

Overview of Hydrogen Production Options for Hydrogen Energy Development, Fuel-Cell Fuel Processing and Mitigation of CO₂ Emissions

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Abstract

This article discusses the processing options for hydrogen production in conjunction with hydrogen utilization, fuel cells, and mitigation of CO₂ emissions. It should be emphasized that molecular hydrogen is an energy carrier but not a primary energy resource, and thus H₂ must be produced using other energy resource. By energy and atomic hydrogen sources, hydrogen can be produced from coal (gasification, carbonization), natural gas and propane gas (steam reforming, partial oxidation, autothermal reforming, plasma reforming), petroleum fractions (dehydrocyclization and aromatization, oxidative steam reforming, pyrolytic decomposition), biomass (gasification, steam reforming, biological conversion), and water (electrolysis, photocatalytic conversion, chemical and catalytic conversion). For fossil fuel-based H₂ production in stationary plants such as coal gasification and natural gas reforming, it would be desirable to develop new approaches that produce hydrogen in a more economical and environmentally-friendly process that also includes effective CO₂ capture or CO₂ utilization as an integral part of the system. A concept called CO-enriched gasification is proposed here for H₂ production from gasification of coal and biomass that may be studied further. For mobile fuel processor, there are major challenges in the development of (1) fuel processor for on-site or on-board production of H₂ that meets the stringent requirement of CO (<10 ppmv) and H₂S (<20 ppbv) for H₂-based proton-exchange membrane fuel cell system, and (2) fuel processor for synthesis gas production for solid-oxide fuel cells that use hydrocarbon fuels. The sulfur contents of most hydrocarbon fuels are too high for use in fuel cell reformer and in anode chamber, if when such fuels meet EPA sulfur requirements in 2006-2010 for automotive vehicles. Removal of organic sulfur before reforming and cleaning inorganic sulfur after reforming would be important for H₂ and syngas production for fuel cells, but conventional desulfurization methods are not suitable for fuel cell applications. Hydrogen energy and fuel cell development are closely related to the control of CO₂ emissions.

Introduction

Hydrogen was first discovered in 1766 by Henry Cavendish (1731-1810) in London, England when he collected it over a metal and described it as "inflammable air". Hydrogen was named in 1783 by Antoine Lavoisier (1743-1794), with the origin of name from the Greek words "hydro" and "genes" meaning "water" and "generator", because when hydrogen burns, water is

produced. The fact that hydrogen reacts with oxygen to produce energy and water (shown below) is the basis of the so-called hydrogen energy, as summarized in [Table 1](#).



Hydrogen energy has the potential to solve many of the major environmental problems that the US and the world are encountering as a result of fossil fuel combustion. However, there remain major challenges in, and thus major opportunities for, hydrogen energy research. There are some general reviews and numerous research articles on various aspects of hydrogen energy [[Momirlan and Veziroglu, 2002](#); [Ogden, 1999](#); [Winter and Nitsch, 1988](#)]. The US Department of Energy has been a strong proponent for research and development related to hydrogen energy development in the US. In his State of the Union Address on January 28, 2003, the US President George W. Bush announced a new hydrogen initiative that is dubbed Freedom Fuel (related to the fuel cell-based Freedom Car) [[DOE EERE, 2003](#)]. The Freedom Car and Freedom Fuel initiatives have certainly stimulated great public interest and more attention in the research community on hydrogen energy. The development of H₂-based energy system requires multi-faceted studies on hydrogen sources, hydrogen production, hydrogen separation, hydrogen storage, H₂ utilization and fuel cells, H₂ sensor and safety aspects, as well as infrastructure and technical standardization. This article discusses the technical processing options for hydrogen production in conjunction with hydrogen utilization, fuel cells, and mitigation of CO₂ emissions, and offers some personal perspective.

Table 1. Principle Thermodynamics of Hydrogen Energy

Thermodynamic Property	Values	State of Water
Reaction	$\text{H}_2 + 0.5 \text{O}_2 = \text{H}_2\text{O}$	
Enthalpy of reaction at 25 °C	$\Delta\text{H}^\circ = -285.8 \text{ kJ/mole (HHV)}$	H ₂ O as liquid
Enthalpy of reaction at 25 °C ^a	$\Delta\text{H}^\circ = -241.8 \text{ kJ/mole (LHV)}^{\text{a}}$	H ₂ O as vapor ^a
Entropy of reaction at 25 °C	$\Delta\text{S}^\circ = -163.3 \text{ J/mole}\cdot\text{K}$	H ₂ O as liquid
Free energy of reaction at 25 °C	$\Delta\text{G}^\circ = -237.2 \text{ kJ/mole}$	H ₂ O as liquid
Free energy of reaction at 80 °C	$\Delta\text{G}^\circ = -228.1 \text{ kJ/mole}$	H ₂ O as liquid
Free energy of reaction at 80 °C	$\Delta\text{G}^\circ = -226.1 \text{ kJ/mole}$	H ₂ O as vapor

a) The heat of vaporization of H₂O is 44 kJ/mole. When the reaction heat involving water as a vapor product is used for calculation, the value is referred to as lower heating value (LHV).

H₂ Production Options

It should be emphasized that molecular hydrogen is an energy carrier but not an energy resource, and thus hydrogen must be produced first. [Table 2](#) summarizes the possible options for H₂ production. By energy and atomic hydrogen sources, hydrogen can be produced from coal (gasification, carbonization), natural gas and propane gas (steam reforming, partial oxidation, autothermal reforming, plasma reforming), petroleum fractions (dehydrocyclization and aromatization, oxidative steam reforming, pyrolytic decomposition), biomass (gasification, steam reforming, biological conversion), and water (electrolysis, photocatalytic conversion, chemical and catalytic conversion).

