. Whether a plant is a first-of-a-kind or *nth* plant may also influence the cost as technology is learned and advanced with time.

The Sherwood plot [49] has proved to be a useful correlation for estimating the separation cost as a function of starting concentration. Figure 1.13 provides a Sherwood plot demonstrating the relationship between cost increase with increasingly dilute gas mixtures. Based upon the previous assumptions from the data plotted in Fig. 1.12, the Sherwood correlation is illustrated in Fig. 1.13. The concentration of each of these species in the flue gas is also listed in Table 1.8. It is clear that an increase in dilution in the flue gas is correlated with an increase in the unit cost of capture. The cost-to-concentration relationship for medium-sulfur coal compared to the low-sulfur coal, *i.e.*, 1270 versus 399 ppm, is also consistent with this trend. Similarly, amine scrubbing for a 477-MW NGCC power plant generating approximately 3.7 mol% CO_2 follows the trend in that it is higher in cost compared to PCC in which the CO_2 concentration is approximately 12 mol% CO_2. Lightfoot and Cockrem [49] described this concept well in a publication titled, What Are Dilute Solutions? Their

Table 1.8 Cost and scale of various coal and natural gas oxidation processes

Process	Price ($/kg)	Concentration (mole fraction)	Emissions (kg/day)	Cost (1000s $/day)
CO_2–PCC	0.045	0.121	8.59×10^6	392
CO_2–NGCC	0.059	0.0373	3.01×10^6	178
SO_x (MS)	0.66	0.00127	8.94×10^4	59.6
SO_x (LS)	2.1	0.000399 (399 ppm)	2.32×10^4	50.4
NO_x	1.1	0.000387 (387 ppm)	1.11×10^4	12.5
Hg	22000	5×10^{-9} (5 ppb)	0.951	21.6

assessment was that the "recovery of potentially valuable solutes from dilute solution is dominated by the costs of processing large masses of unwanted materials." It is interesting to consider DAC in this context as CO_2 is present in the air at similar concentrations of NO_x in flue gas. However, the scale of the CO_2 emissions compared to NO_x as shown in Table 1.8, makes this approach to CO_2 mitigation less desirable than capture from more concentrated sources. Similar to the results of Table 1.8, recent investigations [48, 50] have concluded that cost estimates may be as high as $1000 per ton of CO_2 for DAC.

Defining the Cost of CO_2 Avoided and Captured   Imagine that a CO_2 capture system is installed at a fossil-fuel power plant, and that the energy required to operate the capture system is provided by fossil fuels. In principle, nothing prevents the capture system from emitting more CO_2 than it captures. Such a system would be counterproductive, however. One needs a vocabulary that distinguishes the gross CO_2 removed by a capture device and the net CO_2 that does not enter the atmosphere, which is the gross CO_2 removed minus the CO_2 emitted by the capture system itself. The concepts of gross and net CO_2 prevented from entering the atmosphere are called "captured CO_2" and "avoided CO_2." Avoided CO_2 is always less than captured CO_2 since any capture system will emit some CO_2. Equivalently, the cost of avoided CO_2 (in dollars per ton of CO_2) is always greater than the cost of CO_2 captured.

Figure 1.14 provides a schematic demonstrating the differences between CO_2 captured versus CO_2 avoided for a typical power plant application, assuming that the capture plant captures and stores 90% of the total generated CO_2 emissions and that some CO_2 emissions will be associated with the energy needed to operate the capture process itself. Thus, the cost of CO_2 avoided is the cost of delivering a unit of useful product (in this case, electricity) while avoiding a ton of CO_2 emissions to the atmosphere. Avoidance costs should always include the cost of CO_2 compression, transport and storage since "avoided" means not emitted into the atmosphere.

The cost of CO_2 avoided for a power plant, C_{avo}, is calculated on a net kWh basis by the equation,

$$C_{avo} \left(\$/\text{ton CO}_2 \right) = \frac{\left(\$/\text{kWh}\right)_{cap} - \left(\$/\text{kWh}\right)_{ref}}{\left(CO_2/\text{kWh}\right)_{ref} - \left(CO_2/\text{kWh}\right)_{cap}} \tag{1.13}$$

