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Carbon Dioxide Capture: An Effective Way to Combat Global Warming



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Chapter 1

Overview of Greenhouse Gases and Global Warming

Abstract Evidence proves that the climate is changing due to both natural cycles and anthropogenic influences. The increase in global carbon dioxide concentration, along with that of other greenhouse gases, is a major cause of global warming. Studies indicate that total emissions released from fossil fuels are related to the economy, are still on the rise, and can be stabilized through conscious efforts. Improving land management practices, incorporating carbon sequestration techniques, increasing energy efficiency, and using alternative energy sources are current ways that we can decrease our use of fossil fuels. Some alternative energy sources include waste biomass and cellulosic ethanol, along with others. Current research aims to identify ways to provide affordable fuel sources with little environmental impacts.

Keywords CO₂ · Greenhouse gases · Sequestration

1.1 Evidence for Climate Change

The topic of climate change has induced debate around the world for over a decade. Climate records from thermometers, sediment, corals, and tree rings are all indicators that global temperature is increasing (Zhang et al. 2001). Some scientists point to evidence that the global climate is always cycling through warm and cool periods throughout every hundred thousand years, as to trivialize the climate change claims; however, today, the temperature change has taken place over a span of a 100 years or less.

There are multiple lines of evidence that indicate climate change. As the air temperatures increase, arctic sea ice decreases, rainfall and ocean currents change, and the intensity and frequency of extreme weather events increases. Since recording in 1880, average global temperatures have climbed and the arctic is taking most of the hit. In 1850, Montana's Glacier National Park had glaciers that spanned 21.6 km²; whereas, in 1979, this area decreased to 7.4 km² (Hall and Fagre 2003).

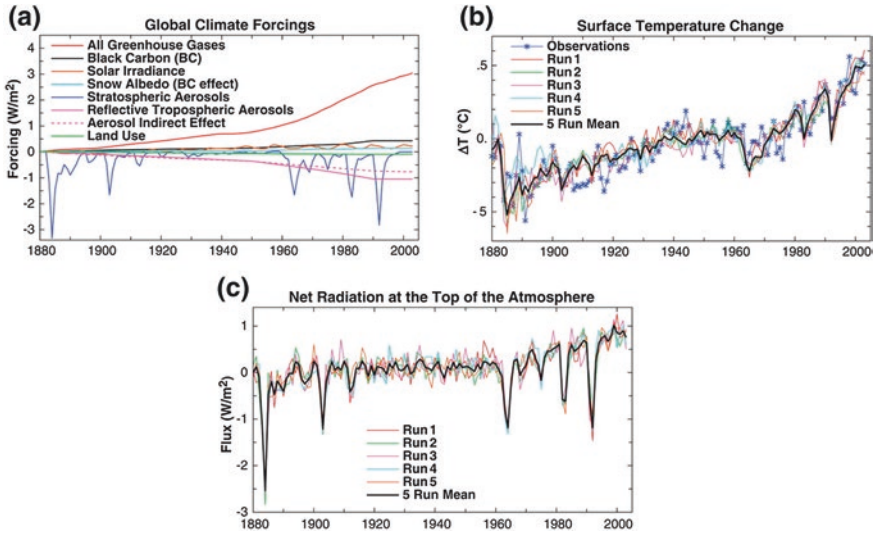
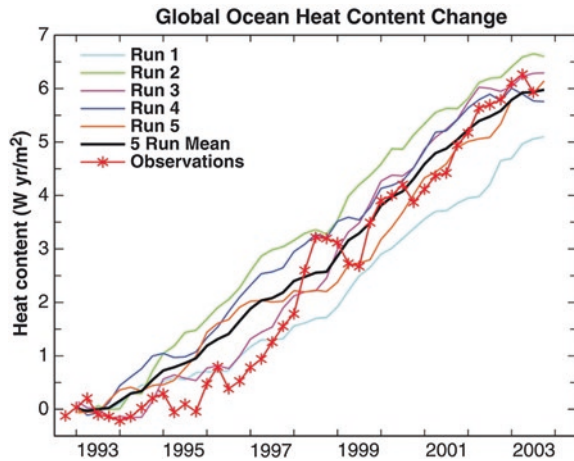


Fig. 1.1 a Forcings used to drive global climate simulations; b simulated and observed temperature change; c net radiation at the top of the atmosphere in the climate simulations (Hansen et al. 2005)

Fig. 1.2 Ocean heat content change between 1993 and 2003 in the top 750 m of world ocean. Five model runs are shown for the GISS coupled dynamical ocean-atmosphere model (Hansen et al. 2005)



Confirmation of the climate change phenomenon ranges beyond changes in annual temperature averages. It's been calculated that the earth is absorbing $0.85\ W/m^2$ from the sun than it is emitting back into space. As the increase in greenhouse gasses alter the energy flux, the surface temperature, ocean heat storage, and net radiation are impacted. Figures 1.1 and 1.2 show the trends of parameters that cause "forcings", or change in the earth's energy balance.

Global warming has been shown to induce an increase in extreme weather events, such as tsunamis (Cynthia Rosenweig 2001), lead to the intensification of forest insects and outbreaks (Logan et al. 2003), impact the global

hydrological cycle (Kay and Davies 2008), induce a rise in sea water level (Church and White 2006), contribute to longer and more damaging forest fires (Vose et al. 2012), shift the range of plants and animal populations (Maclean and Wilson 2011), and cause destruction of coral reefs (Cinner et al. 2013).

1.1.1 Extreme Extremes

Although it has been reported that there's a "pause" in the increases of mean global temperature, there is still an increase in the frequency of extreme temperatures. Seneviratne et al. (2014) studied recent (1979–2012) "extreme extremes" by considering the land area ratio that was affected by temperatures that exceed the 90th percentile of that area. Their analysis shows that high temperature anomalies are amplified.

1.1.2 El Nino

The frequency of extreme El Nino events has increased due to global climate warming (Cai et al. 2014). When the surface temperature along the equatorial Pacific increases more rapidly than the surrounding ocean water, atmospheric convection becomes more prevalent in the eastern equatorial region. Given projections of sea surface temperature and rainfall data under global climate change, Cai et al. (2014) predicted a two-fold increase in extreme El Nino events for the next 2000 years.

1.1.3 Biological Systems

There is sufficient evidence that climatic change is a driving force for shifts in natural systems on a global scale (Parmesan and Yohe 2003). Short-term biological trends within specific ecosystems are significantly due to non-climatic influences, such as land use changes; therefore, Parmesan and Yohe (2003) aimed to analyze the biological trends of over 17,000 species trends on a global scale. Their model considered (1) the ratio of biotic and abiotic changes that match climate change predictions, (2) the extent that competing justification explain those observations, and (3) the confidence that each observation can be attributed to chance. The investigation concluded that with "very high confidence" (as defined by IPCC), climate change has already impacted natural systems. One of the first biological indicators of global warming is the bleaching of coral reefs. Coral reefs have been particularly impacted because they are so sensitive to small changes in water temperature (Glynn 1991). Terrestrial systems have responded to climate change by changing species distributions and community structure. Global warming has also caused a shift in spring events, such as leaf unfolding, blooming date, migration and time of reproduction (Rosenzweig et al. 2008).

1.1.4 Water Cycle

As the global mean temperature rises, there is a direct increase in precipitation, water vapor (another greenhouse gas), mean wind stress, and a decrease in mean sea level pressure. Figure 1.3 shows that temperature increases have caused an increase in column water vapor and precipitation, decrease in mean sea-level-pressure gradient, and change in mean wind stress over the Pacific.

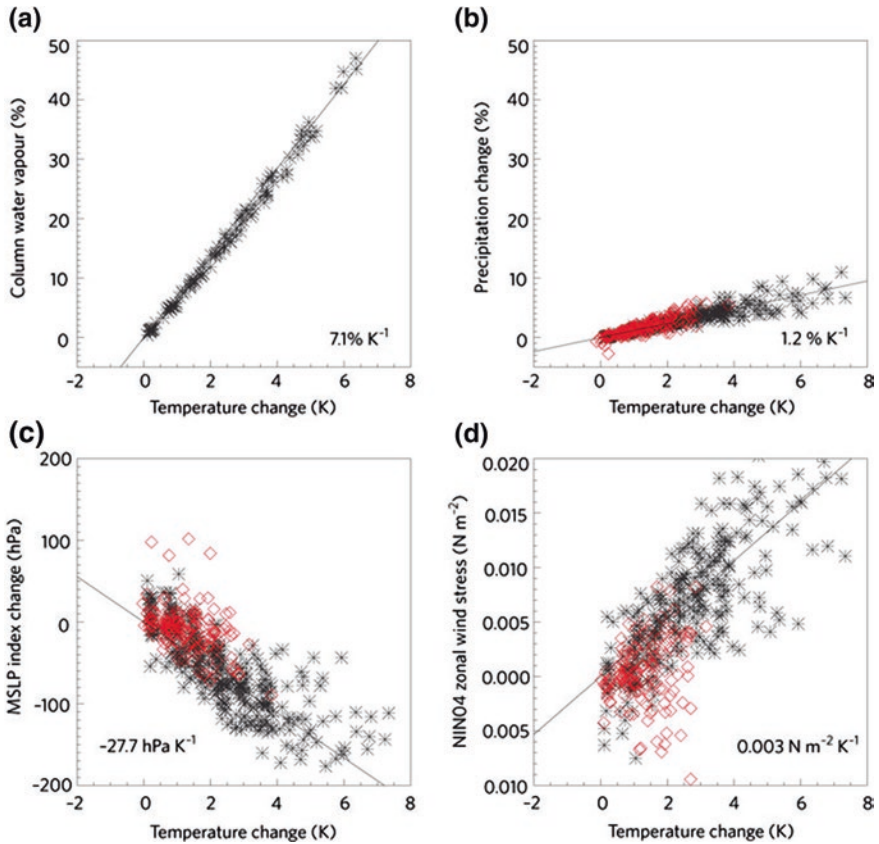


Fig. 1.3 Red diamonds are values derived from the CMIP3 multi-model database, *black asterisks* are values derived from perturbed physics ensembles with the HadCM3 model⁷³; **a** percentage change in global mean column integrated water vapor; **b** percentage global precipitation change; **c** change in the mean sea-level-pressure (MSLP) gradient in hPa across the tropical Pacific basin; **d** changes in the mean wind stress averaged in the NINO₄ region in the central Pacific. *Positive values* indicate a reduction in the strength of the easterly trade winds (Collins et al. 2010)

1.2 CO₂ as a Greenhouse Gas

It is known that greenhouse gases, such as carbon dioxide, methane and nitrous oxide, are a major cause for global warming. Although they occur naturally, human activities increase the concentrations of these gases. Humans are introducing these gases to the atmosphere in a pace much faster than earth's systems can absorb or use them. These gases act as a greenhouse to absorb energy in the form of light; in their energized state, the gases become unstable and energy, in the form of heat, is released and incorporated into the earth's natural cycling.

A recent report by the Intergovernmental Panel on Climate Change confirms that human activities are the main cause for climate change (Vineis 2014). Among all the greenhouse gases, carbon dioxide is the primary one produced by humans. Currently, the principal sources for CO₂ emissions are from energy production, such as the burning of natural gas or coal for heat and power generation. The correlation between GDP and CO₂ levels confirms human contribution to the increases in CO₂ emissions. For instance, when the US GDP increased by 51 % from 1990 to 2004, the total US emissions rose by 15.8 % (US DOC/BEA 2006, <http://www.state.gov/documents/organization/89646.pdf>). Similarly, when the US methane emissions decreased by 10 % from 1990 to 2004, carbon dioxide emissions increased by 20 %. Again, this is considerably due to increases in fossil fuel production (Vineis 2014).

Boer et al. (1992) proposed that if carbon dioxide emissions are doubled, the environmental response would be an annual global warming of 3.5 % the current temperature in Celsius. This will be amplified over land and at higher latitudes, such as in the poles. Further, it's predicted that precipitation and evaporation rates will increase by 4 % with cloud cover decreasing by 2.2 %. This would result in significant decreases of permanent snow over Greenland and increases in precipitation over tropical climates.

1.2.1 Increase in Emissions

It's been found that CO₂ emissions are highly susceptible to instantaneous deviations over time. CO₂ Emissions have an even larger percent variation than world GDP (Peters et al. 2012). Figure 1.4 shows the trend of CO₂ emissions from fossil fuels over time in Pg C (Gt C) per year (black) and the carbon intensity of the economy in g C per US dollar (red). There is a trend line for each of the non-linear divergences in the data. The trend line begins 5 years prior to the crisis to show how each crisis impacts the trend.

