Hydrogen Production Using Solid Fuels

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CONTENTS
4.1 Solid Fuels ............................................................................................................................64
  4.1.1 Supply and Utilization ..................................................................................................64
  4.1.2 Issues Associated with Solid Fuels ..........................................................................67
4.2 Utility Processes ..................................................................................................................68
  4.2.1 Upstream Processes ..................................................................................................68
  4.2.2 Fuel Handling and Air Separation Unit ..................................................................68
  4.2.3 Steam and Electricity: Pressurized Fluidized Bed Combustion .........................69
4.3 Energy Conversion Processes ..........................................................................................70
  4.3.1 Gasification ................................................................................................................71
    4.3.1.1 Gasification Process Design ..............................................................................72
    4.3.1.2 Gasifier Process Optimization .......................................................................74
    4.3.1.3 Fluidized Bed Gasifier .....................................................................................74
    4.3.1.4 Ultrasuperheated Steam Gasification ..............................................................75
    4.3.1.5 Supercritical Water Gasification ....................................................................77
    4.3.1.6 Plasma Gasification .........................................................................................79
  4.3.2 Anaerobic Digestion ....................................................................................................80
  4.3.3 Chemical Looping Processes ......................................................................................83
    4.3.3.1 Syngas Chemical Looping ..............................................................................83
    4.3.3.2 Direct Chemical Looping ...............................................................................85
  4.3.4 Autothermal Reforming ..............................................................................................88
  4.3.5 Hydrogen Separation and Purification Processes ......................................................90
    4.3.5.1 Water–Gas Shift Process ...............................................................................90
    4.3.5.2 Gas Separation Membranes ..........................................................................91
    4.3.5.3 Pressure Swing Adsorption for Hydrogen Purification ...................................93
4.4 Environment Protection Processes ....................................................................................93
  4.4.1 Acid Gas Removal: Sulfur Removal .........................................................................94
  4.4.2 Claus and SCOT Processes: Sulfur Recovery ............................................................95
  4.3 Tar, Ash, and Soot Removal ..........................................................................................95
4.4 CO₂ Capture and Storage .................................................................................................97
Hydrogen is an energy carrier like electricity but with advantageous applications, especially in transportation (through engines and fuel cells). Hydrogen does not occur naturally in large quantities or in high concentrations on Earth. It must be produced from other compounds such as water and hydrocarbons (coal, biomass, solid wastes, natural gas, heavy oils, oil sands, etc).

Solid fuels such as coal, biomass, and solid wastes are increasingly used with water to produce hydrogen, and the energy transfer/conversion processes have been enhanced through recent developments (Gnanapragasam et al., 2010). The search for better uses for solid fuels is gaining prominence rapidly due to environmental imbalances caused by excessive CO$_2$ emissions from solid fossil fuels in energy conversion processes (IPCC, 2008). The impact of global warming has focused efforts on reducing or capturing emissions of CO$_2$ and other greenhouse gases from all energy sources.

Producing hydrogen from solid fuels increases their commercial value, especially for coal in the transportation sector. By converting solid fuels into gases and liquids, two major problems associated with solid fuels are addressed: (1) increasing adaptability to gas/liquid intake processes and (2) enabling cost-effective capture of various pollutants during the solid-to-gas/liquid conversion. A third advantage pertaining to certain solid fuels such as solid wastes is their safe and effective disposal (IEA, 2008b). Collective information on these hydrogen production processes is required to assess the expected outcomes of research and development and other improvement efforts now in place and required in the future.

An extended review of selected technological advances in hydrogen production using solid fuels is presented in this chapter, focusing on energy, environment, and economic sustainability. The advantages and problems associated with new developments are assessed based on research and development involving design, integration, and economics.

The process of producing hydrogen from various solid fuels follows several stages of processes, and the sequence is outlined in Figure 4.1. Solid fuels, depending on their natural occurrence and characteristics, are processed (sometimes with water) to use their exergy for deriving hydrogen through various high- and low-temperature processes. Utility processes involve those that pretreat solid fuels in cleaning, drying, and storing before being used in energy conversion processes. Any system that uses solid fuels in producing hydrogen needs oxygen, steam, and electricity for various stages of hydrogen production, and generating them becomes part of the utility processes.

Energy conversion processes primarily involve converting solid fuels into gaseous and liquid forms for further transformation into hydrogen. As listed in section 3 in Figure 4.1,
Hydrogen Production Using Solid Fuels

Hydrogen production using solid fuels involves gasification, chemical looping, and anaerobic digestion, as discussed in this chapter. Although hydrogen storage is listed as part of energy conversion processes, it is of a different nature that involves issues associated with storing hydrogen for longer periods of time. Hydrogen storage is not discussed here but is covered in another chapter of this book.

FIGURE 4.1
Organizational flowchart of various processes involved in hydrogen production from solid fuels, representing an outline of subject matter discussed in this chapter.
Processes that enable environmental protection by capturing, controlling, and reducing releases of harmful gaseous and solid elements are discussed to provide an understanding of the energy and costs involved in these processes, which can hinder developments of certain technologies for producing hydrogen using solid fuels. To achieve environmental and economic benefits, energy-coordinated process integration is necessary and is discussed toward the end of this chapter.

4.1 Solid Fuels

Solid fuels supply the energy required to split hydrogen from water through various conversion processes, sometimes yielding additional products. Solid fuels as shown in Figure 4.2 include such hydrocarbons as coal, tar sands, oil shale, and bitumen; renewable organic materials such as biomass/charcoal, agricultural residue, and forest residue; and renewable inorganic materials such as municipal and industrial solid wastes.

4.1.1 Supply and Utilization

Reserves of solid fuels are significantly higher than those for other fossil fuels. Of the current global energy use, 80% is supplied by fossil fuels; 13.5% by renewable sources like solar, wind, and geothermal energy; and 6.5% by nuclear energy (Asif and Muneer, 2007). Coal is the most significant contributor among fossil fuels to the current global electricity generation, accounting for 40% (IEA, 2008b). The most abundant fossil fuel on the planet, current estimates of global recoverable coal reserves range from 216 years to over 500 years (British Petroleum, 2003) at present usage rates. By the year 2025, it is expected that the United States will require over 250 GW of new electrical generation
Hydrogen Production Using Solid Fuels

Hydrogen production capacity even without considering replacing old plants (DOE, 2005). Of this new capacity, the International Energy Agency (IEA) estimates that 80 GW will be met through the construction of coal-based power plants, through advanced co-combustion and cogasification processes. Worldwide installed capacity of coal-based plants is expected to increase by over 40% in the next 20 years, exceeding 1400 GW by 2025 (DOE, 2005). When the hydrogen demand becomes equal to that of oil in the transportation sector or electricity in the power sector, solid fuels especially coal will likely have an important role to play owing to their abundance and low market price (IEA, 2008a). Within the member countries of the Organization for Economic Co-operation and Development (OECD), the nature of coal use relative to other energy sources for the last four decades is shown in Figure 4.3. The rapid increase in nuclear and renewable energy in recent years (after 2001 in Figure 4.3) shows the significant efforts of these countries in curbing greenhouse gas emissions.

Only non-agglomerating coal is considered for the purpose of hydrogen production, especially when using gasification as the primary conversion process. In 2007, hard coal (anthracite and bituminous coal) production increased by 6.5% (or 338.0 Mt) to 5542.9 Mt. Brown coal (subbituminous coal) production increased by 0.9% (or 7.9 Mt) to 945.2 Mt, a little above its 1994 level (IEA, 2008a). Total global coal production increased by 5.6%, well above the 10-year average growth trend of 3.4%. Total global coal consumption increased by 6.2% or 271.7 Mtce in 2007, which follows a 4-year trend of annual increases averaging 6.6%. These numbers suggest an increase in worldwide demand for electricity (which is the largest end use for coal), largely due to the migration of vast numbers of potential consumers to the OECD countries, an increase in living standards across the planet and an increase in global population (IEA, 2008b). The total primary energy supply (TPES) by fuel shares for the year 2007 is shown in Figure 4.4, where it is observed that coal delivers up to 26.4% and still maintains the lead role in electricity generation (IEA, 2009). The calorific values of various coals and biomass based on proximate and ultimate analyses are available elsewhere (Parikh et al., 2007).
Biomass capable of use in hydrogen production includes agricultural residues, forest residues, energy crop residues, organic solid wastes, and firewood (charcoal). From data gathered by the IEA (2009) shown in Figure 4.4, only 12.4% is contributed by all renewable resources to the TPES in the world. A contribution of 9.6% is directly from renewable solid fuels such as biomass, residues, and municipal solid waste (MSW).

A total of about 36% of energy contributions are from solid fuels in recent years, providing ample opportunity for producing hydrogen using the energy from these solid fuels. Of the 12.4% renewables in Figure 4.4, 77.3% is shown in Figure 4.5 to be from solid biomass, charcoal, and MSW except for 1.1% from landfill gas, far more than any other renewable energy resources. But biomass tends to be bulky, to deteriorate over time, and to be difficult to store and handle. Compared to coal and oil, biomass has a lower energy density (GJ per unit of weight or volume), which makes handling, transport, storage, and combustion more difficult (IEA, 2006). Although the contribution of solid renewables to the TPES has increased by 9% compared to 1990 levels (IEA, 2009), much of it is used for combustion-based energy systems.

**FIGURE 4.4**

**FIGURE 4.5**
Hydrogen Production Using Solid Fuels

The IEA (2008b) recently compared energy resource types, conversion technologies, and associated policies based on three scenarios (used in Figure 4.6) scaled to the year 2050: (1) the ACT map scenario of the IEA, which implies adoption of a wide range of technologies with marginal costs of up to USD 50/ton of CO$_2$ saved when fully commercialized; (2) the BLUE map scenario, which requires deployment of all technologies involving costs of up to USD 200/ton of CO$_2$ saved when fully commercialized; and (3) the baseline scenario, which reflects developments likely to occur with energy and climate policies implemented to date. While the ACT scenarios are demanding, the BLUE scenarios depend on rapid implementation of unprecedented and far-reaching new policies in the energy sector (IEA, 2008b), which will take more time and effort to implement than the ACT scenarios.

From the data in Figure 4.6, coal appears to be the least favorable fuel for the future owing to its CO$_2$ emissions based on existing commercial-level combustion technologies, which mostly generate electricity. But this trend will change when coal is used for producing hydrogen (Gnanapragasam et al., 2009b), since the downstream processes enable easier capture of CO$_2$ and, when combined with biomass, can also help in reducing overall CO$_2$ emissions. Biomass has tremendous potential (as seen from Figure 4.6) for delivering more energy than coal and other resources by 2050 when the BLUE map is implemented effectively. Thus, it appears to be promising to use biomass for hydrogen production along with high-energy-intensity fuels such as coal.

Industrial inorganic solid wastes such as scrap tires (Stringfellow and Beaumant, 2008) and plastics (Aznar et al., 2006) are also being considered as alternative fuels through effective gasification processes. The supply and utilization of other solid fuels are discussed in detail elsewhere (IEA, 2006, 2007, 2008c; Asif and Muneer, 2007).

### 4.1.2 Issues Associated with Solid Fuels

Solid fuels contain carbon and their use in producing hydrogen results in emissions of CO$_2$, which is currently the most significant greenhouse gas and to which increasing temperatures in the lower atmosphere are attributed (USEPA, 2008). The carbon from solid fossil fuels (shown in Figure 4.2) is of higher concern and requires measures to capture and store underground. Due to the recent necessity to curb CO$_2$ emissions, combustion processes are becoming of decreasing interest to the energy sector (IPCC, 2008). One option to avoid CO$_2$
emissions is the use of renewables, but renewable energy sources that can provide base-load electricity—hydro, biomass, and geothermal—together are not anticipated to be able to satisfy even existing electricity demands and are not climate-neutral when operating continuously (Moriarty and Honnery, 2007). Another possible option, coal gasification with carbon capture and sequestration/storage (CCS), entails large energy and cost penalties using commercially proven methods of CO$_2$ separation (Muradov and Veziroglu, 2008).

In an effort to demonstrate the potential of CO$_2$-free coal-based power generation, a company in Germany has commissioned and is operating a power plant incorporating a complete CO$_2$ capture and sequestration facility (Harrabin, 2008). CO$_2$ capture and separation for gasification (Pennline et al., 2008) involves novel concepts in wet scrubbing with physical sorption, chemical sorption with solid sorbents, and separation by membranes.

Energy crops such as biomass resources are a risk for a sustainable future, since the carbon debt arising from land-use changes can take many years, even centuries, to pay back by using the biomass produced to displace fossil fuels (Fargione et al., 2008). Producing biomass for energy purposes at the expense of either food or fiber supplies, or by increasing deforestation, is of little global benefit (IEA, 2008b).