Table 2. Options of Hydrogen Production Processing Regarding Atomic Hydrogen Source, Energy Source for Molecular Hydrogen Production and Chemical Reaction Processes

Hydrogen Source	Energy Source	Reaction Processes
1. Fossil Hydrocarbons Natural gas ^{a1} Petroleum ^{a2} Coal ^{a1,a2} Tar Sands, Oil Shale, Natural Gas Hydrate	1. Primary Fossil energy ^{b1} Biomass Organic Waste Nuclear energy Solar-thermal	1. Commercialized Process Steam reforming ^{c1} Autothermal reforming ^{c1} Partial oxidation ^{c1} Catalytic dehydrogenation ^{c2} Gasification carbonization ^{c1} Electrolysis ^{c3}
2. Biomass 3. Water (H₂O) 4. Organic/Animal Waste 5. Synthetic Fuels MeOH, FTS liquid, etc.	Photovoltaic Hydropower Wind, Wave, Geothermal 2. Secondary	2. Emerging Approaches Membrane reactors Plasma Reforming
6. Specialty Areas Organic Compound Metal hydride, ch complex hydride Ammonia, Hydrazine Hydrogen sulfide	Electricity ^{b2} H ₂ , MeOH, etc. 3. Special Cases Metal bonding energy Chemical bonding energy	Photocatalytic Solar-thermal chemical Solar-thermal catalytic Biological Thermochemical cycling Electrocatalytic
7. Others	4. Others	3. Others

a1: Currently used hydrogen sources for hydrogen production.

a2: Currently used in chemical processing that produces H₂ as a byproduct or main product.

b1: Currently used as main energy source.

c1: Currently used for syngas production in conjunction with catalytic water-gas-shift reaction for H₂ production.

c2: As a part of industrial naphtha reforming over Pt-based catalyst that produces aromatics.

c3: Electrolysis is currently used in a much smaller scale compared to steam reforming.

Figure 1 shows the current commercial processes and possible future options for H₂ production and related research issues. Figure 2 compares the current commercial process technologies for H₂ production versus the scale of H₂ production based on studies by industrial gas producers as reported in literature [Rostrup-Nielsen, et al., 2003; Gunardson, 1998; HP-Gas, 2002]. Excellent reviews have been published on H₂ production technologies by Rostrup-Nielsen [2002] and on catalysis involved in H₂ production by Armor [1999]. The relative competitiveness of different options depends on scale of production, H₂ purity requirement, catalytic processing methods and energy sources available.

Current commercial processes for H₂ production largely depends on fossil fuels both as the source of hydrogen and as the source of energy for the production processing. Fossil fuels are non-renewable energy resources, but they provide a more economical path to hydrogen

production in the near term (next 5 to 20 years) and perhaps they will continue to play an important role in the mid-term (20 years to 50 years from now). Alternative processes need to be developed that do not depend on fossil hydrocarbon resources for either the hydrogen source or the energy source, and such alternative processes need to be economical, environmentally-friendly, and competitive. An example of an alternative, environmentally-friendly process is biological H₂ production from biomass [Logan et al., 2003].

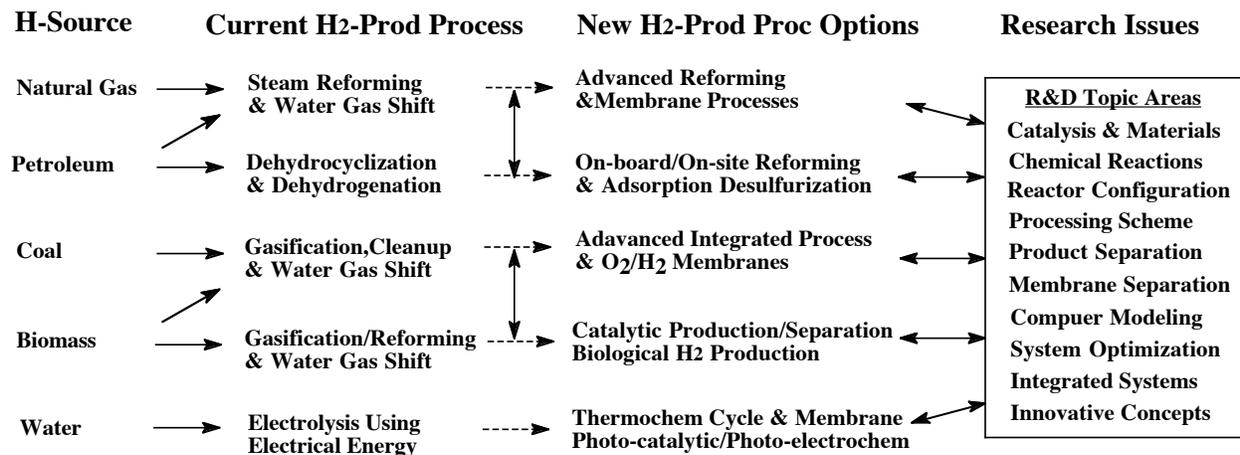


Figure 1. Current processes and possible future options for H₂ production and related research issues.

Some organic substances can be used for hydrogen production, and they includes methanol synthesized via synthesis gas from natural gas and coal (steam reforming, decomposition), ethanol made from biological fermentation of crops and biomass (steam reforming), and sugars or carbohydrates (steam reforming, gasification). For some special applications, hydrogen-containing inorganic compounds such as ammonia and hydrogen sulfide have also been considered as source compounds for hydrogen production (catalytic decomposition).

Regardless of the hydrogen source and energy source, in order for hydrogen energy to penetrate widely into transportation and stationary applications, the costs of H₂ production and separation need to be reduced significantly, e.g., probably by a factor of 2 or more from the current technology.

H₂ separation is also a major issue as H₂ coexists with other gaseous products from most industrial processes, such as CO₂ from chemical reforming or gasification processes. Pressure swing adsorption (PSA) is used in current industrial practice. Several types of membranes are being developed that would enable more efficient gas separation.

H₂ production and separation can be integrated in novel membrane processes that incorporate reaction and separation in the same unit. There are several types of membranes, gas-diffusion membrane, ion-conducting membrane, and catalytic membranes.

