
CHAPTER 1

INTRODUCTION

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1.1 Background

Energy is the backbone of modern society. A clean, relatively cheap, and abundant energy supply is a prerequisite for the sustainable economic and environmental prosperity of society. With the significant economic growth in the Asia Pacific region and the expected development in Africa, the total world energy demands are projected to increase from 462.4 quadrillion BTU in 2005 to much more than 690 quadrillion BTU by 2030,¹ as shown in Figure 1.1. The projected energy supply through 2030 will be drawn from oil, coal, natural gas; renewable forms of energy; and nuclear energy, in that order. Figure 1.1 reveals that fossil fuels account for more than 86% of the world's energy supply.¹

The impact of the global warming induced by the CO₂ emission from fossil energy conversion processes has been an issue of international concern. An energy solution prompted by the combination of ever-increasing energy consumption and rising environmental concerns thus requires a consideration of coupling fossil energy conversion systems with economical capture, transportation, and safe sequestration schemes for CO₂. A long-term energy strategy for low or zero carbon-emission technologies also would include nuclear energy and renewable energy. Nuclear power is capable of generating electricity at a cost comparable with the electricity generated from fossil fuels.² Other than electricity, the heat generated from a nuclear plant can be used for hydrogen generation in hydrogen-producing thermochemical or high-temperature electrolysis plants.³ A variety of social and political issues, as well as

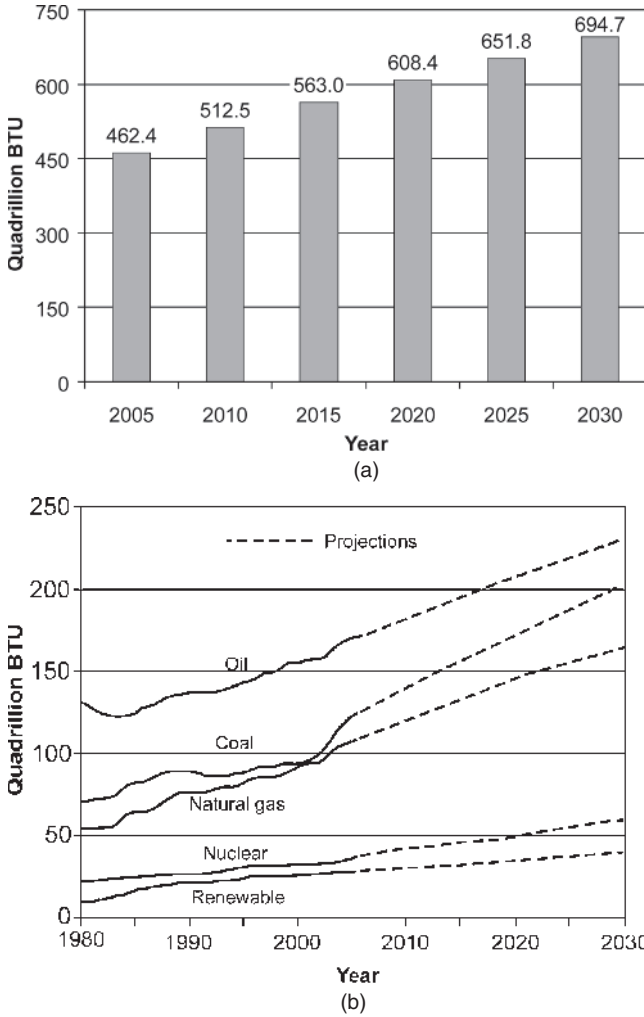


Figure 1.1. Projected global energy (a) demand and (b) supply.¹

operational safety and permanent waste disposal concerns, however, would limit nuclear energy's widespread utilization in overall energy production.^{2,4}

1.1.1 Renewable Energy

Renewable energy (i.e., hydro, wind, solar, biomass, and geothermal) is attractive because of its regenerative and environment-friendly nature. Among the renewable energy sources, hydraulic power provides the largest share of the total renewable energy supply.⁵ For example, in 2005, the world's total hydro-electricity capacity was 750 GW accounting for 63% of the total renewable

energy supply or 19% of the world's electricity supply for that year.⁵ In the United States, hydropower electricity generation is equivalent to 95,000 MW and accounts for 7% of total U.S. electricity generation, supplying 28 million households.⁶ Hydraulic power is less costly compared with other renewable energy sources. Once the hydroelectric plant is built, it does not require a significant amount of operational costs or raw materials. Also, when the overall energy life cycle is considered, a hydroelectric plant emits less greenhouse gases compared with a fossil fuel power plant. Despite these advantages, hydraulic power is subject to geological constraints. Moreover, the construction of hydroelectric plants often can be disruptive to the surrounding ecosystems and the life of inhabitants.⁷

Biomass, defined as “any organic matter, which is available on a renewable basis, including agricultural crops and agricultural wastes and residues, wood and wood wastes and residues, animal wastes, municipal wastes, and aquatic plants”⁸, is a versatile renewable resource that can be converted into electricity, H₂, and biofuels. Biomass can be directly combusted to generate heat or electricity; it also can be gasified to produce syngas for power generation or liquid fuel synthesis. Other than direct combustion and gasification, alcohol-based biofuels such as bioethanol and biobutanol can be produced from sugar or starch crops through fermentation; biodiesel is produced from vegetable oils and animal fats through transesterification; and biogas can be produced from anaerobic digestion of waste or other organic material.⁹ Biomass is often considered to be a carbon neutral energy source, because plant matter is produced from atmospheric CO₂ through photosynthesis. Although biomass is advantageous in several ways, the carbon savings, which are affected by the agricultural practices, for starch-crop-based bioethanol fermentation are doubtful. The life-cycle analysis indicates that the energy consumed in cultivation, transportation and conversion of biomass into bioethanol may be greater than the energy contained in the resulting fuel.^{10,11} According to a more recent study, bioethanol has a positive net energy when the conversion by-products are accounted for properly.¹² The study, however, estimated that ~42 joules (J) of energy from fossil fuels will be consumed to produce 100 J of ethanol from corn through fermentation.

The more advanced cellulosic ethanol production technique, which is under development, converts cellulose such as agricultural residues, forestry wastes, municipal wastes, paper pulp, and fast-growing prairie grasses into ethanol. As a result of the significantly reduced feedstock cost, the cellulosic ethanol production process can be more economical than traditional biofuel production techniques. Moreover, the energy input for generating the biofuel potentially can be reduced, leading to reduction in net CO₂ emissions.¹³ There are, however, technological challenges in the cellulosic biomass pretreatment prior to fermentation. The thermochemical conversion, such as gasification (as in coal gasification), of cellulosic biomass has been considered an attractive approach to generating not only biofuels but also biochemicals and electricity.

Wind, as another source of renewable energy, is used mainly for electricity generation through turbines on wind farms. Wind power can generate electricity at ~5.6 cents per kilowatt-hour.⁴ Under the current tax credit subsidy of 1.9 cents per kilowatt-hour (in 2006 dollars) in the United States, wind power is economically competitive with coal-fired power plants. Within the last decade, the global generation of wind power has increased at an average rate of more than 25% per year.¹⁴ The global capacity of wind turbines reached a record high of 73.9 GW at the end of 2006.¹⁵ The major drawbacks of wind power are its intermittency and highly variable nature, which imposes difficult challenges on grid management. Wind turbines also can be noisy and visually intrusive, but the offshore installation option (turbines installed more than 10 km away from shore) and the recently proposed airborne turbine option¹⁶ would eliminate these aesthetic concerns.

The sum of the solar power that reaches the earth's surface is estimated to be more than 5,000 times the current world energy consumption, and solar electric generation has a higher average power density than any other renewable energy source.¹⁷ Solar energy often is used to generate electricity via photovoltaic cells (solar cells) or heat engines (steam engines or Stirling engines). Apart from electricity generation, solar energy also can be converted into chemical energy such as hydrogen and syngas through solar chemical processes.¹⁸ The major disadvantage of solar power, however, is the high cost of the photovoltaics, which leads to the electricity generated from solar power costing approximately four times that of electricity generated from fossil fuels.¹⁴ The solar chemical processes are still under demonstration in the prototype phase.

Although renewable energy sources are attractive from the environmental viewpoint, they face complex constraints for large-scale application. Even when both the decrease in renewable energy costs and the increase in fossil fuel prices are taken into account, only approximately 8.5% (see Figure 1.1) of the total energy demands in 2030 are projected to come from renewable sources. For primarily economic reasons, fossil fuels, including crude oil, natural gas, and coal, will continue to play a dominant role in the world's energy supply for the foreseeable future.

1.1.2 Fossil Energy Outlook

Among various fossil energy sources, oil is expected to maintain its leading status and its consumption will increase for the foreseeable future. Compared with natural gas and coal, crude oil is relatively easy to be pumped, transported, and processed into high-energy density liquid fuels and chemicals. The 2008 British Petroleum (BP) energy review¹⁹ reported the estimated total oil reserves to be 1.24 trillion barrels, with more than 60% of these reserves located in the Middle East, but the high crude oil prices¹ and limited oil reserves are expected to decrease the share of crude oil in the overall energy supply from 37% to 33%.¹

Dramatic technological advancements have improved the economics of synthetic crude oil production from nonconventional fossil fuels, such as tar sands, extra heavy oil, and oil shale. These new fuels are abundant compared with conventional crude oil reserves. Among them, tar sands and extra heavy oil are relatively cheap to process. The conversion of oil shale into syncrude is economically viable only when crude oil prices are higher than \$70/barrel (in 2004 dollars) using current technologies.⁴ The reserves of tar sands are estimated to be equivalent to about 2.7 trillion barrels of oil, and 81% of the reserves are in Canada; however, only 315 billion barrels are economically recoverable by current technologies.⁴ The estimated tar sand reserves in the United States are between 60 and 80 billion barrels, and approximately 11 billion barrels are recoverable.²⁰ In addition, the Orinoco belt in Venezuela contains large quantities of extra heavy oil. Approximately 270 billion barrels of oil can be recovered from extra heavy oil in this region.²¹ According to the estimates by the U.S. Energy Information Administration, 2.9 trillion barrels of recoverable oil are available from oil shale worldwide. The United States, which has the largest oil shale reserves, has approximately 750 billion barrels of recoverable oil.⁴

The proven natural gas reserves are 180 trillion m³ worldwide, which is equivalent to 1.12 trillion oil barrels. Among these reserves, 0.34 trillion barrels lie in the United States.¹⁹ Natural gas has been a common energy source for heating, electricity generation, and hydrogen production. Major research, development, and commercial efforts in recent years have included an interest in liquefied natural gas and natural gas conversion to chemicals and liquid fuels such as methanol, dimethyl ether, ethylene, propylene, gasoline, and diesel. The efforts devoted to liquid fuel production from natural gas are manifested by the major ongoing gas-to-liquid (GTL) commercial activities with an overall liquid production capacity of more than 70,000 bbl/day (barrels per day) in 2006.²² Figure 1.2 shows the commercial activities in GTL technology using mostly stranded natural gas. The GTL technology is less carbon intensive and is less sensitive to crude oil prices, but the commercial GTL technology is very expensive. For example, the Quarter Petroleum sources in 2009 indicated that the estimated final project cost for the Pearl GTL plant in Qatar that was designed to produce 140,000 bbl/d of the petroleum liquids in 2011 was projected to be more than three times of the original estimate.

The price of natural gas varies significantly with locations and sources. The average natural gas price has been rising during the last several years and is projected to increase continuously for the foreseeable future. Despite the projected price increase, the share of natural gas in world energy consumption is expected to remain at 24% from 2005 to 2030.¹

The demand for coal is expected to increase faster than the demand for both crude oil and natural gas because of coal's relatively low price and abundant supply in some of the largest energy-consuming and developing countries, including China and India. Figure 1.3 and Table 1.1 provide a comparison of world fossil fuel reserves by geological regions. It is expected that the share

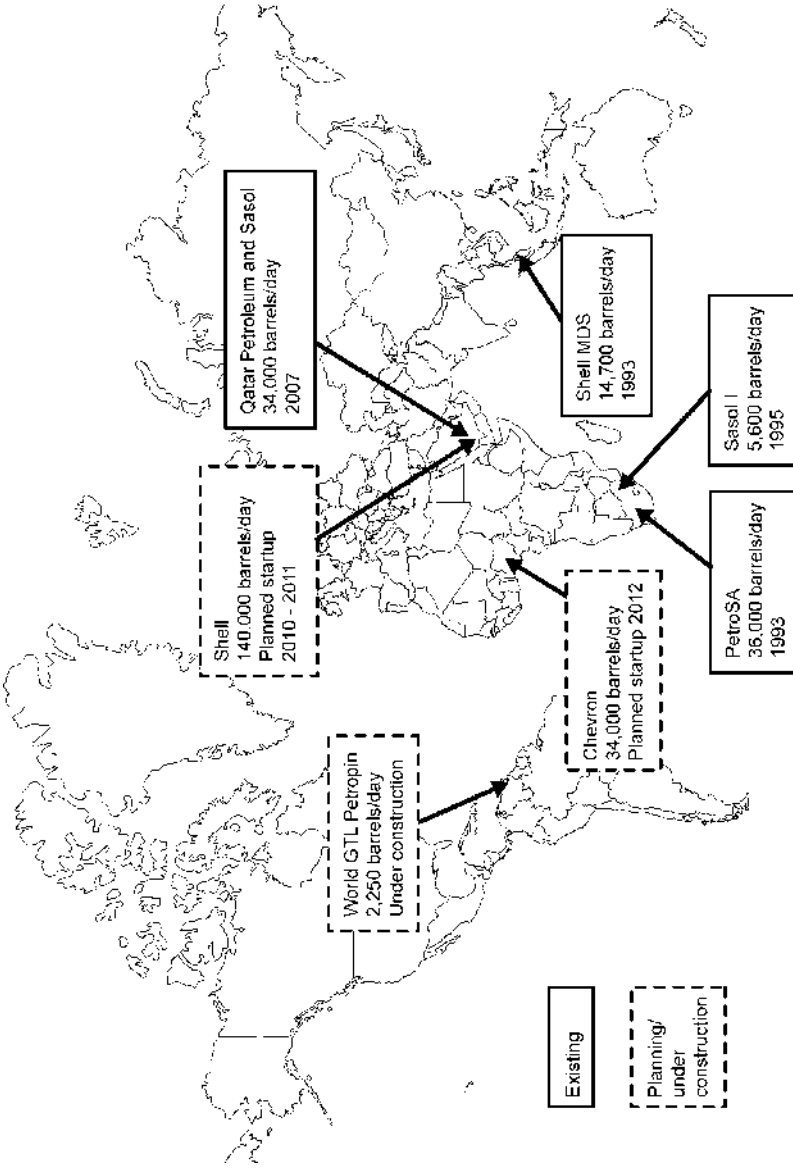


Figure 1.2. Locations and capacities of ongoing commercial technology developments directly associated with natural gas conversion to liquid phase products such as paraffin and olefin.²