During each financial crisis, there is a sharp decrease in CO₂ emissions (Fig. 1.4); however, it rapidly bounces back. For example, in 2010, the impact to CO₂ emissions during the financial crisis was short lived because of the increase in emissions by developing countries, as evidenced in Fig. 1.5. The emissions of the US and other developed countries decreased 8.9 % in 2008–2009 and increased

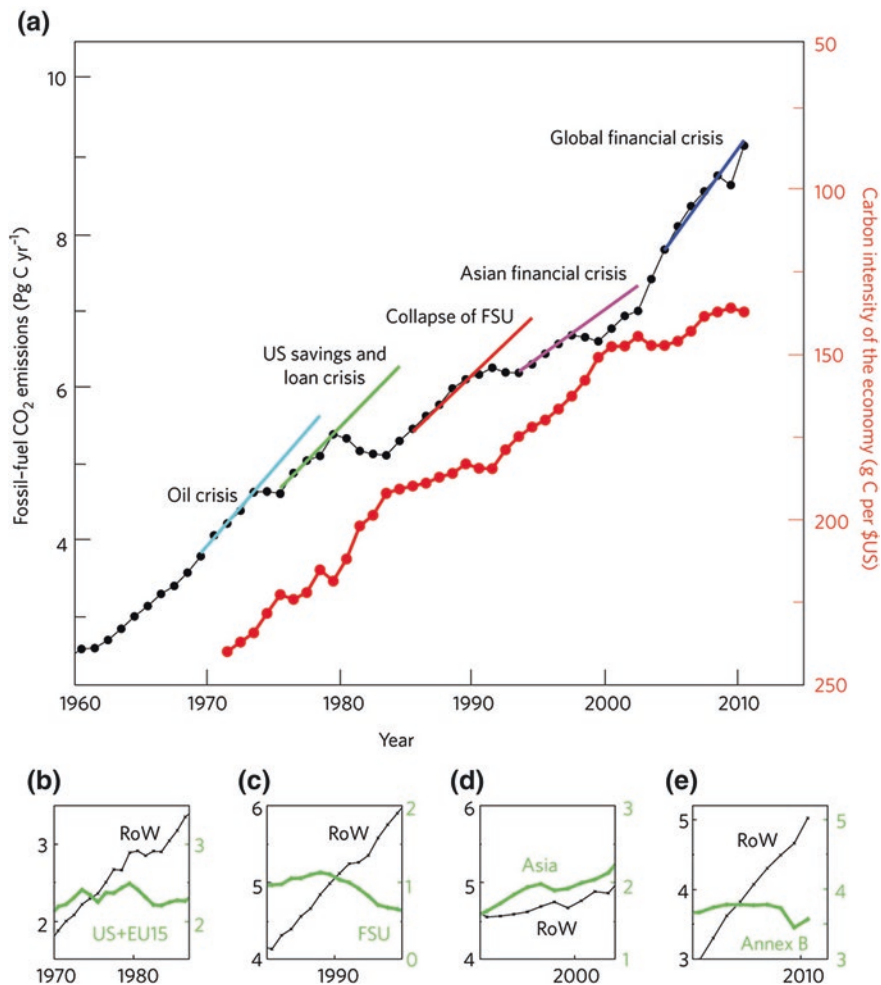


Fig. 1.4 **a** Emissions of CO₂ from fossil-fuel combustion and cement production for the world (Pg C year⁻¹; black curve) and the carbon intensity of world GDP (g C per \$US (2000); red curve, inverted axis). The most important recent financial crises are highlighted with a linear trend fitted to the 5 years before the beginning of each crisis. **b–e** CO₂ emissions (Pg C) for the regions most affected by each financial crisis (right axis) and the rest of the world (RoW; left axis); **b** the oil crisis (1973) and the US savings and loans crisis (1979), where EU15 is the 15 member states of the European Union as of 1995; **c** the collapse of the Former Soviet Union (FSU) 1989); **d** the Asian financial crisis (1997); **e** the recent global financial crisis (2008–2009) (Peters et al. 2012)

slightly (3.4 %) in 2010. On the other hand, in developing countries, the CO₂ emissions continue to rise each year by 4.4 % (2008), 3.9 % (2009), and 7.6 % (2010). This is due to high rates in a few large countries such as China and India. Figure 1.5 shows the trend of CO₂ emissions over time for both “developed”

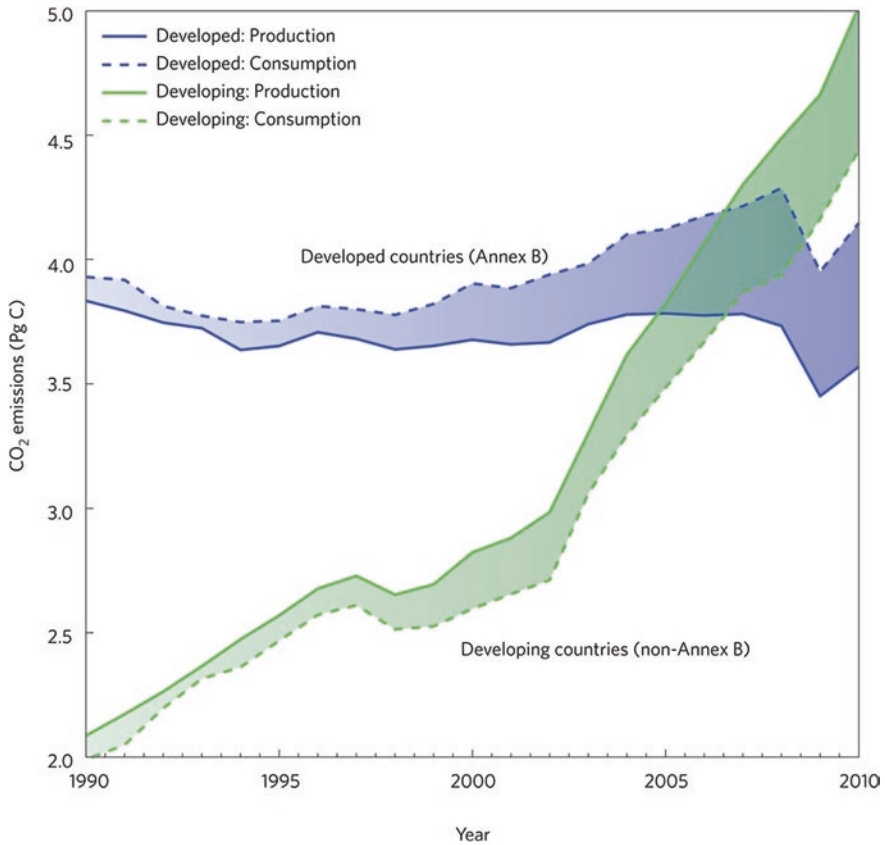


Fig. 1.5 The *shaded areas* are the trade balance (difference) between Annex B/non-Annex B production and consumption. Bunker fuels are not included in this figure (Peters et al. 2012)

and “developing” countries, as defined by the Kyoto Protocol. There is a sharp increase in the CO₂ emissions between 2003 and 2010 in developing countries.

It is estimated that in 2010, half of the total emissions stayed in the atmosphere, which led to one of the largest atmospheric CO₂ growth rates of the last decade. By the end of 2010, the overall concentration of CO₂ in the atmosphere was about 389 ppm. It is estimated that a quarter of the total emissions is deposited in the ocean and the rest is incorporated into natural cycles on land.

In order to lower GHG emissions enough to stabilize global temperature, it is necessary to nearly eliminate anthropogenic CO₂. Nevertheless, atmospheric CO₂ are reversible; if emissions can be reduced enough, the CO₂ level in the atmosphere will decrease because oceans continually take up anthropogenic CO₂. It is agreed that reducing CO₂ emissions is a necessary step for a sustainable world; therefore, a great deal of research attention has been given to designing materials to capture CO₂.

1.3 Actions to Reduce CO₂ Emission

Because CO₂ emissions are on the rise and causing climatic turbulence, it is necessary to take action to reduce the emissions to reduce its effects on the climate and natural systems as a whole. How humans can most effectively reduce this change is highly debated, so it is essential to promote the research on the impacts of CO₂ reduction, particularly the development of predictive tools. To determine how funds should be allocated to fight global warming, scientists model how the support of different CO₂ reduction approaches will impact the overall mitigation of CO₂. Hasselmann et al. (1997) concluded that research concerning technological restructuring for CO₂ capture is of utmost importance, rather than putting funds towards immediately reducing emissions. To limit global warming, CO₂ emissions must drop by half over a few centuries, with a continual decrease thereafter. Therefore, as long as research is advancing, technological restructuring can be implemented over the next century because global warming is based on overall carbon dioxide amounts.

Manne (1997) takes a broad perspective on stabilizing atmospheric concentrations, by exploring the impact that short-term decisions and long-term participation from developing countries will make to limit CO₂ to certain levels. It is suggested by the analysis that a more gradual transition away from fossil fuels is less costly. They believe that policy makers allot GHG insurance dollars towards a blend of options, such as: (1) Research to develop low cost GHG limiting technologies, (2) Reduce uncertainty in the amount of climate change, (3) Immediately reduce emissions, (4) Invest in ways to adapt, should climate change occur.

One way to encourage emission reduction is through increasing fuel prices. Although this will reduce energy usage, technology innovation has been shown to slow down; therefore, it's hard to identify the effect this has on overall CO₂ release. Unless the progression of technology can be estimated and implemented into the model, projections of cost-benefit analysis that consider fuel prices and reduction in energy usage are not realistic (Hogan and Jorgenson 2007).

1.4 Mitigation Techniques

It is widely accepted that it is important to invest in research on techniques to lower the emissions of CO₂ in power production, sequester carbon in agriculture, reduce energy usage, and capture CO₂ from stationary locations.

1.4.1 Land Management Practices

Since 2000, the US government has offered incentives to encourage land management practices that sequester carbon. Examples of these practices include regeneration of previously cleared land and reduced or no-tillage systems on farm land. The USDA projects that carbon sequestration by novel farming practices will increase by 2020 (State 2006).

1.4.2 Biochar Sequestration

Similar to activated carbon, a charcoal-like material called biochar is produced by subjecting biomass to low temperature (300–600 °C) pyrolysis, or heating under an oxygen deficient environment. Naturally, waste organics will convert to a greenhouse gas overtime; however, if this biomass is pyrolyzed, it won't convert to CO₂ for thousands of years. Figure 1.6 shows the inputs, outputs, and applications of biomass subjected to pyrolysis.

Not only does biochar production fix the carbon into a more stable carbon form, it's also responsible for 80–90 % if total uptake of trace HOC in soils. When applied to land, biochar can reduce the emission of other greenhouse gases by binding anthropogenic hydrogen organic compounds (Jeffery et al. 2011). Biochar is also used as a slow release fertilizer and can remove excess nutrients in runoff. It has been shown that as long as the necessary nutrients of nitrogen, phosphorus, and potassium are plentiful, the application of biochar to soil can actually double crop yield (Jeffery et al. 2011). Other benefits of biochar land application are shown in Chap. 3.

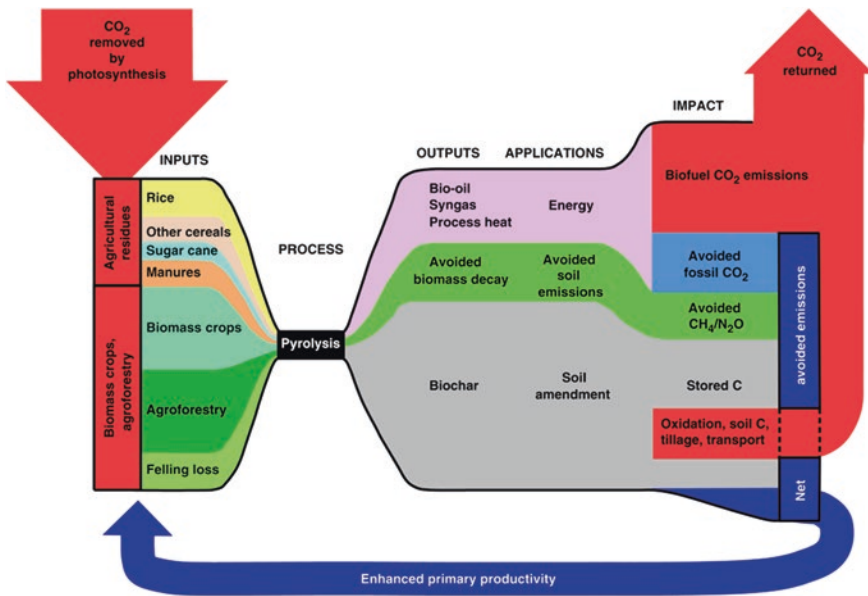


Fig. 1.6 The figure shows inputs, process, outputs, applications and impacts on global climate. Within each of these categories, the relative proportions of the components are approximated by the height/width of the colored fields. CO₂ is removed from the atmosphere by photosynthesis to yield biomass. A sustainable fraction of the total biomass produced each year, such as agricultural residues, biomass crops and agroforestry products, is converted by pyrolysis to yield bio-oil, syngas and process heat, together with a solid product, biochar, which is a recalcitrant form of carbon and suitable as a soil amendment. The bio-oil and syngas are subsequently combusted to yield energy and CO₂. This energy and the process heat are used to offset fossil carbon emissions, whereas the biochar stores carbon for a significantly longer period than would have occurred if the original biomass had been left to decay (Woolf et al. 2010)

1.4.3 Energy Efficiency

Already, research around the world has made improvements to the efficiency of industrial processes. There are countless sources that can be found on how to reduce ones “carbon footprint”, or reduce energy usage. Insulation, programmable thermostats, LED lighting, and water-saving toilets are a few technologies that have been developed to reduce residential energy waste. LEED, Leadership in Energy and Environmental Design, is a certification program with the purpose of designing energy efficient building, homes, and neighborhoods.

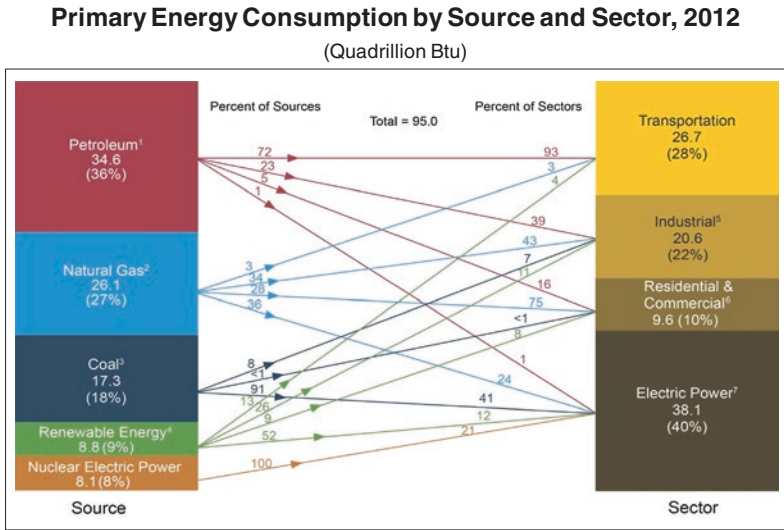


Further, “Energy Star” performance standards are used as a rating system for appliances in “green” or sustainable buildings, giving businesses a positive public view.