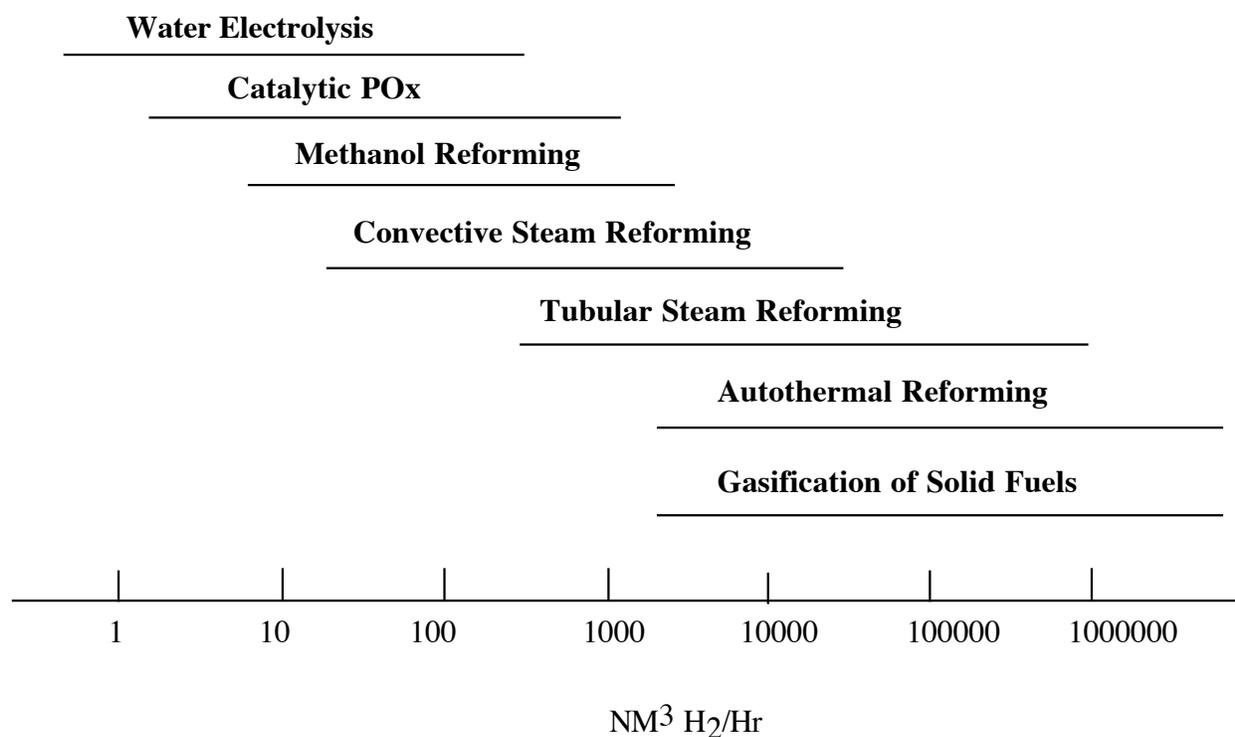


Figure 2. Technology of choices based on the scale of hydrogen demand [Sources: (1) J. R. Rostrup-Nielsen, J. Sehested, N. Udengaard, Paper presented at Am. Chem. Soc. Symp. H₂ Energy for the 21st Century, March 23-27, 2003, New Orleans, LA; (2) H. Gunardson, Industrial Gases in Petrochemical Processing. Marcel Dekker, New York, 1998, 283 pp; (3) HP-Gas. Gas Processes 2002. Hydrocarbon Processing, 2002, (81 (5), 61-121.]. Note: 1 Nm³/h = 847.44 standard cubic feet per day (scfd); 1 million standard cubic feet (MMscfd) = 1180 Nm³/h

A Proposed Concept on CO-Enriched Gasification for H₂ Production from Coal

Because coal resource is much more abundant than natural gas and petroleum in US and many other countries, production of H₂ from coal via gasification is an important path to H₂ energy development in the foreseeable future. Statistically, coal is also the most abundant fossil energy resource in the world [Song and Schobert, 1996]. An excellent review of coal gasification technologies has been published by Stiegel and Maxwell [2001]. There are major technical challenges for developing more economical system for coal-based hydrogen and synthesis gas production coupled with CO₂ capture and sequestration, including the following aspects: more efficient gasification for H₂ production purpose, sulfur-tolerant catalysts for water-gas-shift reaction; efficient removal of hydrogen sulfide from hot gas; effective separation of CO₂ from H₂ in the presence of steam [Xu et al., 2003], and permanent sequestration of CO₂ as solid mineral [Maroto-Valer et al., 2002].

A concept called CO-enriched gasification (COEG) is proposed here, as illustrated in Figure 3, for coal and biomass gasification that may be studied further. Coal gasification typically occurs at very high temperatures and the heat utilization (heat transfer to make steam) at very high temperature is not very efficient, thus incorporation of an endothermic chemical reaction may be helpful. CO-enriched coal gasification involves CO-enriching reaction [eq.(2)]

using recycled CO₂ and exothermic oxidation reactions (eqs. 3 and 4). CO-enriched gasification of coal can be achieved by integrating reactions of 3 co-reactants-steam, CO₂, and oxygen with carbon (coal) (eqs. 1-4). It is similar in principle to the tri-reforming concept recently proposed by the author for natural gas [Song, 2003]. CO₂ can be recovered by either conventional method or by using the CO₂ “molecular basket” [Xu et al., 2002, 2003] and recycled for the gasification. The COEG could be a more effective way compared with H₂ production via steam gasification (eq. 1). Compared to conventional processes, CO-enriched gasification is expected to be superior for H₂ production purpose because each CO molecule gives an additional H₂ molecule upon water gas shift reaction (eq. 5). The proposed CO-enriched gasification is based in part on a recently reported concept of tri-reforming of natural gas which involves 3 reactions simultaneously-CO₂ reforming, steam reforming and partial oxidation of methane [Song, 2001; Song et al., 2002]. This reaction produces CO-rich gas due to addition of CO₂ as a co-reactant (eq. 2), and such CO-rich gas will produce more H₂ since CO will produce more H₂ molecule upon water-gas-shift reaction (eq. 5). Such gasification can also be conducted in the presence of biomass. Previous studies have shown that coal gasification reactivity is higher in steam than in carbon dioxide [Messenbock et al., 1999]. Certain catalysts can change the reactivity or reaction rate in CO₂ gasification, and it is possible that an integrated oxidative CO₂-steam gasification can proceed to the extents suitable for enhanced H₂ production.