Other issues regarding solid fuels such as washing, drying, ash removal, and solid pollutant removal are well understood and managed in existing solid fuel–based energy systems and are discussed further elsewhere (de Souza-Santos, 2004; Rezaiyan and Cheremisinoff, 2005; Higman and Burgt, 2008).

### 4.2 Utility Processes

Utility processes are those that involve preparing solid fuels for actual energy conversion processes where hydrogen production begins in gaseous or liquid forms.

#### 4.2.1 Upstream Processes

Upstream processes (in Figure 4.1) involve cleaning, blending, and upgrading solid fuels to enhance the quality of feedstock, thus improving the efficiency of various downstream conversion processes (CanmetENERGY, 2005) and also simplifying the separation of pollutants associated with solid fuels (NEDO, 2004). Some of the upstream cleaning processes that are in use in Japan and other larger importers of coal include (1) using a cartridge system, where all solid feedstocks are blended to form a uniform mixture containing a standardized composition; (2) treating the feedstock with solvents to clean the fuel of unusable residue; (3) blending of high-sulfur, high-grade coals with low-sulfur, low-grade coals and high-ash biomass (to avoid sintering); and (4) upgrading low-grade solid fuels with pretreatment using heavy oils (NEDO, 2004). These upstream processes likely will eventually be part of every energy conversion facility in the world, due to the long-term environmental and economic benefits and the desire of governments to implement energy efficiency policies (Eldridge et al., 2009) for improving the sustainability of operating existing and future energy systems.

#### 4.2.2 Fuel Handling and Air Separation Unit

Solid fuels arriving at energy transfer plants need temporary storage, drying, crushing/milling, and internal transportation mechanisms. The handling of solid fuels consumes
some energy with operation and maintenance costs and is vital to the functioning of systems that produce hydrogen using energy from solid fuels. Due to their availability and widespread use (de Souza-Santos, 2004), solid fuel handling is mature and is not discussed in detail here. Commercially, ProcessBarron (www.processbarron.com) is one of several private companies that specializes in design, manufacture, and commissioning of integrated solid fuel handling equipment for a given energy conversion system.

The nature of integration of such fuel handling equipment within the system should entail limited wastes in all forms (energy, material, and cost). For example, storing the right type of fuel in a feasible environment reduces energy requirements for drying and transportation. Using waste heat from various processes within the system, to dry high-moisture feedstocks before crushing, increases the specific energy output of the fuel and overall system energy efficiency.

Air separation (Kerry, 2006) is crucial to enable both oxyfuel combustion and oxyfuel gasification processes that result in gaseous CO\textsubscript{2} only at the exhaust (after hydrogen separation). This makes the CO\textsubscript{2} underground storage much easier by compressing only CO\textsubscript{2}. Removing N\textsubscript{2} from air also increases the residence time of high-temperature synthetic gas (syngas) within the gasifier. When N\textsubscript{2} is not removed from air, the high nitrogen content in the gasifier yields syngas with a low heating value, 4–6 MJ/Nm\textsuperscript{3} based on HHV (McKendry, 2002). Oxygen and steam gasification on the other hand may produce a gas with a medium heating value, 10–18 MJ/Nm\textsuperscript{3} based on HHV (Hofbauer et al., 2003).

Air separation units (ASUs) consume a considerable amount of electric power, up to 10% of that for the entire system, especially in larger systems using cryogenic separation (Li, 2007), thus requiring a careful assessment of the need for only high-quality processes (Kerry, 2006). Membrane-based gas separation units (ion transport membranes [ITMs]) have been proven to be cheaper to install than cryogenic-based air separation by about 8% (Stiegel, 1999), and they also consume less power and are likely to prevail in most hydrogen-producing systems in the future.

### 4.2.3 Steam and Electricity: Pressurized Fluidized Bed Combustion

Circulating fluidized bed (CFB) combustors operating at atmospheric pressure are commercially established globally, that is, more than 400 power units are in operation around the world (Kavidass et al., 2000), with approximately 3000 operating CFB boilers in China alone (Yue et al., 2009). Fluidized beds are particularly suited to the combustion of low-quality coals, and most existing circulating fluidized bed combustion/combustor (CFBC) plants burn such materials along with biomass in cofiring mode. Moving to supercritical cycles is a logical step for very large CFB units (IEA, 2008b). A 460 MW supercritical unit is under construction at Lagisza, Poland, with start-up anticipated in 2009. This unit is expected to have a thermal efficiency of 70%. CFB combustor-based power plants using oxygen instead of air (known as oxy fuel combustion) are advantageous for CO\textsubscript{2} capture (Anthony, 2008; Manovic et al., 2008). There are hundreds of atmospheric CFB combustors operating worldwide, including a number of plants as large as 250–300 MW. Designs for larger supercritical CFBC units (600 MW capacity) are being developed (IEA, 2008b) with still higher efficiencies.

Any system that produces hydrogen involves processes that need high-quality steam and electricity, which may be produced on-site with a pressurized fluidized bed combustion unit. This process is of particular interest when considering the energy, environment, and economic benefits through integration and was developed by the US Department of Energy and industry partners (Weinstein and Travers, 2002). The process is still under development but is moving into demonstration
and commercial stages owing to its small- and medium-scale capacities and higher operating efficiencies, above 70% (IEA, 2008b).

Pressurized fluidized bed combustion is employed at high pressures in combined cycles, with the boiler exhaust gases routed to generate additional power through heat recovered from the gas turbine exhaust. The combined gas and steam cycle achieves efficiencies up to approximately 44% (DOE, 2007). The first of such units had a capacity of about 80 MW, but two larger units are operating in Karita and Osaki, Japan, the former using supercritical steam (IEA, 2008b).

Incorporating advanced pressurized fluidized bed combustion/combustor (PFBC), with a thermal efficiency exceeding 70%, would enhance the use of nongasifiable solid feedstock, such as certain types of biomass, which then may be cofired with coal in the advanced PFBC to produce process steam and electricity.

4.3 Energy Conversion Processes

Much research on converting solid fuels to hydrogen is in early stages, but developments are expected to accelerate in the near future as the demand for hydrogen increases in various applications. Recent research into processes for converting solid fuels to gaseous forms indicates that such processes have a significant potential for commercialization and should be able to achieve industrial-scale production levels (Gnanapragasam et al., 2010).

Hydrogen derived from coal is slated to be the primary objective in the fuel program of the US Department of Energy (Lior, 2008), and research is ongoing to develop modules for coproducing hydrogen from coal via systems integrated with advanced coal power plants at prices competitive with crude oil (DOE, 2007).

Primary conversion processes in producing hydrogen from solid fuels include direct processes such as gasification, anaerobic digestion, fermentation, and liquefaction (Chmielniak and Sciazko, 2003). There are also direct chemical looping (DCL) processes such as the iron oxide cycle and indirect thermochemical cycles based on copper–chloride and sulfur–iodine. Some of these processes (copper–chloride and sulfur–iodine cycles) are undergoing extensive research for commercial development and implementation (IEA, 2008b) and thus are not discussed here. The process diagrams in this chapter are wherever possible self-explanatory.

Coal, biomass, solid wastes, and oil sand coke (Furimsky, 1998) are potential gasification fuels for syngas production and methanol synthesis (Chmielniak and Sciazko, 2003). Applications of these processes depend on feedstock characteristics, volume of production, and postconversion processes to manage wastes and by-products (Higman and Burgt, 2008). A review of decarbonization processes for fossil fuels ranging from natural gas to coal (Muradov and Veziroglu, 2008) has identified the commercial potential of new technologies, which suggests various uses for solid carbon after CO$_2$ sequestration.

The average energy and exergy conversion efficiencies of syngas from solid fuel gasification (76% and 75%, respectively) are found to be higher than those for hydrogen (64% and 55%) production from gasification (Bargigli et al., 2004). However, coal-to-syngas conversion generates a significant amount of solid waste, and the material intensity is much higher for syngas than for natural gas and hydrogen (21 and 39 g/g, respectively), indicating a higher load on the environment that should be dealt with carefully.

Technoeconomic comparisons of hydrogen production via steam–CH$_4$ reforming (SMR), coal and biomass gasification, and water electrolysis have been reported (Langer et al., 2007).
Increases in natural gas prices are observed to make coal gasification as well as biomass gasification competitive, provided its technological barriers are overcome (including feedstock processing and postconversion of products). A comparison of electricity and hydrogen production processes, from coal and natural gas with CO$_2$ capture, for various technologies and for large-scale and decentralized systems (Damen et al., 2006, 2007), demonstrated that a short-term net power efficiency of 32%–40% is achieved by an integrated gasification combined cycle (IGCC) system with production costs of 4.7–6.3 €ct/kWh.

Coal gasification forms the central element of IGCC systems and has the greatest fuel flexibility of advanced technologies for power generation (Beer, 2007). Current commercial gasification technologies are also well adapted to using biomass and other low-value feedstocks that have high ash residues (Liu and Niksa, 2004). Gasification also permits the control and reduction of gaseous pollutant emissions (Trapp, 2005) and a possible low-cost approach to concentrate CO$_2$ emissions at high pressure to facilitate underground sequestration.

### 4.3.1 Gasification

Presently, gasification is the only commercial, large-scale option for converting solids to gases (Rezaiyan and Cheremisinoff, 2005) and one of the cleanest conversion technologies for solid fuels. Academic and industrial research has improved production capabilities and operating efficiencies in recent years. The gasification of carbonaceous, hydrogen-containing fuels is an effective method for thermal hydrogen production (Stiegel and Ramezan, 2006) and is considered a key technology in the transition to a hydrogen economy (Collot, 2006). Gasification converts solid fuels into a syngas comprised mainly of CO, CO$_2$, H$_2$, CH$_4$, H$_2$O, and other constituents in minor concentrations (Higman and Burgt, 2008). Syngas production offers the possibility of obtaining multiple products that can be used for different applications. Gasification has the highest energy conversion efficiency relative to other solid fuel conversion technologies (Beer, 2000). One particular version of a commercial gasification process is shown in Figure 4.7, as an example of the initial stage of solid fuel conversion.

Producing hydrogen from syngas is a significant step in the clean coal technology roadmap as realized by many countries including Canada (CanmetENERGY, 2005), Japan (NEDO, 2004), and the United States (DEO, 2002). Gasification carries great significance for coal and dry biomass, while for wet biomass and sewage, other conversion processes such as anaerobic digestion and supercritical water gasification (SCWG), respectively, appear advantageous due to the higher moisture content in the feedstock (Mozaffarian et al., 2004).

The British Gas–Lurgi (BGL) gasifier shown in Figure 4.7 is a countercurrent, moving-bed, slagging gasifier operating at pressures of 25 bar or higher (NETL, 2000). The reactor vessel is water cooled and refractory lined. The coal and/or biomass mixture is fed into the top of the gasifier via a lock-hopper system and reacts while moving downward through the gasifier. The coal’s ash/mineral matter is removed from the bottom of the gasifier as molten slag through a slag tap, then quenched in water, and removed. Steam and oxygen are injected through tuyere nozzles near the base of the gasifier and react with the coal as the gases move up. This countercurrent action results in a wide temperature difference between the top and the bottom of the gasifier. After gas conversion, the ash and unconverted char from coal/biomass end up as slag and get collected at the bottom of slag lock after cooling. The typical operating temperature for this type of gasifier is from 600°C to 1900°C (Higman and Burgt, 2008). The gasifier can be characterized due to this temperature profile as being divided into drying, devolatilization, gasification, and combustion zones from top to bottom, respectively.
Experimental and modeling investigations of long-stick wood gasification in a top-lit updraft fixed-bed gasifier describe common problems of many gasifier designs (Saravanakumar et al., 2007). They produce so much tar that the gas cleanup equipment cost is several times the gasifier cost. Fluidized beds typically produce 0.5%–4% tars, while updraft biomass gasifiers produce 10% tars. Both stratified downdraft and top-lit updraft gasifiers produce much lower tar levels, typically 0.1%. For the gasifier, the top-lit updraft mode is found to provide more satisfactory overall performance (NETL, 2000); the BGL gasifier (Figure 4.7) belongs to this category.