1.4.4 Alternative Energy Sources

By far, petroleum is the most used energy source; however, efforts are being made to reduce our dependence on petroleum and coal. Natural gas, which is cleaner burning than fossil fuels, is accessed from underground reservoirs, but is becoming limited. Therefore, it is important that we derive natural gas from renewable sources, such as biomass and find other forms for fuel generation, such as cellulosic ethanol.

Different forms of energy production, such as biomass combustion and anaerobic digestion are some ways to reduce the environmental impact of power generation.



¹ Does not include biofuels that have been blended with petroleum—biofuels are included in "Renewable Energy."
² Excludes supplemental gaseous fuels.
³ Includes less than 0.1 quadrillion Btu of coal coke net imports.
⁴ Conventional hydroelectric power, geothermal, solar photovoltaic, wind, and biomass.
⁵ Includes industrial combined-heat-and-power (CHP) and industrial electricity-only plants.
⁶ Includes commercial combined-heat-and-power (CHP) and commercial electricity-only plants.

⁷ Electricity-only and combined-heat-and-power (CHP) plants whose primary business is to sell electricity, or electricity and heat, to the public. Includes 0.2 quadrillion Btu of electricity net imports not shown under "Source."
 Notes: Primary energy in the form that it is first accounted for in a statistical energy balance, before any transformation to secondary or tertiary forms of energy (for example, coal is used to generate electricity). * Sum of components may not equal total due to independent rounding.
 Sources: U.S. Energy Information Administration, *Monthly Energy Review* (January 2014), Tables 1.3, 2.1-2.6.

Fig. 1.7 The figure from the EIA shows the breakdown of energy sources (2011)

By using petroleum and underground methane, like that extracted from shale reservoirs, we release new carbon into the atmosphere; therefore, creating a net increase in CO₂ level. Using renewable bioenergy, rather than fossil fuels that are sequestered underground, is one way to lower anthropogenic CO₂ in the atmosphere. Currently, those used gas wells can be filled with greenhouse gases that have been recaptured after energy production; this CO₂ capture technology will be discussed in the following chapters (Fig. 1.7).

In 2012, petroleum and coal are the source of 54 % of the energy consumed in the US. Natural gas contributed to 27 % of energy and renewable and nuclear energy make up 17 %. Right now, renewable energy only makes up a small fraction of the transportation, industrial, and residential sectors; however, with increased technology (i.e., hydrogen powered cars) it could play a larger role. With the creation of new technology and discovery of energy reservoirs, natural gas has potential to contribute to more energy in the industrial sector.

1.4.4.1 Natural Gas

We can reduce our carbon dioxide output by using natural gas rather than fossil fuels. Natural gas drilling has been shown to be a promising way of accessing

methane because it can be cleaner burning (i.e., less CO₂ emissions), and found abundantly in deep shale structures. Nevertheless, there is concern about its impact on other aspects of the environment, such as if methane leaks into water systems.

1.4.4.2 Biomass Combustion

Another way of obtaining methane for use in the heating applications is from biomass combustion. Biomass combustion is a proven technique for producing power, while still utilizing a renewable resource. One concern of this technology is in the emission of gaseous and particulate pollutants (i.e., NO_x). Staged combustion technologies have been developed that can reduce NO_x up to 50 % (in wood) and 80 % for biofuels with high nitrogen content. Selective catalytic reduction and selective non-catalytic reduction are secondary methods used to rid the flue gas of NO₂. These techniques use urea or ammonia to reduce NO_x to N₂, with up to 90 % efficiency (Nussbaumer 2003).

When biomass is the input for energy conversion processes, the result is a CO₂ neutral cycle. In general, the production is less costly than with fossil fuel input; however, the transition cost from raw fuel to purified gasoline and diesel could be higher. The study found that, in Sweden, if 125 TWh/year of biomass, which apparently can be produced from logging, straw, and energy crops is utilized for energy, more than one-half of CO₂ emissions in Sweden can be eliminated (Gustavsson et al. 1995).

1.4.4.3 Fuel Cells

Clean energy systems such as fuel cells have energy efficiency up to twice that of internal combustion engines and look promising; however, both durability and cost are still problem areas. The most expensive parts of the fuel cell include the membrane, bipolar plates, and the electrocatalyst. Efforts are currently being made to encourage enhancement of hydrogen storage technologies, such as metal hydrides and carbon-based storage materials. Storage must release H₂ at a relatively low temperature so that the operation efficiency is not harmed. In order to address the need for new storage technology, a hydrogen storage project by the DOE has developed centers of Excellence for Metal Hydrides, Chemical Hydrides, and Carbon-based Materials to identify and develop new hydrogen storage materials that meet the targets (Chalk and Miller 2006).

Specifically, hydrogen and oxygen powered cars are attracting significant research attention. The reaction of hydrogen and oxygen produces water through the PEM fuel cell that utilizes a proton exchange membrane. With hydrogen-fueled cars, the major barrier is in the storage of hydrogen. One solution is to bind hydrogen to materials with high surface area through physisorption (Ross 2006).

1.4.4.4 Biomass to Liquid Automotive Fuel

Since 2002, Volkswagen and Daimler working with CHOREN Industries, a producer of gasification technology for carbonaceous materials, in Freiberg, Germany, to build a BTL, or biomass to liquid synthetic biofuels plant, with a capacity of 200,000 tonne/year, 10–15 of the BTL plants could save up to 3 million tonnes of CO₂ by 2020 and could reduce GHG by 90 % without competing with food production (Cozier 2007).

1.4.4.5 Cellulosic Ethanol

Cellulosic ethanol is produced from lignocellulose, the structure that makes up the majority of plants; therefore, the feedstock is easy to cultivate in large quantities. The hardest part of using cellulosic ethanol is to extract the cellulose and convert the cellulose to glucose. This process is typically performed by enzymes, which can be really expensive (Fig. 1.8).

Cellulosic biomass undergoes an enzymatic pretreatment step, which breaks down the biomass to release sugar, next cellulose is broken down to glucose and fermented to ethanol, which is recovered and used for electricity.

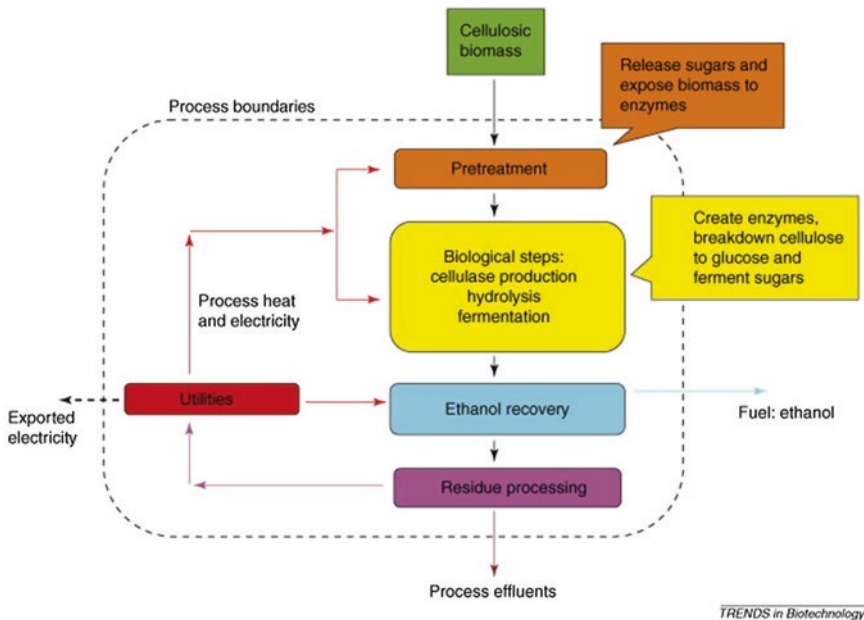


Fig. 1.8 A simplified process of cellulosic ethanol production (Wyman 2007)

1.5 Conclusion

Increases in carbon dioxide emissions have already impacted global temperatures, correlating to a shift in biological and climate systems. Actions have been taken in agriculture, industry, transportation, and in the private sector to mitigate CO₂ emissions. The majority of anthropogenic CO₂ comes from power and industry sector. Large stationary power plants are practical locations to implement CO₂ capture technology and current research aims to make this process cost effective.

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Chapter 2

Overview of CO₂ Capture Technology

Abstract Until cost-effective alternative energy sources are available, it is necessary to capture harmful waste gases at the source (i.e., smoke stacks). CO₂ gas can be captured prior to combustion, through an oxyfuel combustion stage, or after combustion. Currently, the most common way to separate carbon dioxide gas is through an amine-scrubbing system in post-combustion scenarios; however, this method can be costly and byproducts are harmful to the environment. For this reason, absorbents, adsorbents, membranes, gas hydrates, and chemical looping processes are considered as methods for CO₂ gas capture. Industries such as iron and steel and cement industries can also incorporate CO₂ separation and capture technologies. Once CO₂ is captured, it can be transported through pipelines and stored in geological formations and ocean reservoirs.

Keywords Adsorbent • Absorbent • Post-combustion

2.1 Rationale for CO₂ Capture Technology

It would be ideal to change the fuel source from carbon based ones to cleaner energy alternatives, such as wind and solar; however, until these can be developed at competitive prices, it is important that we have ways to capture CO₂ from existing and new power plants that use conventional and renewable fuels.

Stationary point sources, like power plants, are practical locations to implement CO₂ capture technology, because electricity generation contributes to 41 % of total CO₂ emissions (Sumida et al. 2012). Technologies that can effectively capture CO₂ from stationary point sources thus have developed recently.

2.2 Research on Carbon Capture and Storage (CCS)

In general, CCS refers to the research and development aimed at finding viable ways to capture and transport a concentrated stream of CO₂ and then store it in underground reservoirs or oceans. CCS provides a tentative solution for continued use of fossil fuels, until the technology to transition to more sustainable energy sources is developed (Herzog 2001).

According to Herzog (2001), CCS has 4 components:

- (1) Capture
- (2) Compression
- (3) Transport
- (4) Injection

There is significant storage capacity in both land and water reservoirs. Although the ocean and deep saline formations have the greatest potential capacity (1000's GtC), depleted oil and gas reservoirs and coal seams have a worldwide capacity on the magnitude of 100s GtC. Terrestrial reservoirs have less capacity (10s GtC) (Herzog 2001).

2.3 Carbon Capture Processes in Power Plants

There are 3 gas production scenarios where CO₂ can be separated in power plants. At this time, capturing 90 % of CO₂ from power plants would add \$0.02/kWh; 75–80 % of this cost results from capture and compression processes (Herzog 2001). Figure 2.1 depicts the gas capture pathway for the three areas of energy production.

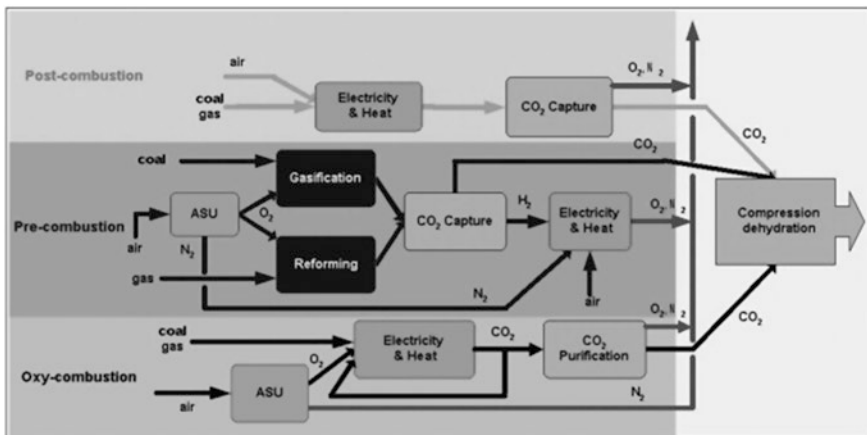


Fig. 2.1 The three CO₂ capture processes (Kanniche et al. 2010)

2.3.1 Pre-combustion

In the precombustion CO₂ capture process, coal/fossil fuel undergoes gasification and after syngas is produced, a water-gas shift (WGS) reactor prepares the syngas for extraction of fuel gas and CO₂. Therefore, CO₂ must be separated from H₂ after the gasification process. This occurs at a high pressure (1000 times higher than flue gas in post-combustion) and the remaining H₂ goes on to participate in the combustion process (Sumida et al. 2012).

2.3.2 Oxy-fuel Combustion

This is a nitrogen-free combustion technique that produces highly concentrated CO₂ flue gas streams. Oxygen Transport Membranes (OTMs) have already been developed to separate the oxygen from CO₂; another technique involving partial flue gas recycling (FGR) can be implemented to existing boilers. Nevertheless, current oxygen production techniques are costly, so in order to apply this oxy-fuel to industry, a wide range of advancements must be made.

There are a few variations of oxy-fuel combustion are currently in the conceptual phase of research.

In the Matiant Cycle, CO₂ from fuel combustion in oxygen is used to replace N₂ in air. The excess is extracted through valves. The main advantage is that a N₂ and CO₂ separation is not needed; the disadvantage is that a CO₂ turbine is required.