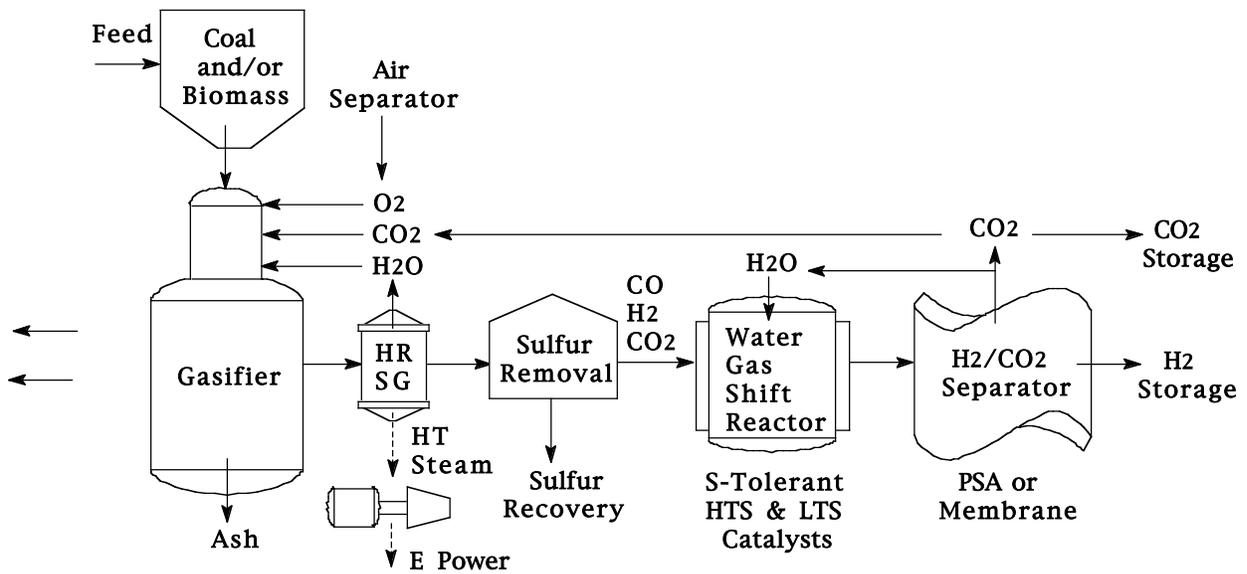
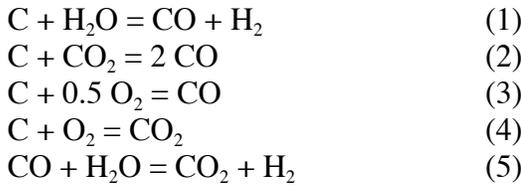


Figure 3. Conceptual scheme of the proposed CO-Enriched Gasification (COEG) process for H₂ production from coal and/or biomass.

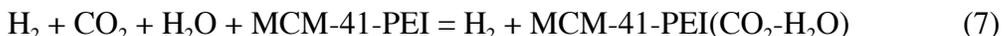
Sulfur-Tolerant Catalyst Needed for Water Gas Shift for H₂ Production from Coal

For conversion of coal-derived CO to H₂ and CO₂ by water-gas-shift reaction (eq. 6), sulfur-tolerant catalyst would be preferred. Because gas from coal gasification contain H₂S in high concentrations (e.g., 20000 ppm), conventional approach is to remove H₂S before water gas shift reaction because the current industrial catalysts are extremely sensitive to sulfur of any form. While sulfur removal is necessary, it is inevitable for gas to contain a trace amount of H₂S. Current commercial Fe-Cr₂O₃-Al₂O₃ catalyst (HTS) and Cu-ZnO-Al₂O₃ (LTS) catalyst are sensitive to poisoning by sulfur (H₂S), even at just a few ppm level. It would be desirable if sulfur-tolerant and active catalyst can be developed for water-gas-shift reaction. It may be worthy to explore more transition-metal sulfide based catalysts for developing sulfur-tolerant water-gas-shift catalysts. Based on our prior work on catalytic coal liquefaction in the presence of water [Song et al., 2000] and sulfur-tolerant catalyst for hydrogenation [Song and Schmitz, 1997], we believe certain transition metal sulfide based catalyst can be effective WGS catalyst in the presence of hydrogen sulfide.



Separation of CO₂ from Gas Mixture Following LT-WGS

For the proposed concept to work, we need effective separation of CO₂. We have proposed a CO₂ “molecular basket” concept for effective separation of CO₂ from H₂ in the presence of steam. Our recent results with mesoporous molecular sieve of MCM-41 modified with a branched polymer polyethyleneimide show that the CO₂ “molecular basket” of MCM-41-PEI type is very effective for separation of CO₂ from simulated flue gas, and the presence of steam further enhanced the capacity of the CO₂ separation [Xu et al., 2002, 2003]. This concept could be applied in principle for separation of CO₂ and H₂O from H₂, as in the mixture from low-temperature water-gas-shift reaction (represented by eq. 7), thus enabling the CO₂ recovery and use for gasification by the proposed COEG process. The CO₂ can also be stored for other uses and for permanent sequestration such as mineral sequestration.



On-board/On-site H₂ production for Fuel Cells

Fuel cell converts chemical energy directly to electricity. It is intrinsically much more efficient than conventional combustion/heat-based energy conversion systems and is an important new path for efficient, clean and sustainable energy development., for which The original device for fuel cell was invented by Sir William Grove in UK in 1839, has emerged as a very promising energy device for the 21st century [Larminie and Dicks, 2000]. A major reason for the greater interest in hydrogen energy now worldwide is that the technologies of fuel cells using H₂ as a fuel have advanced to the extent where many people begin to see its major commercial application potentials. There are five types of fuel cells including polymer electrolyte membrane fuel cell (PEMFC), alkali fuel cell, phosphoric acid fuel cell, molten carbonate fuel cell, and solid oxide fuel cell (SOFC). Among the five types, SOFC and PEMFC are the two most promising fuel cells [Larminie and Dicks, 2000].