**4.3.1.1 Gasification Process Design**

The two combustion-related factors of greatest impact on gasifier design and operation have been reported to be (1) fuel reactivity and (2) slag flow as it runs down the refractory walls and out of the bottom of the reactor under gravity (Wall, 2007). A gasification product gas with tar content below the targeted limit of 2 g/m³ can be achieved only under special conditions in terms of gasifier design and operation as well as feedstock characteristics (Corella et al., 2006).
The main chemical reactions that occur inside the gasifier with appropriate energy conditions (Ptasinski et al., 2007; Mountouris et al., 2008) are as follows:

**Exothermic combustion reaction:**

\[
C + O_2 \rightarrow CO_2; \quad \Delta H = -393.5 \text{ kJ/mol} \tag{4.1}
\]

**Endothermic Boudouard equilibrium process:**

\[
C + CO_2 \rightarrow 2CO; \quad \Delta H = 172.6 \text{ kJ/mol} \tag{4.2}
\]

**Endothermic heterogeneous water–gas shift (WGS) reaction:**

\[
C + H_2O(g) \rightarrow CO + H_2; \quad \Delta H = 131.4 \text{ kJ/mol} \tag{4.3}
\]

**Exothermic hydrogenation gasification:**

\[
C + 2H_2 \rightarrow 2CH_4; \quad \Delta H = -74.9 \text{ kJ/mol} \tag{4.4}
\]

After formation, these gases tend to react based on local temperature and pressure gradients and nonequilibrium conditions. Depending on the amount of steam available, the following reactions may occur within the gasifier and in the WGS reactors in the H_2 system:

**Endothermic CH_4 decomposition:**

\[
CH_4 + H_2O \rightarrow CO + 3H_2; \quad \Delta H = 206.12 \text{ kJ/mol} \tag{4.5}
\]

**Exothermic WGS reaction:**

\[
CO + H_2O \rightarrow CO_2 + H_2; \quad \Delta H = -41.2 \text{ kJ/mol} \tag{4.6}
\]

At high gasifier temperatures, the sulfur in coal reacts with CH_4 and steam to form H_2S in a two-step process (Patnaik, 2002) as shown in the following discussion; this is removed using stages of separation processes, the descriptions for which can be found in the literature (Garcia et al., 2006):

\[
CH_4 + 2S \rightarrow CS_2 + 2H_2 \tag{4.7}
\]

\[
CS_2 + 2H_2O \rightarrow 2H_2S + CO_2 \tag{4.8}
\]

The overall reaction in the gasifier, considering the use of CO_2 as a coal carrier gas and using oxygen instead of air for gasification, may be represented as

\[
\dot{n}_{\text{coal}} \left( y_{C}C + y_{H_2}H_2 + y_{N_2}N_2 + y_{O_2}O_2 + y_{S}S + y_{\text{ash}} \right) + \dot{n}_{\text{O}_2}O_2 + \dot{n}_{\text{CO}_2}CO_2 + \dot{n}_{\text{steam}}(H_2O) \rightarrow
\]

\[
\dot{n}_{\text{syn}} \left( y_{\text{CO}_2}CO_2 + y_{CO}CO + y_{pH_2}H_2 + y_{\text{CH}_4}CH_4 + y_{H_2O}H_2O + y_{pN_2}N_2 \right) + \dot{n}_{\text{H}_2S}H_2S + \dot{n}_{\text{ash}} \tag{4.9}
\]

where

- \( y \) is the molar fraction
- \( n \) is the molar flow rate
- \( p \) denotes the product
4.3.1.2 Gasifier Process Optimization

An assessment of the performance of a gasifier operating without air preheating and using a higher-moisture-content fuel (over 10% moisture by weight) demonstrates the benefits of high-temperature air preheat (Young and Pian, 2003). Performance was observed to improve minimally by drying a manure–waste fuel to below 10% moisture. An investigation of the selection of IGCC candidate coals using a pilot-scale gasifier operation showed that high-ash coal (about 17% by weight) yields less than 60% cold-gas efficiency (Yun et al., 2007). To improve the efficiency for such low-reactivity coal, it is suggested that the gasifier design should permit increased reaction time and the option of char recycling and that methods of inducing higher mixing of coal powder with reacting gases be considered. Since all types of coal can be gasified, gasification appears promising for the production of hydrogen from coal. Gasification plants are also advantageous, compared to other coal-based alternatives, for CO\(_2\) capture (Collot, 2006) as mentioned earlier.

An optimization of catalytic steam gasification of biomass at low temperatures for hydrogen production suggests that higher temperatures and steam flow rates increase syngas yield (Moghtaderi, 2007). At 600°C and high steam content (about 90%), hydrogen production can be optimized with the help of a catalyst when using biomass. The status of catalytic gasification of biomass, similarities and differences between dry and wet processes, and challenges for future research and development from both catalysis and process viewpoints have been discussed (van Rossum et al., 2008).

The influences on hydrogen production of gasifier operating temperature, pressure and coal type, and steam-to-carbon ratio that have been examined based on chemical equilibrium (Wang et al., 2006) suggest that the operating pressure in the gasifier be maintained at 20–30 bar for enhanced CO\(_2\) partial pressure and capture efficiency. The appropriate gasifier temperature is between 625°C and 850°C, for which more than 70% hydrogen can be obtained with a production efficiency of 46.45%. The overall system also cogenerates hydrogen and power with near-zero emissions.

An energy analysis of the biomass gasifier showed (Mahishi and Goswami, 2007) that the optimum conditions for hydrogen production occurred at a gasification temperature of 1000 K, a steam–biomass ratio of 3 and an equivalence ratio of 0.1, achieving a 54% energy efficiency for the gasifier. A similar thermodynamic analysis (Gnanapragasam et al., 2009a) of the performance of a gasification process under varying steam-to-coal (S/C) and oxygen-to-coal (O/C) ratios in the gasifier yielded a range of syngas compositions as given in Table 4.1. These values are based on a Gibbs free energy minimization equilibrium model for the gasifier when using anthracite coal with an HHV of 32.85 MJ. From Table 4.1, it is evident that, when 80% S/C and 70% O/C are used, the hydrogen produced is the highest (37 vol.%) and that the remaining CO will be converted to hydrogen and CO\(_2\) during the WGS reaction stage. The amount of CO\(_2\) emission is directly proportional to the carbon in the feedstock.

4.3.1.3 Fluidized Bed Gasifier

A novel fluidized bed gasifier fitted with water-cooled sampling probes for measuring the axial gas concentrations at various gasifier heights has been reported (Ross et al., 2007). Three distinct zones are observed in the gasifier. In the first zone (the bottom third of the distance from the distributor), with a temperature below 950°C, char combustion and gasification reactions dominate. In the second zone, with a temperature between 800°C and 900°C, the devolatilization products from the biomass combine with the char
Hydrogen Production Using Solid Fuels

4.3.1.4 Ultrasuperheated Steam Gasification

A new method for gasifying carbonaceous materials to syngas comprises the formation of an ultrasuperheated steam (USS) composition containing mainly water vapor, CO₂, and highly reactive free radicals (Lewis, 2007). The USS at temperatures ranging from 1316°C to 2760°C is a clear colorless flame; when it comes into contact with carbonaceous materials (feedstock), rapid gasification occurs to form a syngas. The syngas generated from USS gasification has a higher hydrogen fraction (more than 50%) than other gasification processes (Pei and Kulkarni, 2008). When used within an IGCC system, the overall efficiency is found to be lower, suggesting that USS gasification is more suitable for hydrogen production than power generation.

The USS gasifier is a long cylindrical reactor with a steel casing for the high-pressure (above 30 bar) operation and a ceramic lining (Lewis et al., 2002; Ryu, 2004) to resist the high temperatures of up to 2500°C. The pulverized coal or biomass is fed from the top into a pilot burner as shown in Figure 4.8, which initiates with some propane aided by synthetic air the high-temperature flame, which is a combination of 79% steam and 21% oxygen. The flame disintegrates hydrogen from steam, allowing the syngas to have a higher hydrogen fraction (more than 50%) than other gasification processes (shown in Table 4.1). The reactor

### Table 4.1

Simulated Syngas Volumetric Composition (without Nitrogen) for Four S/C Inlet Ratios and Five O/C Inlet Ratios, Considering an Anthracite Feedstock When Gasifier Operates at 20 bar, 1173 K

<table>
<thead>
<tr>
<th>S/C (%)</th>
<th>O/C (%)</th>
<th>H₂</th>
<th>CO</th>
<th>CO₂</th>
<th>CH₄</th>
<th>H₂O (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>70</td>
<td>0.19</td>
<td>0.74</td>
<td>0</td>
<td>0.07</td>
<td>0</td>
</tr>
<tr>
<td>40</td>
<td>70</td>
<td>0.31</td>
<td>0.61</td>
<td>0</td>
<td>0.03</td>
<td>0.01</td>
</tr>
<tr>
<td>60</td>
<td>70</td>
<td>0.35</td>
<td>0.52</td>
<td>0.05</td>
<td>0.02</td>
<td>0.03</td>
</tr>
<tr>
<td>80</td>
<td>70</td>
<td>0.37</td>
<td>0.46</td>
<td>0.09</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>40</td>
<td>90</td>
<td>0.25</td>
<td>0.63</td>
<td>0.12</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>40</td>
<td>100</td>
<td>0.28</td>
<td>0.59</td>
<td>0.04</td>
<td>0.00</td>
<td>0.02</td>
</tr>
</tbody>
</table>

*Source: Adapted from Gnanapragasam, N.V. et al., Energy Conserv. Manage., 50, 1915, 2009a.*

gasification reactions. The third zone is the freeboard with a temperature of 800°C and below, where variations in the main gas components occur due to the WGS reaction.

In the case of a fluidized bed gasifier, the fuel is gasified in a bed of small particles fluidized by a suitable gasification medium such as air or steam. The concern for climate change has increased the interest in biomass gasification for which fluidized bed gasifiers are particularly popular, occupying nearly 20% of the market (Basu, 2006). Fluidized bed gasifiers are divided into the following two major types: (1) bubbling and (2) circulating. Depending on the fuel and the application, the gasifier operates at a temperature within the range of 800°C–1000°C and at atmospheric and pressurized conditions. The hot gas from the gasifier passes through a cyclone, which separates most of the solid particles associated with the gas and returns them to the bottom of the gasifier for recirculation. An air preheater located below the cyclone raises the temperature of the gasification air and indirectly controls the temperature inside the gasifier.

also generates a tremendous amount of heat, thus enabling self steam generation. The flame is maintained by using some portion of the syngas generated.

The ASU is mandatory for this type of gasifier, since the higher hydrogen percentage depends on the synthetic air composition; thus, oxygen becomes important for high-temperature combustion. This adds to the power requirement for the compressors unless membrane-based separation is used (Stiegel, 1999). The USS process is burner-based, not reaction-based, offering the end user a wide choice of reactor designs. There are no exothermic oxidation reactions within the reactor. Downstream of the USS steam envelope, gasification becomes a steam-only gasification and/or steam reforming process inherently resistant to the production of tars (Sieger and Donovon, 2002). No ash slagging occurs despite very high temperatures (Ryu et al., 2004), which makes the USS process ideal for small-scale hydrogen production.
Hydrogen Production Using Solid Fuels

Wood char with a lower higher heating value than that of anthracite (about 2–3 MJ/kg) still is able to produce about 37% hydrogen for about 63% of its weight compared to anthracite, as can be seen from Table 4.2 when USS composition is at 80% steam and 20% CO₂. The data in Table 4.2 are mainly for steam gasification since no oxygen is supplied, thus belonging to a second type of USS process with temperatures ranging from 300°C to 700°C. This particular USS process does not require an ASU, reducing the penalty on the overall energy efficiency.

### 4.3.1.5 Supercritical Water Gasification

This process is aimed at generating hydrogen from the biogenic feedstock sewage sludge (Gasafi et al., 2007; Li et al., 2009). The process exploits the specific physical and chemical properties of water above its critical point \( T = 374°C, P = 221 \text{ bar} \). These properties allow for a nearly complete conversion of the organic substance contained in the feed material to an energy-rich fuel gas containing hydrogen, CO₂, and CH₄. The characteristics of SCWG are examined and compared to other energy conversion technologies by modeling an overall energy system (Yoshida et al., 2003). A SCWG combined cycle is determined to be the most efficient conversion process for biomass with high moisture content. The breakeven point between thermal gasification and SCWG is approximately 40% biomass moisture content.