The Graz cycle uses water and CO₂, under a high temperature gas turbine and low temperature steam cycle, to separate CO₂.

Chemical Looping Fuel is oxidized by a metal oxide, rather than air, to improve the efficiency of the production of CO₂ and water. This can be condensed to a nearly pure CO₂ stream (Gupta 2003).

2.3.3 Post-combustion

In post combustion capture, fossil fuel is converted to energy prior to the CO₂ capture process. The major challenge is in separating the low concentration of CO₂ (16–16 %) out of the high concentration of N₂ gas (73–77 %). In this scenario, one characteristic challenge is the lower pressure of CO₂ flow. There needs to be a balance between selectivity to CO₂ verses other gases and the ability to desorb the CO₂. Chemical absorption tends to produce strong bonds, resulting in a high regeneration cost.

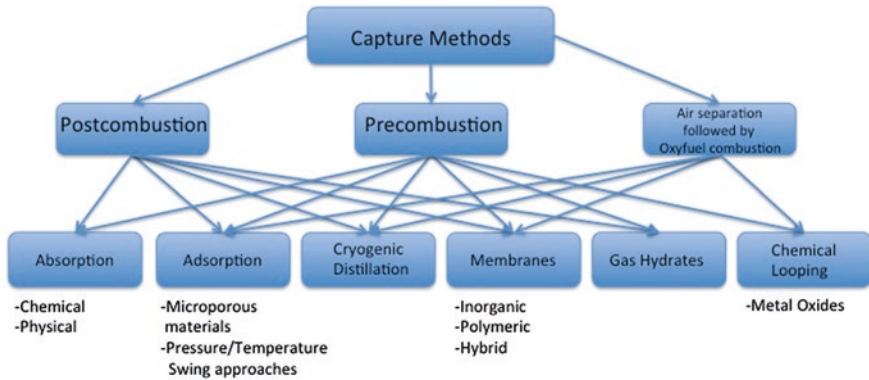


Fig. 2.2 Carbon dioxide capture methods possible for each combustion location, based on (D’alessandro et al. 2010)

2.4 CO₂ Capture Technology at Different Stages

Figure 2.2 lays out several general options for carbon dioxide capture. Post-combustion capture technology is the most developed and the processes of adsorption (surface binding of gases), absorption, distillation, membrane separation, and gas hydrates have been determined to be potential mechanisms for CO₂ capture in this area of energy production. This book will focus on the selection of CO₂ sorption materials, rather than other processes that are less researched.

2.5 Selection of Capture Technology

It is more costly to retrofit a CO₂ capture system into existing plants than for new coal fire plants because of less efficient heat integration and site-specific difficulties requiring adaptation of the capture system. The selection of CO₂ capture technology is based on the fuel composition, the heat, the influence of water, the resulting partial pressure of the gas mixture, and the configuration of the power plant (Rao and Rubin 2002).

2.5.1 Absorbents

One historically attractive method for separating gaseous compounds is to have the target gas selectively absorb into a liquid. Several commercial gas separation technologies depend on the interactions between gases and pure liquids, to remove CO₂ from natural gas. The goal of chemical scrubbing is to differentially dissolve

the target gas into the liquid phase. Another method of separation is comprised of a reaction between the target gas and a liquid solute (Bates et al. 2002).

Currently, there is a large energy penalty for CO₂ capture. For example, the most commonly used and most highly developed technique uses an aqueous alkanolamine absorbent, which contributes to an energy penalty of nearly 30 % the output of the power plant. Not only does this require large capital investment, but the driving cost of CO₂ capture for amine-based systems is related to the solvent regeneration processes, as CO₂ can only be released under high temperature. Further, current materials that are used on these large gas flow applications form waste products that require careful handling and storage and the materials become unstable after heating, which limits regeneration.

2.5.2 Adsorbents

Solid adsorbents are considered promising as they can be designed to have a large capacity and selectivity for gas adsorption. The porosity and structure of the framework can be further modified to optimize the selection of CO₂ over other gases that are present within the industrial gas stream (Sumida et al. 2012). A more detailed summary on the research progress of absorbents and adsorbents will be presented in the next chapters.

2.5.3 Cryogenic Distillation

Distillation columns are used to separate CO₂ from the other gases such as N₂ and CH₄ by condensation and vaporization cycles. These gases are separated based on their different vapor pressures (yielding different boiling points) and volatilities. Flue gas is compressed into a fluid, pretreated to remove water, sent through a series of heat exchangers, and finally is distilled to separate liquefied CO₂ from gaseous N₂, CH₄, or H₂ (Wilcox 2012).

2.5.4 Membranes

Membranes are used as an alternative to liquid amine absorption, but are less developed. They are selective to certain gases, such as CO₂, due to their specific porosity, shape, and electrostatic interactions.

2.5.5 Gas Hydrates

Gases, such as CH₄, CO₂, and water form gas hydrates, or ice-like inclusion crystals at specific temperatures and partial pressures under the presence of

tetrahydrofuran (THF). These crystals are separated and subsequently decomposed to create a CO₂ rich stream. At this time the system is costly and inefficient; the rate of hydrate formation needs to be improved (Linga et al. 2007)

2.5.6 Chemical Looping

The general principle of the chemical looping process is to cycle a metal/metal oxide through reduction and oxidation reactors, which then oxidizes the fuel to produce CO₂ and H₂O from CH₄; therefore, having inherent CO₂ capture potential. This is practical for use in oxyfuel combustion (Brandvoll and Bolland 2004).

2.6 Carbon Capture Process in Power Plant Applications

2.6.1 Iron and Steel Production

Iron and steel industries already employ CO₂ capture technologies to enhance the quality of flue gas. In the iron industry, when the gas is reduced, both Directly Reduced Iron (DRI) and CO₂ are produced and should be separated. The steel industry frequently will use a blast furnace during the production. The gas emissions include a mixture of N₂, H₂, CO₂, and CO. 20 % of the mixture is CO₂ and CO. The carbon dioxide capture is performed using membrane separation (where H₂ is removed), followed by an expansion turbine. The resulting CO₂ is compressed and stored. Figure 2.3 depicts this capture process (Gielen 2003).

2.6.2 Cement Production

The concentration of CO₂ in flue gas from cement production (14–33 %) is higher than that from power generation sources; therefore cement kilns are good places to apply CO₂ capture processes. The CO₂ could be captured by amine scrubbing, but the regeneration heat is inaccessible; oxyfuel combustion could be used, if the high CO₂ concentration doesn't negatively affect the process (Bosoqa 2009).

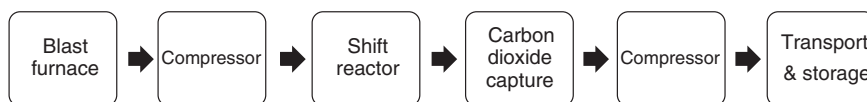


Fig. 2.3 CO₂ capture and storage system process for a conventional blast furnace. Adapted from Gielen (2003)

2.6.3 Purification of Natural Gas Streams

In natural gas purification there is a need to remove CO₂, H₂S, and from CH₄ (Gupta 2003). This would improve pipeline capacity and reduce compression horsepower. When feed and output gases are at high pressure, membrane technologies are most practical; whereas, at low pressure, adsorbing materials can be applied (Echt 2012).

2.7 Transport and Storage of CO₂

2.7.1 Transport

There are several ways that have been researched to transport CO₂ after the gas is captured from gas streams. It can be transported via pipelines under or over-ground, by tankers, or in ships across the ocean. This sort of transportation technology is mostly developed because of the current and historical need to transport natural gas. Finally, the captured CO₂ can be stored in underground reservoirs (Anderson and Newell 2004).

2.7.2 Storage

In its gas form, CO₂ can be sequestered in geological formations and ocean reservoirs, such as deep saline reservoirs, depleted oil and gas wells, and unmineable coal seams. Oceans and geologic formations are the most suitable sites. Residence time for CO₂ in geologic reservoirs is at least thousands of years, but ocean storage is less secure. Oceans closely cycle with the atmosphere, so 15–20 % of stored CO₂ will escape over hundreds of years. Because of this cycling, environmental impacts due to ocean storage are important to define. PH drops due to the reduction of CO₂ with seawater, but the impact can be avoided if the injection technique disperses the CO₂. On the other hand, when planning to use geologic storage, safety is a key consideration (Herzog 2001).

One practical benefit of injecting CO₂ into depleted oil and gas wells is that the pressure of the injection can actually facilitate more extraction of natural gas. Depleted coalmines and salt reservoirs have been employed as well. Nevertheless, with global emissions of 30 Gt per year, underground storage would fill; therefore, efficient conversion of CO₂ to transportation fuel is currently studied as a promising advancement (Sumida et al. 2012).

2.8 Conclusion

In order to counteract the growth of CO₂ emissions, carbon can be either converted into a more sustainable form (i.e., biochar) or captured as a gas and buried in underground (i.e., depleted gas mines) or ocean reservoirs. The implementation

of carbon capture technologies is, at this time, most practical in post-combustion scenarios, where CO₂ is separated from N₂ gas at low pressure.

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Chapter 3

Adsorbents for CO₂ Capture

Abstract Solid adsorbents are promising for applications in post-combustion CO₂ capture scenarios. Some adsorbents include zeolites, activated carbon, carbon nanotubes, zeolites, and silicon-based adsorbents. The materials are characterized by their surface functional groups, porosity, surface area, pore size, metal ligands, and electrostatic interactions to determine their potential as adsorbents for CO₂. Organic adsorbents are promising for low temperature CO₂ adsorption because of their surface properties, such as high surface area, which enables it to be modified by adding additional metals and functional groups. Carbonaceous materials can be physically or chemically activated in order to enhance capture. Biochar, a material known for its benefits to agriculture, can also be used to capture CO₂. Modified Organic Frameworks (MOFs) combine metal ions and organic ligands to produce a crystalline porous network that is capable of selectively binding molecules at high capacity. Other solid adsorbents include zeolites, clays, silica-based adsorbents, and metal oxide-based adsorbents.

Keywords Activated carbon · Biochar · MOF · Zeolite

3.1 Adsorbents Overview

It was proposed by the Intergovernmental Panel of Climate Change (IPCC) that, with the recent advances in the production of new porous materials, the application of a full-scale CO₂ adsorption facility would be feasible. Comparative studies such as Lu et al. (2008) discuss the use of promising adsorbents such as zeolites, activated carbon, carbon nanotubes, zeolites, and silicon-based adsorbents. When either physically or chemically activated, silicon and zeolites fix carbon through a mineral carbonation reaction, while organic frameworks bind to CO₂ through weak physical bonding and basic functional groups.

Gas adsorption onto adsorbents can act through both chemisorption and physisorption. Physisorption is mainly controlled by the van der Waals forces between

the surface of the adsorbent and the adsorbate molecules, such as CO₂; therefore, the surface area and pore size of the adsorbents play huge roles. In the chemisorption of gases, surface functional groups play an important role and interact with adsorbate molecules mainly through weak chemical bonds. Physical adsorbents, due to their weak interaction energy, can be regenerated at relatively low temperatures and therefore low energy and cost.

Common adsorbent frameworks for CO₂ capture include activated carbon and zeolites (Zaman and Lee 2013). When carbon is modified with additional metal ions, metal oxides, and amine-metal composites, it is considered a Metal Organic Framework (MOF) (Li et al. 2011).

3.2 Determining the Feasibility for CO₂ Capture

How do we determine which adsorbent is the best for post-combustion CO₂ capture? In terms of general physical properties, the materials are characterized by their surface functional groups, porosity, surface area, pore size, metal ligands, and electrostatic interactions (Li et al. 2011). The heat of formation can also be an indicator of the bond type and strength (D'alessandro et al. 2010).

3.2.1 Screening Adsorbents

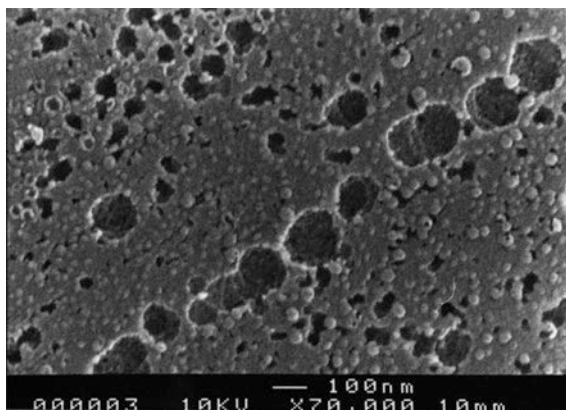
Molecular modeling can aid in selection of adsorbents for gas separation by screening a large number of materials and providing insight into mechanism of CO₂ adsorption (Sumida et al. 2012). At low pressures, uptake correlates with the heat of absorption; at intermediate pressures, uptake correlates with the surface area; and at the highest pressures, uptake correlates with free volume available within the adsorbents. In one study, Yazaydin et al. (2009) screened 14 MOF's at 0.1 bar and 25 °C. The results showed that the best performing metals for CO₂ adsorption were Zn, Mg, Ni, CO, and dioxybenzenedicarboxylate.

3.2.2 Properties that Are Screened for

3.2.2.1 Surface Area

The Brunauer-Emmett-Teller (BET) method is often used to determine the surface area of an adsorbent (Dogan et al. 2006). In this method nitrogen gas is isothermally pumped through a vacuum chamber at constant temperature and changing relative pressure (P/P_0) to develop an isothermal model (Lowell and Shields 1991). Higher surface area has been correlated to enhanced gas adsorption because of the increased availability for more active sites (Sumida et al. 2012).