Figure 4 outlines the fuel processing steps and options for different fuel cell applications [Song, 2002]. There are major challenges in the development of (1) fuel processor for on-site or on-board production of H₂ that meets the stringent requirement of CO (<10 ppmv) and H₂S (<20

ppbv) for H₂-based proton-exchange membrane fuel cell system, and (2) fuel processor for synthesis gas production for solid-oxide fuel cells that use hydrocarbon fuels. The sulfur contents of most hydrocarbon fuels are too high for use in fuel cell reformer and in anode chamber, if when such fuels meet EPA sulfur requirements in 2006-2010 for automotive vehicles. Removal of organic sulfur before reforming and cleaning inorganic sulfur after reforming would be important for H₂ and syngas production for fuel cells, but conventional desulfurization methods are not suitable for fuel cell applications [Song, 2002; Song and Ma, 2003]. Figure 5 and Figure 6 show the concepts and processing steps in an integrated fuel cell systems [Song, 2002].

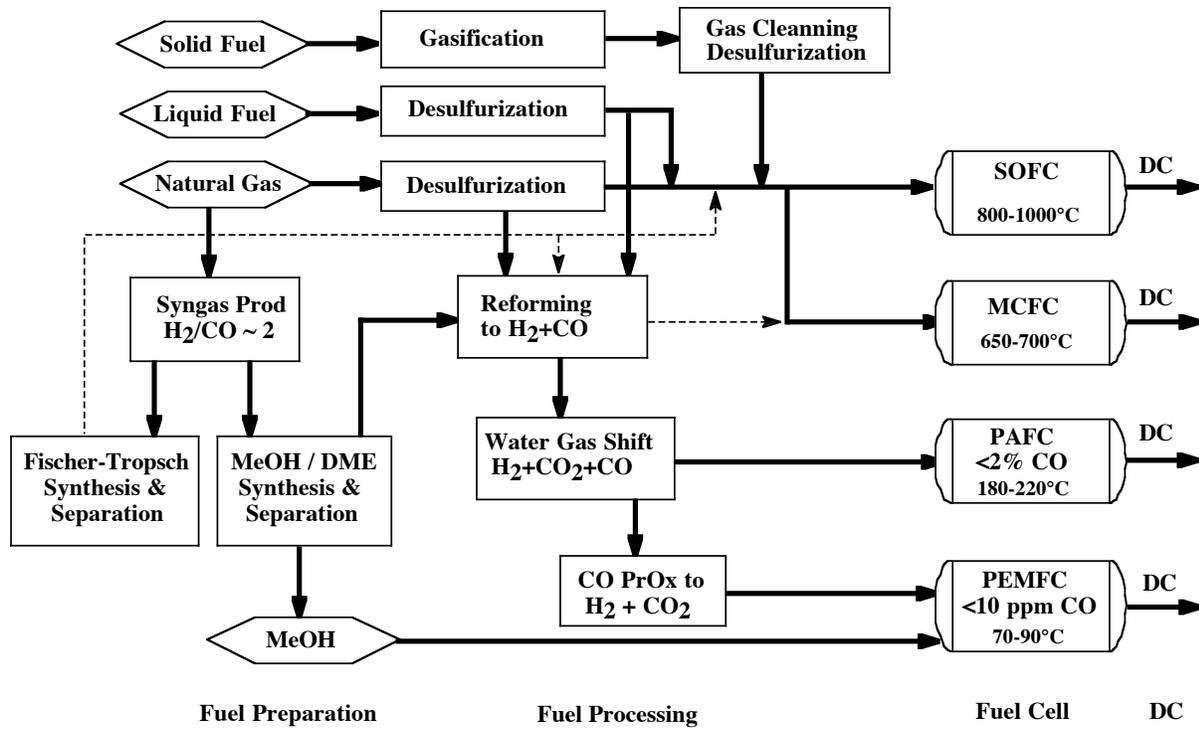


Figure 4. The concepts for fuel processing of gaseous, liquid and solid fuels for high-temperature and low-temperature fuel cell applications [Song, 2002].

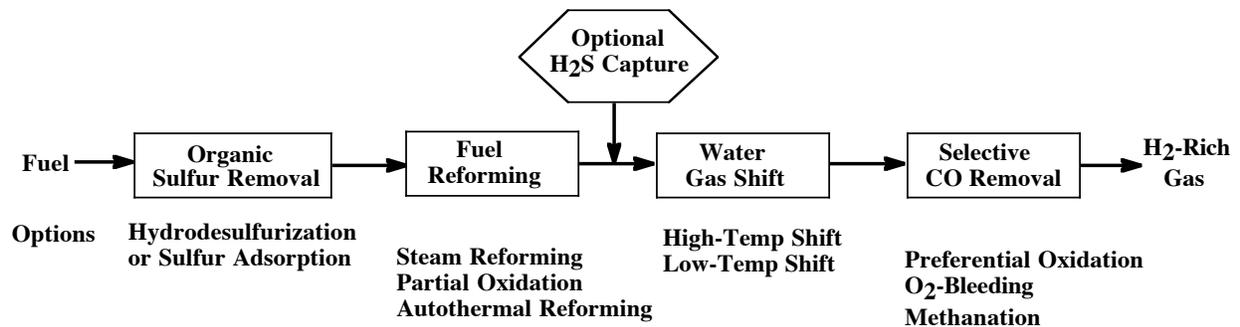
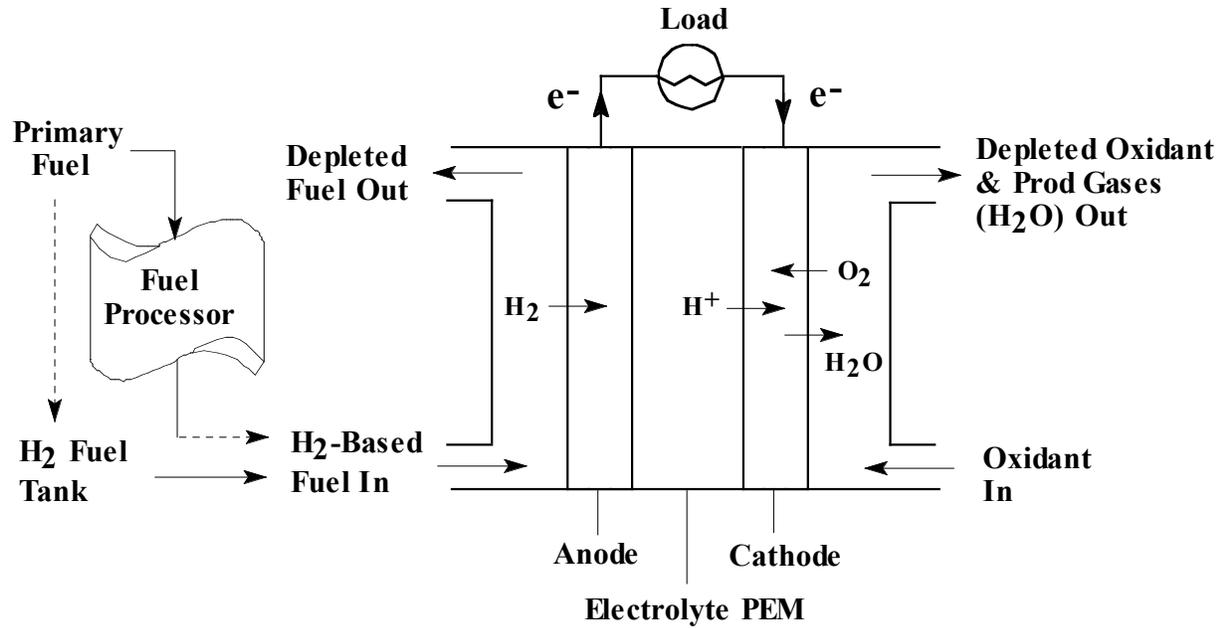