Gas yields, carbon gasification efficiency, and the total gasification efficiency increase with increasing temperature and reaction time and decreasing feed concentration (Yamaguchi et al., 2009). Hydrogen yield increases from 7% mole fraction to over 30% for an increase of reaction temperature from 600°C to 800°C for the gasifier shown in Figure 4.9. Among the parameters varied, temperature and feed concentration are found to have the most significant effect on the SCWG reaction behaviors. Higher temperatures and lower feed concentrations favor coal utilization for hydrogen production, promoting the reforming reaction of CH₄ and CO (Lu et al., 2008). The SCWG of brown coal requires

### TABLE 4.2

Experimental Syngas Volumetric Composition for Four Test Cases Involving Two Different USS Compositions with Char and Coal

<table>
<thead>
<tr>
<th>Syngas Composition (Volume Fraction of Dry Gas)</th>
<th>Wood Char</th>
<th>Anthracite Coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Test Cases</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel composition (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moisture—1.6</td>
<td>0.323</td>
<td>0.37</td>
</tr>
<tr>
<td>Volatile matter—21.8</td>
<td>0.254</td>
<td>0.236</td>
</tr>
<tr>
<td>Fixed carbon—78.2</td>
<td>0.4</td>
<td>0.373</td>
</tr>
<tr>
<td>Ash—1.4</td>
<td>0.02</td>
<td>0.019</td>
</tr>
<tr>
<td>Fuel feed rate (g/s)</td>
<td>2.5</td>
<td>4</td>
</tr>
<tr>
<td>USS composition</td>
<td>30% H₂O, 70% H₂O, 30% CO₂, 20% CO₂</td>
<td>80% H₂O, 80% H₂O, 20% CO₂</td>
</tr>
<tr>
<td>H₂</td>
<td>0.321</td>
<td>0.367</td>
</tr>
<tr>
<td>CO</td>
<td>0.243</td>
<td>0.203</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.409</td>
<td>0.402</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.019</td>
<td>0.014</td>
</tr>
</tbody>
</table>

a catalyst for achieving a high utilization efficiency that leads to a high hydrogen production closer to the theoretical limit.

To improve hydrogen production when using SCWG with biomass, an alkali, such as NaOH, KOH, Na₂CO₃, K₂CO₃, and Ca(OH)₂, is used as a catalyst or promoter. Of these, potassium carbonate (K₂CO₃) is found to catalyze gasification of the cellulose (in biomass) with the formation of more hydrogen and less CO (Guo et al., 2007). The activity of K₂CO₃ is higher than that of Ca(OH)₂ and K₂CO₃ cannot capture CO₂. A summary of the catalytic
mechanism of $\text{K}_2\text{CO}_3$ for biomass gasification in supercritical water (SCW) occurs as given in the following (Sinag et al., 2003):

$$\text{K}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{KHCO}_3 + \text{KOH}$$

(4.10)

$$\text{KOH} + \text{CO} \rightarrow \text{HCOOK}$$

(4.11)

$$\text{HCOOK} + \text{H}_2\text{O} \rightarrow \text{KHCO}_3 + \text{H}_2$$

(4.12)

$$2\text{KHCO}_3 \rightarrow \text{H}_2\text{O} + \text{K}_2\text{CO}_3 + \text{CO}_2$$

(4.13)

$$\text{H}_2\text{O} + \text{CO} \leftrightarrow \text{HCOOH} \leftrightarrow \text{H}_2 + \text{CO}_2$$

(4.14)

More hydrogen was also obtained for cellulose gasification with the mixture of $\text{K}_2\text{CO}_3$ and $\text{Ca(OH)}_2$, and the $\text{CO}_2$ capture is enabled in this particular case. The processes within the SCWG system provide opportunities for waste energy integration, thus enabling a self-sustained process with feedstock delivering the corresponding product of syngas with a higher hydrogen fraction.

### 4.3.1.6 Plasma Gasification

Plasma gasification is another process for producing a hydrogen-rich syngas. The process has no limitation on feedstock characteristics and smaller requirements of air/oxygen and is a pyrolysis process becoming commercially popular in solid waste management facilities around the world (especially in Canada, Europe, Japan, and the United States). It is mostly used for efficient and clean disposal of municipal solid wastes and garbage (Carabin and Gagnon, 2007). When coal is gasified in a steam and air environment under arc plasma conditions, hydrogen production is enhanced (Galvita et al., 2007). The steam environment is estimated to increase syngas output by 30%–40% for plasma gasification compared to an air environment.

Efforts on process development and energy optimization for plasma gasification of sewage sludge have suggested (Mountouris et al., 2006) that a moisture content ($w/w$) of about 0.4 produces maximum hydrogen with lower CO, for 0.3 mol/mol of dry waste at a temperature of 1273 K. But at lower moisture content (about 0.1) for almost the same amount of hydrogen produced, an equal amount of CO is also produced, thus enabling higher overall hydrogen production, through the WGS process. Sewage treatment using plasma gasification indicates (Mountouris et al., 2008) that integration of predrying and electrical energy production processes (or hydrogen) not only is self-sufficient from an energy point of view but leads to the availability of additional electrical energy for distribution. The primary roadblock to performance of plasma gasification is the amount of moisture in the feedstock, and the sensitivity is shown in Table 4.3. Correlating with the data from Mountouris et al. (2006), the moisture content of feedstock is not critical for hydrogen production although it is for electricity generation, as seen from the data in Table 4.3. The equilibrium model based on plasma gasification demonstrates that an input of 250 tons/day of sewage sludge with 68% moisture yields a net electric power output of 2.85 MW.

From an energy viewpoint, the ratio of power available for material treatment (after all power losses are subtracted from the arc power) to the total arc power (as shown in
Figure 4.10) increased with increasing arc power from 0.35–0.41 at arc power 95–100 kW to 0.41–0.46 for arc power higher than 130 kW for wall temperatures of 1100°C–1200°C. The ratio is lower for higher wall temperatures (Van Oost et al., 2009).

Plasma gasification above 1300 K when using biomass appears to produce higher fractions of hydrogen in syngas (Van Oost et al., 2009) than at 800 K, ranging from 28% to 46% by volume. Due to their high costs, plasma systems have been used primarily for the vitrification of high-toxicity waste and mainly at the pilot scale (Moustakas et al., 2008). As these systems become more accepted and their designs simpler, their use will likely be more extensive. Plasma gas used in gasifiers for vitrification also belongs to this category and can result in a significant waste reduction volume, ranging from about 5:1 for ash input to maximum 50:1 for solid waste (Minutillo et al., 2009). A better solution can be achieved using air as the plasma gas and adding oxygen to sustain the waste gasification. Then, the plasma gasification efficiency is 69%.

### 4.3.2 Anaerobic Digestion

Anaerobic digestion is similar to SCWG for producing syngas and substitute natural gas (SNG) by converting wet biomass with moisture of about 70–95 wt.% (Mozaffarian et al., 2004). Anaerobic digestion is a biological process that occurs in the absence of air and has been used to convert organic wastes to biogas, that is, a mixture of CH₄ (55–75 vol.%) and CO₂ (25–45 vol.%). During anaerobic digestion, typically 30%–60% of the solid input is converted to biogas. The by-products consist of an undigested residue and various water-soluble substances that may act as nutrients for algae growth and other biodigesters. Depending on the digestion system (wet or dry), the average residence time is between 10 days and 4 weeks. The anaerobic digestion of biomass and organic waste streams has the potential to facilitate energy recovery and sustainability from biodegradable waste (Duerr et al., 2007). With current developments in reformer technologies, hydrogen can be

<table>
<thead>
<tr>
<th>Moisture Content (% w/w)</th>
<th>Oxygen (mol/mol)</th>
<th>Net Thermal (MW)</th>
<th>Net Electrical (MW)</th>
<th>Syngas Heating Value (kWh/Nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero gasification energy (when the energy for gasification is self-sustained)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.2</td>
<td>0.53</td>
<td>−1.07</td>
<td>4.17</td>
<td>1.12</td>
</tr>
<tr>
<td>10.23</td>
<td>0.55</td>
<td>−0.92</td>
<td>4.04</td>
<td>1.03</td>
</tr>
<tr>
<td>14.68</td>
<td>0.57</td>
<td>−0.77</td>
<td>3.90</td>
<td>0.96</td>
</tr>
<tr>
<td>20.50</td>
<td>0.60</td>
<td>−0.54</td>
<td>3.71</td>
<td>0.86</td>
</tr>
<tr>
<td>27.04</td>
<td>0.64</td>
<td>−0.25</td>
<td>3.45</td>
<td>0.74</td>
</tr>
<tr>
<td>29.88</td>
<td>0.66</td>
<td>−0.10</td>
<td>3.33</td>
<td>0.69</td>
</tr>
<tr>
<td>34.92</td>
<td>0.70</td>
<td>0.19</td>
<td>3.07</td>
<td>0.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Moisture Content (% w/w)</th>
<th>Oxygen (mol/mol)</th>
<th>Gasification Energy (MW)</th>
<th>Net Electrical (MW)</th>
<th>Syngas Heating Value (kWh/Nm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zero net thermal energy (when net thermal energy is self-sustained)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.68</td>
<td>0.213</td>
<td>−3.92</td>
<td>2.12</td>
<td>2.14</td>
</tr>
<tr>
<td>20.50</td>
<td>0.348</td>
<td>−2.77</td>
<td>2.45</td>
<td>1.52</td>
</tr>
<tr>
<td>27.04</td>
<td>0.535</td>
<td>−1.18</td>
<td>2.90</td>
<td>0.95</td>
</tr>
<tr>
<td>29.88</td>
<td>0.613</td>
<td>−0.52</td>
<td>3.09</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Hydrogen Production Using Solid Fuels

Produced from CH₄-derived anaerobic digestion of organic waste material, much of which is currently landfilled through autothermal reforming (ATR).

Factors affecting anaerobic digestion operation and performance of such system as shown in Figure 4.11 include physical composition of the manure, manure type and manure collection method, and frequency of feeding the digester, along with suitable conditions for bacteria growth, for biogas energy production (Brown et al., 2007). Anaerobic bacteria grows and performs best under optimal temperatures in the range of 95°F–105°F, which has an optimal retention time range of 10–30 days and an optimal pH range of 7–8.5.

The production of biogas through anaerobic digestion offers significant advantages over other waste treatment processes (Ward et al., 2008), including the following:

- Production of less biomass sludge compared to aerobic treatment technologies.
- Success in treating wet wastes of less than 40% dry matter.
- More effective pathogen removal. This is especially true for multistage digesters or if a pasteurization step is included in the process.
- Minimal odor emissions, as 99% of volatile compounds are oxidatively decomposed upon combustion, for example, H$_2$S forms SO$_2$.
- A high degree of compliance with many national waste strategies, implemented to reduce the amount of biodegradable waste entering landfills.
- A slurry is produced (digestate), which is an improved fertilizer in terms of both its availability to plants and its rheology.
- A source of carbon-neutral energy in the form of biogas.
Hydrogen Production Using Solid Fuels

There are four important biological and chemical stages of anaerobic digestion (Gerardi, 2003):

- **Hydrolysis**: A chemical reaction where particulates are solubilized and large polymers converted into simpler monomers, when one or more water molecules are split into hydrogen and hydroxide ions.
- **Acidogenesis**: A biological reaction where simple monomers are converted into volatile fatty acids.
- **Acetogenesis**: A biological reaction where volatile fatty acids are converted into acetic acid, CO$_2$, and hydrogen. The acetate is produced by anaerobic bacteria from a variety of energy sources such as hydrogen and carbon.
- **Methanogenesis**: A biological reaction where acetates are converted into CH$_4$ and CO$_2$, while hydrogen is consumed by the formation of CH$_4$ by microbes known as methanogens.

The material drawn from the anaerobic digester is called sludge or effluent. It is rich in nutrients (ammonia, phosphorus, potassium, and more than a dozen trace elements) and is an excellent soil conditioner and feed for algae growth (Goodman, 1999). Digester sizing and process details are available elsewhere (Goodman, 1999; Gerardi, 2003; Pandey, 2004).

### 4.3.3 Chemical Looping Processes

**Chemical looping combustion (CLC)**, developed in the mid-1990s, uses metallic oxide as an oxygen carrier for combustion (Ishida and Jin, 1995). The fuel, mostly gases similar in composition to syngas, reduces the metal oxide to the corresponding metal at low temperature in the first reactor. In a second reactor, the metal is oxidized using oxygen in moistened air at high temperature to form the metal oxide, which is recycled to the first reactor. Hydrogen is produced from water in the second reactor. During the reaction in the first reactor, the oxygen in the metal is transferred to the carbon in the fuel forming CO$_2$ and water (Yu et al., 2003; Jin and Ishida, 2004; Fan et al., 2008). The water is condensed to separate CO$_2$ and send it to storage. This process exhibits a greater potential for CO$_2$ separation compared to membrane separation of CO$_2$.

Experimentation and process modeling and simulation suggest that a maximum coal-to-hydrogen conversion efficiency of 80% can be achieved using coal DCL (Fan et al., 2008; Gnanapragasam et al., 2009b). Some problems with this process include temperature issues relating to metal oxide (very high temperatures destabilize the structure) and sizing the reactor to control reaction rates (Fan et al., 2008).