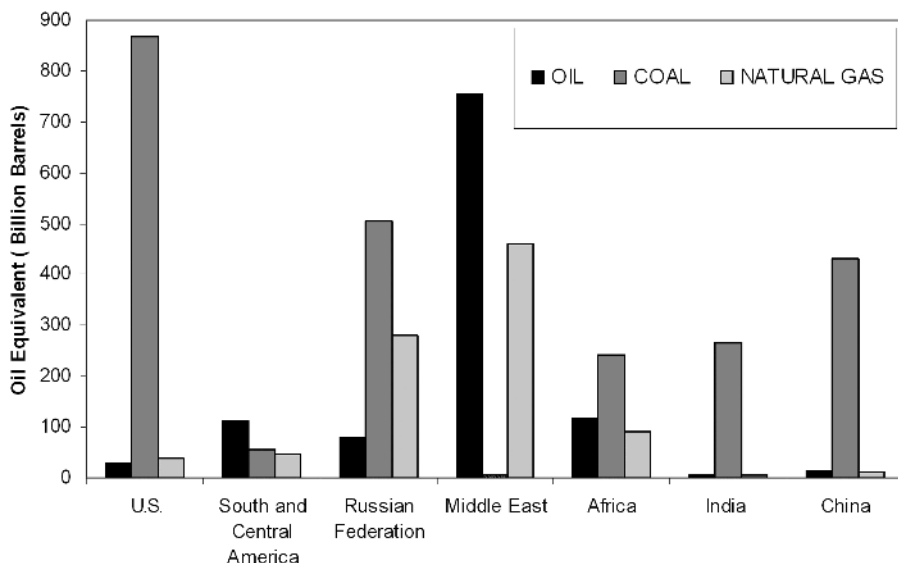


Figure 1.3. World fossil fuel reserve distributions (1 million ton of oil equivalent equals 1.111 billion m³ of natural gas, 1.5 million ton of hard coal, or 3 million ton of lignite).¹⁹

TABLE 1.1. World Fossil Fuel Reserves¹⁹

	Oil (10 ⁹ Barrels)	Natural Gas (10 ¹² m ³)	Coal (10 ⁶ t)
United States	29.4	5.98	242,721
South and Central America	111.2	7.73	16,276
Russian Federation	79.4	44.65	157,010
Middle East	755.3	73.21	1,386
Africa	117.5	14.58	49,605
China	15.5	1.88	114,500
India	5.5	1.06	56,498
Rest of the World	124.1	28.27	209,492
Total	1,237.9	177.36	847,488

of the energy supplied by coal will increase from 26% to 29% in the next three decades (2005–2030).¹

The United States possesses more than 26% of the total coal reserves in the world, and, based on the current consumption rate, these reserves will last for approximately 250 more years.²³ Currently, more than a third (40%) of the electricity generated worldwide comes from coal, whereas in the United States about half of the electricity is generated from coal. Most of the current coal-based power plants are combustion power plants. With improvements over traditional coal combustion technology and the development of new technologies, such as the integrated gasification combined cycle (IGCC), the dominance

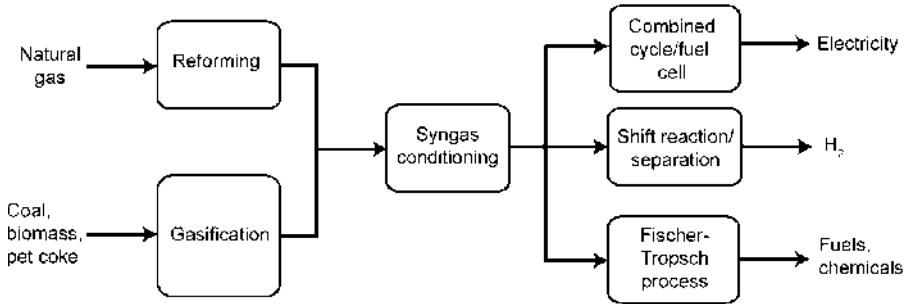


Figure 1.4. Cogeneration of electric power, chemicals, and fuels from coal gasification or natural gas reforming.

of coal in electricity generation is expected to continue well into the 21st century.⁴ In the United States, the Energy Vision 2020 of the U.S. Department of Energy (DOE) has embraced clean coal technology as part of the response to the urgent need for independence from nondomestic energy resources.

Similar to natural gas, coal also can be used for liquid fuel and chemical synthesis. In the well-known commercial indirect coal-to-liquid (CTL) process, coal is first gasified into syngas, a gas mixture that contains H₂ and CO. The coal-derived syngas is then conditioned and liquefied through Fischer–Tropsch synthesis. An alternative method for coal liquefaction involves direct liquefaction of coal using hydrogen under very high pressure (up to 210 atm) in the presence of catalysts. The first direct coal liquefaction commercial plant was commissioned for operation at 6,000 ton of coal per day in 2009 in China. The cost of such a direct coal liquefaction process, however, is higher than that of the indirect CTL process, but the direct coal liquefaction process produces more liquid fuels.²⁴ Figure 1.4 presents the process flow diagrams to coproduce various products from different carbonaceous feedstock from coal gasification or natural gas reforming. Although liquid fuel synthesis processes using coal, biomass, or natural gas are much more capital intensive than oil refining, they can become economical if the crude oil price is high. As shown in Figure 1.4, syngas derived from coal gasification or natural gas reforming shares a similar downstream processing scheme in the cogeneration of electricity, hydrogen, chemicals, and/or liquid fuels. There are processing similarities of biomass, petroleum coke, and other carbonaceous feedstock to coal. In the next section, the energy conversion processes concerned with coal as feedstock are discussed.

1.2 Coal Combustion

In a power plant, coal can be burned in a variety of combustors or boilers such as a pulverized combustor, a stoker combustor, or a fluidized bed combustor.²⁵

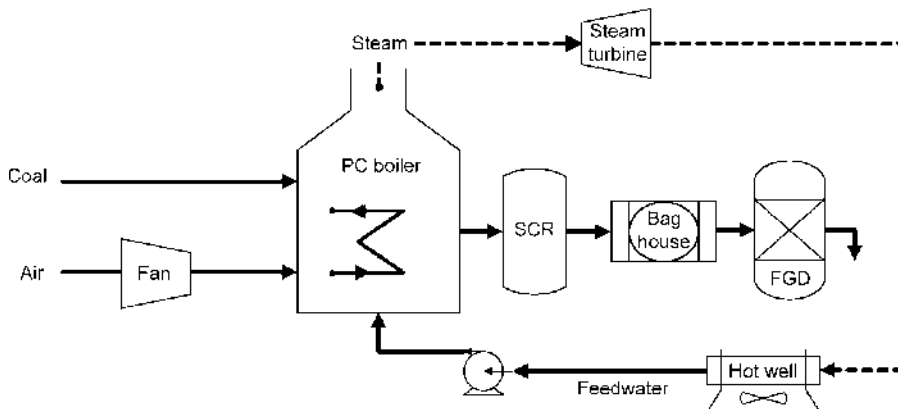


Figure 1.5. Simplified schematic diagram of a pulverized coal combustion process for power generation (PC: pulverized coal; SCR: selective catalytic reduction; FGD: flue gas desulfurization; - - - steam).

The heat of combustion is used to generate high-pressure, high-temperature steam that drives the steam turbine system to generate electricity. Currently, pulverized coal (PC) fired power plants account for more than 90% of the electricity generated from coal.²⁶ The schematic flow diagram of a PC power plant is illustrated in Figure 1.5.

In a PC power plant, coal is first pulverized into fine powder with more than 70% of the particles smaller than $74\mu\text{m}$ (200 mesh). The pulverized coal powder is then combusted in the boiler in the presence of $\sim 20\%$ excess air.²⁵ The heat of combustion is used to generate high-pressure, high-temperature steam that drives the steam turbine system based on a regenerative Rankine cycle for electricity generation. Although the underlying concept seems to be simple, the following challenges need to be addressed for modern PC power plants: enhancement of energy conversion efficiency; effective control of hazardous pollutants emission; and CO_2 capture (and sequestration).

1.2.1 Energy Conversion Efficiency Improvement

An increase in combustion process efficiency leads to reduced coal consumption, reduced pollutant emissions, and potential cost reduction for electricity generation. The first-generation coal-fired power plants constructed in the early 1900s converted only 8% of the chemical energy in coal into electricity (based on the higher heating value, HHV).²⁷ Since then, a significant improvement in plant efficiency has been made. Thermodynamic principles require higher steam pressures and temperatures for a higher plant efficiency. The corrosion resistance of the materials for boiler tubes, however, constrains the maximum pressure and temperature of the steam. Most of the PC power plants currently under operation use subcritical PC (Sub-CPC) boilers that produce

steam with pressures up to 22 MPa and temperatures around 550°C. The energy conversion efficiencies of traditional sub-CPC power plants typically range from 33% to 37% (HHV).²⁸

With an increase in the steam pressure, supercritical PC (SCPC) power plants were first introduced in the early 1960s in the United States.²⁷ Supercritical power plants use steam with a typical pressure of ~24.3 MPa and temperatures up to 565°C, leading to a plant efficiency of 37%–40%.²⁸ Many supercritical power plants were constructed in the 1960s and 1970s in the United States. However, because of the low reliability of the boiler materials, the further application of the SCPC technology essentially was halted in the United States in the early 1980s. The development of high-performance super alloys coupled with increasing environmental concerns and the rising cost of coal during the last two decades has stimulated the revival of supercritical technology, especially in Europe and Japan, leading to the reduction of sub-critical boilers in newly installed plants.

Recent advances in coal combustion technologies are highlighted by the generation of ultra-supercritical (USCPC) steam conditions that can provide even higher process efficiencies. The ultra-supercritical condition refers to operating steam-cycle conditions above 565°C (>1,050°F).²⁸ The pressure and temperature of the steam generated from existing ultra-supercritical power plants can reach 32 MPa and 610°C, which corresponds to an energy conversion efficiency of more than 43%.^{28,29} The global ongoing research and development (R&D) activities on PC boilers focus on the development of superalloys that can sustain steam pressures up to 38.5 MPa and temperatures as high as 720°C. It is expected that a plant efficiency of more than 46% can be achieved under such conditions.^{28–30} Other efforts in ultra-supercritical technology include minimizing the usage of superalloys, improving the welding technique, and optimizing the boiler structure design to minimize the length of the steam line to the steam turbine.²⁹

Apart from PC boilers, fluidized bed combustors (FBCs) using either turbulent fluidized beds or circulating fluidized beds (CFBs) also are being used for steam and power generation worldwide. In these processes, limestone is injected to capture SO_x formed during coal combustion. Compared with PC boilers, the FBC has lower SO_x and NO_x emissions.^{31,32} Furthermore, it has superior fuel flexibility.³³ Most commercial FBC plants operate under atmospheric pressure, with energy conversion efficiencies similar to sub-CPC power plants. Higher efficiencies can be achieved by operating the FBC at increased pressures.^{33–35} The pressurized fluidized-bed combustor (PFBC) generates a high-temperature, high-pressure exhaust gas stream, that drives a gas-turbine/steam-turbine combined cycle system for power generation. In an advanced PFBC configuration, fuel gas is generated from coal via particle oxidation and pyrolysis. The fuel gas is combusted to drive a gas turbine (topping cycle). Such a process has the potential to achieve an energy conversion efficiency of more than 46%.³⁴ The capital investment for PFBC is higher than PC power plants with a similar efficiency.³⁶ Other potential challenges to the PFBC technology

TABLE 1.2. Energy Conversion Efficiencies (HHV) of Various Coal Combustion Technologies and Energy Penalty for CO₂ Capture Using MEA^{28,38–43}

Technology	Sub-CPC	SCPC	USCPC	AFBC	PFBC
Base case efficiency (%) HHV	33–37	37–40	40–45	34–38	38–45
MEA retrofit derating (%) ^a	30–42	24–34	21–30	~35 ^b	~30 ^b

^aDecrease in energy conversion efficiency when a retrofit MEA system is used to capture 90% of the CO₂ in the flue gas.

^bEstimate based on ASPEN simulation.

include scale-up, high-temperature particulates/alkali/sulfur removal for gas turbine operation and mercury removal from the flue gas.^{33,37} Currently, the usage of the PFBC is low. Table 1.2 compares the performance of different coal combustion technologies.

1.2.2 Flue Gas Pollutant Control Methods

Modern coal-combustion power plants need to be able to capture environmentally hazardous pollutants released from coal combustion. Such pollutants include sulfur oxides, nitrogen oxides, fine particulates, and trace heavy metals such as mercury, selenium, and arsenic. Methods for capturing these contaminants from the flue gas streams abound. The challenges, however, lie in the efficient and cost-effective removal of these contaminants.

The traditional method for SO_x removal uses wet scrubbers with alkaline slurries. The wet scrubber is effective, but it is costly and yields wet scrubbing wastes that must be disposed. Alternative methods include more cost-effective lime spray drying and dry sorbent duct injection. The lime spray drying method employs a slurry alkaline spray yielding scrubbing wastes in solid form, which eases waste handling. Dry sorbent duct injection employs a dry alkaline sorbent for direct in-duct injection, circumventing the use of the scrubber. Recent pilot tests have used reengineered limestone sorbents (i.e., PCC precipitated calcium carbonate) of high reactivity, yielding a sorbent sulfation efficiency of more than 90%, compared with less than 70% with ordinary limestone sorbent. The result indicates a viability of the dry sorbent duct injection method with very active sorbents.^{44–46} The NO_x is commonly removed by selective catalytic reduction (SCR). Other methods that can be employed include a low NO_x burner and O₃ oxidation. The recent pilot testing of the CARBONOX process using coal char impregnated with alkaline metal revealed a high NO_x removal efficiency at low flue gas temperatures.⁴⁷ The trace heavy metals such as mercury, selenium, and arsenic can be removed by calcium-based sorbents and/or activated carbon.^{44,48}

The techniques to control the flue gas pollutants indicated above are well developed. An effective capture (and sequestration) of CO₂, an important greenhouse gas (GHG) that accounts for 64% of the enhanced greenhouse effect⁴⁹ is, however, a challenging task.

1.3 CO₂ Capture

As noted, excessive accumulation of CO₂ in the atmosphere can cause serious climate changes. Anthropogenic activities, primarily resulting from fossil fuel usage, have contributed to the increase of the atmospheric CO₂ concentration from the preindustrial level of 280 ppm to the current value of 380 ppm.⁵⁰ Moreover, under the current carbon emission growth rate, the atmospheric CO₂ concentration could reach 580 ppm—a threshold value to trigger severe climatic changes—within just 50 years.⁵¹

After years of controversy, the Intergovernmental Panel on Climate Change (IPCC) conclusively determined in 2007 that the increase in anthropogenic greenhouse gases was the cause for the worldwide temperature rise. Because of its relative abundance compared with other greenhouse gases, CO₂ is by far the most important of these gases and accounts for up to 64% of the enhanced greenhouse effect.⁴⁹ The CO₂ represents ~15% of the flue gas stream from coal-combustion power plants and the total amount of CO₂ produced from coal-based power plants accounts for more than 40% of all anthropogenic CO₂ emissions.⁵² Proper CO₂ management is, therefore, important. In a fossil-fuel-based power plant, the CO₂ management involves three steps: capture including separation and compression; transportation; and sequestration. Among the three steps, the CO₂ capture is the most energy-consuming.^{28,53}

The existing techniques for CO₂ capture from PC power plants include the well-established monoethanolamine (MEA) scrubbing technology. Figure 1.6(a) shows the schematic diagram of the MEA scrubbing process with key stream conditions.^{54–56} In this process, the flue gas is first cooled to ~40°C before entering the absorber where fresh amine solvent is used to absorb CO₂ in the flue gas stream. The spent amine solvent with a high CO₂ concentration is then regenerated in the stripper under a higher temperature (100–150°C), and CO₂ is then recovered at low pressures (1–2 atm). A large amount of high-temperature steam is required to strip the CO₂ in the regeneration step.⁵⁶ Thus, although the theoretical minimum work for MEA scrubbing is as low as 0.11 MWh/ton CO₂ or equivalently, a parasitic energy consumption of ~12%⁵⁷ used for steam generation and CO₂ compression for transportation, it is estimated that the actual energy consumption using amine scrubbing can reduce the power generated from the entire plant by as much as 42%.⁴⁰ This energy consumption amounts to ~70%–80% of the total cost in the overall three steps of carbon management, that is, carbon capture, transportation, and sequestration.^{53,58} As a result, a process that can reduce the energy consumption in the CO₂ capture step will be vital for CO₂ management in coal-fired power plants.