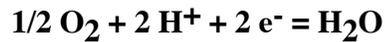
Figure 5. Steps and current options for on-site and on-board processing liquid and gaseous hydrocarbon fuels and alcohol fuels to produce H₂-rich gas for low-temperature fuel cells (PEMFC) [Song, 2002].



Anode (Fuel) Reaction:



Cathode (oxidant) Reaction:



Total Reaction:



Figure 6. Concept of proton-exchange membrane fuel cell (PEMFC) system using on-board or on-site fuel processor, or on-board H₂ fuel tank [Song, 2002].

CO₂ Emission Control Related to H₂ Production

Hydrogen energy and fuel cell development are closely related to the mitigation of CO₂ emissions. Fuel cell using hydrogen allows much more efficient electricity generation, thus can decrease CO₂ emission per unit amount of primary energy consumed or per kilowatt•hour of electrical energy generated. For fossil fuel-based hydrogen production such as coal gasification, it would be desirable to develop new approaches that produce hydrogen in a more environmentally-friendly process that also includes effective CO₂ capture or CO₂ utilization as an integral part of the system.

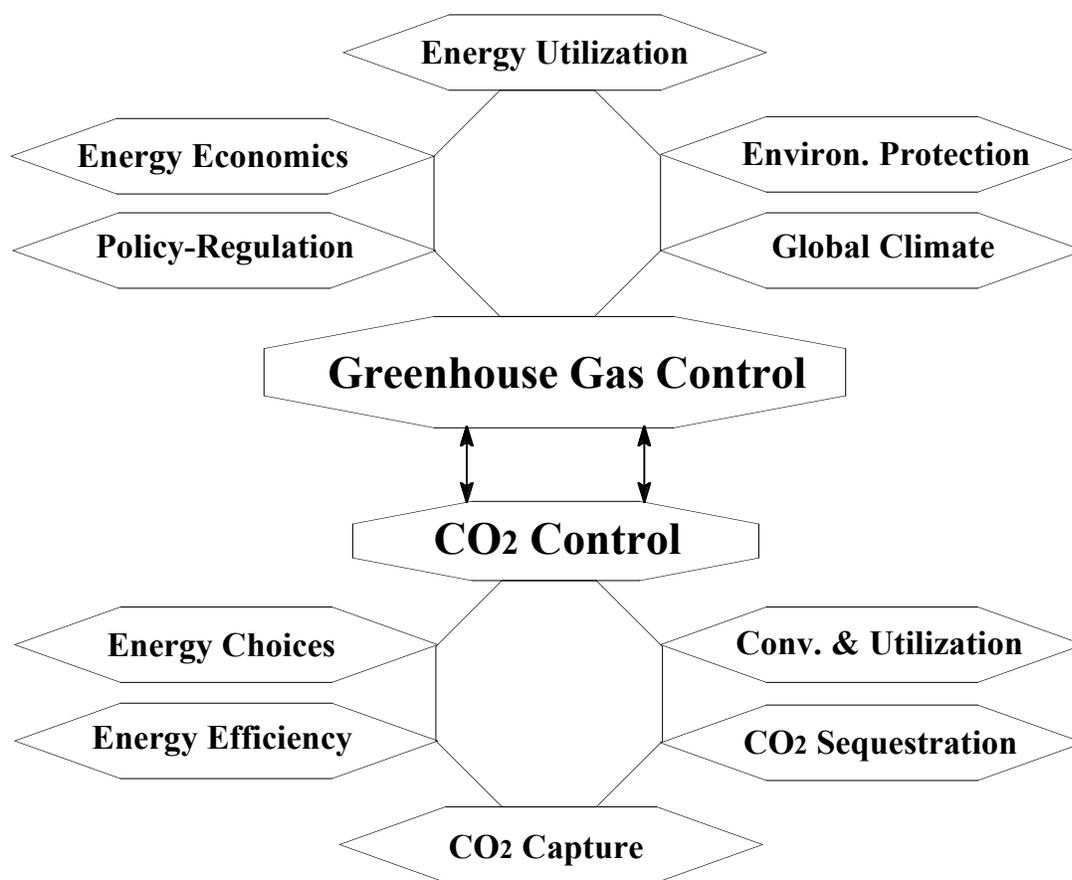


Figure 7. Key issues for control of greenhouse gas and related technical areas for CO₂ control [Song, 2002b].