Fig. 3.1 SEM magnifications of activated carbon samples show a hollowed structure with pores from 10 to 100 nm in size (Brasquet et al. 2000)



Sometimes gas may be released at sub-atmospheric pressures, as is the case with flue gas from power plants and from sour natural gas wells. Therefore, it is important to have a high density of metals, which interact with CO₂ molecules best at around 1 atm. In this case, the strength of the molecular bond, measured by the heat of adsorption, is increasingly indicative of CO₂ capture capacity.

3.2.2.2 Pore Size

The pore size of adsorbents is also important to consider, as this impacts the selectivity of the material to certain gases as opposed to others. The pore size, along with surface area, can be modified by chemical activation or physical activation (Li 2011). Under high-pressure (i.e., 4.5 MPa), CO₂ capture applications, such as in pressure-swing adsorption, a high volume of large micropores or small mesopores are required; however, narrow micropore volume should be kept to a minimum (Casco et al. 2014) (Fig. 3.1).

3.2.2.3 Electrostatic Interactions

This property impacts the selectivity of gases. In post-combustion capture, the main concern is separating CO₂ and CH₄. MOFs with ordered microdomains have different electrostatic field strengths can separate the molecules. For example, lithium cations have been incorporated onto organic frameworks by chemical reduction or ion exchange and have been successful in capturing CO₂ (Bae et al. 2011). The separation of CO₂ from N₂ can be performed due to physical differences in the radii of the molecules. It is assumed that all MOFs preferentially adsorb CO₂ over N₂ and CH₄, so that specific property isn't fundamentally interesting; rather, the research focus must be on finding inexpensive adsorbents with remarkable capacity and selectivity (D'alessandro et al. 2010).

3.2.2.4 Gravimetric CO₂ Uptake

This refers to the amount of CO₂ adsorbed per unit mass of material. This shows how much mass of adsorbent is needed to form the adsorbent bed. Thermogravimetric Analysis is used to quantify the amount of CO₂ that is adsorbed to the surface of the material. A metal balance is often used to determine the mass change as gas flows through an orifice at a set flow rate.

3.2.2.5 Volumetric Capacity

This term refers to how densely the CO₂ can be stored within the adsorbent. This is an important parameter to know when determining the volume of the adsorbent bed.

3.2.2.6 Heat of Formation

Similar to enthalpy of adsorption, heat of formation can be quantified by a thermogravimetric analysis by taking the integral of the heat flow in J/s over a period of time at 25 °C (Pires et al. 2000). The change in heat flow is caused by the binding reaction between the gas molecules and carbon framework. Physical adsorption typically produces a heat of adsorption between 5 and 40 kJ mol⁻¹; whereas, chemical adsorption is typically between 40 and 800 kJ mol⁻¹ (Chang and Chen 2006). The enthalpy of adsorption is an indicator for the strength of bond between the pore surface and the CO₂. Although a high enthalpy of adsorption indicates high selectivity, it may make regeneration difficult. It's necessary to optimize the binding strength of CO₂ to have high selectivity and low regeneration energy. If the binding strength is too low, the volume of the adsorbent bed will be large; however, if too high, the cost of regeneration will be high. The combination of these values will determine the heating and therefore, regeneration efficiency (Sumida et al. 2012).

3.2.2.7 Gas Selectivity

Not only is it important to assure a large CO₂ adsorption capacity, but when considering low pressure scenarios, it's also necessary to assess CO₂/N₂ and CO₂/CH₄ selectivity. In flue gas applications, it's important to separate the CO₂ from the N₂ component of the gas stream. In order to upgrade natural gas, it's important to selectively adsorb CO₂ from the natural gas stream. Liu (2012) used metal modified organic frameworks with immense surface areas (up to 6250 m²/g) to capture CO₂, with ranges between 10 and 40 mol/kg m²/g at 50 bars and room 25 °C.

3.2.3 Langmuir Isotherm

Langmuir isotherm can be employed to model the adsorption of CO₂ on adsorbents. As the CO₂ mol fraction increases, so does the equilibrium selectivity on the adsorbent. The linear form of Langmuir's isotherm model is given by the following equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \left(\frac{1}{Q_o} \right) C_e$$

where C_e is the equilibrium concentration of the adsorbate, q_e the amount of adsorbate adsorbed per unit mass of adsorbate at the equilibrium, and Q_o and b are Langmuir constants related to adsorption capacity and rate of adsorption, respectively.

3.3 Organic Adsorbents

For low temperature adsorption, a broad range of micro/mesoporous materials, such as activated carbon, have been shown to be promising adsorbents for CO₂. This is because of their high surface area, which promote physical adsorption and therefore, easy regeneration. Because of natural surface groups, they can be modified with metals and nitrogenous groups to enhance their selectivity towards gases.

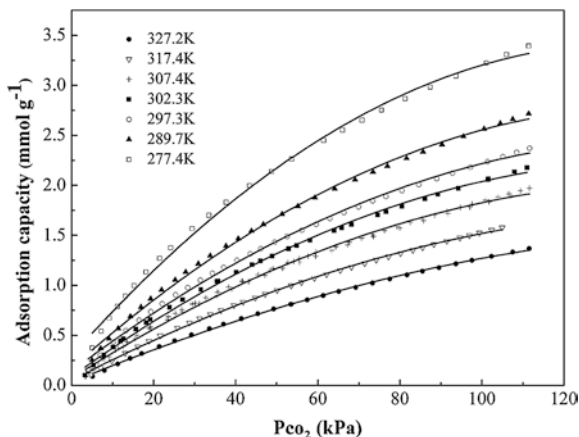
3.3.1 Activated Carbon

Activated carbon is often produced through physical or chemical activation. In physical activation, a physical agent, such as steam is used; whereas, in chemical activation, a chemical reagent is used to alter the properties of the resulting carbon for optimal adsorption. To optimize the adsorption of AC, it is important that the adsorbent has high surface area and highly developed porosity, especially micro- and mesoporosity.

3.3.1.1 Physical Activation

One way to increase the surface area and pore volume of carbon materials is to expose the material to supercritical fluids. This supercritical activation decreases the surface tension, while not permitting the structure to collapse when organics are removed by heat. By supercritical drying, surface area is increased even more than when solvent exchange is used. One example activated carbon can adsorb 12 mmol CO₂ per gram at the high pressure of 4 MPa. The material

Fig. 3.2 Isotherm for adsorption of CO₂ on activated carbon (Samanta et al. 2012)



shows complete regeneration because the physisorption mechanism is employed. Adsorption can be modeled using Henry's law, and is directly proportional to the pressure (Drage et al. 2009).

Figure 3.2 shows experimental data and model results of the adsorption process of CO₂ onto activated carbon through a change in pressure from 0 to 120 kPa. As the temperature of adsorption increases, the amount of CO₂ adsorbed decreases. The highest adsorption is reached at a temperature of 277 K.

3.3.1.2 Chemical Activation

The procedure to make chemically activated carbon materials is quite simple, as described by Sevilla (2011), who activated biomass with KOH. The solvent is combined with the feedstock in 2:1 and 4:1 (KOH:feedstock) ratios. The KOH modified feedstock is pyrolyzed between 600 and 800 °C and washed with 10 % HCl to remove salts. It is then rinsed with DI water and oven dried. The surface area of the resulting carbon is enormous (BET SA = 2200–2400 m²/g). Results show that as the production temperature, at which the feedstock was pyrolyzed at, increased from 600 to 800 °C, the resulting adsorption of CO₂ increased too. A major conclusion of their study was that narrow micropores, rather than mesopores are important for CO₂ adsorption.

3.3.2 Biochar

3.3.2.1 Introduction to Biochar

Biochar can be used to address some of the most urgent environmental problems of our time—soil degradation, food insecurity, water pollution from agrichemicals, and climate change... (Johannes Lehmann, Soil Sciences, Cornell University)

One might recognize the word biochar (or “black carbon”) because of its known applications in agriculture, but its capacity for capturing carbon dioxide is less known. Similar to activated carbon, biochar is porous carbon framework that has received attention for its ability to remove contaminants, sequester carbon in soils, and concurrently improve soil quality (Jeffery et al. 2011). The pyrolysis process, which involves heating under anaerobic conditions, produces this pyrogenic form of carbon that is less susceptible to degradation/mineralization. In regards to supply, biochar can be generated from waste biomass and agricultural/forest residue, so the source is abundant.

3.3.2.2 Environmental Benefits of Biochar

Biochar production and burial removes carbon dioxide indirectly from the atmosphere through plants, while improving the soil quality and acting as a fertilizer (Glaser et al. 2009). For example, soil scientist demonstrated the use of biochar plus chemical amendments (N, P, K fertilizer and lime) on average doubled grain yield over four harvest compared with the use of fertilizer alone (Tenenbaum 2009).

Because of the relatively large surface area of biochar and abundant pore spaces that include extensive micropores, there is huge potential for soil improvement applications. Without releasing carbon, biochar is capable of remaining in soil for centuries (maybe even millennia). Based on European emissions of about 1.1 Gt of carbon per year, it is estimated that biochar land application could offset around 9 % of Europe’s emissions (Barrow 2012). Not only does biochar fix carbon by binding anthropogenic hydrogen organic compounds in soil, it also provides a microhabitat for beneficial soil organisms and enables moisture retention and adsorption of nutrients. It can increase ion exchange capacity of soils, improve soil moisture retention, raise pH, retain N on permeable soils, bind agrochemicals and reduce phosphate and nitrate pollution (Barrow 2012).

3.3.2.3 Economic Benefits of Biochar

There are 3 main economical benefits of using biochar (Matovic 2011):

1. Can be produced by relatively simple processes
2. Can be produced wherever there is biomass and soil
3. Improves soil quality

3.3.2.4 Biochar’s Carbon Dioxide Capture Potential

Because biochar can be derived from different types of feedstocks under various conditions, it is also important to advance current understanding the governing CO₂ sorption mechanisms to optimize the development and production of biochar-based CO₂ adsorbent.

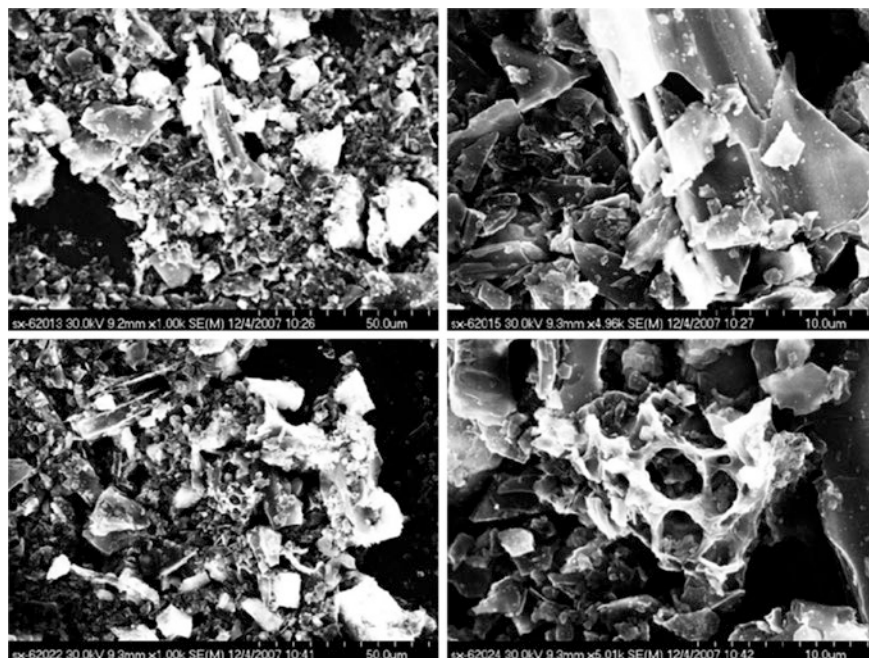


Fig. 3.3 SEM images of biochar (Lee et al. 2010)

Biochar has unique surface properties that give it excellent potential for CO₂ capture because it tends to be polar, hydrophilic, and has an extensive porous structure (Fig. 3.3) with comparatively high surface area-to-weight ratios (Sun et al. 2014). Biochar is not only more environmentally friendly, but also 10× cheaper than AC and other common CO₂ capture materials because it is often produced from various waste biomass residues through one-step slow pyrolysis at relatively low temperatures without sophisticated equipment.

Creamer et al. (2014) determined that biochar could be used as a low-cost CO₂ capture material. Six types of biochars were prepared from two commonly used feedstock materials through slow pyrolysis at 300, 450, 600 °C and were assessed for their sorption of CO₂ and the adsorption kinetics of CO₂ onto the biochars were measured and modeled (Fig. 3.4).

Experimental data showed that biochar could be a promising framework for CO₂ capture with adsorption comparable to many commonly used commercial adsorbents. Because the adsorption of CO₂ was mainly through physisorption, biochars with larger surface area generally showed better adsorption ability, although the presence of nitrogenous groups also promoted the adsorption.

Further, the biochar was able to release the captured CO₂ with an elevation in temperature. Figure 3.5 shows this linear relationship between temperature and CO₂ adsorption, confirming the physisorption mechanism.