The chilled ammonia process, illustrated in Figure 1.6(b), is another solvent-based CO₂ capture technology, in which ammonium carbonates and bicarbonate slurries are used to capture the CO₂ in the flue gas stream at 0–10°C and atmospheric pressure. The CO₂-rich solvent is then regenerated at 110–125°C and 20–40 atm. The capability to regenerate CO₂ at increased pressures reduces the energy consumption for CO₂ compression. Based on the studies by the

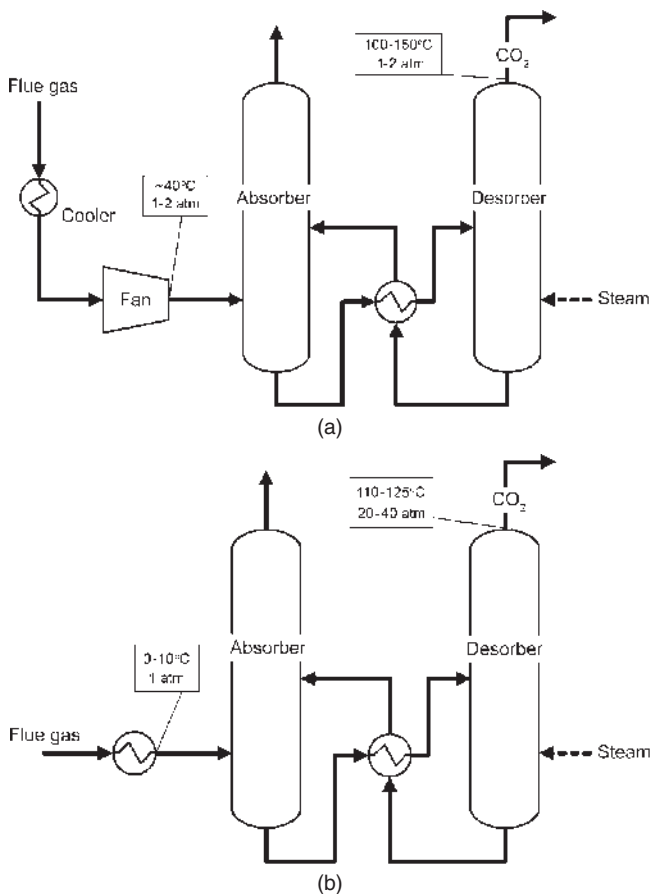


Figure 1.6. Conceptual schematic of (a) MEA scrubbing technology for CO₂ separation and (b) chilled ammonia technology for CO₂ separation.

Electric Power Research Institute (EPRI) and ALSTOM, the overall energy penalty for CO₂ capture is estimated to be lower than 16% when the chilled ammonia process is used.^{59,60} A 5-MW_{th} (megawatts thermal) equivalent chilled ammonia process demonstration plant, jointly supported by ALSTOM and EPRI, is currently under construction at We Energies' Pleasant Prairie Power Plant in Wisconsin.⁶¹ American Electric Power (AEP) is also planning to demonstrate the chilled ammonia process at the 20-MW_e (megawatts electricity) scale, starting in 2009, before building a 200-MW_e commercial-level chilled ammonia retrofit system in 2012.⁶²

Similar to solvent-based CO₂ scrubbing techniques, high-temperature sorbents such as limestone, potassium carbonates, lithium silicates, and sodium carbonates can be used to capture CO₂ in the flue gas at increased temperatures.^{63,64} With good heat integration, these solid sorbents can be effective in

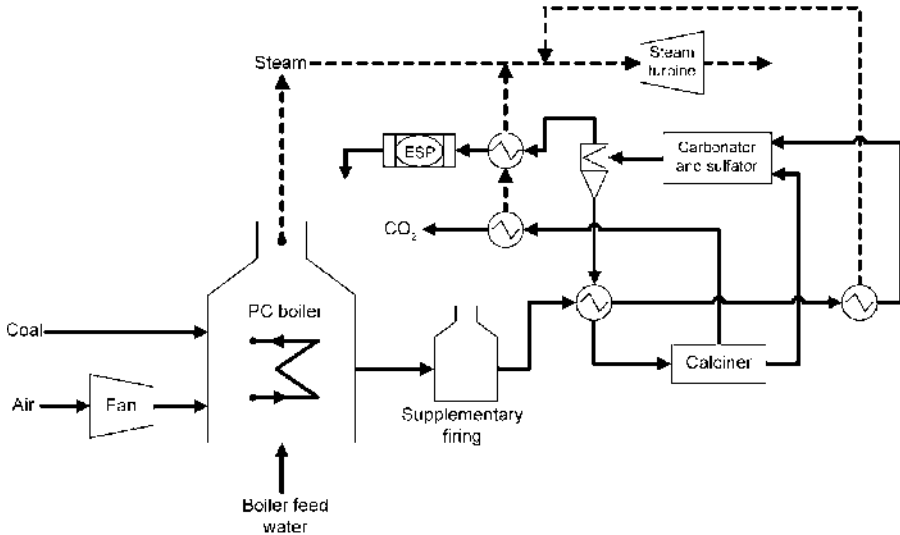


Figure 1.7. Conceptual scheme of carbonation–calcination reactions integrated with a 300-MWe coal-fired power plant depicting heat integration strategies (--- steam).

the CO_2 capture. One heat integration scheme is of particular relevance, which is based on the carbonation–calcination reactions using hydrated lime, natural limestone, or reengineered limestone sorbents at $600\text{--}700^\circ\text{C}$ for CO_2 capture.⁶⁵ Figure 1.7 delineates the heat integration scheme for retrofitting the carbonation–calcination reactions to an existing PC power plant. In the process, both CO_2 and SO_2 in the flue gas are captured by the calcium-based sorbents in the carbonator operated at $\sim 650^\circ\text{C}$, forming CaCO_3 and $\text{CaSO}_3/\text{CaSO}_4$. The carbonated sorbent, CaCO_3 , is then regenerated to calcium oxide (CaO) sorbent in the calciner at $850\text{--}900^\circ\text{C}$, yielding a pure CO_2 stream. In the Carbonation–Calcination Reaction (CCR) Process developed at the Ohio State University (OSU), the regenerated CaO may or may not be followed by the hydration reaction before it is injected to the flue gas stream. The sulfated sorbent and fly ashes are removed from the system by means of a purge stream. With an optimized energy management scheme, the CCR Process consumes $15\%\text{--}22\%$ of the energy generated in the plant.^{66,67} The Process is being demonstrated in a $120\text{-KW}_{\text{th}}$ (kilowatts thermal) plant at OSU (see Section 6.3). Another calcium-based process using CaCO_3 is being demonstrated at CANMET Energy Technology Center in Canada.⁶⁸ The CANMET process captures CO_2 at a substantially higher Ca:C molar ratio compared with that in the CCR Process. At low temperatures ($\sim 590^\circ\text{C}$), separation of CO_2 also can be carried out by an adsorption approach using a K_2CO_3 promoted hydrotalcite sorbent through a pressure/temperature swing process.⁶⁹

To generalize, several retrofit systems under different stages of development can be used to capture CO_2 from existing power plants. As PC power plants will continue to provide a significant portion of the electricity needs

well into the 21st century,⁷⁰ these CO₂ capture systems are essential to mitigate the environmental impact from coal burning. As noted, CO₂ capture and compression from coal combustion flue gas are costly and energy intensive. Promising approaches to reduce the overall carbon footprint of a coal-based plant are to devise coal conversion processes that are intrinsically advantageous from a carbon management and energy conversion standpoint. Such approaches are described in Sections 1.5–1.7.

In addition to the previous CO₂ capture methods, oxy-fuel combustion provides another means for carbon management in coal-fired power plants. In this method, pure oxygen, instead of air, is used for coal combustion. As a result, a concentrated CO₂ stream is generated, avoiding the need for CO₂ separation, but the energy-consuming cryogenic air separation step will reduce the overall plant efficiency by 20%–35%.^{28,41,53} This process has been demonstrated by the Babcock & Wilcox Company on a 1.5-MW_{th} pilot scale PC unit. Demonstration on a 30-MW_{th} unit is under way. The ongoing pilot-scale studies on oxy-fuel combustion include those carried out by ALSTOM, Foster-Wheeler, CANMET Energy Technology Center, Vattenfall, and Ishikawajima-Harima Heavy Industries (IHI).⁷¹

1.4 CO₂ Sequestration

Although the cost of CO₂ sequestration represents a relatively small portion of the total carbon management cost, it is necessary to achieve permanent and efficient sequestration of the stream containing CO₂. For storage capacities, geological,⁷² mineral⁷³ and ocean⁷⁴ based sequestration—each capable of storing much more than ~10³ Gt (gigatons)—could reduce significantly current anthropogenic carbon emission levels, which are estimated to be 6 to 8 Gt of carbon per year, for several hundred years.⁷⁵

The oceans, being natural absorbers of CO₂, are already processing a large fraction of the emission. Various injection methods have been investigated to enhance oceanic CO₂ uptake, including dissolution of CO₂ at a depth below the mixed layer of oceans and bottom injection of CO₂, forming lakes of dense CO₂. This CO₂ reacts with seawater to form a clathrate, a cage structure with approximately six water molecules per CO₂. Although ocean sequestration is promising in terms of carbon sequestration capacity, the environmental impact caused by changed ocean chemistry may be the most significant factor determining the acceptability of oceanic storage.

Currently, considerable interest in storage means is focused on geological sequestration. The ideal geological formations that can be used for geological CO₂ sequestration include depleted oil and gas reservoirs (200–500 Gt of carbon, GtC), deep unmineable coal seams (100–300 GtC), and deep saline aquifers (10²–10³ GtC). Mined salt domes and rock caverns also are considered to be viable options.⁷⁵ Injecting CO₂ into such depleted reservoirs is similar to the well-established and effective practice of using supercritical CO₂ for enhanced oil and gas recovery (EOR). The uncertainty of this practice for CO₂

storage, however, lies in the long-term stability of the reservoirs.⁷⁶ When injected into the coal bed, CO_2 can replace adsorbed CH_4 in a molar ratio of $\sim 2:1$. By doing so, coal beds can serve as both a CO_2 reservoir and a source for methane production.⁷⁴ The first large project that applies geological sequestration to contain carbon emissions uses a saline formation as the CO_2 repository. In this project, CO_2 from Statoil's Sleipner West gas reservoir in the North Sea is injected into an aquifer under the sea floor.⁷⁷ The graphic representation, given in Figure 1.8, illustrates the operation of the aquifer sequestration.

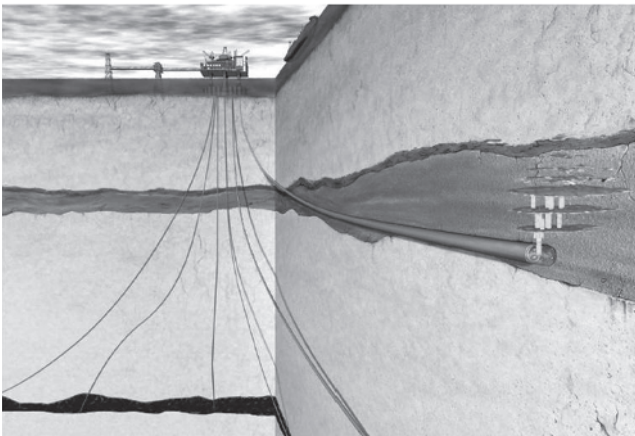
The Sleipner field – CO_2 Treatment and Injection



StatoilHydro

(a)

Sleipner CO_2 Injection



StatoilHydro

(b)

Figure 1.8. (a) The Sleipner gas field center in the North Sea. (b) the Sleipner CO_2 injection into the Utsira Saline formation at 1,000m below sea bottom.⁷⁷ Photos: courtesy of StatoilHydro.

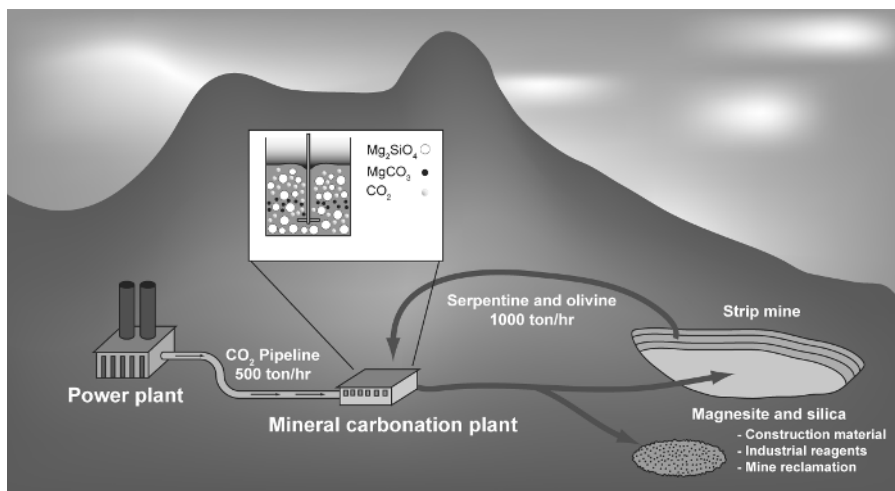


Figure 1.9. CO₂ sequestration by mineral carbonation.⁷⁹

Geological sequestration is attractive because of the technological readiness and low injection costs. There are, however, some concerns such as the consideration that most of the actual costs will be associated with future monitoring of the injected CO₂ because the accidental release of CO₂ could result in the devastating suffocation of humans and animals similar to the incidents that occurred in Nyos, Cameroon, in 1984 and 1986. Thus, monitoring technology will play a key role in the success of the geological sequestration method.⁷⁸

Mineral sequestration of CO₂ can be conducted in a chemical reactor, as shown in Figure 1.9, in order to achieve a high reaction rate of immobilization of carbon in a mineral matrix. The reaction between CO₂ and most minerals is slow in nature. Serpentine (Mg₃Si₂O₅(OH)₄) and olivine (Mg₂SiO₄), however, were found to be two of the most promising minerals that could be used in the mineral sequestration because of their ability to form carbonates and their abundant availability.⁷⁹ In the mineral sequestration process, Mg in serpentine is dissolved in solution and reacts with dissolved CO₂ to form MgCO₃, which is environmentally benign. A pH swing process that dissolves Mg at a low pH and precipitates MgCO₃ under a high pH offers a viable approach for mineral sequestration of CO₂, while producing value-added solid products.⁸⁰ The cost of the carbon mineral sequestration process is still higher than that of the geological sequestration process. Thus, optimization is ongoing to improve its economic feasibility.

Another important sequestration method is bio-based. This method also mimics the natural capture of carbon. One of the largest natural carbon flows through the environment is driven by photosynthesis. Plants take up CO₂ and water, and turn them into reduced carbon compounds such as starch and cellulose. Thus, forestation and agricultural fixation of carbon, either in biomass

or soil, can play a role in carbon sequestration. Currently, researchers are investigating various biosystems such as ocean fertilization and algae production to capture CO_2 at a rapid rate.