CO₂ capture involves chemical or physical separation of CO₂ from gas mixtures. Common methods include absorption using an agent such as monoethanol amine, physical adsorption using solid adsorbent, chemical adsorption using the above-mentioned CO₂ “molecular basket”, and cryogenic separation at low temperatures, and membrane separation (see below). Depending on further study and verification, the proposed COEG process concept shown in Figure 3 could possibly facilitate the CO₂ recycling for high-temperature heat utilization and H₂ production on the one hand, and produce concentrated CO₂ that facilitates CO₂ storage/sequestration on the other hand. CO₂ sequestration refers to long-term storage of CO₂ in various reservoir locations with large capacity, such as mineral carbonation, geologic formations, ocean, aquifers, and forest. Permanent storage of CO₂ as carbonate has some intrinsic merit when compared to ocean sequestration [Maroto-Valer et al., 2002]. As can be seen from the thermodynamic analysis shown in Figure 8 [Song, 2002b], carbonate would be far more stable among most carbon-containing compounds, and reaction of CO₂ with calcium salt to form calcium carbonate is thermodynamically feasible.

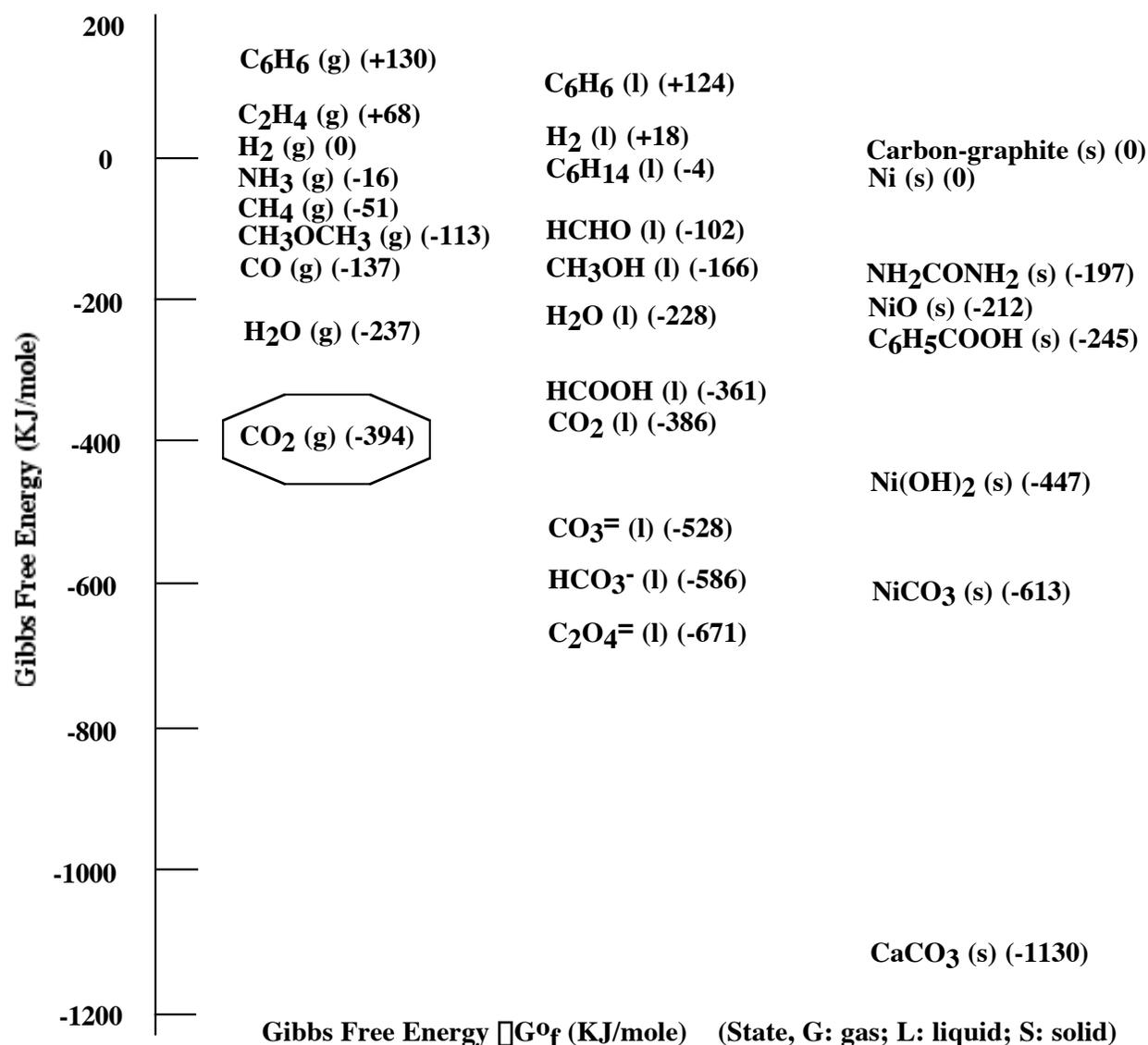


Figure 8. Gibbs free energy of formation for CO₂ and related molecules [Song, 2002b].

Future Perspectives

Development of H₂-based energy system require multi-faceted studies on hydrogen sources, hydrogen production, hydrogen separation, hydrogen storage, H₂ utilization and fuel cells, H₂ sensor and safety aspects, as well as infrastructure and technical standardization.

On the other hand, hydrogen energy is one form of energy but unlike the primary energy sources, hydrogen energy is a form that must be produced from chemical transformation of other substances first before being used. The production and utilization is also associated with various energy resources, fuel cells, CO₂ emissions, H₂ emission, safety and infrastructure issues. The technical communities of researchers also need to explore the following global questions that I believe are important, and more studies are needed to answer these questions:

- Should we use hydrogen in the future as energy carrier for transportation? Does the hydrogen energy solve the potential global warming problem by reducing CO₂?