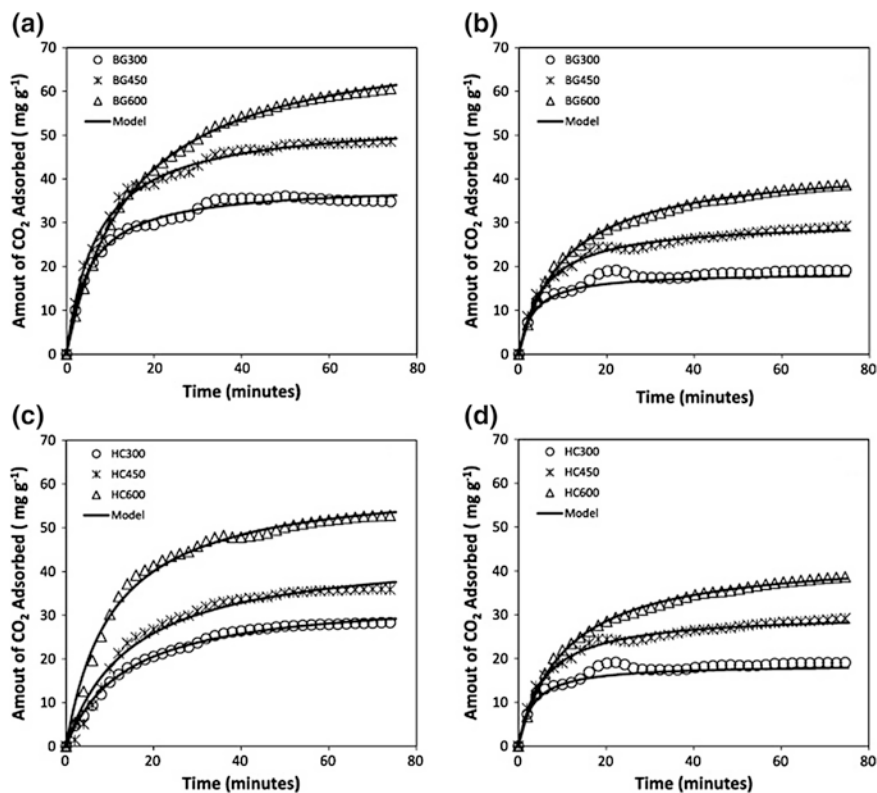


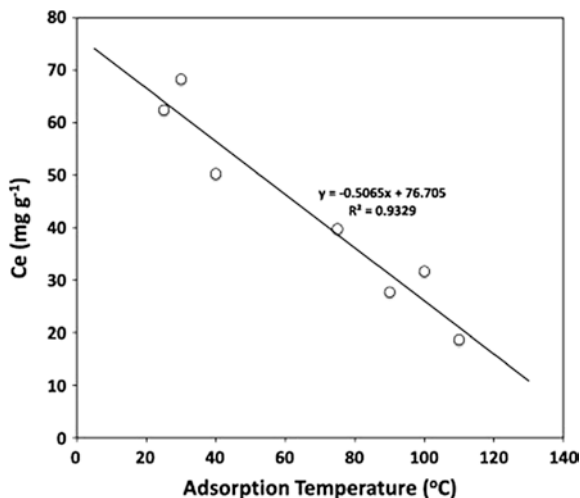
Fig. 3.4 CO₂ adsorption kinetics of biochars derived from hickory wood (HC) and sugarcane bagasse (BG) at different pyrolysis temperatures (300, 450, 600 °C) assessed at two different adsorption temperatures (25 and 75 °C). **a** BG, 25 °C; **b** BG, 75 °C; **c** HC, 25 °C; **d** HC, 75 °C (Creamer et al. 2014)

Because of all these advantages, biochar is a promising CO₂ capture material that can be used to reduce anthropogenic CO₂ emission and to mitigate global warming (Creamer et al. 2014).

3.3.3 Metal Organic Framework (MOF)

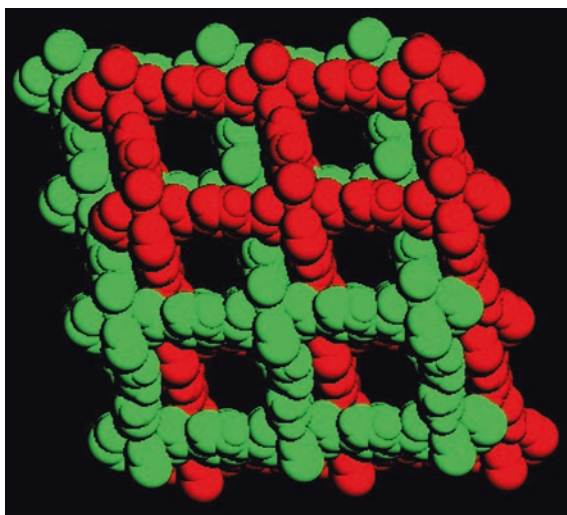
The introduction of functional groups with a high affinity for CO₂ into pores of organic materials has been employed as strategy to enhance the adsorption capacity and selectivity of CO₂ adsorption (Sumida et al. 2012). The general idea, when producing a metal organic framework for gas adsorption, is to combine metal ions

Fig. 3.5 Desorption of CO₂ from BG600 over temperature increase (Creamer et al. 2014)



and organic ligands to produce a crystalline porous network that is capable of selectively binding molecules at high capacity and releasing these molecules completely at non-prohibitive energy cost. Figure 3.6 shows a 1-D image of a MOF with micropores. A flexible, or stimuli-responsive MOF is produced to respond to physical and chemical stimuli of various kinds in a tunable fashion by molecular design and have shown additional advantages for selective adsorption and separation of CO₂. MOFs are characterized by the type of metal-nodes which affect the framework dynamics, such as the “breathing and swelling” of the system during interactions with outside molecules. They are synthesized and screened with the

Fig. 3.6 One-dimensional micropores in metal organic framework (Bastin et al. 2008)



objective to have remarkable stability under various conditions. This property enables the MOFs to capture and separate gases at room temperature (or higher) and at relatively low pressure (Schneemann et al. 2014).

Compared to zeolites, MOFs can be more easily modified to capture CO₂ at different pressures, as the pore structure and chemical composition are more accessible to be modified (Li et al. 2011). The material synthesis is considered “low cost” in relation to other solid adsorbents, such as zeolites, which is only affordable at the research scale. In order to decrease the cost of synthesis, the process must be scaled up (Li et al. 2011).

3.3.3.1 Synthesis of MOF

A variety of synthesis temperatures, solution compositions, concentrations, and production techniques have been employed to produce optimal MOF's for different applications. Some of the production techniques include: mechanochemical procedures, sonication-assisted synthesis, and microwave heating. It is important that these frameworks can be scaled up to an industrial level. In order for the material to capture a significant amount of gas, it is important that the surface area is huge. This allows for the maximum amount of active surface sites. Further, in order to selectively capture certain gases, the framework must be “flexible” enough so that both the pore size and bonding of functional groups can be modified.

3.3.3.2 Amine Modified MOF's

Amines and their derivatives are used also to introduce chemical bonding between the MOF's and CO₂. The heat of adsorption, an important tool in characterizing the chemical bonding, can reach up to 90 kJ/mol when using amine modified MOF's (Li 2011).

3.4 Other CO₂ Adsorbents

3.4.1 Silica-Based Adsorbents

Grafting amine groups to solid sorbents with high surface area, such as mesoporous silica, helps overcome issues associated with liquid absorption, such as corrosiveness and costly regeneration (Hicks et al. 2008). Silica is promising not only because of its porosity, but also because its surface can be functionalized easily by ligands with a variety of electronic effects. The variety of electronic effects is beneficial when one is concerned with optimizing the basicity of the

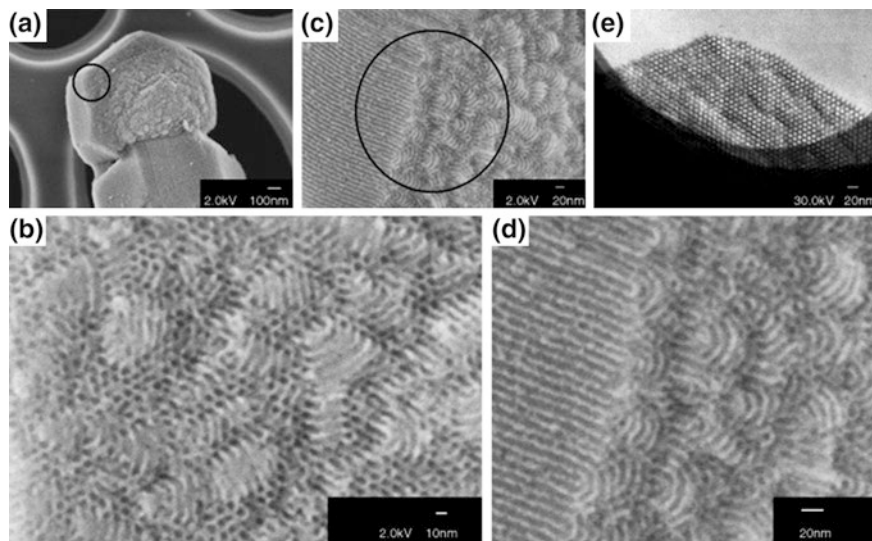


Fig. 3.7 SEM (a–d) and STEM (e) images of SBA-15 mesoporous silica. *Circled areas* in (a) and (c) are enlarged in (b) and (d) respectively (Che et al. 2003)

structure and therefore the strength of bonding between the surface and the gas molecules (Zelenak et al. 2008). Figure 3.7 shows the mesoporous structure of silica that makes it promising for CO₂ capture applications.

3.4.2 Metal Oxide-Based Absorbents

Calcium oxide works to capture CO₂ by carbonation in which calcium oxide reacts with CO₂ to produce calcium carbonate (Lu et al. 2006; Li et al. 2005). The reaction is reversible and proceeds via decarbonation. CaO-based sorbents have a variety of morphological properties, such as different pore structures and particle size, which affect their carbonation ability. Like other adsorbents, the uptake of CO₂ is very much related to pore volume and BET surface area. With increasing carbonation, the material forms a powder layer, so the surface area becomes extremely low and the CO₂ uptake is limited significantly (Lu et al. 2006).

Because of the different physical and electrostatic properties on metals, making a composite out of a combination of metal oxides can enhance the capture of CO₂. One example is in the synthesis of the composite metal oxide Ca₁₂Al₁₄O₃₃. The composite utilizes the carbonation reaction, which produces calcium carbonate under CO₂ flow and the calcination reaction, which releases the CO₂ under N₂ flow at high temperatures (1173 K). The regeneration of CaO and Ca₁₂Al₁₄O₃₃ metal-oxide composites is very expensive because the decarbonation reaction is necessary to unbond the carbon dioxide (Li et al. 2005).

3.4.3 Zeolites

Zeolites, microporous aluminosilicate minerals, have been actively researched for over 50 years; however, only a small fraction has been discovered. Recent advancements in high-throughput synthesis and characterization have made it possible to produce zeolites with new structure, topologies, and pore metrics for a variety of applications (Phan et al. 2010). The high chemical and thermal stability of zeolites allow for the topography, crystallinity, and porosity to be preserved under organic physical reactions, such as in reflux with organic solvents, alkaline solution, and boiled water. In order to access new applications for zeolites, high throughput analysis is used to synthesize zeolites with a variety of metal ions and “functionalizable” organic units (Phan et al. 2010). Figure 3.8 shows an example of a basic zeolite structure made up of aluminum and silica.

Even under low-pressure gas situations, zeolites can have high CO₂ uptake capacity, complete reversibility, high thermal stability, and greater selectivity towards CO₂ than MOFs (Phan et al. 2010). When evaluating the potential for zeolites to capture CO₂, it is popular to research a variety of zeolitic frameworks that are composed of different functional groups and structural dimensions, yielding different molecular interactions, pore size, and stability. They are evaluated for their selectivity towards CO₂ and their capacity for CO₂ storage.

Some zeolitic imidazolate frameworks can hold up to 83 L of CO₂ with only 1 L of material, due to their high porosity (Banerjee et al. 2008). The separation of CO₂ from a CO₂/CO mixture is particularly difficult; nevertheless, the adsorption is completely reversible. Breakthrough experiments at room temperature show complete retention of CO₂ and passage of CO through pores (Banerjee et al. 2008). It is even proposed that due to the flexibility of the zeolitic framework, structures can be functionalized to induce the catalysis of CO₂ into a usable fuel (Phan et al. 2010).

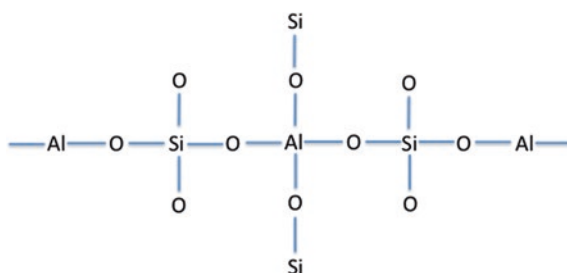


Fig. 3.8 Basic zeolite structure

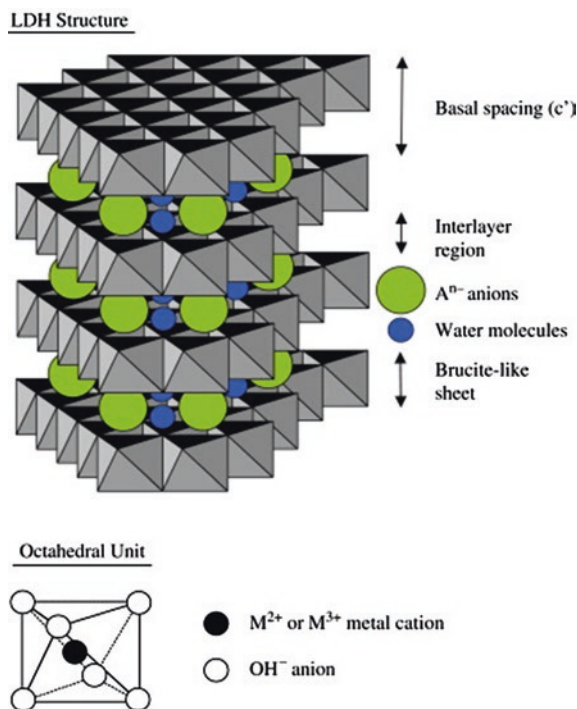


Fig. 3.9 Schematic representation of the LDH structure (Goh et al. 2008)

3.4.4 Clays/Layered Double Hydroxides (LDHs)

3.4.4.1 Introduction

LDHs are positively charged brucite-like layers. These positively charged layers are developed from the trivalent cations that partially substitute for the divalent cations. Figure 3.9 shows the organization of an LDH structure. Anions and water molecules in the interlayer regions compensate for this extra charge. Reddy et al. (2006) studied the ability for LDH structure produced at a variety of calcination temperatures to capture CO₂. The calcination temperature of 200 °C, gave the optimal surface area, while also enabling the decomposition of calcium carbonate, which generates basic sites. Both chemical and physical interactions are involved in the CO₂ adsorption process; therefore, the process was found to be 88 % reversible (12 % irreversible) (Reddy et al. 2006).