The preceding discussion suggests that there are several carbon sequestration methods currently being investigated and developed. It is desirable to consider multiple sequestration methods concurrently for carbon sequestration resulting from its massive flux of emission. A life-cycle analysis is needed to ascertain the amount of CO_2 sequestered relative to the cost and energy requirements for each sequestration method employed.

1.5 Coal Gasification

For many years, commercial efforts on clean coal processes have focused on coal combustion for power generation. Nonetheless, the development of new processes mindful of higher energy conversion efficiencies for electricity generation, as well as of variability in product formation, has generated considerable interest. Because of the unpredictable crude oil price and concern over carbon management, the development of clean coal technology (CCT) has led to serious consideration of gasification as a commercial coal processing route. Coal gasification schemes can provide a variety of products in addition to electric power. It is noted that from the carbon management viewpoint, gasification also is a preferred scheme over combustion because of a higher CO_2 concentration and a lower volumetric gas flow stream from which CO_2 is to be separated.

The commercial operation for gasification dates back to the late 18th century when coal was converted into town gas for lighting and cooking. Since the 1920s, there have been numerous different gasification processes developed for the production of syngas, hydrogen, chemicals, liquid fuels, and/or electricity.^{82,83} Figure 1.10 shows a general scheme of the coal gasification process.⁸¹ The heart of a coal gasification process is the coal gasifier. Figure 1.11 shows several types of gasifiers that can be classified generally based on the state of fluidization of the particles, including a moving bed gasifier, a bubbling/turbulent bed gasifier, and an entrained flow gasifier. The moving bed gasifier is characterized by dense downward movement of particles with a significant axial temperature gradient. The bubbling/turbulent bed gasifier is operated under the bubbling or the turbulent fluidization regime in dense-phase fluidization with a uniform temperature distribution in the bed.⁸⁴ The entrained flow gasifier, however, is operated under the pneumatic conveying regime in dilute-phase fluidization with a uniform temperature in the gasifier. The bubbling fluidization regime is characterized by the flow of gas bubbles with an increased tendency of bubble coalescence when the gas velocity increases, whereas the turbulent fluidization regime is characterized by the flow of gas bubbles with an increased tendency of bubble breakup when the gas velocity increases. The pneumatic conveying regime in dilute-phase fluidization is represented by

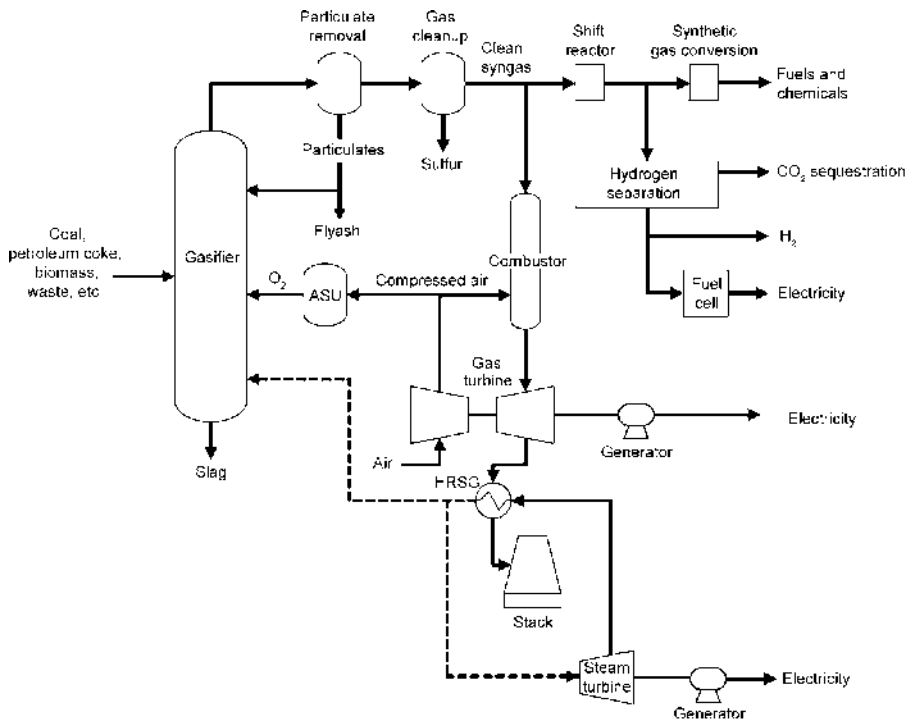


Figure 1.10. Schematic diagram of coal gasification processes (--- steam).⁸¹

dilute transport of solid particles in clustering or nonclustering form.⁸⁴ Most modern gasifiers adopt an entrained-flow design thanks to better fuel flexibility, carbon conversion, and syngas quality.⁸²

Figure 1.12 shows examples of three different designs for the entrained bed gasifier. The design varies with the manner in which coal/coal slurry and gaseous reactants are introduced and heat is removed. Furthermore, different gasifiers have different feeding rates of water/oxygen, and as a result, the composition of the syngas at the outlet of the gasifier varies. The Shell gasifier, shown in Figure 1.13, uses water to cool the membrane-based gasifier walls, and the dry coal powder feedstock is introduced along with oxygen at the side of the gasifier. In addition, the Shell gasifier typically adopts a gas quench configuration, in which a recycled cold syngas stream is introduced to the gasifier at the raw syngas exit to quench the molten ash entrained in the raw syngas. The quenching would prevent the molten ash from agglomeration.

The common features of entrained flow gasifiers include high operating temperature, low water feed rate, and a high CO/H₂ ratio in the raw syngas. In a typical gasification process using an entrained-flow gasifier, the high-temperature, high-pressure raw syngas (~1,300°C, ~25 atm) is produced from the gasifier and contains such pollutants as particulates, H₂S, COS, and mercury.

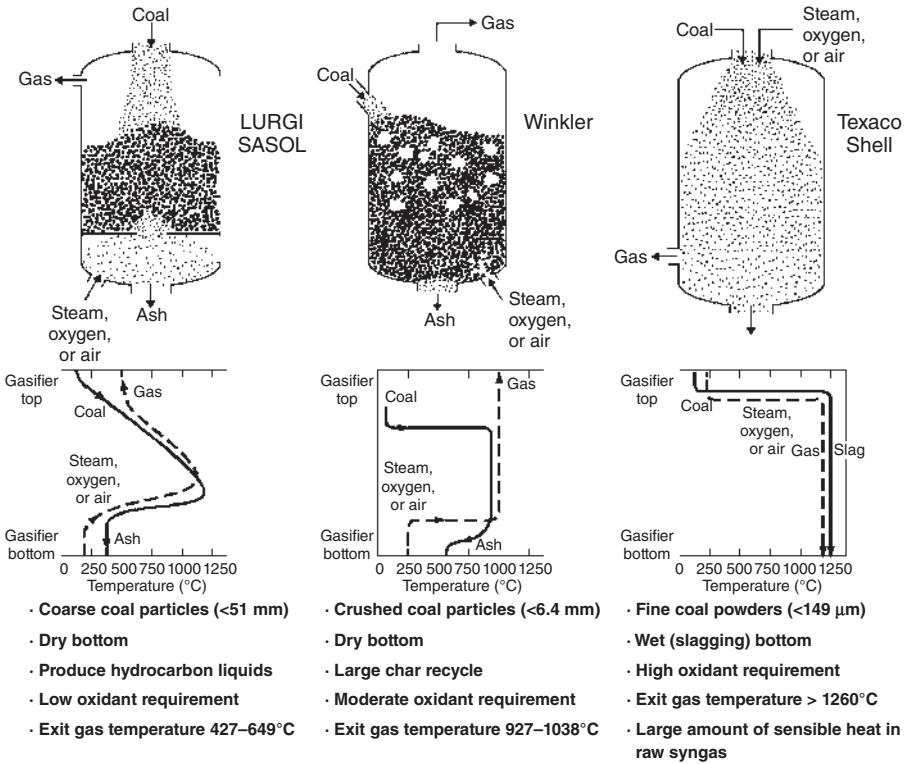


Figure 1.11. Schematic diagrams and temperature distributions of various gasifiers.²⁵

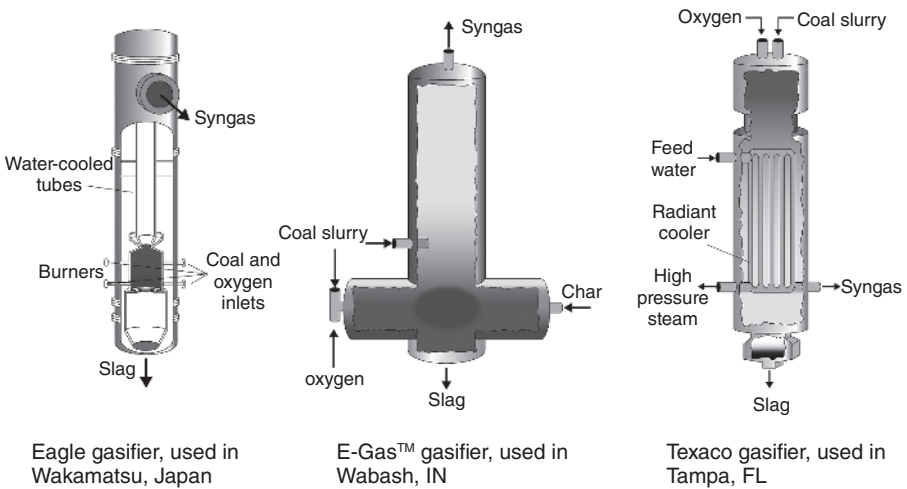


Figure 1.12. Schematic configurations of various entrained flow gasifiers.^{85–87}

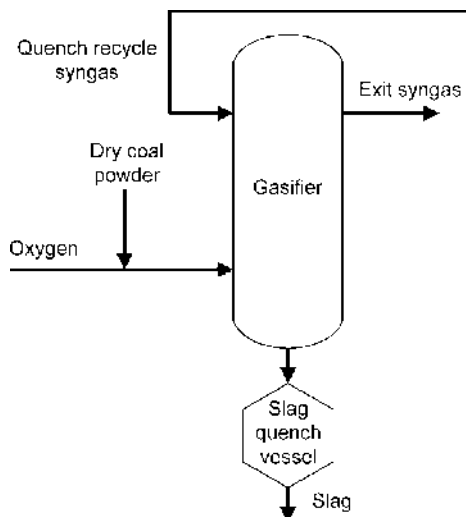


Figure 1.13. Schematic diagram of the key flow streams around the Shell gasifier.²⁵

The raw syngas is first cooled by water quenching or by passing it through heat exchangers. It then flows through a dry ceramic filter system or a wet scrubber system where fly ash is removed. A hydrolysis unit then is used to convert COS in the syngas into H₂S and CO₂. This syngas stream is further cooled to near ambient or even lower temperature and passes through a solvent-based sulfur removal unit.²⁵ Mercury and other trace metals in the H₂S cleaned syngas are removed subsequently by activated carbon using a fixed bed operated at ~35°C and 60 atm. The activated carbon usually is impregnated with 10–15 wt.% sulfur, which would react with mercury to form HgS, a stable compound that is suitable for long-term storage.⁸⁸ Different processing routes can be followed after the syngas is cleaned up. For electricity generation, the syngas can be introduced directly into a combustion turbine to generate electricity. The high-temperature exhaust gas from the combustion turbine is then sent to a heat recovery steam generator (HRSG) to produce high-temperature and high-pressure steam to drive a steam turbine to generate more electricity. The gasification process that involves both gas turbines and steam turbines for electricity generation is known as the IGCC process. The overall energy conversion efficiency for the IGCC can exceed ~45% when carbon capture is not required.⁸⁹ For hydrogen generation, the syngas is introduced to the water–gas shift (WGS) reactor that converts CO into hydrogen and CO₂. The gas then passes through the acid gas removal units and pressure swing adsorption (PSA) units to separate out H₂ from CO₂. The PSA tail gas with low H₂ concentration can be combusted in a gas turbine to generate electricity for parasitic energy use. The hydrogen can be a fuel source for either fuel cell or gas turbine operations. The hydrogen also can be used as a makeup gas to tune



Figure 1.14. Tampa Electric's Polk IGCC Power Station Unit 1. Photo courtesy of Mr. Mark J. Hornick of Tampa Electric.



Figure 1.15. Air Products's LPMEOH process demonstration unit for methanol synthesis using syngas from coal gasification with slurry bubble column reactor, located at the Eastman Chemical site in Kingsport, Tennessee. U.S. DOE Topical Report No. 11, April 1999, under DOE contract #DE-FC22-92PC90543. Photo: courtesy of Debbie Bauer, Corporate Communications of Air Products.

up the CO/H_2 ratio to 1/2 so that it can be used for Fischer–Tropsch synthesis, which converts CO and H_2 to liquid hydrocarbons or chemicals. It is noted that the raw syngas from the gasifier usually has a CO/H_2 ratio ranging from 1.4/1 to 2/1.²⁵ The key to innovative gasification technology development lies in well-conceived process integration and intensification.

The current development of coal gasification processes varies from conceptual to pilot demonstration to commercial scale. Figure 1.14 shows the coal/petcoke IGCC plant at Polk County, FL, which has been producing 260-MW electricity on grid. The plant uses the Texaco gasifier shown in Figure 1.12. The coal-to-liquid technology can be exemplified by the production of methanol from syngas derived from coal gasification. The commercial plant of Eastman Chemicals, which produces methanol at a capacity of 5,000 ton/d, is shown in Figure 1.15. Figure 1.16(a) shows a commercial slurry bubble column reactor with 5-m ID developed by Sasol for the production of gasoline, diesel, and wax at a capacity of 2,500 bbl/d using syngas from coal or natural gas as feedstock.



Figure 1.16. (a) Sasol's 5-m ID F-T reactor for coal-to-liquid synthesis. (b) Sasol's Oryx gas-to-liquid plant in Qatar, which consists of two low-temperature Fischer–Tropsch SPD (slurry-phase distillate) reactors with a capacity of 17,000 bbl/d each, producing a primary product of low-sulfur diesel oil using the feedstock of reformed natural gas. It shows one reactor of 10-m ID in front, with another of the same size behind it. Photo: courtesy of Sasol Limited.

A slurry bubble column reactor of 10-m ID for Fischer–Tropsch synthesis, which is shown in Figure 1.16(b), is currently operated at a capacity of 17,000 bbl/d for GTL applications.