Exergy analysis allows meaningful efficiencies and losses to be evaluated for energy systems and corresponding design improvements to be identified (Dincer and Rosen, 2007). Such an analysis suggests that the net power efficiency of a power generation system incorporating CLC exceeds that of a conventional power system by reducing combustion irreversibilities (Anheden and Svedberg, 1998). Of the various metal oxides that can be used for the syngas redox process, iron oxide (Fe$_2$O$_3$) has been identified as permitting the highest conversion of syngas to combustion products (CO$_2$ and water) along with a high conversion of steam to hydrogen (Gupta et al., 2007).

#### 4.3.3.1 Syngas Chemical Looping

**4.3.3.1.1 Reduction Reactor**

The syngas produced from the gasifier contains mostly CO, H$_2$, CO$_2$, and CH$_4$ (Li et al., 2001), and it reduces the metal oxide (Fe$_2$O$_3$) to the constituent metal (Fe and FeO). The advantage
of using iron oxide (Fe$_2$O$_3$) as the oxygen carrier is that it does not involve catalytically dependent reactions (Gupta et al., 2007). The gaseous products are CO$_2$ and steam. The steam is condensed to obtain sequestration-ready CO$_2$. The reactions of CO in the syngas with iron oxide and wustite (FeO) are given as follows:

\[
\text{Fe}_2\text{O}_3 + \text{CO} \rightarrow 2\text{FeO} + \text{CO}_2 \quad (4.15)
\]

\[
\text{FeO} + \text{CO} \rightarrow \text{Fe} + \text{CO}_2 \quad (4.16)
\]

Similarly, the reactions of hydrogen in the syngas with iron oxide and wustite (FeO) are as follows:

\[
\text{Fe}_2\text{O}_3 + \text{H}_2 \rightarrow 2\text{FeO} + \text{H}_2\text{O} \quad (4.17)
\]

\[
\text{FeO} + \text{H}_2 \rightarrow \text{Fe} + \text{H}_2\text{O} \quad (4.18)
\]

The reactions in Equations 4.15 through 4.18 occur at a pressure of 30 atm and a temperature ranging from 750°C to 900°C within the process shown in Figure 4.12. The particle size for the iron oxide is 2–10 mm. The reduction reactors in the syngas chemical looping (SCL) system are set with inert conditions for CH$_4$ since the model does not allow CH$_4$ to react with the iron oxide, thus completing the reactions in Equations 4.15 through 4.18 and enabling the production of hydrogen (Hoffman, 2005). In the SCL system, therefore, the CO$_2$ stream contains the unreacted CH$_4$, depending on the inlet conditions. These data are included in the results.

4.3.3.1.2 Oxidation Reactor

This reactor operates at 30 atm and 500°C–700°C to oxidize the metal produced in the reduction reactor using steam. The products are 99% pure hydrogen and magnetite (Fe$_3$O$_4$). The reactions are as follows:

\[
\text{Fe} + \text{H}_2\text{O}_{(g)} \rightarrow \text{FeO} + \text{H}_2 \quad (4.19)
\]

\[
3\text{FeO} + \text{H}_2\text{O}_{(g)} \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2 \quad (4.20)
\]

Both reactions are slightly exothermic and some of the heat may be used for preheating the feedwater to make steam. Hydrogen production using CLC of the syngas is indirect with the use of iron oxide. The actual hydrogen in the syngas is converted to water (Equations 4.17 and 4.18). These oxidation reactions are similar with a principal purpose as that of the SCL system to produce hydrogen as in the case of the DCL system in Figure 4.14.

4.3.3.1.3 Combustion Reactor

The magnetite formed in the oxidation reactor enters the combustion reactor where it reacts with oxygen to form a more stable form of iron oxide III (Fe$_2$O$_3$). A significant amount of heat is produced during the oxidation of Fe$_3$O$_4$ to Fe$_2$O$_3$. The reaction is

\[
4\text{Fe}_3\text{O}_4 + \text{O}_2 \rightarrow 6\text{Fe}_2\text{O}_3 \quad (4.21)
\]

The gas composition of exhaust (N$_2$ + O$_2$ in Figures 4.12 and 4.14) includes the remaining oxygen after the reaction in Equation 4.21 and the corresponding nitrogen.
Chemical looping with oxygen uncoupling (CLOU) is a novel method to burn solid fuels in gaseous oxygen without the need for an energy-intensive ASU (Mattison et al., 2008). The CO$_2$ from combustion is inherently separated from the rest of the flue gases. The reaction rate of petroleum coke was found to be approximately 50 times higher when using CLOU compared to the reaction rate of the same fuel with an iron-based oxygen carrier in conventional CLC.

**4.3.3.2 Direct Chemical Looping**

The DCL process removes the gasification process from the hydrogen production route. Rather, it has a fuel reactor that first combusts some feedstock to generate the temperature required for the endothermic reactions as described in Equations 4.24 through 4.28.
4.3.3.2.1 Fuel Reactor

The principal difference in the DCL system (Figure 4.13) relative to the SCL system (Figure 4.12) is the absence of the gasifier and the addition of a fuel reactor. The latter is an extended form of reduction reactor, and its chemical reactions are discussed as follows. The fuel reactor can be modeled as three separate Gibbs reactors (rigorous reaction and multiphase equilibrium based on Gibbs free energy minimization) linked together by restricting products from each of the three reactors: partial combustion, fuel reactor top, and fuel reactor bottom (see Figure 4.13). The reactions and conditions in the fuel reactor, based on Fan et al. (2008) and Mattison et al. (2008), are as follows:

- **Partial combustion**: Coal devolatilization and partial combustion occur (where the formula for coal used here represents Pittsburgh #8 coal, although a different coal similar in composition is used in the calculations) as follows:

  \[
  \text{C}_{11}\text{H}_{10}\text{O} \rightarrow \text{C} + \text{CH}_4 \quad (4.22)
  \]

  \[
  \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \quad (4.23)
  \]

- **Fuel reactor top**: Char gasification and iron oxide reduction occur as follows:

  \[
  2\text{C} + \text{O}_2 \rightarrow 2\text{CO} \quad (4.24)
  \]

  \[
  \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \quad (4.25)
  \]
Hydrogen Production Using Solid Fuels

2C + H₂ → CO + H₂ \hspace{1cm} (4.26)

CH₄ + 4Fe₂O₃ → CO₂ + 2H₂O + 8FeO \hspace{1cm} (4.27)

- **Fuel reactor bottom**: Wustite (FeO) reduction occurs, following the reactions in Equations 4.15 and 4.16.

The overall chemical reaction within the fuel reactor (Fan et al., 2008) is

\[ \text{C}_{11}\text{H}_{18}\text{O} + 6.44\text{Fe}_2\text{O}_3 + 3.34\text{O}_2 \rightarrow 11\text{CO}_2 + 5\text{H}_2\text{O} + 12.88\text{Fe} \] \hspace{1cm} (4.28)

The residence time for the coal char in the fuel reactor is between 30 and 90 min (Fan et al., 2008), depending on operating temperature (750°C–900°C) and pressure (1–30 atm). The reaction in Equation 4.27 enables the conversion of CH₄ in the gas stream to CO₂ and H₂ while reducing iron oxide (Fe₂O₃). Thus, in the DCL system, the CO₂ stream may not contain CH₄, unlike the SCL system.

Figures 4.14 and 4.15 show the range (from 15 to 25 kg/s) of air mass flow rate into the gasifier for the SCL system and into the fuel reactor for the DCL system, on the horizontal axis. The distributions of the production of H₂, CO₂, and CH₄ are plotted in Figure 4.14 for the corresponding change in inlet air mass flow rate to the gasifier in the SCL system. In Figure 4.15, a similar distribution is shown for the DCL system, except for CH₄ since
it is consumed within the process (Equation 4.27) and not produced along with \( \text{H}_2 \) and \( \text{CO}_2 \) as in the SCL system. Since \( \text{CH}_4 \) is not converted to hydrogen or any other form in the SCL system, the \( \text{H}_2 \) output rate in Figure 4.14 increases with air inlet flow rate until the air inlet flow rate reaches 19 kg/s, when \( \text{CH}_4 \) is no longer produced in the gasifier of the SCL system. The results in Figures 4.14 and 4.15 are based on simulations of the SCL and DCL systems when anthracite coal is used at a rate of 5 kg/s. Theoretically, the DCL system is better than the SCL system in producing more hydrogen at low oxygen input (Gnanapragasam et al., 2009b), but this observation has not been confirmed at large scales.

### 4.3.4 Autothermal Reforming

Hydrogen production from coal-derived methanol via ATR has been reported to have fewer trace impurities than other coal-based hydrogen production processes, mainly due to higher operating temperature generated by the partial oxidation step (Yoon and Erickson, 2008) as shown in Figure 4.16. Coal-based methanol has been shown to have higher amounts of trace hydrocarbons than chemical-grade methanol derived from natural gas, so hydrogen production from coal-derived methanol via ATR is feasible considering fuel cell applications.

Natural gas and the thermolysis gases from petroleum and coal can be thermally decomposed to manufacture hydrogen and vapor-deposited carbon materials, in the form of nanoparticles, fibrous materials, or pyrolytic carbon solids (Halloran, 2008). Coal thermolysis can produce hydrogen from coke oven gas and carbon materials from fabricated cokes.
The combined manufacture of hydrogen and carbon materials would be economical if the market value of the hydrogen and solid carbon materials were greater than the value of coal as a fuel.

ATR uses oxygen and CO\(_2\) or steam in a reaction with CH\(_4\) to form syngas (Xuan et al., 2009). The reaction takes place in a single chamber where the CH\(_4\) is partially oxidized. The reaction is exothermic due to the oxidation. When the ATR uses CO\(_2\), the H\(_2\)/CO ratio produced is 1:1; when the ATR uses steam, the H\(_2\)/CO ratio produced is 2.5:1.

The exothermic reaction in the ATR process when using CO\(_2\) is

\[
2\text{CH}_4 + \text{O}_2 + \text{CO}_2 \rightarrow 3\text{H}_2 + 3\text{CO} + \text{H}_2\text{O} \tag{4.29}
\]

and when using steam is

\[
4\text{CH}_4 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 10\text{H}_2 + 4\text{CO} \tag{4.30}
\]

The outlet temperature of the syngas is between 950\(^\circ\)C and 1100\(^\circ\)C, and the outlet pressure can be as high as 100 bar (Mahecha-Botero et al., 2008). The main difference between SMR and ATR is that SMR uses no oxygen. The advantage of ATR is that the H\(_2\)/CO can be varied, which is particularly useful for producing some second-generation biofuels, such as dimethyl ether (DME, CH\(_3\)OCH\(_3\)) that requires a 1:1 H\(_2\)/CO ratio. For the generation of hydrogen, the use of steam in the flow of processes in the ATR system is shown in Figure 4.16. The broken lines in Figure 4.16 denote SMR, while the solid lines denote the ATR process.
4.3.5 Hydrogen Separation and Purification Processes

Hydrogen is generated from the gasification process and available in the syngas, but it needs to be separated before and after WGS reaction. Chemical looping does not require physical hydrogen separation since it is a thermochemical process and enables cheaper separation (Andrus, 2009). After hydrogen is separated, it still contains other gaseous elements in smaller amounts that need to be removed for highly purified hydrogen.

4.3.5.1 Water–Gas Shift Process

WGS catalysts have been commercially developed for use by the petrochemical industry (Leach, 1984; Twigg, 1996). Presently, there is renewed interest in the WGS reaction because of its importance in reforming fuels to hydrogen for use in fuel cells. Since biomass gasification yields relatively high CO/H₂ ratios, higher hydrogen contents can be achieved using commercial CO shift catalysts in two fixed-bed reactors operated in series: a high-temperature shift reactor (HTSR) for rapid reaction and a low-temperature shift reactor (LTSR) to shift thermodynamic equilibrium to very low levels of CO (Zhang et al., 2005). The high-temperature shift reaction takes advantage of faster kinetics at elevated temperatures to convert about 75% of the CO into H₂. Conversion is, however, limited by thermodynamic equilibrium, which favors hydrogen formation at low temperatures. Accordingly, the gas is slightly cooled and passed through a second LTSR to convert most of the remaining CO to H₂.