3.5 Conclusion

Adsorbents are promising materials for the capture of carbon dioxide in post combustion gas. Compared to absorbents, adsorbents tend to have lower energy requirements for regeneration. Two of their important properties include high surface area, meaning many exposed sites for binding molecules, and abundant functional groups that selectively encourage molecular attraction of carbon dioxide. Organic (carbon-based) adsorbents, such as biochar, are specifically useful because they are polar and hydrophilic. Organics can even take on additional functionalization by the addition of nitrogenous groups or metal oxides to facilitate affinity of the adsorbent to the carbon dioxide. Other inorganic adsorbents can also be used for CO₂ capture. For example, zeolites are natural or synthetic minerals and can incorporate a variety of cations. They are promising due to the diversity of different molecular interactions, pore size, and stability that can be useful in a variety of applications.

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Chapter 4

Absorbents for CO₂ Capture

Abstract CO₂ can be absorbed through either physical or chemical pathways. In order to increase efficiency of capture/separation, decrease cost, and reduce negative environmental impacts, it is necessary that absorbents have high net cyclic capacity, high absorption rate, good chemical stability, low vapor pressure, and low corrosiveness. Aqueous solutions of alkanolamines, including primary amines (monoethanolamine), secondary amines (diethanolamine), and tertiary amines (methyldiethanolamine), and combinations of the three are commonly used to remove acidic gases like CO₂ from flue gas. Each material has its favorable and unfavorable properties; it is important to design a material with an optimal balance, as increased efficiency and bond strength results in the need for higher regeneration energy and therefore money. Ionic liquids are highly adaptable and are thermally stable, which makes them also good candidates to be employed in CO₂ capture systems; however, are still in the research phase of development.

Keywords Alkanolamine · Ionic liquid · Regeneration energy

4.1 Search for the Optimal Absorbent

According to Rao and Rubin (2002), the optimal CO₂ absorbent must have the following characteristics:

- (1) High net cyclic capacity
- (2) High reaction/absorption rate
- (3) Good chemical stability
- (4) Low vapor pressure
- (5) Low corrosiveness

To optimize CO₂ capture and sequestration feasibility, it is important to focus on the key parameters that affect performance, cost, and environmental implications of a diversity of technologies. When using aqueous monoethanolamine (MEA) or

other amine-based absorbents, the performance is based on the mass flow rate of CO₂ in the flue gas, the desired CO₂ capture efficiency, the MEA concentration, and the CO₂ loadings in the solvent. Because MEA removes other acid gases like NO₂ and SO_x, there might be a need for additional solvent. The amount of heat depends on the type of absorbent and the amount of compression that is needed. This is the main parameter that factors into the cost of the process. Although the amine-based CO₂ absorption process reduces the emissions of particulate matter and acid gases, it creates several new waste products, such as ammonia gas (Rao and Rubin 2002).

4.2 Physical Absorbents

4.2.1 Mechanism

The physical absorption of a CO₂ can be described by Henry's Law, which dictates the amount of gaseous acids absorbed into a liquid. At constant temperature, the amount of dissolved gas is directly related to the partial pressure of the gas. The solubility of gases is temperature dependent and based on Henry's constant (Breeding 1993). The operation of CO₂ physical absorption technology is based on this principle. Industrial processes that yield a high concentration of CO₂, such as natural gas, synthesis gas, and hydrogen production, capture in CO₂ low temperature and high-pressure conditions. Similarly, CO₂ can be desorbed at reduced pressure and elevated temperature (Yu et al. 2012). When searching for an absorbent, it is important that the physical absorbent is stable (not highly corrosive).

4.2.2 Processes

The Selexol Process uses dimethylether or propylene glycol and can be applied to remove both CO₂ and H₂S under a low temperature operation. This is a fairly well commercialized process due to the low vapor pressure and low toxicity. Further, the absorbent is stable and easily regenerated (Yu et al. 2012). The Rectisol Process uses methanol as an absorbent to capture acidic gases. It's the preferred method for separating H₂S, but can also be used in CO₂ capture (Hochgesa 1970). Purisol is a low energy process that uses the chemical N-methylpyrrolidone. Morphosorb is a relatively new process that uses morpholine as the absorbent. The operation cost is relatively low (30–40 % less than Selexol process). The Fluor process uses propylene carbonate, which enables a high solubility of CO₂; however, requires a partial pressure of higher than 50 psig (Yu et al. 2012).

4.3 Alkanolamine Absorbents

4.3.1 Introduction to Liquid Amines

Aqueous solutions of alkanolamines, such as MEA, are commonly used to remove acidic gases like CO₂ from flue gas. These amine-based absorbents can be categorized into three groups: primary amines such as MEA and diglicolamine (DGA); secondary amines, diethanolamine (DEA) and di-isopropanolamine (DIPA); and tertiary amines, methyldiethanolamine (MDEA) and triethanolamine (TEA), and have been widely employed for the removal of CO₂ (Rodriguez-Flores et al. 2013). Recently, with call for high regeneration efficiency, materials such as 2-amino-2-methyl-1-propanol (AMP) are being produced that have been engineered with both favorable and unfavorable characteristics. The “unfavorable” characteristics will enhance the regeneration efficiency due to the weaker bond.

4.3.1.1 MEA

In the early 1990s researchers investigated ways to optimize the recovery of CO₂ from flue gas (Erga et al. 1995). A variety of absorption-steam stripping using amines, such as MEA, were considered under different CO₂ concentrations/loads. In comparison to other alkanolamines, MEA has high reactivity, low solvent cost, and low molecular weight. These properties give it high capacity for CO₂ absorption and reasonable thermal stability. Nevertheless, the CO₂ desorption of MEA requires higher energy consumption than other alkanolamines. Furthermore, its reaction is more corrosive than other alkanolamines and results in the high formation of degradation products and carbamate; therefore, it is important that new absorbents are screened to optimize the absorption rate and regeneration efficiency (Ma'mun et al. 2007).

4.3.1.2 Diethanolamine (DEA)

Secondary amines like DEA receive attention because of their lower regeneration energy and lower a degradation rate than primary amines (e.g., MEA); however, DEA does not have as high of CO₂ capture performance as MEA (Veawab et al. 2002). Because primary and secondary amines are sterically unhindered, they form carbonate as a byproduct that could reduce their loading capacity for CO₂. Regardless, they are preferred over the sterically hindered tertiary amines because they are more reactive. Both DEA and MEA can react with CO₂ even at low concentrations.

4.3.1.3 AMP and Blended Systems

Like tertiary amines, AMP, or 2-amino-2-methyl-1-propanol, is a sterically hindered amine form, so it does not contribute to amine formation. In a study by Barzagli et al. (2010), AMP is capable of capturing the most CO₂ out of DEA and MDEA (methyldiethanolamine). Because of the assortment of favorable and unfavorable characteristics between the alkanolamine chemicals, studies have focused on combining the chemicals to produce the optimal absorbent. Compared to single amines, a blend of different amine types can significantly enhance the absorption efficiency (in the range 7–14 %) (Barzagli et al. 2010).

4.3.2 Amine-Based Carbon Dioxide Capture Systems

Figure 4.1 shows the process of carbon dioxide absorption via the amine scrubbing process. The flue gas that is produced through the post-combustion stage enters a reactor that is filled with an amine-based absorbent, such as MEA. The absorbent binds with the CO₂ gas, but not with the other gases, such as N₂. In the amine scrubbing process, the formation of ammonium carbamate is the chemical mechanism for the entrapment of CO₂. The other gases are released through the top of the absorption tank, because they are not bound to the solvent. The CO₂-bound solvent sinks into a separate pipe and is pumped into the desorption tank. The bond between the amine-solvent and CO₂ is broken due to increases in temperature, and the CO₂ is bubbled out into a separate tank. The solvent is regenerated by the addition of heat (Rao and Rubin 2002).

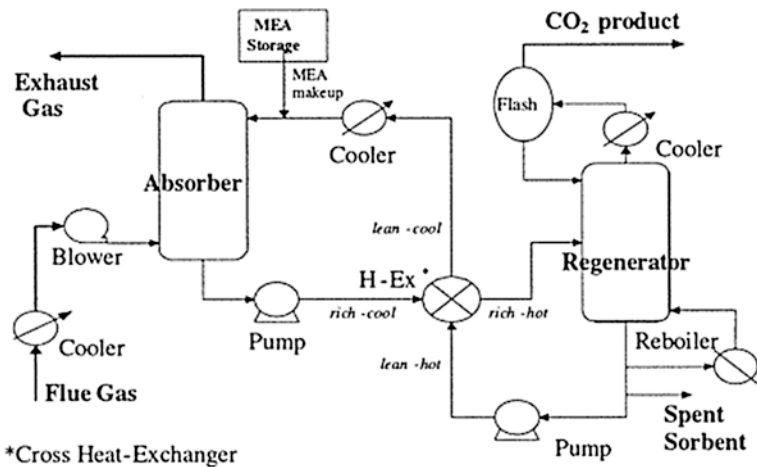


Fig. 4.1 CO₂ capture from flue gases using amine-based system (Rao and Rubin 2002)

Table 4.1 MEA cost model parameters and nominal values, adapted from Rao and Rubin (2002)

| Capital cost elements | Nom. value | O&M cost elements | Nom. value |
|--|---------------------|---------------------------------------|----------------------------------|
| Process area costs (nine areas) | | Fixed O&M costs (FOM) | |
| Total process facilities cost | PFC ^{a, b} | Total maintenance cost | 2.5 % TPC |
| Engineering and home office | 7 % PFC | Maintenance cost allocated to labor | 40 % of total maint. cost |
| General facilities | 10 % PFC | Admin & support labor cost | 30 % of total labor cost |
| Project contingency | 15 % PFC | Operating labor | 2 jobs/shift |
| Process contingency | 5 % PFC | | |
| Total plant cost (TPC) = sum of above | | Variable O&M costs (VOM) | |
| Interest during construction | Calculated | Reagent (MEA) | \$1250/tonne MEA |
| Royalty fees | 0.5 % PFC | Water cost | \$0.2/m ³ |
| Preproduction costs | 1 month VOM&FOM | CO ₂ transport cost | \$0.02/tonne CO ₂ /km |
| Inventory (startup) cost | 0.5 % TPC | CO ₂ storage/disposal cost | \$5/tonne CO ₂ |
| Total capital reqmt (TCR) = sum of above | | Solid waste disposal cost | \$175/tonne waste |

4.3.3 Cost-Benefit Analysis of MEA Sorption

Table 4.1 lists out example cost parameters and nominal values. The major cost is in the purchase of reagent (MEA). In this model, the reagent cost is \$1250/tonne MEA. The amount used is dependent on the flow rate of CO₂. In this table, the energy consumed by the process is processed internally through the total process facilities cost and subtracted from the overall efficiency of the system.

Because the amine scrubbing process has several downfalls, such as amine-solvent volatilization, high-energy consumption during regeneration, unfavorable degradation, and corrosion issues, it is necessary to develop new solvents and processes for the absorption of CO₂.

4.4 Ionic Liquids

4.4.1 Introduction to Ionic Liquids

In recent years, ionic liquids have received increasing research attention as promising materials for carbon dioxide capture. The properties of ionic liquids make them highly adaptable for the development of new processes. Ionic liquids

have been developed that have negligible vapor pressure and therefore, solvent vapor shouldn't become lost into the gas stream (Bates et al. 2002). Further, they are thermally stable, and have a tunable chemistry (Bara et al. 2010).

4.4.2 Selection of Ionic Liquids

When choosing an ionic liquid, CO₂ removal efficiency and solvent stability are assessed. In order to predict the capture ability of material, the properties of the liquid that we consider include: vapor pressure, heat capacity, density, viscosity, surface tension, and thermal conductivity.

Examples of ionic liquids include: 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim]-[BF₄])₁₃ and 1-butyl-3-methylimidazolium bis((trifluoromethyl)-sulfonyl)imide ([Bmim][Tf₂N])₁₄. These are best at higher pressures, rather than one atmospheric pressure, which is less desirable for post-combustion CO₂ capture.

4.4.3 Status of Ionic Liquids for CO₂ Capture

Currently, ionic liquids for CO₂ capture are still in the research phase of development; however, because they are liquid absorbents, could employ a similar setup to liquid amine absorbents and therefore, adapted relatively quickly into the large-scale applications. One simulation compared the energy efficiency of capturing carbon dioxide using ionic liquids versus conventional MEA capture process and it was claimed that the specific ionic liquid used 16 % less energy (Huang et al. 2014). Ionic liquids also have potential to be used in pre-combustion capture processes.

4.5 Conclusion

In conclusion, both physical and chemical absorbents have proven to be effective CO₂ capture materials; however, they may have significant drawbacks. Increased efficiency and bond strength results in the need for higher regeneration energy and therefore money. MEA systems have been used for decades to separate CO₂ from flue gas streams; however, the incorporation of the technology significantly decreases the energy efficiency of power plant. Some other promising materials include secondary and tertiary amines, AMP, ionic liquids, or a blend of amine absorbents. Additional research on the mechanisms of absorption and how this relates to properties of the absorbents is still needed to form an optimal material.