Challenges to existing coal gasification processes include significant energy consumption in the alteration of temperatures and pressures of the syngas in the pollutant removal process. Technologies that can enhance pollutant and product separation and chemical reactions at increased temperatures are being developed. These technologies include high-temperature sorbents for H₂S removal; sulfur-tolerant catalysts for water-gas shift reactions; metallic, ceramic, polymeric, or hybrid membranes for CO₂, H₂ and/or H₂S separation; and catalysts with high selectivity for the Fischer–Tropsch synthesis. For the membrane technology, when applied to the water-gas shift reaction with *in situ* removal of either CO₂ or H₂ from the reacting product gases, it can enhance the water-gas shift reaction conversion significantly. The variables that dictate the membrane performance include the types of the materials used (organic, inorganic, or hybrid), the permeability and selectivity properties, the tolerance level toward pollutants, and the physical strength in enduring the high-pressure drop across the membrane. Factors that affect the economical viability of the membrane-based gasification technologies include the cost and reliability of the membranes. Membranes can be used in product separation when coupled with reactor operation. Process simulations indicate that by using H₂- or CO₂-selective membranes, the energy penalty for CO₂ capture in a coal-to-hydrogen process can be reduced.^{90–92}

In addition to vigorous commercial activities on the IGCC process, novel clean coal processes, characterized by high-energy conversion efficiencies and ease in implementing product and/or pollutant separation strategies, are now at various stages of development. The novel coal reforming processes being developed worldwide include the Zero Emission Coal Alliance (ZECA) Process, the HyPr-Ring Process, the GE Fuel-Flexible Process, the ALSTOM Process, the chemical looping combustion processes, and the OSU's Syngas Chemical Looping Process, CDCL Process, and Calcium Looping Process. These new processes employ the chemical looping concept, and some are at the demonstration level. In the next section, the fundamental concept and characteristics of chemical looping technology and its process applications are discussed.

1.6 Chemical Looping Concepts

A given reaction can be decomposed into multiple subreactions in a reaction scheme using chemical intermediates that are reacted and regenerated through the progress of the subreactions. A reaction scheme of this nature is referred to as chemical looping. An ideal chemical looping scheme is to design the subreactions in such a manner that the exergy loss of the process resulting

from this reaction scheme can be minimized while allowing the separation of the products and/or pollutants generated from the reactions to be accomplished with ease, thereby yielding an overall efficient and economical process system.

Achieving a high process efficiency for the energy conversion to products such as electricity, H_2 , and liquid fuels while maintaining low pollutant emissions represents a major challenge for any fossil fuel conversion system. This is particularly the case for coal, which is the most carbon intensive among all the available fossil energy resources. To achieve a high process efficiency, a proper energy management strategy is necessary. Furthermore, to assess the effect of the strategy, it is desirable to resort to the analysis of the energy conversion process based on the thermodynamic concept of exergy, or availability. Exergy and its application to such an analysis are briefly explained in the following discussion.

The exergy of a system is defined as the maximum amount of usable work extractable from the system during a transformation that brings the system into equilibrium with a reference state.⁹³ The ambient environment commonly is used as the reference state. The exergy rate is the ratio between the available work and the total amount of energy. The second law of thermodynamics indicates that energy degrades in all irreversible processes, or in equivalent terms, exergy loss will occur in any nonideal process. Although it is not possible to eliminate the energy degradation, the exergy loss in a process can be minimized through strategic energy management. A useful approach to improving an existing system is to identify the steps where the largest irreversibility occurs and to minimize these losses.

Energy with a low exergy rate can be integrated into energy with higher exergy rates to improve the overall energy conversion efficiency of the process.⁹⁴ The following two examples illustrate how energy integration can be used to minimize exergy loss whose results are calculated with the assumptions follows:

1. The environmental temperature is $T_0 = 273.15\text{ K}$, and the environmental pressure is $P_0 = 101,325\text{ Pa}$.
2. The reference substance for carbon and CO is 400 ppm CO_2 , the reference substance for H_2 is pure water, and the reference substance for Fe, FeO, and Fe_3O_4 is pure Fe_2O_3 .
3. The upper limit for the gas turbine operating temperature is 1,800 K.
4. Coal is considered as pure carbon.
5. Heat can be integrated with a 100% efficiency whenever feasible.
6. The enthalpy of devaluation is defined as the enthalpy change for a substance from the current state to its reference state.
7. The feedstock in the outside of the reaction loop is at the environmental state.

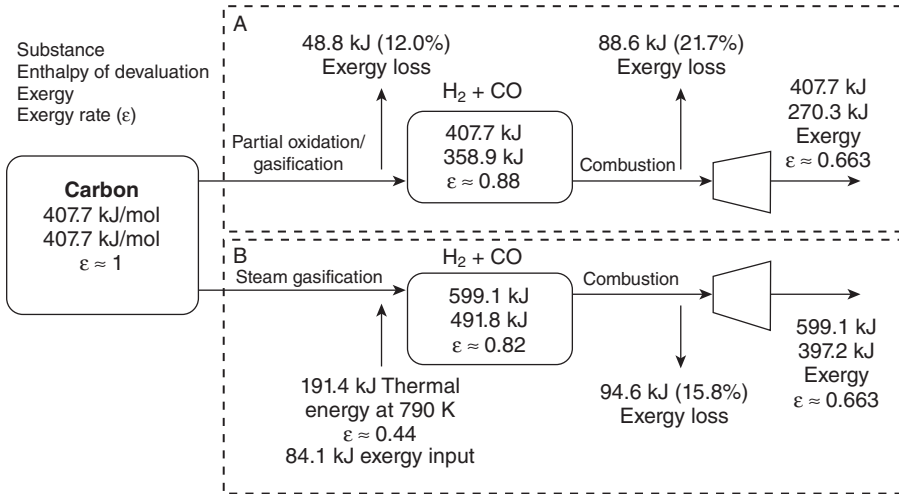


Figure 1.17. Exergy recovering schemes for carbon gasification/gas turbine system, showing scheme A (top) and scheme B (bottom).

Scheme A in Figure 1.17 shows two major steps of the traditional IGCC process. In the first step, coal reacts with oxygen and steam to form syngas; in the second step, syngas generated in the first step is combusted to drive the gas turbine/steam turbine combined cycle. As shown Figure 1.17, both steps in scheme A are highly irreversible and involve inevitable exergy loss. Specifically, in the first step, carbon is oxidized partially to provide the heat needed in the steam carbon reaction. Although no heat loss is assumed, 12% exergy is lost from the formation of syngas, which has a lower exergy rate ($\epsilon = 0.88$) than that of carbon ($\epsilon = 1$). In the second step, 21.7% exergy is lost from the limitation on the gas turbine operating temperature. An operating temperature of 1,800 K would correspond to an exergy rate of 0.663 from combustion, which is much lower than the exergy rate of the syngas ($\epsilon = 0.88$). Thus, with a total of 33.7% exergy loss, the energy conversion efficiency of scheme A, which is equivalent to the exergy conversion efficiency in this specific case, cannot exceed 66.3% for electricity generation. To improve the theoretical energy conversion efficiency, the exergy loss in scheme A should be minimized. One option for reducing the exergy loss is to incorporate the low exergy rate energy into carbon. This option leads to scheme B.

In scheme B, the thermal energy with a low exergy rate ($\epsilon = 0.44$ at 790 K), which is abundant in a typical IGCC process, is integrated into the gasification step. The thermal energy would provide the heat needed for the steam carbon reaction to form H_2 and CO_2 . This approach serves two purposes: (1) Exergy loss can be avoided by the heat integration through incorporation of the low exergy rate thermal energy into the endothermic steam carbon reaction; and (2) less exergy loss would occur in the combustion step because of a smaller

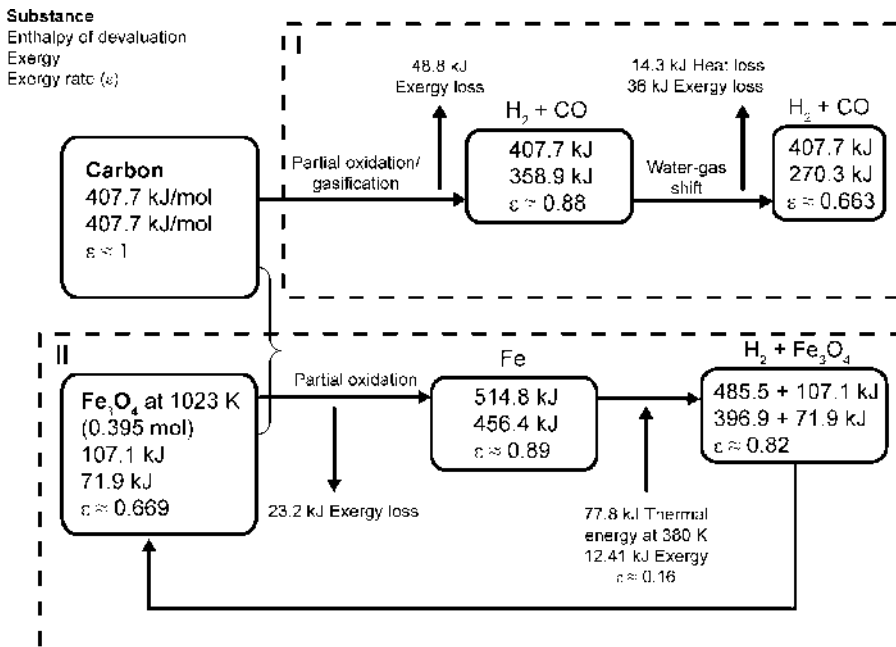


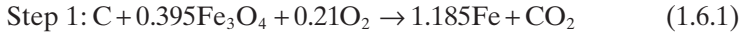
Figure 1.18. Exergy recovering scheme for carbon gasification-water-gas shift process, scheme I (top) and scheme II (bottom: the reaction temperature is assumed to be 1,123 K for scheme II).

exergy rate difference between H_2 and the thermal energy at the combustion temperature. By recovering the thermal energy, more than half of the exergy loss can be avoided in scheme B.

Other than heat recovery, the choice of suitable chemical intermediates and optimization of the chemical reaction scheme often can decrease drastically the exergy loss for an energy conversion process. Figure 1.18 illustrates two schemes in the second example for H_2 generation from coal.

Scheme I represents a traditional route where carbon is converted into syngas followed by the water-gas shift reaction to produce hydrogen. Similar to the previous example, the gasification step would lead to 12% exergy loss from partial oxidation. The second step in scheme I, the water-gas shift reaction, will lead to another 8.8% exergy loss from the conversion of CO into H_2 , which has both lower enthalpy devaluation and a lower exergy rate. In the previous calculation, the exergy in the low-temperature waste heat generated in the WGS reaction is not taken into account. The energy required for separating hydrogen from CO_2 also is neglected.

Scheme II offers an alternative approach using the chemical looping concept. Here, Fe is used as a chemical intermediate to convert carbon into hydrogen. Also, two steps are involved in scheme II. The reactions are as follows:



A small amount of O_2 is introduced in the first reaction to provide the heat needed to reduce Fe_3O_4 to Fe. Much less exergy loss occurs in step 1 (23.1 kJ) compared with the traditional gasification step (48.8 kJ). This is from the recovery of a low-exergy-rate chemical, Fe_3O_4 ($\epsilon = 0.669$), which reacts with carbon ($\epsilon = 1$) to form a chemical, Fe ($\epsilon = 0.89$), of a medium exergy rate. With H_2O introduced into the system under ambient conditions, the steam-iron reaction in step 2 of scheme II requires only a small amount of low grade heat, rendering the ease in balancing the heat required of this step. A zero exergy loss is achievable in step 2 of scheme II. As a result, a traditional gasification-water-gas shift process would lead to at least 68.7-kJ exergy loss for every mole of H_2 generated. On the other hand, when the chemical looping process is used with Fe- Fe_3O_4 as the looping media, the exergy loss can be reduced to 14.7 kJ for each mole of H_2 generated. Thus, the exergy loss for H_2 production is reduced by more than four times using the chemical looping process.

Note that the results presented in the examples are based on a set of assumptions given earlier. Thus, they represent only the upper bound of the energy conversion efficiencies in the conversion process. Nevertheless, because of the common assumptions used in assessing the process options, the results obtained serve as a good guide for relative comparisons of these options. To generalize, an efficient energy conversion process should comprise steps that are less irreversible. The following are general guidelines in devising reaction schemes that are thermodynamically advantageous:

1. Highly exothermic reactions that take place at low temperatures should be avoided.
2. Whenever products with lower exergy rates are produced, energy with an even lower exergy rate than the products should be incorporated into the reactants to minimize the exergy loss. The carrier of the low grade energy can be either heat or chemical substances.
3. The excessive heat generated from exothermic reactions should be integrated into chemical energy by integration with endothermic reactions whenever possible; this integration requires that the exothermic reactions operate under a similar or higher temperature than do the endothermic reactions.
4. One single reaction with high exergy loss can be dissociated into a set of reactions employing appropriate chemical intermediates. This new reaction scheme may be subject to less exergy loss.

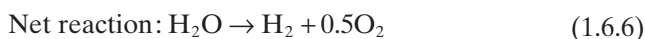
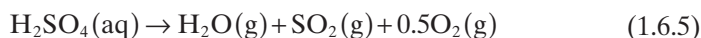
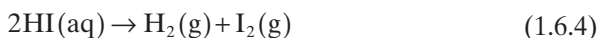
As illustrated in Figure 1.18, the choice of the reaction scheme is based on one that can minimize the exergy loss. In the rest of the section, examples of

chemical reaction schemes that encompass reactions in a looping manner are described. Rather than directly converting feedstock (reactants) into products, the chemical looping strategy uses a series of reaction schemes to generate end products through transformations of certain chemical intermediates. By doing so, as noted, the exergy loss in the conversion process potentially can be minimized. The ideal approach to conduct the chemical looping reaction scheme is to employ a self-sustaining medium that can assist the chemical transformation during the conversion process. The medium also is intended to alleviate the reaction barrier and minimize energy loss in the formation of the product.

An ideal medium, in either solid or fluid form, to be selected for use should possess such properties as high reactivity at proper temperature and pressure ranges, physical integrity, chemical stability, favorable equilibrium toward intermediate product formation, spontaneity of intermediate reaction scheme, ease in intermediate product separation, and moderate exothermic to endothermic heat of reactions. For the chemical looping system to be applicable to process operation, other factors to be considered include simplicity of the chemical looping scheme, ease in heat integration, and process economics. The chemical looping principles discussed earlier can be applied to reaction systems for chemical synthesis or to separation systems for chemical separation. Salient reaction looping examples that may not be related to energy conversion are described as follows:

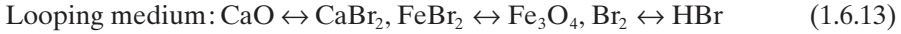
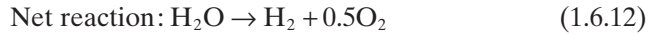
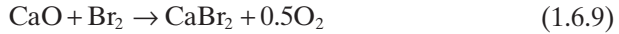
A. Water Splitting for Hydrogen and Oxygen Production

A-1. I₂ and SO₂ Loopings



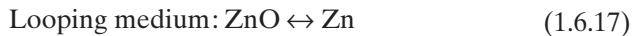
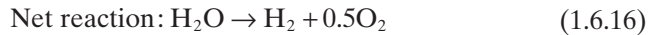
The water-splitting iodine–sulfur (IS) process produces hydrogen and oxygen. The gaseous SO₂ and I₂ liquid react with water to produce two acids, HI and H₂SO₄. This reaction is called the Bunsen reaction. Aqueous HI and H₂SO₄ are separated using a liquid–liquid separator, and then each acid is decomposed at 500°C and 850°C, respectively. I₂ and SO₂ obtained after the decomposition of the acids are recycled to the Bunsen reaction.⁹⁵

A-2. CaO, FeBr₂, and Br₂ Loopings



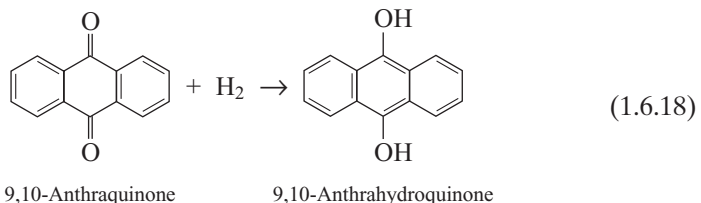
A bromine system produces hydrogen using metal bromides and bromine as looping media. Calcium oxide and hydrogen bromide are obtained from a high-temperature steam reaction with calcium bromide. Hydrogen can be recovered from a mixture of steam and hydrogen bromide generated from the steam and iron bromide reaction.⁹⁶