The WGS reactors in Figure 4.17 are arranged to obtain the maximum hydrogen production. The WGS reaction, Equation 4.6, is carried out in two reactors placed in series, including a HTSR and LTSR. These reactors operate at temperatures of about 350°C–400°C.
Hydrogen Production Using Solid Fuels

and 190°C–210°C, respectively (Perna, 2008). The catalysts employed to improve the reaction rate are sulfur tolerant, thus enabling the sulfur removal unit to be downstream of the shift units (Chiesa et al., 2005). The syngas exiting the LTSR is cooled at the operating temperature of the acid gas removal (AGR) unit.

The steam-to-carbon ratio ($S_{\text{SHIFT}}/C$) in the WGS reactors in Table 4.4 is defined as the ratio of the mass flow rate of the feed coal to the mass flow rate of the water input to the shift units, in the range 0.6–1.2. It is assumed that the mass fraction input to the HTSR is 0.67. The syngas converted after the WGS process is similar in composition to Table 4.4.

The catalytic tar process in combination with high- and low-temperature WGS reactors upgrades hydrogen in the raw gas from 5.8–8.8 vol.% to as high as 27–29 vol.% (Zhang et al., 2005). The CO concentration of 13–15 vol.% in the raw gas is reduced to less than 0.5 vol.%. The conversion of CO in the high-temperature WGS reaches 75%–80%, while the CO conversion by the combination of high- and low-temperature WGS reactors exceeds 95% (Mahecha-Boteroa et al., 2009).

### 4.3.5.2 Gas Separation Membranes

Gas separation using membranes of various kinds, primarily differentiated by the membrane material, is a rapidly evolving field (Li, 2007). The most common commercial materials for membranes include metallic, ceramic, and polymeric substances and, recently, carbon-based nanotubes or pores in compact grid arrangements (Kerry, 2006). It was reported in 2004 that membrane use in power cycles and fuel production using fossil fuels through the integration of membrane technologies has not been fully explored (Bredesen et al., 2004). Since then, several integration works have been reported, including design optimization and feasibility assessments using techno-economic analyses of the membranes for power and fuel production systems (Amelio et al., 2007; Rezvani et al., 2009). New combustion processes with porous membrane integration have also been recently reviewed (Mujeebu et al., 2009), providing a broader picture of membrane applications in energy conversion processes: mainly air separation and CO$_2$ and H$_2$ separation.

| TABLE 4.4 |
| Characteristics of the Syngas from LTSR at Different $S_{\text{SHIFT}}/C$ Ratios in the Conditions of Maximum Hydrogen Production |
| $S_{\text{SHIFT}}/C$ | 0.6 | 0.8 | 1 | 1.2 |
| $S/C$ | 0.7 | 0.6 | 0.4 | 0.2 |
| Molar Composition (%) | | | | |
| H$_2$ | 49.95 | 48.92 | 49.58 | 50.15 |
| CO$_2$ | 33.28 | 32.44 | 32.39 | 32.28 |
| CO | 0.89 | 0.55 | 0.61 | 0.72 |
| H$_2$O | 14.34 | 16.61 | 15.96 | 15.4 |
| H$_2$S | 0.5 | 0.49 | 0.49 | 0.49 |
| CH$_4$ | 0 | 0 | 0 | 0.01 |
| N$_2$ + Ar | 1 | 1 | 1 | 1 |
| Hydrogen Flow Rate (kg/kg coal) | | | | |
| H$_2$ | 0.156 | 0.159 | 0.161 | 0.162 |

Of the current noncryogenic technologies for oxygen separation, membranes such as the ITM provide clean, efficient, and economic means of producing oxygen (Li, 2007). Ionic conducting or ionic and electronic conducting ceramic dense membranes are of particular interest due to their 100% selectivity for oxygen, with three to four orders of magnitude higher flux than the best organic membranes.

Carbon separation membranes (CSMs) are ceramic hollow fiber membranes that provide a good alternative. Ceramic hollow fiber membranes are not commercially available at present, mainly due to the lack of techniques to produce the ceramic membrane with a thin and dense separation layer in a hollow fiber form (Li, 2007). Hollow fiber membranes are frequently produced from polymeric materials and can provide the highest membrane area per unit packing volume, achieving densities as high as 8,000–10,000 m²/m³ (Li, 2007). However, this configuration is seldom used in ceramic membranes because of its poor mechanical strength. An early effort at gas separation, via the development of glass hollow fiber membranes (Way and Roberts, 1992), yielded membranes that were too fragile for industrial uses. Many other attempts have been made to develop fabrication techniques for hollow fiber ceramic membranes (Smid et al., 1996; Brinkman et al., 2000; Luyten et al., 2000; Tan et al., 2001; de Jong et al., 2004; Xu et al., 2004; Liu et al., 2006).

A fundamental process for noncryogenic separation of industrial gases is permeation (Kerry, 2006), which involves the diffusion of a substance in solution through a barrier or membrane. Permeability is the capacity of a porous material (membrane) for transmitting a fluid. The membranes used for permeation simulation in this work may be one or a combination of thin, dense, and continuous films formed from cellulose acetate or polymers.

The separation of a component in a gas mixture is carried out in three steps, in which the component dissolves in the membrane wall, diffuses through the membrane material, and is desorbed on the opposite side of the membrane wall. This procedure can be defined by Henry’s law of solubility and by Fick’s law of diffusivity, while noting that the solubility of a gas in a liquid is proportional to the partial pressure of the gas. These laws can be expressed as follows:

Feed gas solubility in the polymer:

\[ z_{IP} = S_i P_i x_i \] (4.31)

Fick’s law inside membrane material:

\[ \frac{Q_i}{A} = \frac{D_i (x_i - y_i)}{L_p} \] (4.32)

Permeate solubility in the polymer:

\[ z_{IP} = S_i P_p y_i \] (4.33)

The operating performance of any polymeric membrane is characterized by two factors: (1) permeability (which defines productivity, the transport rate for a given species in the feed stream, and, therefore, the cost of the system) and (2) selectivity (which in turn defines recovery or purity of the selected stream). Expressions for permeability and selectivity can be derived from Equations 4.31 through 4.33 (Fleming and Dupuis, 1993). For oxygen separation from air, N\(_2\) is more permeable than O\(_2\) due to the higher molar fraction of N\(_2\) in air, whereas H\(_2\) is more permeable than CO\(_2\) due to the lower molar fraction of CO\(_2\) in the exhaust gas stream after WGS reaction.
4.3.5.3 Pressure Swing Adsorption for Hydrogen Purification

The quality of the hydrogen produced can be a major issue for automotive applications. The pressure swing adsorption (PSA) unit produces hydrogen with 99.999% of purity, operates at above 20 bar, and reaches H\(_2\) separation efficiencies in the range 85%–90%. The PSA purge gas (waste gas) can be used to superheat steam or can be combusted for power generation in a gas turbine combined cycle (Perna, 2008). New hydrogen plants are almost invariably designed using PSA for final hydrogen purification (Hamelinck and Faaij, 2002).

PSA is based on the difference in adsorption behavior between different molecules (Katofsky, 1993). The process separates components of a gas stream by selective adsorption to a solid at high pressure and subsequent desorption at low pressure. This adsorption/desorption is a batch process, but by placing two beds in parallel, it operates nearly continuously. While adsorption takes place in one bed, the other is desorbed (LaCava et al., 1998). First, activated carbon in the set of beds \(A\) selectively adsorbs nearly all CO\(_2\) and all H\(_2\)O. The remaining gas then passes to the second set of beds \(B\) containing a zeolite molecular sieve, which selectively adsorbs essentially all the remaining compounds and some hydrogen. The overall recovery of hydrogen is increased by recycling some of the desorbed gas from the \(B\) beds (LaCava et al., 1998). There is a trade-off in that the recycled gas must be recompressed and cooled to near-ambient temperature, adding to capital and operating costs, and a slightly larger PSA unit will also be needed. As with the methanol synthesis loop, some of the recycled gas must be purged to prevent the buildup of CH\(_4\) and other nonhydrogen gases. Recovery rates of over 90% are achievable, and the product purity is extremely high: 99.999%.

In PSA, species other than hydrogen are selectively adsorbed on a solid adsorbent, for example, activated carbon and 5A zeolite (Ruthven et al., 1994), at a relatively high pressure by contacting the gas with the solid in a packed column in order to produce a hydrogen-rich gas stream. The adsorbed species are then desorbed from the solid by lowering the pressure and purging with high-purity product hydrogen, and the PSA waste gas is generated. Continuous flow of product is maintained by using multiple, properly synchronized adsorption beds.

In a pressure swing adsorption (PSA) facility for H\(_2\) purification, the impurities are adsorbed at high pressure, while H\(_2\) passes through the adsorber vessel. When the vessel is full, it is disconnected from the process and the pressure is decreased, thus releasing most of the impurities (Rydén and Lyngfelt, 2006). A small fraction of the produced H\(_2\) is needed for purging and regeneration of the adsorbers, so the H\(_2\) recovery is limited to about 90%. The off-gas from the adsorber vessel consists of CO\(_2\), purge H\(_2\), unreformed CH\(_4\), some CO, and minor fractions of other impurities. PSA is a batch process, but by using multiple adsorbers, it is possible to provide constant flows. The pressure drop for H\(_2\) is usually about 0.5 bar. There is no need for power, heating, or chemicals.

4.4 Environment Protection Processes

When producing hydrogen from coal, pollutants of various forms are released at various conversion stages to the Earth’s surface and lower atmosphere. Only gases that form in large quantities, such as H\(_2\)S, carbonyl sulfide (COS), and CO\(_2\), and solids, such as ash, tars, and other nonenergy solid wastes, are discussed as part of pollution-control processes. These have to be managed for a sustainable environment without long-term damage to the
balance in the ecosystem. This section discusses some of the primary measures in managing these hazardous wastes that result in using coal and other solid fossil fuels. These processes improve the sustainability of hydrogen production systems that use solid fuels.

4.4.1 Acid Gas Removal: Sulfur Removal

Sulfur appears as SO$_2$ (only in combustion processes), H$_2$S, and COS in syngas after the energy conversion of sulfur-rich solid fuels (all solid fossil fuels). Sulfur in raw coal is converted to H$_2$S and COS in the gasifier, and most of the COS is converted to H$_2$S in the WGS reactors. In systems without the WGS process and CO$_2$ removal (Kohl, 1997), COS is typically hydrolyzed to H$_2$S in a catalytic bed at about 200°C.

AGR units (shown in Figure 4.18) are based on chemical absorption and physical absorption for atmospheric and pressurized configurations, respectively (Perna, 2008). AGR removes 99.9% of the H$_2$S, which is converted to elemental sulfur via Claus and shell claus
off-gas treating (SCOT) plants. The efficiency of the CO₂ capture unit is assumed equal to 95%. Prior to CO₂ capture, H₂S is removed from the syngas (containing 0.6% H₂S by volume) by physical absorption in CH₂OCH₃ of polyethylene glycol (Selexol). The WGS reactors included in H₂ plants and electricity plants with CO₂ capture greatly elevate (relative to electricity plants with CO₂ venting) the CO₂/H₂S ratio in the syngas and thus promote significant cocapture of CO₂ along with H₂S in the H₂S absorption tower.

Since essentially all of the sulfur in the gasifier feedstock is converted to H₂S, the amount of H₂S produced is totally dependent on the sulfur content of the feedstock. Note that coal has a relatively high sulfur content, while biomass has a relatively low sulfur content. Generally, the AGR processes lower the H₂S content of the syngas to less than 4 ppm, which means that, in essence, all of the H₂S produced in the gasifier must be processed in the sulfur recovery system.

4.4.2 Claus and SCOT Processes: Sulfur Recovery

The type of sulfur recovery system required is dependent on the required sulfur recovery efficiency, the quantity of sulfur to be removed, and the concentration of the H₂S in the acid gas. The required sulfur removal/recovery efficiency will vary depending on location; however, the gasification industry claims that the technology has near-zero pollution, so it necessitates the industry to install the best available control technology. Currently, H₂S removal efficiencies of 99.9% can be economically achieved (Nagl, 2005).

The Claus process has been the main sulfur recovery process for applications with large amounts of sulfur (greater than 20 long tons per day), relatively high H₂S concentrations (greater than 15%), and consistent inlet conditions. However, the Claus process is limited by chemical equilibrium to removal efficiencies of approximately 98% if three catalytic reactor stages are employed. To achieve higher removal efficiencies, a tail gas treating unit is required. For over 30 years, the preferred tail gas treating process has been the SCOT process. In that process, the tail gas from the Claus unit is heated to approximately 300°C in an in-line burner, which serves the dual purpose of heating the gas stream and producing a reducing gas, which is needed in the downstream reactor. The effluent from the burner is then passed over a cobalt–molybdenum catalyst. In the reactor, all of the SO₂, COS, and CS₂ are converted to H₂S by a combination of hydrogenation and hydrolysis reactions. The reactor effluent gas is then cooled and processed through a typical amine unit, which is selective to the absorption of H₂S. The recovered H₂S is then recycled back to the Claus unit, and the remaining gas is sent to an incinerator prior to exhausting to the atmosphere.