such that $\left(\$/\text{kWh}\right)_{ref}$ and $\left(\$/\text{kWh}\right)_{cap}$ represent the cost per net kWh of electricity produced by the reference and capture plant, respectively and $\left(CO_2/\text{kWh}\right)_{ref}$ and
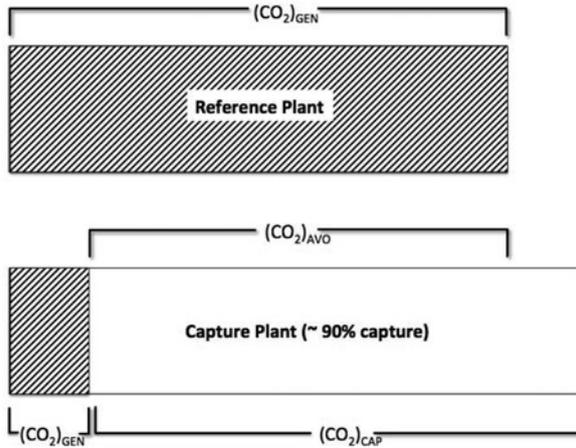
Fig. 1.14 Schematic demonstrating the difference in CO_2 captured versus CO_2 avoided for a point-source capture scenario. Here, the capture plant produces the same useful product output as the reference plant, so additional capacity is needed to operate the capture system. For a power plant all values are typically normalized on the net kWh generated

$\left(^{CO_2}/_{kWh}\right)_{cap}$ represent the tons of CO_2 emitted to the atmosphere per net kWh of electricity produced by the reference and capture plant, respectively.

In contrast, the cost per ton of CO_2 captured, C_{cap}, can be calculated by the equation,

$$C_{cap} \left(\$/tonCO_2\right) = \frac{\left(^{\$}/_{kWh}\right)_{cap} - \left(^{\$}/_{kWh}\right)_{ref}}{\left(^{CO_2}/_{kWh}\right)_{cap}} \qquad (1.14)$$

such that the numerator again represents the incremental cost of the capture system, while the denominator is the quantity of CO_2 captured, with all values again normalized on the net plant output. The key difference from Eq. (1.13) is that the capture cost does not include the cost of energy to operate the capture system; nor does it typically include the costs of CO_2 transport and storage. Thus, the cost per ton captured is always less than the cost per ton avoided.

For a co-generation power plant that produces both electricity and heat, costs and emissions can be normalized on the total equivalent thermal energy output (in kJ). For other types of point sources, such as an oil refinery stack or a cement plant, costs and emissions would be normalized on the relevant measure of useful output (*e.g.*, barrels of oil or tons of cement) when calculating the cost of CO_2 avoided or captured.

Cost for Direct Air Capture For CO_2 removed directly from the atmosphere (a concept being developed, but not yet practiced on a commercial scale) there is no reference plant or specific product associated with the capture system, as with point sources. Nonetheless, the concepts of gross and net CO_2 removal from the

Fig. 1.15 Schematic
demonstrating the difference
between CO_2 captured versus
CO_2 generated for a DAC
scenario
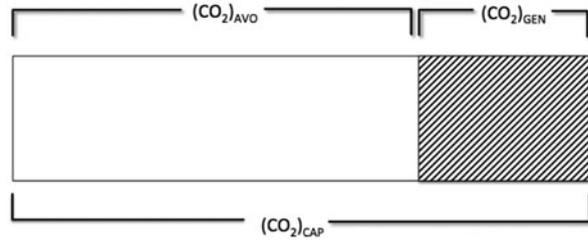
atmosphere are analogous to those associated with emission prevention. The two
analogous concepts are again called CO_2 captured (gross) and CO_2 avoided (net).
The amount and cost of CO_2 captured in the case of DAC is defined in the same way
as the previous method, namely the incremental cost of the capture system divided
by the amount of CO_2 captured. Thus,

$$C_{cap,DAC}\left(\$/\text{ton } CO_2\right) = \frac{\left(\$/\text{yr}\right)_{DAC}}{\left(CO_2/\text{yr}\right)_{DAC}} \qquad (1.15)$$

where the numerator is the levelized annual cost of the capture system and the
denominator is the annual average amount captured.

Figure 1.15 shows a schematic demonstrating the difference between avoided
versus captured. In the case of DAC there is only a capture plant since the CO_2
emissions are captured directly from air, compressed, transported, and stored (or
sequestered). Similar to the point source definition, however, allowance is made for
the generation of emissions associated with the purchased energy resource(s) used
to fuel the DAC plant and the energy required to capture a given number of tons of
CO_2 from the air. Effectively, the cost of CO_2 avoided is the cost of the capture plant
(plus transport and storage costs) divided by the *net* amount captured, rather than
the total amount.

The cost of CO_2 avoided, $C_{avo,DAC}$, in the case of DAC can be calculated by,

$$C_{avo,DAC}\left(\$/\text{ton } CO_2\right) = \frac{\left(\$/\text{yr}\right)_{DAC}}{\left(CO_2/\text{yr}\right)_{DAC} - \left(CO_2/\text{yr}\right)_{gen}} = \frac{\left(\$/\text{yr}\right)_{DAC}}{\left(CO_2/\text{yr}\right)_{net}} \qquad (1.16)$$

such that the numerator represents the total annualized cost of building and operating
the DAC plant and the denominator represents the net number of tons captured
per year from the DAC plant. Energy to operate the plant typically will be some
combination of electricity and heat sourced by fossil fuels or renewables.

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