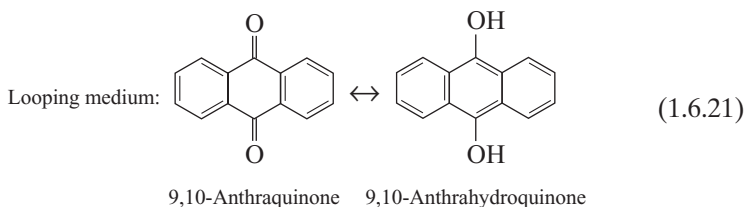
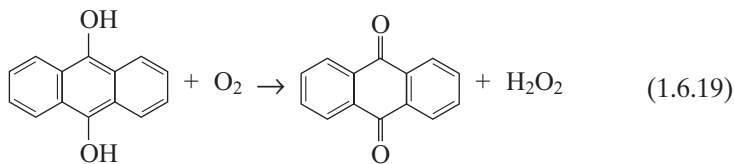
A-3. Zn Looping



For this process, parabolic mirrors concentrate sunlight over a small area to achieve high-temperature heat. This heat can be transferred to chemical energy by dissociating ZnO into Zn and O at $\sim 1,700^\circ\text{C}$ in a solar reactor. Zinc then reacts with steam at $\sim 400^\circ\text{C}$ to regenerate ZnO, yielding hydrogen. Also, different metal oxides other than zinc oxide also can be used. Compared with other processes of hydrogen production, such as chemical looping, given in cases A-1 and A-2, this process requires the reaction to occur at a higher temperature; however, renewable solar energy can be used as the energy source for ZnO dissociation.⁹⁷

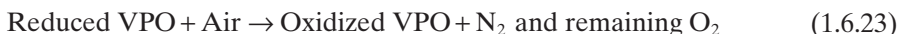
B. Production of Hydrogen Peroxide





Hydrogen peroxide is formed by the reaction of oxygen with the looping intermediate, 9,10-anthrahydroquinone. Another looping intermediate, 9,10-anthraquinone, is formed which is then separated and reacts with H_2 to form 9,10-anthrahydroquinone. The looping process is then repeated.⁹⁸

C. Production of Maleic Anhydride from Butane



The maleic anhydride production from butane catalyzed by oxidized vanadium phosphorous oxide (VPO), which also serves as an oxygen carrier, was developed by DuPont in the 1990s. Maleic anhydride is an essential component for spandex fibers and copolyester elastomers. The butane oxidation and conversion to maleic anhydride occur in a circulating fluidized bed system, as shown in Figure 1.19. In this system, butane is oxidized in a riser with oxidized VPO to form maleic anhydride. Reduced VPO is then oxidized using air in a turbulent fluidized bed regenerator. Thus, the VPO particles loop around the reactors in an oxidized or reduced state. The particles, that usually contain inert support, require sustaining mechanical and thermal stresses in the looping operation.⁹⁹ This looping process was demonstrated well at the bench and pilot scales. Its commercial operation, however, was hampered, that was noted to be caused by the scale-up effects of the CFB reactor on the reactant contact time and the solid particle holdup in the CFB system.¹⁰⁰

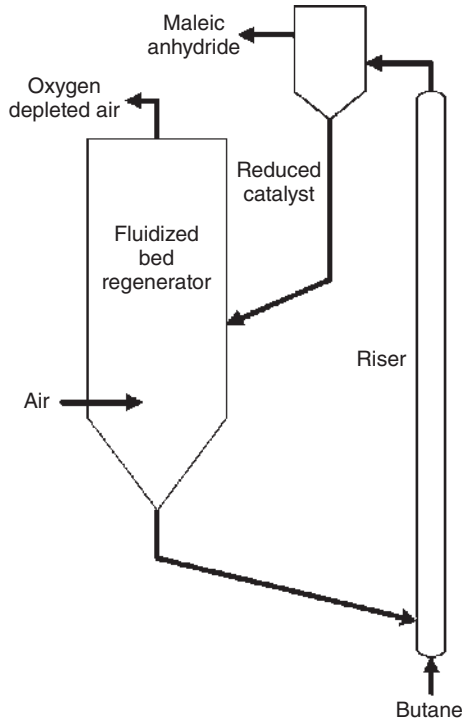
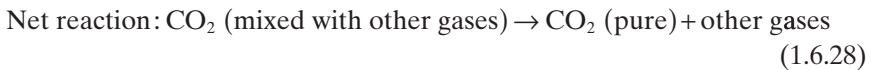


Figure 1.19. Circulating fluidized chemical looping system for production of maleic anhydride.

The inadequacy for sustainable commercial operation principally may be from the chemical and mechanical viabilities of the VPO particles and their associated effects on the transport properties and overall reaction kinetics of the particles in performing their catalytic and looping functions in the circulating fluidized-bed system.

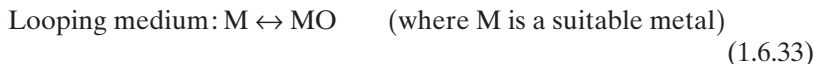
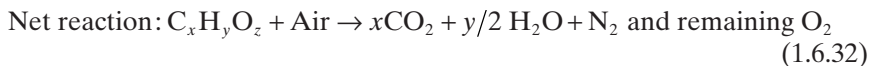
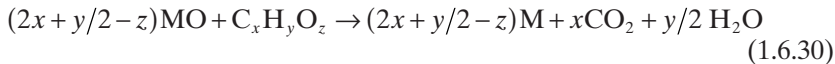
Several examples of chemical looping reactions of relevance to carbonaceous fuel conversions and processes are discussed as follows:

A. CO₂ Separation Using Calcium-Based Sorbent



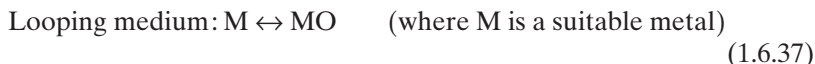
This reaction scheme can be applied to the separation of CO₂ from a gas mixture where CaO is used as the looping medium. These looping reactions can be conducted by varying the temperature and/or pressure in gasification or combustion systems. As these reactions are carried out at high temperatures, proper heat integration would yield a high thermal efficiency of the process, leading to a low-energy penalty for CO₂ capture.¹⁰¹

B. Combustion of Carbonaceous Fuel to CO₂



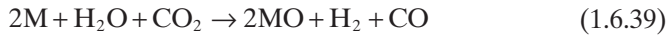
Instead of direct combustion of carbonaceous fuel using air to produce heat and hence electricity, this reaction scheme uses metal oxides (MOs) as the looping medium. The first reaction in the scheme uses MO to convert carbonaceous fuel into a steam and CO₂ mixture from which high-purity CO₂ can be separated. The second reaction, which is the combustion of reduced metal (M) with air, liberates heat. This process, by decoupling combustion into two reactions that occur in two different reactors, allow expeditious CO₂ separation from the combustion products.^{102,103}

C. Gasification of Carbon to H₂

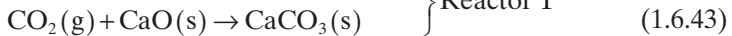
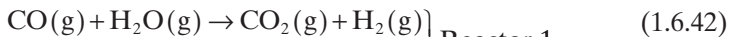


The only difference between this looping scheme and the combustion of carbonaceous fuel to CO₂ above is the oxidation agent used for the second reaction. In this example, steam is used instead of air, yielding a reaction product of hydrogen, instead of heat. Furthermore, the advantages of this looping reaction route over the traditional gasification and water-gas shift route for H₂ production include the ease of CO₂ separation. With a suitable metal employed, the reactions can proceed at an optimized temperature with a minimal exergy loss.¹⁰⁴

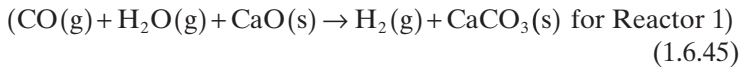
D. Gasification of Carbon to Syngas



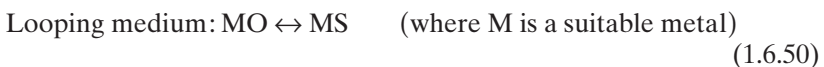
Similar to scheme C, when CO_2 is used as the reacting gas along with H_2O in the second reaction, syngas with any combination of concentrations of CO and H_2 can be produced. Thus, the subsequent reactions that synthesize chemicals and fuels based on CO and H_2 can proceed under optimum CO and H_2 concentration conditions.

E. H_2 Production from the Water–Gas Shift Reaction

Net reaction: $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$



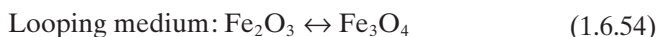
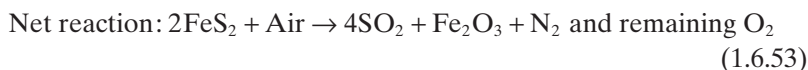
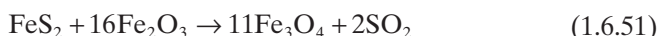
The introduction of CaO looping particles in a water–gas shift reaction would chemically react with CO_2 generated *in situ*, thereby driving the equilibrium toward the formation of H_2 . With highly efficient looping particles, nearly 100% conversion of CO can be achieved. Thus, H_2 of high purity can be produced and a sequestration-ready CO_2 stream can be generated from the calciner¹⁰⁵ where the calcination reaction occurs.

F. Separation of H_2S 

In this scheme, a sorbent such as ZnO first is used to react with H_2S in a gas mixture. The spent sorbent, MS , is then regenerated using O_2 . This reaction

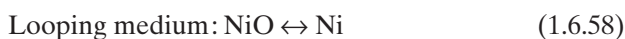
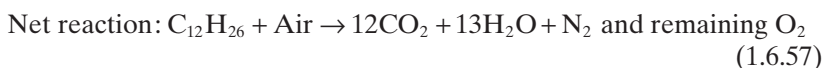
is commonly used in a high-temperature gas cleaning of sulfur in the gasification process.¹⁰⁶

G. Production of S from FeS or FeS₂



These reactions are of relevance to mineral processing. In this reaction scheme, sulfur in pyrite (FeS₂) or in pyrrhotite (Fe_(1-x)S, x = 0 to 0.2) is extracted using hematite (Fe₂O₃) as a looping medium. The reaction scheme generates SO₂, which is then reduced to sulfur in a separate reaction.¹⁰⁷

H. Combustion with Dodecane Liquid Fuels



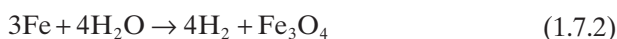
In these reactions, the carbonaceous fuel used is dodecane that is introduced into the reducer in liquid form. The reduction reactions yield a concentration of CO₂ near 100% without formation of carbon on the surface of the oxygen carrier NiO.¹⁰⁸ The oxygen carrier NiAl_{0.44}O_{1.67} also can be used to yield a similar liquid fuel conversion behavior in the reducer.¹⁰⁹

1.7 Chemical Looping Processes

With the pressing needs for efficient and cost/energy effective separation scheme for CO₂ emission control in the coal conversion processes, the chemical looping technique has evolved as an important alternative to the traditional techniques. In this section, a historical perspective on the development of the chemical looping processes for carbonaceous fuel conversions is given. Several representative chemical looping processes that currently are being developed are discussed briefly here with details of some of them presented in later

chapters. Although gaseous and liquid chemical looping media such as molybdenum oxide vapor and molten iron oxide-tin could be used to convert carbonaceous fuels, commercial operation of such looping systems may not be practical and can be much more challenging than that of using the solid looping medium. Therefore, the chemical looping processes considered in this book involve only the solid chemical looping medium.

The principles of chemical looping for carbonaceous fuel conversion were first applied for industrial practice between the late 19th century and the early 20th century. Howard Lane from England was among the first researchers/engineers who conceived and successfully commercialized the steam-iron process for hydrogen production using the chemical looping principle. With the aid of the iron oxide chemical intermediate, the steam-iron process generates H_2 from reducing gas obtained from coal and steam through an indirect reaction scheme. The reaction scheme for the steam-iron process can be represented by



The first commercial steam-iron process based on the Howard Lane design was constructed in 1904. Hydrogen plants based on the same process were then constructed throughout Europe and the United States, producing 850 million ft^3 of hydrogen annually by 1913.¹¹⁰ After the development of Lane's invention, a German scientist named Anton Messerschmitt simplified the design of the steam-iron process. The improved design reduced the cost of the equipment and maintenance of the steam-iron plant.¹¹⁰ The Lane Process and Messerschmitt Process diagrams are shown in Figures 1.20(a) and (b), respectively. Although further improvements were made subsequently, the steam-iron process only partially converts the reducing gas. Moreover, the iron-based looping medium has poor recyclability, especially in the presence of sulfur.¹¹⁰⁻¹¹³ With the introduction of less costly hydrogen production techniques using oil and natural gas as feedstock in the 1940s, the steam-iron process became less competitive and was then phased out. This process is discussed in detail in Chapter 4.