Although many of these processes are mature, when integrated with hydrogen production, process optimization becomes essential for improving the overall energy efficiency.

4.3 Tar, Ash, and Soot Removal

The presence of tars in the product gas is a significant challenge in the commercial utilization of coal and biomass product gas (syngas) as a source of sustainable energy. Tar is formed in the gasifier and comprises a wide spectrum of organic compounds, generally consisting of several aromatic rings. Simplified tars can be separated into heavy and light tars (Higman and Burgt, 2008). Heavy tars condense as gas temperature drops and cause notable fouling, efficiency loss, and unscheduled plant shutdowns. The tar dew point, that is, the temperature at which tars start to condense, is a critical factor. Light tars like phenol or naphthalene have limited influence on the tar dew point but are not less problematic.
Light tars like phenol chemically pollute the bleed water of downstream condensers and aqueous scrubbers. Naphthalene is important as it is known to crystallize at the inlet of gas engines increasing needs for maintenance and service.

Conventional gas tar cleaning is based on wet scrubbing and on a wet cleaning with an electrostatic precipitator (ESP). In some new processes (Zwart et al., 2008), the tar removal principle is based on a multiple-stage scrubber in which gas is cleaned by a special scrubbing oil. In the first stage, the gas is cooled with scrubbing oil. Heavy tar particles condense and are collected, after which they are separated from the scrubbing oil and can be recycled to the gasifier, together with a small bleed. In the second stage, lighter gaseous tars are absorbed with scrubbing oil. In the absorber column, the scrubbing oil is saturated by these light tars. This saturated oil is regenerated in a stripper. Hot air or steam is used to strip the tars of the scrubbing oil. All heavy and light tars can be recycled to the gasifier where they are destroyed and contribute to the energy efficiency. Tar waste streams are efficiently recycled this way.

The raw syngas generated in a partial oxidation gasifier also includes carbon soot that is removed and recovered from the syngas by scrubbing with water (as shown in Figure 4.19). The scrubbing water contains one or more high-temperature surfactants that allow greater soot concentrations in the water-scrubbing quench zone of the gasifier. The carbon soot is separated from the scrubbing water with the aid of scrubbing oil. The separation of the carbon soot from the scrubbing water is enhanced with the aid of one or more surfactants that render the soot particles hydrophobic and oleophilic (Jahnke, 2003). The recovered carbon soot is ultimately recycled to the gasifier to recover the energy value of the carbon during the partial oxidation reaction. The overall energy efficiency of the gasification process can be

FIGURE 4.19
Syngas carbon soot removal unit. (Adapted from Gasification, 2nd edn., Higman, C. and van der Burgt, M., Copyright 2008, with permission from Elsevier.)
increased by removing all or a significant portion of the water from the soot mixture before recycling the soot. Separating the soot from the water allows for independent regulation of the soot and water recycle streams, depending on the reaction conditions in the gasifier.

Other solid particles from mostly syngas are removed at several stages. Char particles are collected in a syngas cooler and cyclones and recycled to the gasifier. Slag from the gasifier is water quenched and removed through a lock hopper (Collot, 2006). Syngas is quenched with recycled cleaned cooled water. Raw syngas is then dedusted in ceramic candle filters. Molten ash is tapped off and quenched with water in the bottom of most types of gasifiers. Ash is commonly removed from the gasifier by a revolving grate and depressurized in a lock hopper.

### 4.4 CO₂ Capture and Storage

The current challenge for using carbonaceous solid fuels in producing hydrogen is the capture and disposal/storage of CO₂ in an environmentally feasible manner (EcoEnergy, 2008). Based on a performance evaluation of state-of-the-art commercial technology for hydrogen coproduction (Chiesa et al., 2005), a system that converts 57%–58% of the coal lower heating value (LHV) to hydrogen while exporting to the grid electricity amounting to 2%–6% of the coal LHV, in contrast to decarbonizing coal in IGCC electricity generation (which entails a loss of 6%–8% points of electricity conversion when capturing CO₂ as an alternative to venting it), CO₂ capture for hydrogen production incurs a minor energy penalty (2% points of export electricity). Some of these losses are attributable to the number of intermediate processes involved in producing hydrogen from coal, including several for pollution control.

The hydrogen from various gas streams, subsequent to cleaning and particle separation, is accompanied by CO₂, which can be stored (Damen et al., 2007) and used for different applications. After further cooling of syngas from gasifiers, H₂S is removed from the syngas using a physical solvent (Selexol) and CO₂ is removed from the syngas (again using Selexol). After being stripped from the solvent, the CO₂ is dried and compressed to 150 bar for pipeline transport and underground storage (Higman and Burgt, 2008). Three paths for the CO₂ are possible, as shown in Figure 4.1. The commercial route is already applied by several industries for using and storing CO₂ in various forms. The current commercial applications include industrial use of CO₂ in large refrigeration systems making dry ice, enhanced oil recovery, and manufacturing of various chemicals. Also some CO₂ produced within the hydrogen production system may be used for transporting solid fuels into high-pressure reactors.

The second option of storage involves sending the remaining CO₂ for large-scale underground storage (IEA, 2008b). Such processes are being implemented commercially in recent years through a process known as geological sequestration (GS), where the CO₂ is compressed and placed in deep underground aquifers, depleted oil and gas reservoirs, and dried underground coal beds. Some large-scale CO₂ storage projects are already in operation and under construction, while others are the subject of feasibility studies (NETL, 2009).

There is an upcoming and promising third option of disposing CO₂, converting CO₂ into microalgae using sunlight and water, via algae-based artificial photosynthesis (in Figure 4.1). Microalgae are microscopic photosynthetic organisms. They generally produce more of the kinds of natural oils needed for biodiesel extraction (Sheehan et al., 1998). Autotrophic
algae enable the photosynthesis process by utilizing light, CO$_2$, and water to grow the candidate algae (depending on the conditions available for growth). Heterotrophic algae use thermal energy from waste heat applications, CO$_2$, and nutrients derived from biogas effluents, leachate in landfills, and wastewater from fermenting processes. Some of the advantages of algae include (Sheehan et al., 1998) the following:

- Use of far less water than traditional oilseed crops.
- More efficient conversion of solar energy because of their simple cellular structure.
- Capable of producing 30 times the amount of oil per unit area of land, compared to terrestrial oilseed crops.
- Capable of taking the waste (zero-energy) form of carbon (CO$_2$) and converting it to a high-density liquid form of energy (natural oil).
- Growth that is directly proportional to the surface area and the area of exposure to sunlight (only for autotrophs).
- Use of optical fiber–based reactor systems (only for autotrophs) developed by Japanese researchers that could dramatically reduce the amount of surface area required for algae production.
- Three main ingredients of microalgae: carbohydrates, protein, and natural oils.
- Fuel production concepts:
  - Production of CH$_4$ gas through biological or thermal gasification: breakdown of any form or organic carbon into CH$_4$
  - Production of ethanol through fermentation: most effective for conversion of carbohydrate portion of algae
  - Production of biodiesel: applies exclusively to the natural oil fraction of the microalgae
- Ability to produce up to 60% of their body weight in the form of triacylglycerols (TAGs), making it an alternative source for biodiesel than the oilseeds.
- Transesterification: reacting TAGs with simple alcohols creates a chemical compound known as alkyl ester or, more commonly, biodiesel.
- Not dependent on land area if algae are grown in large existing aquatic environments, although for large-scale production, a sizable portion of the land (nonagricultural land) area is needed.

There is also a fourth option not denoted in Figure 4.1, which is the mineral storage of CO$_2$, in which CO$_2$ is reacted with naturally occurring magnesium (Mg)- and calcium (Ca)-containing minerals to form carbonates. This process has several advantages, the most significant of which is the fact that carbonates have a lower energy state than CO$_2$, which is why mineral carbonation is thermodynamically favorable and occurs naturally (Shackley and Gough, 2006). Thus, the carbonates are stable and are unlikely to convert back to CO$_2$ under standard conditions. On the same basis, CO$_2$ recycle or reuse is another option that involves metal oxides such as Fe$_2$O$_3$, ZnO, and CaO to split CO$_2$ into CO and oxygen, for use in various processes (Kodama and Gokon, 2007). The latter option, in which CO$_2$ is split into CO and oxygen is an artificial photosynthesis process; it is a greenhouse-type concept for controlled feeding of biologically engineered plants that can consume, in a controlled environment, high volumes of CO$_2$ to store carbon and emit oxygen (Collings and Critchley, 2005).
4.5 Economic Benefits through Process Integration

Several paths exist to obtain hydrogen from water using energy from solid fuels, but the sustainability of these paths remains partly dependent on the economics of the overall system. This section presents an overview of the benefits of appropriate process integration toward economic sustainability of hydrogen production using solid fuels as the energy source.

Biomass is likely to remain a major solid fuel in driving the hydrogen economy. By the year 2050, according to the VTT report estimates (IEA, 2008b), agricultural and forestry residues and wastes will be the most cost-competitive types of biomass, with only around 30% of total bioenergy coming from specialized energy crops. Only current technologies and crop yields are used in this assessment, and population growth is taken to be zero. Larger biomass-based plants can achieve economies of scale, but this can be more than offset by the increased transport distances needed to obtain the required volume of biomass. The costs of delivered biomass vary with country and region due to factors including variations in terrain, labor costs, and crop yields. On average in Europe, the cost of operating a forwarder is USD 67–104/h, chipping costs USD 148–213/h, transport costs USD 91–143/h, and loading/unloading costs USD 40–83/h.

The coal sector is well established from mining to transportation to distribution and utilization, enabling economic development in several countries around the world (IEA, 2008a). Some current and possible future integration benefits are given in the following.

### 4.5.1 Integration of Energy Conversion and Waste Management Processes

Integrated processes, such as the one shown in Figure 4.20, create opportunities to improve the use of solid fuels, thereby reducing the associated environmental pollution and helping meet growing energy demands (Gnanapragasam et al., 2010). Numerous small-scale integrated projects for end users, such as combined power generation with hydrogen production and CO₂ capture, and their benefits have been investigated (Chiesa et al., 2005;

![FIGURE 4.20](image1)

Example of process integration aimed at centralized hydrogen production for energy, environment, and economic benefits.
Handbook of Hydrogen Energy

Damen et al., 2006; Shoko et al., 2006; Stiegel and Ramezan, 2006; Turner et al., 2008). New energy conversion technologies are also being developed and adopted due to the potential markets for efficient processes. Gasification as shown in Figure 4.7 is a promising conversion process that is expected to achieve significantly higher efficiencies for coal/biomass conversion to electricity and transport fuels (Beer, 2000).

4.5.1.1 Benefits of Process Integration

In large-scale process integration, solid fuels are converted via various industrial-scale integrated processes to convenient energy forms and ultimately to hydrogen. The benefits of such systems include the following:

1. Multiple uses of feedstock: Input solid fuels are converted to hydrogen, increasing efficiency and decreasing waste generation.

2. Demand-based production: Since each feedstock has a different market value, a proper blend of the cheapest and most efficiently used feedstocks can be used to reduce operating costs as well as to conserve rare fuels.

3. Process applicability: Based on the market value and demand for hydrogen, some of the processes are used for producing other products such as chemicals, reducing operating costs while utilizing the full potential of the facility.

4. Resource availability: Proven coal reserves and potentially consistent biomass supplies (IEA, 2006, 2007, 2008; Asif and Muneer, 2007), as well as the challenges associated with solid waste disposal (e.g., lack of landfills, special needs depending on the nature of waste), contribute to sustainability by being flexible in terms of allowable feedstocks.

5. Proven technologies: The processes considered have been tested or proven in industry so as to ensure high efficiency and low pollution with optimized performance.

6. Opportunities: When combining several processes for multiple products, new opportunities are provided for improving and developing these processes.

7. Centralized pollution control: Integration provides a major advantage by permitting centralized pollution control (reducing the overall energy consumption), which increases the capture efficiency for many pollutants, for example, SO$_2$, H$_2$S, COS, NO$_x$, and CO$_2$.