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Chapter 5

CO₂ Reduction and Utilization

Abstract As CO₂ capture technology is employed extensively, the volume of CO₂ that is released through various processes has potential to surpass the limited amount of storage capacity. One sustainable way to deal with CO₂ is to convert it into a usable form, such as for energy. The major obstacle for CO₂ reduction is that the reaction isn't energetically favorable; therefore, it is necessary to use catalysts to incite this reaction. Photocatalytic reactions are performed in a variety of conditions, such as under UV light exposure or concentrated sunlight in the presence of a catalyst and water. A variety of transition metal complexes, such as TiO₂, SiO₂, and metal decorated nanoparticles have been studied for their potential as photocatalysts. Current research is being funded to expand our knowledge on how to best use or convert captured CO₂.

Keywords Reduction · Photocatalyst · TiO₂

5.1 Introduction to the Reduction of CO₂

As discussed in Chap. 1, there are various methods to fix carbon or store captured carbon dioxide. However, numerous processes release CO₂ as a byproduct and global storage capacity for CO₂ is naturally limited. A more sustainable option for the mitigation of CO₂ is to reduce it to usable forms, such as CO or methanol. The major obstacle for CO₂ reduction is that the reaction isn't energetically favorable, making the challenge such a hot topic (Ahmed et al. 2011).

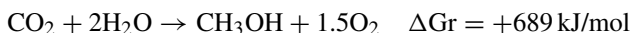
5.1.1 Photocatalysis

In chemistry, catalysts are used to accelerate reactions, and in the case of photocatalysis, a photoreaction is initiated by absorbed light. Photocatalytic activity (PCA) is determined by the catalyst's ability to produce electron-hole pairs, which in

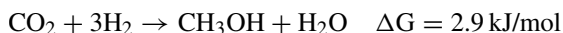
turn, generate free radicals that undergo secondary reactions, such as water-splitting and oxidation of organic matter. Recently, photocatalysis has been suggested to be a potential cost-effective way for CO₂ reduction (Li et al. 2014).

5.2 Thermodynamics of the Catalysis Process

Natural reduction of CO₂ with water is thermodynamically unfeasible without the significant addition of energy, indicated by a large positive ΔG .



The reaction using H₂ as a reduction agent requires much less energy.



However, the production of H₂ from water splitting, is energy intensive



As shown by above, it's energy intensive to reduce CO₂ to hydrocarbons, so it is necessary to use catalysts to incite this reaction. Nevertheless, the reaction: $\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- = \text{HCOOH}$, provides the hydrogen ion, H⁺ and enables energy to be released through the reaction with CO₂ to produce hydrocarbons. The problem is that splitting H₂O to get H⁺ is also difficult. Catalysts would need to be added to the water-splitting reaction to lower energy expenditure. In summary, the known processes of reducing CO₂ to hydrocarbon products require the addition of energy. This can be provided in either the form of light (photocatalysis) or heat (thermocatalysis). This chapter only discusses advancements in photocatalysis to reduce CO₂.

5.3 Photocatalytic Reactions

Photocatalytic reactions are performed in a variety of ways. One method is to circulate H₂ and CO₂ gas over a photoreaction cell exposed to UV light. The reaction cell can be prepared by dispersing a catalyst (i.e., a metal composite) evenly on a flat quartz surface. Depending on the catalyst, different wavelengths and energy intensities are needed. For example, for a zinc-copper-aluminum-gallium LDH catalyst, the wavelength used is 555 nm with an intensity of 28–42 mW/cm² at a temperature between 305 and 313 K (Ahmed et al. 2011).

5.3.1 *Choosing a Catalyst*

The general idea of catalysis is that a metal complex will directly bind the CO₂ molecule and form a single reaction product, while simultaneously desorbing a reduction product, such as carbon monoxide or polyethylene (Fu et al. 2012).

A variety of transition metal complexes have been studied for their potential as catalysts for the reduction of CO₂. TiO₂, SiO₂, ZnO, CdS, GaP, and SiC are some examples. These can be applied to solid frameworks, thin films, rods/tubes, or react within aqueous mixtures. The form that these compounds are in corresponds to the selective formation of different reduction products. For example, Wang et al. (2011) noted the potential to combine molecular catalysts with metal organic frameworks to produce highly active heterogeneous catalysts that reduce carbon dioxide, using solar energy.

5.3.2 *Testing the Catalysts*

Using nano-TiO₂/N catalyst, Michalkiewicz (2014) achieved a CO₂ adsorption capacity of 120 mg/g, at a pressure of 40 bars. TiO₂ is used as a photocatalyst, so when exposed to UV light, it is able to stimulate the reduction of carbon dioxide. Freundlich equation was used to model the adsorption of CO₂ by the catalyst. In order to quantify the reduction of CO₂, the nanoparticles were suspended in water within a semi-batch reactor. Carbon dioxide gas was pumped through the reactor to purge the system, and then the UV light, at the center of the reactor was turned on. Gas samples were collected from the outflow of the system and their concentrations were analyzed using gas chromatography. At about 1 h, the adsorption of CO₂ reached an equilibrium conversion to methanol, with a yield of about 20 μmol/g. The authors concluded that the presence of nitrogen in the material enabled higher CO₂ adsorption, which would be due to the basic groups on the nitrogen. Surface area is also shown to be an important factor for achieving high yield in carbon dioxide reduction (Michalkiewicz 2014).

5.3.3 *Common Catalysts*

Although TiO₂ has been used in many developments on photocatalysis, it has poor CO₂ selectivity. There is considerable room for improvement on the development of CO₂ reduction photocatalysts and it's still too early to focus on a single material, as there are actually a variety of metal oxides that should be explored.

5.3.3.1 TiO₂

Titanium dioxide has often been used as a photocatalyst for the oxidation of organic contaminants, for the degradation of crude oil, and for the sterilization of microbes on food contact surfaces (Ni et al. 2007).

TiO₂ nanoparticles have been shown to catalyze the conversion of CO₂ to hydrocarbons like methane, under UV radiation, even in the presence of water vapor. In the anatase and rutile phases, TiO₂ nanoparticles under UV light drive electrons across the band gap. These electrons react with water vapor to produce hydroxyl radicals and protons (Tan et al. 2006).

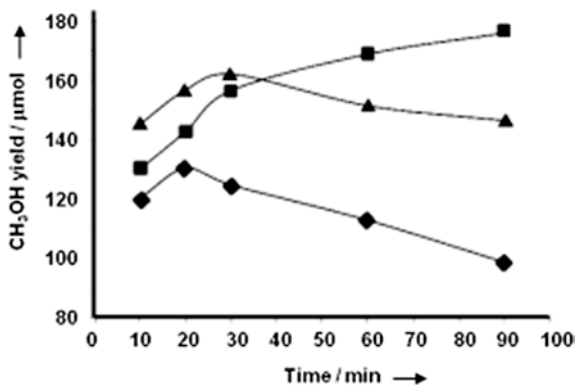
In the energy field, under UV light, TiO₂ nanoparticles can convert water to H₂ gas through a process called “water-splitting” (Ni et al. 2007). Nevertheless, the efficiency of this energy conversion is very low and several methods, such as dye sensitization and metal ion-implantation, have been developed to improve the productivity of the reaction (Ni et al. 2007).

5.3.3.2 Other Metal Oxides

Zinc oxide is the second most popular metal oxide for photocatalysis, as it can be used in a variety of conditions (Navalon et al. 2013). The photoactivity of zinc oxide is influenced by microstructure, crystal size, morphology, and crystal orientation (Navalon et al. 2013).

Like with TiO₂, ZnO aids in the production of methanol (as well as CO and CH₄) from the reduction of CO₂. The production decreases as a function of time, which indicates that under reaction conditions, the product is not stable (Navalon et al. 2013). Figure 5.1 compares CH₃OH yield during the photoreduction of CO₂ using 355 nm laser irradiation over three types of photocatalysts: TiO₂ (◆), NiO (■), and ZnO (▲). Both ZnO and NiO have higher yield of methanol than TiO₂.

Fig. 5.1 Photoreduction of CO₂ using TiO₂ (◆), NiO (■), and ZnO (▲) as catalysts (Navalon et al. 2013)



5.3.3.3 Metal Decorated Carbon Nanoparticles

There is increasing research on the applications of carbon nanoparticles, such as graphene and fullerene for photocatalysis (Yang et al. 2013). In particular, metal decorated carbon nanoparticles can be constructed from a variety of molecular complexes, considered for use in a variety of gas storage, compound separation, and heterogeneous catalysis application (Wang et al. 2011). Even without metal coating, visible-light irradiation promotes charge separation in carbon nanoparticles (Navalon et al. 2013); however, when gold and copper are used to coat these carbon nanoparticles, the metal-carbon complex can effectively enhance the charge separation on the carbon (Navalon et al. 2013).

The metal coated nanoparticles can be produced by a simple method (Navalon et al. 2013):

- (1) Treat water-soluble CNP's with nitric acid
- (2) Functionalizing with a poly(ethyleneglycol)diamine
- (3) Coat CNP's with metal nanoparticles

The use of carbon nanoparticles enhances the surface area by providing a framework for the metals and also contributes to the separation of charge.

5.3.3.4 Layered Double Hydroxides

Layered double hydroxide (LDH) catalysts have been developed for the photocatalytic conversion of carbon dioxide to methanol (Ahmed et al. 2011). One particular LDH that can be used in the photocatalysis was formed with zinc copper aluminum and gallium. When exposed to UV light under H_2 flow, CO is the major product that is formed with the use of Zn-Al-LDH (620 nm/h/g); however, with the inclusion of copper and gallium, the methanol formation rate increased to 160 nm/h/g (Ahmed et al. 2011). A methanol selectivity of 88 % was achieved using this Zn-Cu-Ga hydroxide layered material (Ahmed et al. 2011).

5.3.3.5 Nickel Supported on Silica-Alumina

Nickel supported on silica-alumina can also catalyze the reduction of CO_2 to methane, under UV light (Sastre et al. 2014). The process is relatively efficient with a CO_2 conversion rate above 90 % and selectivity of 95 % (Sastre et al. 2014).

5.3.4 Comparison of Catalytic CO_2 Photoreduction Systems

In a review article, Navalon et al. (2013) gave a good summary of various catalytic systems employed for CO_2 photoreduction (Table 5.1). The review article also indicates that catalysts can be effective in both UV and visible light in order to

Table 5.1 Summary of the various catalytic systems employed for CO₂ photoreduction, adapted from Navalon et al. (2013)

| Catalyst | Light source | Conditions | Product |
|---|--------------------------------|--|--|
| ZnO, NiO | Laser at 355 nm | 0.3 g catalyst, 70 mL water | H ₂ , CH ₃ OH |
| Ga ₂ O ₃ | 300 W Xe lamp | 50 mg catalyst, 3 mmol water | CH ₄ |
| Ru, Cu, Au; Ag/ALa ₄ Ti ₄ O ₁₅ | 400 W high pressure Hg lamp | 0.3 g catalyst 360 mL water, ambient conditions, continuous CO ₂ flow | CO, H ₂ |
| ZnGa ₂ O ₄ ; RuO ₂ /ZnGa ₂ O ₄ | 300 W Xe lamp | 0.1 g catalyst, 4 mL DI water | CH ₄ |
| CdS | 500 W high pressure Hg lamp | 70 μmol catalyst, 3 mL CH ₃ CN, 2-propanol | HCOOH, CO, H ₂ , CH ₃ CHO |
| [Zn ₃ Ga(OH) ₈] + 2[Cu(OH) ₄] ₂ - H ₂ O | 500 W Xe lamp | 0.1 g catalyst, 1.67 mmol H ₂ | CH ₃ OH |
| NiO/InTaO ₄ | Sunlight | 1.2 bar total pressure, 0.02 bar water vapor | CH ₃ OH |
| Pt-Cu/ZnO/K ₂ Ti ₆ O ₁₃ | Concentrated sunlight | 0.3 g catalyst, 4 mL DI water | CH ₃ OH |

produce a diversity of hydrocarbon products, such as CO, CH₄, CH₃OH, and HCOOH. Selectivity for these products depends on the conditions, catalyst, and light source.

5.4 CO₂ Reuse Research

The American Recovery and Reinvestment Act (ARRA) funds projects that capture CO₂ from industrial sources and as a part of this, the US Department of Energy has recently decided to fund 12 projects that aim to find innovative uses for carbon dioxide (Energy 2014).

Some ideas include converting CO₂ into mineral carbonates (Alcoa, Inc.), sodium hydroxide and cement substitutes (Calera Corp.), polycarbonates (Novomer Inc.), liquid fuels (Renewable Energy Institute International), and pipeline quality synthetic natural gas (Research Triangle Institute).

Other funded projects research ways to utilize the CO₂ to facilitate the renewable energy production. One example is to use CO₂ to cultivate the production of algae that will be converted into algal oil, biofuel and/or fertilizer, which is done at facilities across America such as Sunrise Ridge Algae, UOF LLC, Touchstone Research Lab, and Physical LLC (Energy 2014).

5.5 Conclusion

Because the capacity of CO₂ storage reservoirs is limited, it is more sustainable to convert the CO₂ to methanol or other usable forms. The major drawback is the high-energy penalty of reducing CO₂; therefore, catalysts are needed to facilitate the reactions. Photocatalysts such as metal oxides are being used for the photoreduction of CO₂; further, when these photocatalysts are produced as nanoparticles or nanocomposites, their conversion efficiency is even better. A wide range of catalytic systems has been studied, but research is still needed to optimize the catalysts and the conversion processes.

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