In the 1950s, the chemical looping scheme was proposed for CO_2 generation used for the beverage industry. Oxides of copper or iron were used as the looping particles, and carbonaceous material was used as the feedstock.¹¹⁴ The Lewis and Gilliland Process for CO_2 production made use of two fluidized bed reactors, the CO_2 generator and the metal oxide regenerator, for continuous operation. Both reactors initially were heated using hot gases. After achieving a temperature of $\sim 850^\circ C$ in the generator, metal oxide flow started. It was then

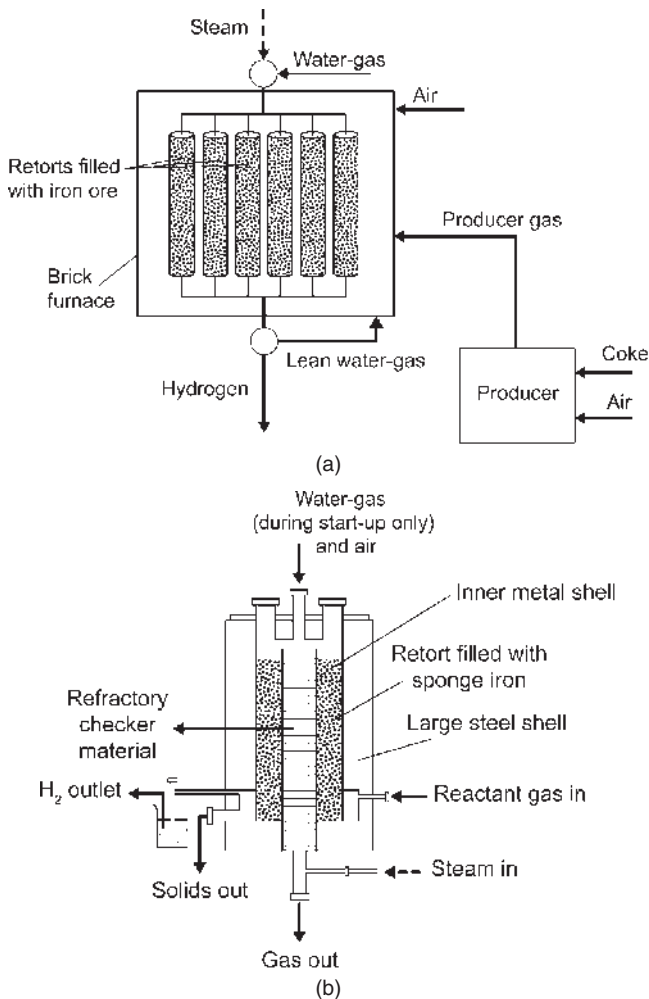


Figure 1.20. Initial steam-iron processes using fixed bed: (a) Lane Process;¹¹³ (b) Messerschmitt Process.¹¹³

followed by the initiation of the flow of fuels such as methane, syngas, and/or solid carbonaceous fuels. Steam and/or recycled CO₂ are used as fluidizing gases in the generator. The regenerator used fluidizing air, which oxidized the reduced metal oxide. The process flow diagram is shown in Figure 1.21. Alternative designs using moving beds and alternating fixed beds also were considered.¹¹⁴

In the early years, the adoption of a chemical looping strategy was mainly prompted by the lack of effective chemical conversion/separation techniques in the generation of the product. In contrast, modern applications of chemical

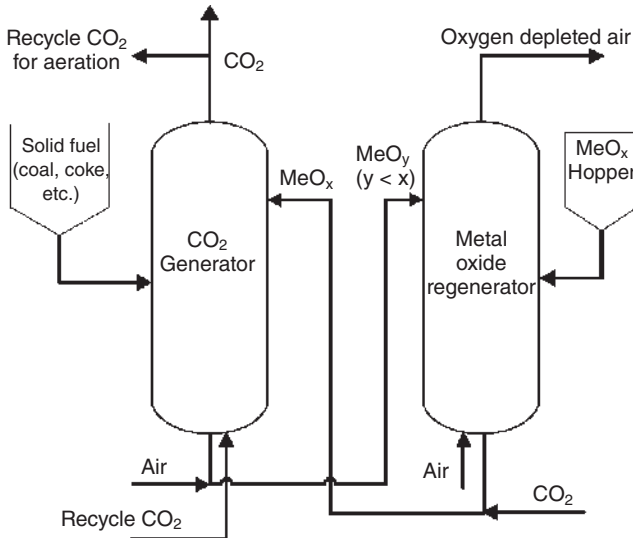


Figure 1.21. Fluidized bed chemical looping for CO₂ generation using solid fuel.¹¹⁴

looping processes are prompted by the need for developing an optimized reaction scheme that minimizes the exergy loss involved in the chemical/energy conversion system.^{115–118} Also driven by the envisaged CO₂ emission control, the recent developments in chemical looping systems have focused on the efficient conversion of gaseous carbonaceous fuels such as natural gas and coal-derived syngas,^{66,104,115–117,119,120} and solid fuels such as petroleum coke and coal,^{121–123} whereas CO₂ separation is achieved through the looping reaction scheme.

Several examples of modern chemical looping processes using coal or coal-derived syngas as feedstock are described in this section. These processes include the ZECA Process, chemical looping combustion processes, the Syngas Chemical Looping Process, the Coal-Direct Chemical Looping Process, the GE Fuel-Flexible Process, the ALSTOM Hybrid Combustion-Gasification Process, the HyPr-Ring Process, and the Calcium Looping Process.

In the ZECA Gasification Process, conceived by Los Alamos National Laboratory in the United States, coal reacts with steam and recycled H₂ to produce methane. The methane is subsequently reformed to produce H₂ and finally electricity using a solid oxide fuel cell with a reported overall electricity generation efficiency of ~57%.^{124,125}

In the chemical looping combustion (CLC) processes, carbonaceous fuel such as coal-derived syngas or natural gas first reacts with metal oxide (e.g., nickel oxide) in the reducer, where metal oxide is reduced to metal (e.g., nickel). The reaction products are CO₂ and steam, from which CO₂ is readily separable. Metal that exits from the reducer enters the combustor where it

reacts with air to regenerate the metal oxide. The metal oxides is then recycled back to the reducer. The heat of oxidation is carried by the high-temperature, high-pressure spent air from the combustor. The spent air is used to drive a steam turbine/gas turbine combined cycle system for electricity generation. Figure 1.22 shows a simplified chemical looping combustion process for electricity generation using coal-derived syngas as feedstock. Figure 1.23 shows a simplified block diagram of the Syngas Chemical Looping (SCL) Process.

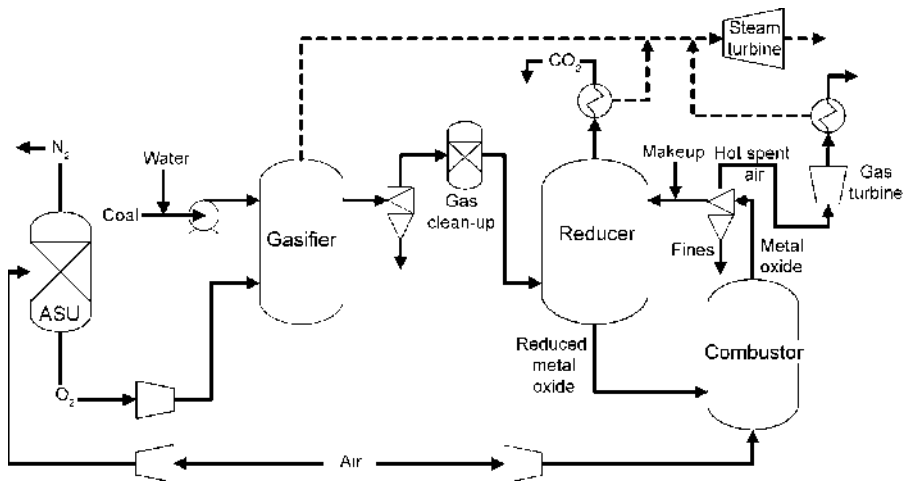


Figure 1.22. Schematic diagram of CLC process (--- steam).

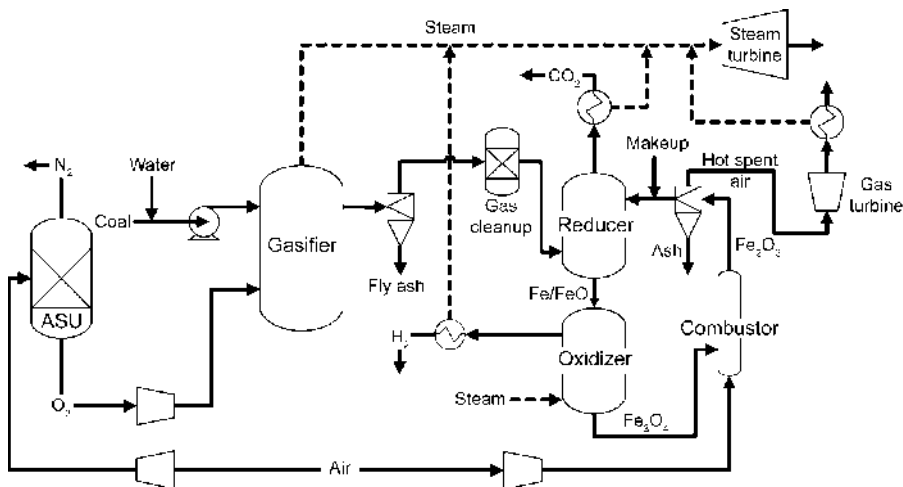


Figure 1.23. Schematic diagram of the Syngas Chemical Looping (SCL) Process (--- steam).

Compared with the CLC process, the SCL process has the flexibility to coproduce hydrogen and electricity.^{104,126–128}

There are three main reactors in the SCL process: the reducer, the oxidizer, and the combustor or combustion train. In the reducer, coal-derived syngas with moderate levels of pollutants (i.e., HCl, NH₃, sulfur, and mercury) is used to reduce specially tailored iron oxide composite particles that can undergo multiple reduction–oxidation cycles. The syngas is converted completely into carbon dioxide and water, whereas the iron oxide composite particles are reduced to a mixture of Fe and FeO at 750–900°C. The Fe/FeO particles leaving the reducer are then introduced into the oxidizer, which is operated at 500–750°C. In the oxidizer, the reduced particles react with steam to produce a gas stream that contains only H₂ and unconverted steam. The steam easily can be condensed out to obtain a high-purity H₂ stream. Meanwhile, the Fe and FeO are regenerated to Fe₃O₄. The Fe₃O₄ formed in the oxidizer is regenerated further to Fe₂O₃ in an entrained flow combustor that also transports solid particles discharged from the oxidizer to the reducer inlet, completing the chemical loop. A portion of the heat produced from the oxidation of Fe₃O₄ to Fe₂O₃ can be transferred to the reducer through the particles, whereas at the high pressure and high temperature, spent air produced from the combustor can be used to drive a gas turbine/steam turbine combined cycle system to generate electricity for parasitic energy consumption. In yet another configuration, a fraction or all of the reduced particles from the reducer can bypass the oxidizer and be introduced directly to the combustor if more heat or electricity is desired. Hence, both chemical looping reforming and chemical looping combustion concepts are applied in the SCL system, rendering it a versatile process for H₂ and electricity coproduction.

Another type of chemical looping processes that drastically simplify the coal conversion scheme is represented by The Ohio State University's (OSU's) Coal-Direct Chemical Looping Process as shown in Figure 1.24. Here, a specially tailored, highly reactive Fe₂O₃ particle similar to that used in the SCL Process is used for converting coal to hydrogen. In this process, Fe₂O₃ particles are introduced into the reducer, together with fine coal powder. By using suitable gas–solid contacting patterns, coal will be gasified into CO and H₂. The reductive gas will react with Fe₂O₃ particles to form Fe and FeO, while producing a highly concentrated CO₂ and H₂O flue gas stream. H₂O in the flue gas can be condensed readily, leaving a sequestration-ready CO₂ stream. The reduced Fe/FeO particles from the reducer enter the oxidizer to react with steam to generate hydrogen while being oxidized to Fe₃O₄. The resulting Fe₃O₄ exiting from the hydrogen production reactor will be conveyed back to the reducer pneumatically. During the particle conveying, the Fe₃O₄ particle will be oxidized to its original state, that is, Fe₂O₃. Compared with other looping processes, the Coal-Direct Chemical Looping Process characterizes a much simpler coal conversion scheme with a hydrogen production efficiency (on an HHV basis) of close to 80%.¹²⁹

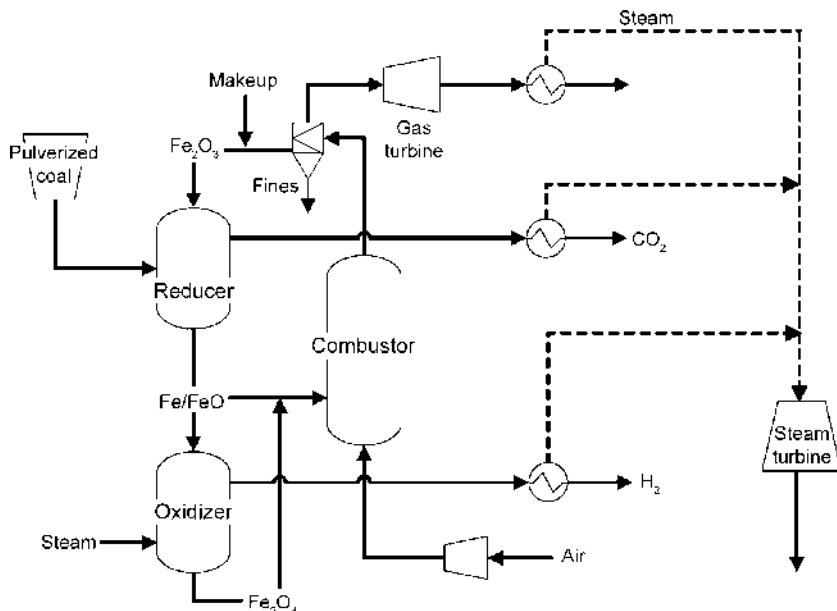


Figure 1.24. Schematic diagram of the Coal-Direct Chemical Looping Process (- - - steam).

Apart from coal or syngas, the chemical looping technique also can process other carbonaceous fuels, making the utilization of by-products from the fossil fuel processing industry possible. Moreover, the generation of H_2 via steam makes the chemical looping process compatible with any existing system that is a net producer of low grade heat such as low-pressure, low-temperature steam. This is possible because water can be used to extract the heat of any exhaust stream with temperatures higher than 100°C to produce steam, which can, in turn, be used for hydrogen production in the chemical looping oxidizer. By doing so, the latent heat of the steam can be stored in the H_2 produced in the form of chemical energy, which has a higher exergy ratio. The latent heat also can be stored in liquid fuels. The key to the high efficiency of this process is the staged reactions in the looping reactors and the design of highly reactive and highly recyclable particles.

The HyPr-Ring Process developed in Japan involves coal gasification using pure oxygen and steam. This process closely follows the concept of the Carbon Dioxide Acceptor Process developed by the Consolidation Coal Company and later the Conoco Coal Development Company in the 1960s and 1970s.¹³⁰ Figure 1.25 illustrates the HyPr-Ring Process. In gasification, coal is fed along with calcium oxide, steam, and oxygen to the gasifier. The presence of excess steam in the gasifier drives the reaction toward the formation of H_2 . Calcium oxide captures CO_2 generated in the water-gas shift reaction, resulting in a

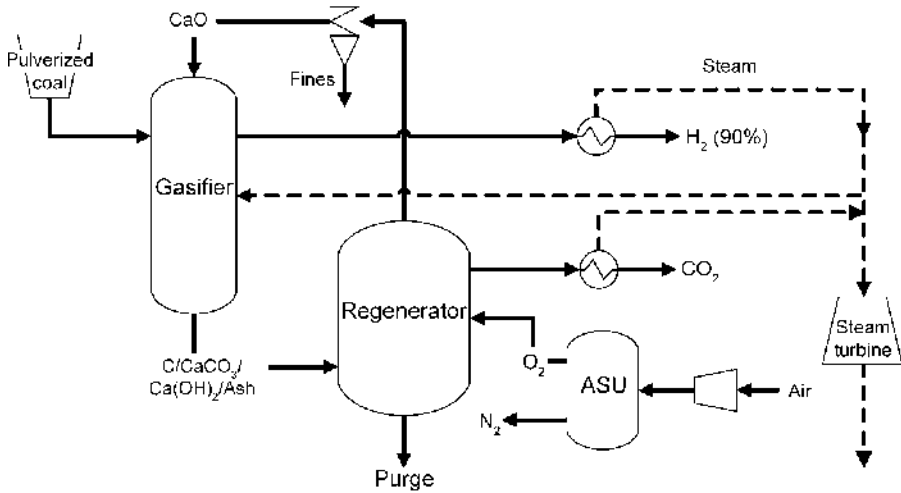


Figure 1.25. Schematic diagram of the HyPr-Ring Process.

product gas stream of $\sim 90\%$ H_2 mixed with methane. The solids from the gasifier consist of mostly used CaO sorbents (CaCO_3) and some unconverted carbon, which is to be introduced to a regenerator along with oxygen. The heat generated by combusting the unreacted carbon allows the calcination reaction to be carried out for CaO regeneration while producing a high purity of CO_2 for sequestration. It is estimated that a 77% (HHV) H_2 production efficiency can be achieved using this process without taking into account the energy consumption for CO_2 compression.¹³¹

The Calcium Looping Process (CLP) developed by OSU is closely related to the reactive CO_2 separation strategy from the coal combustion flue gas stream, given in Figure 1.7, using high-temperature sorbents. The process requires the calcium-based sorbent to be of high reaction capacity and to have a high ability for regeneration, while maintaining viability of the sorbent for more than 100 or more cycles of usage. The design of sorbent particles that possess the requisite characteristics is thus crucial to the viability of the process. Figure 1.26 describes a gasification process represented by the CLP.