4.5.1.2 Challenges in Large-Scale Process Integration

Integration poses several challenges including potential incompatibility of processes and the need for additional accessory units that increase costs and reduce overall system efficiency. The demand for hydrogen energy is not yet large, in part because infrastructure for hydrogen is not yet widely available. Much of the public and the media view coal as dirty based on data from existing power plants, which lack the pollution-control technologies capable of achieving near-zero emissions, confusing information and lack of awareness about cleaner technologies for using solid fuels. The project in Figure 4.6 has various stages of analysis, including thermodynamic, material, economic, environmental, market, and optimization. These stages should detail the benefits of implementing such a system into the existing energy infrastructure. The multiproduct and integrated nature of the system enables efficient use of coal, biomass, and municipal solid waste in producing electricity, hydrogen, and chemicals simultaneously, thereby contributing to making energy systems more sustainable.
4.5.1.3 Economics of Process Integration

Gasification appears to be a more advantageous use of biomass than combustion, but a comprehensive economic analysis of biomass gasification systems suggests that the costs of plant construction are high compared with conventional plants while there are environmental benefits (Dowaki et al., 2005). Hence, an appropriate business model may be available in the future. Gasification has been proven to be the most advantageous conversion process for the initial stages of a hydrogen production facility. However, for gasification to play a major role in the near future, capital and operating cost must be reduced and reliability and performance improved (Collot, 2006).

There are currently several research and industrial development projects worldwide on IGCC and integrated gasification fuel cell (IGFC) systems (Shoko et al., 2006). In such systems, there is a need to integrate complex unit operations including gasifiers, gas separation and cleaning units, WGS reactors, turbines, heat exchangers, steam generators, and fuel cells. The IGFC systems tested in the United States, Europe, and Japan employing gasifiers (types include Texaco, Lurgi, and Eagle) and fuel cells have resulted in energy conversion efficiencies of 47.5% (HHV), which is much higher than the 30%–35% efficiency of conventional coal-fired power generation. IGCC and IGFC are currently not viable economically compared with current coal-utilization technologies, but further efficiency improvements and reductions in gaseous pollutant emissions could render the technologies more competitive. Hydrogen produced from coal-based gasification has recently been shown to be competitive with production from natural gas provided the cost of natural gas remains above $4/10^6 Btu, and the reliability of gasification-based processes can be demonstrated to be high (Stiegel and Ramezan, 2006). These authors suggest that the cost of producing hydrogen from coal could be reduced by 25%–50%, even with the capture and sequestration of CO₂.

Energy conversion efficiencies are greatest for natural gas–based systems due to the fuel characteristics. The costs of hydrogen production for natural gas and coal/biomass are much lower than for electrolysis (which presently has only a 4% market share) due to the volume of production (which is much higher for hydrogen from fossil fuels) and the mature state of the technology. A comparison of efficiencies and costs for various hydrogen production methods (Shoko et al., 2006) shows steam reforming of natural gas to be the most beneficial, with high efficiencies (65%–75% based on LHV) and low production costs (USD 5–8/GJ). Gasification of biomass and coal has an overall efficiency of 42%–47% (LHV) with an average production cost at USD 9–13/GJ, while water electrolysis has the lowest efficiency (35%–42% HHV) and the highest production cost (on average USD 20/GJ).

4.5.2 Cost of Hydrogen Production: Impact of CO₂ Capture on Various Technologies

The costs of hydrogen production with coal-based technologies are compared with those for established technologies in Figure 4.21. With current technologies, large-scale hydrogen production can be attained with SMR and coal gasification with CO₂ capture from the shifted syngas, resulting in a CO₂ capture efficiency of 85%–90% (Damen et al., 2006, 2007). The conversion efficiency, including electricity inputs and outputs in primary terms, is 73% for SMR and 59%–62% for coal gasification. Investment costs are approximately 550 and 840 €/KWh for 1000 MWh SMR and coal gasification plants, respectively. The costs of hydrogen produced by SMR are dominated by fuel and feed costs, which makes coal gasification more favorable, especially if energy prices rise increasingly. Hydrogen production costs for SMR are estimated at 9.5 €/GJ and an optimally designed coal gasification
plant with electricity export may reach 7 €/GJ. CO₂ avoidance costs compared to identical plants without CO₂ capture are 23 and 5 €/ton of CO₂ for SMR and coal gasification, respectively. The penalty for CO₂ capture is compared in Figure 4.22 with other hydrogen production technologies, based on data compiled by SDTC (2006). The rectangular boxes in Figures 4.21 and 4.22 identify processes relating to hydrogen production using solid fuels.

Advanced large-scale ATR and coal gasification systems with ion-transfer membranes enable hydrogen production with 90% CO₂ capture at efficiencies of 73% for ATR and 69% for coal gasification (Damen et al., 2006, 2007). Investment costs for these systems are estimated at nearly 300 and 600 €/kWh, resulting in hydrogen costs of 8.1 and 6.4 €/GJ and CO₂ avoidance costs of 13 and 5 €/ton CO₂ for ATR and coal gasification, respectively.

A membrane reformer enables small-scale hydrogen production with relatively low-cost CO₂ capture. A 2 MWh plant may achieve efficiencies of 65% and investment costs of around 600 €/kWh (including hydrogen compression to 480 bar), resulting in a hydrogen cost of nearly 17 €/GJ, considering gas and electricity prices for small industrial users. Although the desire to reduce CO₂ emissions and capture emitted CO₂ is growing, the investment cost for solid fuel–based hydrogen production will likely remain the main hurdle.

4.5.3 Comparison of Hydrogen Production: Efficiency and Overall Costs

When carbon sequestration is coupled with natural gas steam reforming or coal gasification for hydrogen production, there is 14%–16% expected increase in the production cost of hydrogen (Tzimas and Peteves, 2005). Hydrogen production costs will decrease for coal and biomass once a market is established, likely as shown in Table 4.5, in which current data are compared with data for the year 2020. Natural gas is presently the most
Hydrogen Production Using Solid Fuels

Hydrogen Production Using Solid Fuels

Hydrogen Production Using Solid Fuels

Advantageous feedstock in terms of efficiency, CO₂ capture, hydrogen production costs, capital investment and specific operation, and maintenance costs (Langer et al., 2007).

Coal is superior to biomass, with lower capital costs, feedstock costs and availability, and hydrogen production costs. But coal has higher operating costs when coupled with CO₂ capture. With CO₂ capture, the investment cost decreases for coal due to the integration of various processes. Hydrogen production costs based on direct conversion concepts have been projected for 2020 (Langer et al., 2007). The comparison is made for the following processes: natural gas steam reforming, conventional small scale (NGSRS) at 22 €/GJ; natural gas steam reforming, conventional large scale with carbon capture (NGSTLCC) at 11 €/GJ; gasification large (coal); gasification large (coal, sequestration); ATR—Med; ATR—small (PSA); ATR—small (membrane); SMR—large; SMR—large (sequestration); SMR—small; SMR—small (PSA); SMR—small (membrane); SMR—small (PSA); SMR—small (PSA); SMR—small (membrane); SMR—large (sequestration); Gasification large (coal); Gasification large (coal, sequestration); ATR—Med; ATR—small (PSA); ATR—small (membrane); Electrolysis (coal); Electrolysis (grid mix); Electrolysis (wind and grid); Electrolysis (wind); Electrolysis (solar); Solar hydrogen reforming—small; Solar hydrogen reforming—large; Waste hydrogen capture; Waste hydrogen capture large; Waste hydrogen capture—small.

FIGURE 4.22

TABLE 4.5
Comparison of Hydrogen Production for Different Feedstocks

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Natural Gas to H₂</th>
<th>Natural Gas to H₂ with CO₂ Capture</th>
<th>Coal to H₂</th>
<th>Coal to H₂ with CO₂ Capture</th>
<th>Biomass to H₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Overall efficiency (%)</td>
<td>80</td>
<td>75</td>
<td>55</td>
<td>65</td>
<td>55</td>
</tr>
<tr>
<td>Specific capital investment (€/MWₐₐ)</td>
<td>333,000</td>
<td>380,000</td>
<td>834,000</td>
<td>745,000</td>
<td>932,000</td>
</tr>
<tr>
<td>Specific operation and maintenance costs (€/MWₐₐ)</td>
<td>18,000</td>
<td>43,000</td>
<td>38,000</td>
<td>79,000</td>
<td>39,000</td>
</tr>
<tr>
<td>Feedstock costs (€/GJ)</td>
<td>5.4</td>
<td>5.4</td>
<td>2.1</td>
<td>2.1</td>
<td>4.27</td>
</tr>
<tr>
<td>H₂ production costs: present (€/GJ)</td>
<td>8.6</td>
<td>10.0</td>
<td>8.6</td>
<td>10.5</td>
<td>12.0</td>
</tr>
<tr>
<td>H₂ production costs: 2020 (€/GJ)</td>
<td>10.1</td>
<td>11.1</td>
<td>8.4</td>
<td>8.7</td>
<td>10.2</td>
</tr>
</tbody>
</table>


* Conversion of coal and biomass to hydrogen is via gasification.
conventional coal gasification, large scale (CCGL) at 10 €/GJ; conventional coal gasification, large scale with carbon capture (CCGLCC) at 11 €/GJ; advanced coal gasification, large scale with carbon capture (ACGLCC) at 9 €/GJ; and biomass gasification, large scale (BGL) at 10 €/GJ.

4.5.4 Cost of Hydrogen in World Markets

Current decentralized hydrogen production costs more than USD 50/GJ, but various centralized production options similar to the process integration shown in Figure 4.20 promise, in the long run, hydrogen prices between USD 10/GJ and USD 15/GJ. While retail hydrogen prices are sensitive to prices of feedstocks (e.g., natural gas and electricity), the cost of hydrogen through natural gas reforming may decrease to less than USD 15/GJ of H₂ by 2030, and through electrolysis, it may decrease to less than USD 20/GJ of H₂. The projected cost of hydrogen from coal gasification in centralized IGCC plants with CCS is even lower—below USD 10/GJ (IEA, 2008b). Long-term costs for high-temperature water splitting could range from USD 10/GJ (using nuclear) to USD 20/GJ (using solar heat). Higher costs are projected for other technologies.

In addition to production facilities, infrastructure needs to be developed to distribute, store, and deliver hydrogen to vehicles. The overall investment cost for this infrastructure, worldwide, is likely to be in the trillions of US dollars (DOE, 2008). Overall, the retail price of hydrogen for transportation users, reflecting all feedstock-related, capital (infrastructure), and operating costs, appears likely to remain well above USD 1.00/L of gasoline equivalent, for the foreseeable future.

4.6 Summary

This review of various stages for obtaining hydrogen using solid fuels, through selected research and development efforts on aspects of hydrogen production from solid fuels, indicates the potential for significant improvements in applications of existing processes in different ways:

- Gasification is an established primary conversion process for producing hydrogen from solid fuels, and research is ongoing in terms of design, modeling, optimization, and market applications.
- Some processes have significant applications in energy markets, including those that use plasma for gasification, SCW for gasification, and USS for gasification, as well as a solar-thermal process for direct dissociation of carbon and hydrogen from solid fuels.
- Several system-integration projects have been proposed and tested based on the applicability of associated processes to increase hydrogen production and improve overall system productivity with additional products.
- Breakthrough conversion technologies or processes that differ fundamentally from those used at present and that can increase efficiency by more than 10%–15% do not exist presently at research or commercial levels. The reason for this
observation is that energy research efforts are widespread, with the focus on core technologies driven by market interests and demand.

- The requirements for alternative transportation fuel sources for clean and sustainable energy sources for power generation and less dependence on outside markets will in the near future likely drive increased research and development on new conversion processes. Circumstances at the present time appear adequate for promoting the rapid development of fundamentally different technologies for the conversion of solid fuels to hydrogen. Pressure is increasing on governments, industry, investors, and researchers to find alternatives.

A major shift is expected over the next few years in the way research is performed on the conversion of solid fuels into various energy forms, and hydrogen will likely receive the highest priority. Some research directions for converting solid fuels to hydrogen likely to receive attention include the following:

- Direct conversion of solid fuels to hydrogen and determining ways to reduce the number of steps in the processes
- Decreasing exergy losses for processes and systems and finding ways in process designs to make exergy use more efficient
- Sizing process units to reduce waste heat and entropy creation while maintaining performance
- Improving or optimizing system integration, accounting for convenient installation (closeness to resource location is preferred for municipal solid waste and landfills), low capital costs, low operating and maintenance costs, low emissions, and comparable overall efficiencies (although higher than existing plants is preferred)

The cost of hydrogen from solid fuels is expected to become competitive and may become lower than other sources, based on an adequate hydrogen infrastructure and combined research efforts from the academic and industrial workforce.

The information amalgamated here is intended to provide a useful resource that can aid researchers pursuing advanced methods for hydrogen production using solid fuels.

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Hydrogen Production Using Solid Fuels

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Hydrogen Production Using Solid Fuels


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