As shown in Figure 1.26, the CLP is integrated into a coal gasification system capable of electric power generation, H_2 production, and Fischer–Tropsch synthesis for fuels and chemicals. The coal gasifier is operated at high pressures and high temperatures. In the gasifier, reactions of coal, steam, and air/pure oxygen take place in fluidized beds in a variety of contact modes. As the syngas mixture exits from the gasifier, steam is introduced for a water–gas shift reaction downstream for converting CO to H_2 , whereas calcium oxide also is introduced to remove CO_2 in the WGS product gas stream, forming calcium carbonate (CaCO_3). The removal of CO_2 allows the WGS reaction to proceed with full conversion of CO to H_2 without thermodynamic constraints.

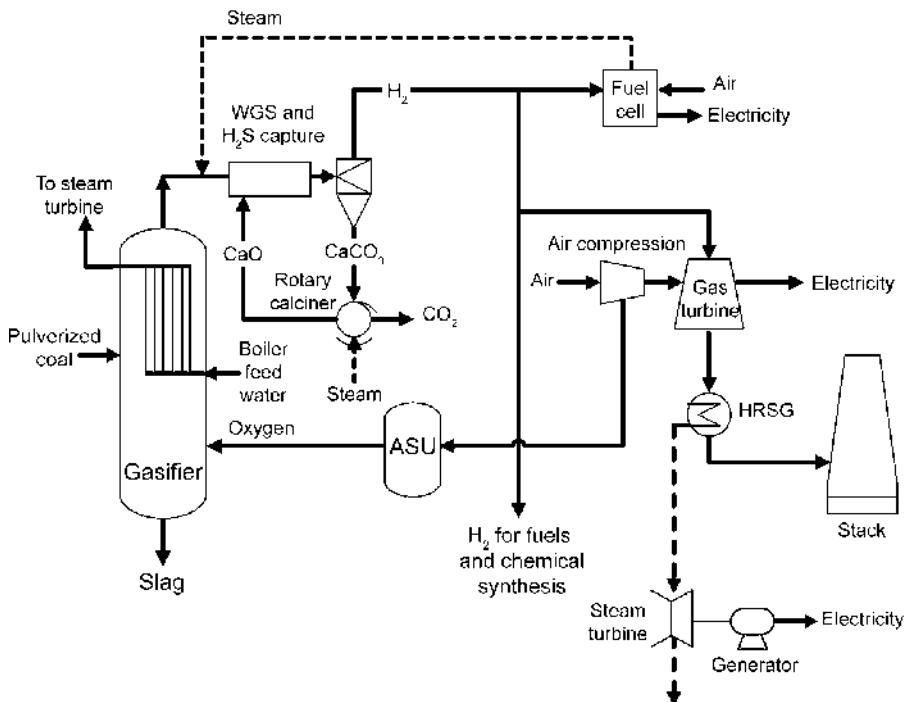


Figure 1.26. Schematic diagram of the CLP.⁶⁶

Thus, this process can be tailored to enhance the H_2 concentration to the maximum extent possible. Calcium oxide also removes acid gases (i.e., H_2S and HCl). At the exit of the WGS reactor, the reacted $CaCO_3$ particles are captured by a high-temperature cyclone, and the spent solids are then sent to a calciner for regeneration that converts $CaCO_3$ back to CaO . The regeneration may also involve a hydration step. In that case, the sorbent introduced to the process will be in hydrate form. The calcined gas mixture will be of high-purity CO_2 with some H_2S that can be economically compressed for sequestration. If necessary, H_2S can be separated from the CO_2 stream before sequestration. The hydrogen-enriched fuel gas can be further purified for fuel cell applications or used for electric power generation without any low-temperature cleanup requirements. The calcium looping scheme achieves a process intensification goal in that it reduces the excess steam requirement, while removing CO_2 and acid gases, including H_2S , providing a sequestrable CO_2 stream, and producing a high-purity H_2 stream.

The GE Fuel-Flexible Process takes different types of feedstock such as coal and biomass to coproduce H_2 and electricity. The fundamental process concept for the fuel-flexible process is similar to the HyPr-Ring Process except that, for conducting the calcination reaction, instead of pure oxygen, metal

oxide is used. As a result, the reaction scheme for this process involves two chemical loops and, hence, two different looping media. The two loops are operated using three interconnected fluidized bed reactors. In the first reactor, coal is partially gasified with steam to form a mixture of H_2 , CO and CO_2 . The CO_2 is captured by calcium-based sorbents to form $CaCO_3$. The depletion of CO_2 results in an enhanced water–gas shift reaction toward the formation of H_2 . Moreover, sulfur in the coal also can be captured by the sorbent-forming $CaSO_3$. As a result, a high-purity H_2 stream is obtained from the first reactor. The solids in the first reactor, which mainly consist of reacted sorbents ($CaCO_3$, $CaSO_3$) and unconverted carbon, are introduced to the second reactor where high-temperature steam is injected. In this reactor, the unconverted carbon reacts with a high-temperature oxygen carrier (mainly Fe_2O_3) from the third reactor to form reduced metal; furthermore, the heat carried by the oxygen carrier and the high-temperature steam provide heat to regenerate the spent sorbents coming from the first reactor. Therefore, a high-concentration CO_2/SO_2 gas stream is generated from the second reactor. The third reactor regenerates the reduced oxygen carrier obtained from the second reactor by reacting it with air. Heat from all the hot exhaust gas streams is used for steam generation to drive the turbine system. Thus, the products from this process are pure hydrogen from the first reactor and electricity from the turbines. Meanwhile, the CO_2 stream from the second reactor is ready for sequestration. In this process, part of the solids needs to be discharged during the operation to avoid ash accumulation and to maintain solid reactivity.¹³² The overall energy conversion efficiency for the fuel-flexible process is estimated to be 60% (HHV) with 50–50 hydrogen and electricity coproduction. Figure 1.27 illustrates the overall scheme of the process.

The ALSTOM Hybrid Combustion-Gasification Process (Figure 1.28) contains three different operational configurations for the purpose of effective operations: (1) indirect coal combustion for heat generation, (2) coal gasification for producing syngas, and (3) coal gasification for producing hydrogen.¹³⁴ For the first and second configurations, one chemical loop is used, whereas for the third configuration, two chemical loops are used. In the first configuration, two main reactors are used with calcium sulfate as the looping medium. The calcium sulfate is reduced to calcium sulfide by coal in the first reactor, forming a high-purity CO_2 stream. The calcium sulfide formed is then combusted in the second reactor with air. Part of the heat generated from the combustor is used to compensate for the heat required for coal gasification in the first reactor, whereas the rest is used to produce high-temperature, high-pressure steam for electricity generation. The second configuration, although similar, uses a much higher coal-to- $CaSO_4$ ratio and a higher steam feed rate for the first reactor. Thus, the reduction of $CaSO_4$ is accompanied by the formation of CO and H_2 resulting from the presence of an excessive amount of carbon and steam. In this configuration, most of the heat generated in the combustor is used to offset the heat required for coal gasification in the first reactor. The product for this configuration is syngas, and most of the carbon in coal is

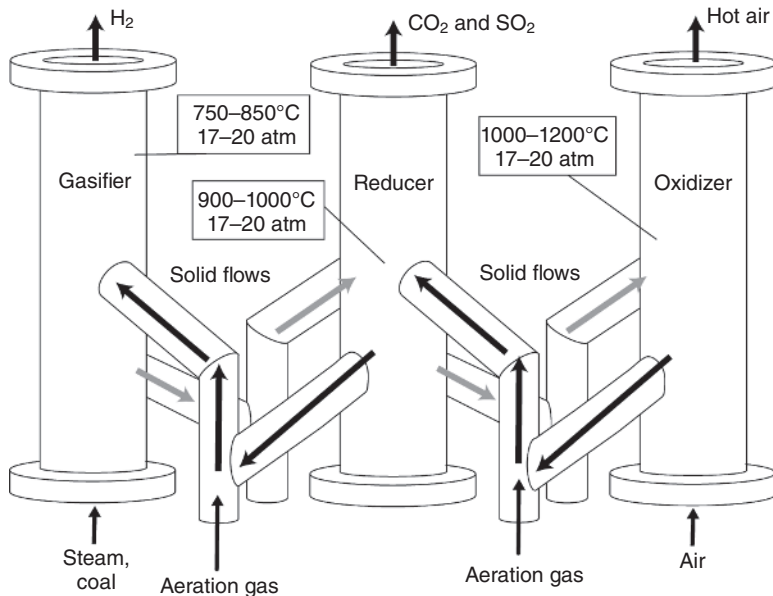


Figure 1.27. Schematic diagram of the fuel-flexible gasification-combustion process.¹³³

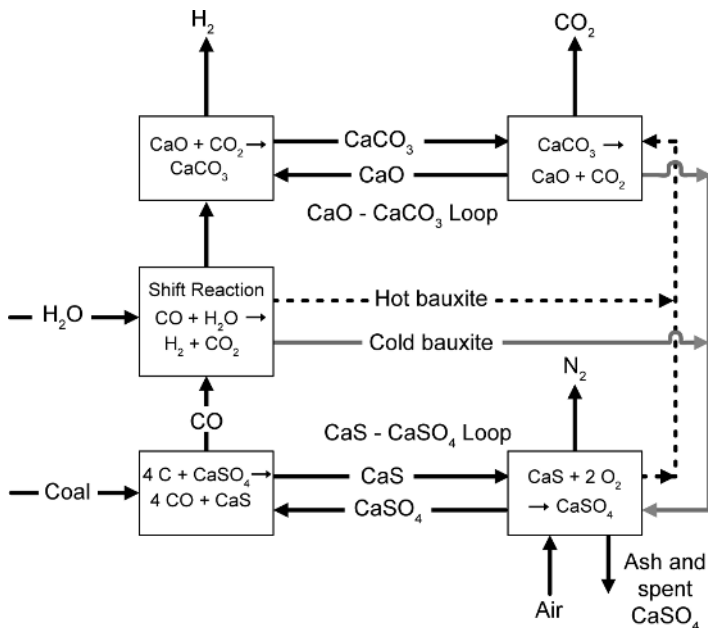


Figure 1.28. Schematic diagram of the ALSTOM Process.¹³⁵

converted to gaseous CO and H₂. Thus, there is no carbon capture necessary. In the third configuration, as shown in Figure 1.28, however, pure hydrogen is produced with the introduction of the third reactor (calciner) and an additional chemical loop—a calcium oxide/calcium carbonate loop. The idea is to introduce even more steam than the second configuration to conduct the WGS reaction in addition to the reduction reaction of CaSO₄. Calcium oxide is used in the first reactor to capture the CO₂ generated by the WGS reaction and thus drives the reaction toward the formation of pure H₂ as the product. The heat integration of this configuration includes the utilization of part of the heat generated from calcium sulfide combustion to calcine calcium carbonate in the calciner, forming CO₂.¹³⁵ In all the configurations, bauxite is used as the heat carrier, transferring the heat from the exothermic reaction (CaSO₄ formation) to the endothermic reaction (calcination reaction).

Note that the processes discussed earlier have high-energy efficiencies for H₂/electricity production. Moreover, they have integrated the CO₂ capture into the process. As an example, the energy conversion efficiencies from the ASPEN simulation for the SCL Process, the Coal-Direct Chemical Looping (CDCL) Process, and the CLP are compared in an efficiency chart with those of the state-of-the-art processes that generate H₂ or electricity from coal in a carbon-constrained scenario as given in Figure 1.29.¹³⁶ The figure shows that significantly improved energy conversion efficiencies are realized with near full carbon capture using the novel chemical looping concept.

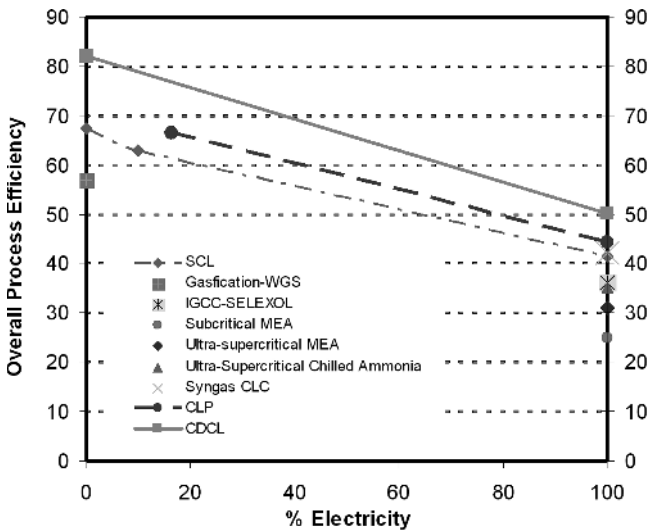


Figure 1.29. Efficiency comparisons among various technologies for H₂/electricity production from coal.

It is, thus, evident from the preceding discussion that coal gasification schemes can be efficient and versatile in generating a variety of products, including hydrogen, liquid fuels, and chemicals in addition to electric power. From a carbon management viewpoint, gasification is a preferred scheme over conventional combustion. The coal conversion processes in the future will inherently be of high energy and economic efficiencies with a reaction pathway that generates readily separable streams of products and pollutants, including carbon dioxide. The chemical looping processes that are being actively pursued worldwide possess such desirable characteristics. Their applications to coal conversion, therefore, represent a promising direction for the optimum coal conversion process development.

1.8 Overview of This Book

In this book, the current carbonaceous fuel conversion technologies based on chemical looping concepts are detailed in the context of traditional or conventional technologies. The key features of the chemical looping processes as well as their ability to generate a sequestration-ready CO₂ stream are discussed thoroughly. The looping media employed in the processes are mainly in solid form, whereas the carbonaceous fuels can be in solid, liquid, or gas form. As the success of the chemical looping technology depends strongly on the performance of the particles, Chapter 2 is devoted entirely to the subjects of solid particle design, synthesis, properties, and reactive characteristics. The looping processes can be applied for combustion and/or gasification of carbon-based material such as coal, natural gas, petroleum coke, and biomass directly or indirectly for steam, syngas, hydrogen, chemical, electricity and liquid fuel production. The details of the energy conversion efficiency and the economics of these looping processes for combustion and gasification applications in contrast to those of the conventional processes are given in Chapters 3–5. Chapter 3 describes the chemical looping processes for combustion using solid carbonaceous fuels, syngas, or natural gas as feedstock. Chapter 4 illustrates chemical looping processes for gasification using gaseous fuels as feedstock such as syngas, natural gas, and light hydrocarbons. Chapter 5 describes the chemical looping processes for gasification using solid carbonaceous fuels as feedstock such as coal. Finally, Chapter 6 presents additional chemical looping applications that are potentially beneficial, including those for H₂ storage and onboard H₂ production, CO₂ capture in combustion flue gas, power generation using fuel cells, steam-methane reforming, tar sand digestion, and chemicals and liquid fuel production. A CD is appended to this book that contains the chemical looping simulation files, and the simulation results based on the ASPEN PLUS software for such reactors as gasifier, reducer, oxidizer, and combustor, and for such processes as conventional gasification processes, SCL Process, CLP, and CCR Process.

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