- Should we rely on hydrogen for residential and stationary electrical power generation? Would distributed on-board and/or on-site H₂ production using conventional fuels be more desirable if the technology can be developed ?
- Would transportation and storage of H₂ produced from centralized plants through various means be more desirable in the future?
- What are the key technical, environmental and socio-economical factors that must be clarified for global hydrogen energy development ?
- What should we use as hydrogen source for molecular H₂ production in the future, and what energy source should we use for the production processing in the future?
- If the currently dominant fossil fuels ever become so scarce to the extent that H₂ becomes a dominant energy carrier at some point in the long-term future, what will the world use as resources for materials and chemical feedstocks (that are currently derived largely from fossil fuels)? Should the societies reduce consumption of fossil hydrocarbon resources, regardless the location of such resources, and save them for future generations ?

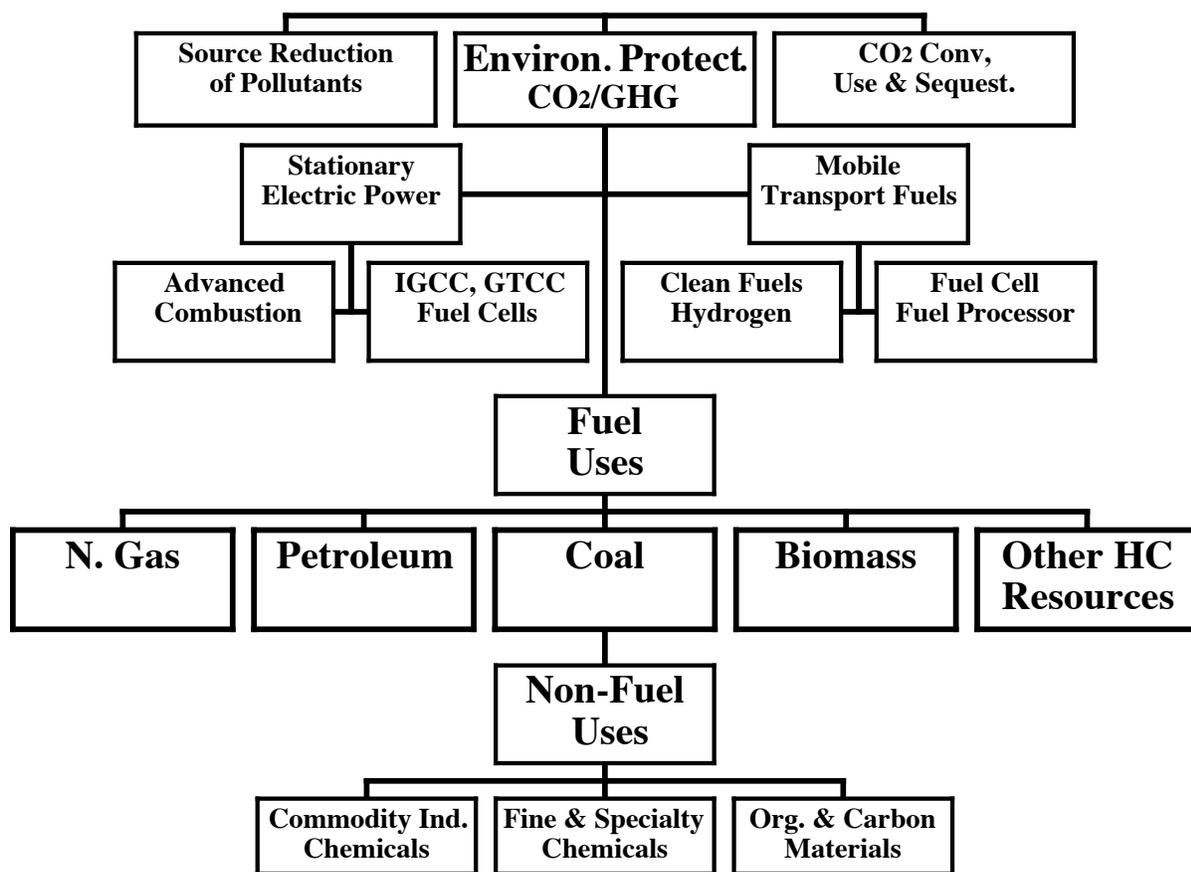


Figure 9. A personal vision for research towards comprehensive and effective utilization of hydrocarbon resources in the 21st century.

Figure 9 presents a personal vision for research towards comprehensive and effective utilization of hydrocarbon resources in the 21st century. No single energy source will satisfy the needs of societies in the long term. The best-possible scenario for future energy system is a balanced mix of various forms of renewable energies and resources used in combination.

It is important to think about the above questions in the context of sustainable energy development. To begin with end in mind, I believe the world could be better served if the energy research community explores the future energy issues in a comprehensive and integrated fashion [Song, 2001, 2002c, 2002d]. For comprehensive utilization research, we should look at different uses of hydrocarbon resources, for fuel uses and non-fuel uses, that are equally important although different in volume [Song and Schobert, 1993, 1996; Schobert and Song, 2000; Song, 2001, 2002c, 2002d].

Finally, it should be mentioned that a recent computational study at CalTech points out possible/potential environmental impacts of hydrogen energy in the future (hydrogen leak, estimated at up to 10-20% of total H₂ produced in the future, could cool the Earth's stratosphere due to additional water formed from hydrogen at high altitudes and disturb the ozone chemistry) [NaTrompme et al., 2003]. Another study at MIT indicates limitations of hydrogen energy development for transportation by fuel cell cars with respect to its effect on greenhouse gas reduction [Weiss et al., 2003]. More experimental and theoretical studies regarding possible long-term effects are needed to clarify the related issues.

Concluding Remarks

H₂ production is a major issue in hydrogen energy. It should be kept in mind that hydrogen is an energy carrier but not an energy resource, and thus hydrogen must be produced. By energy and atomic hydrogen sources, hydrogen can be produced from coal (gasification, carbonization), natural gas and propane gas (steam reforming, partial oxidation, autothermal reforming, plasma reforming), petroleum fractions (dehydrocyclization and aromatization, oxidative steam reforming, pyrolytic decomposition), biomass (gasification, steam reforming, biological conversion), and water (electrolysis, photocatalytic conversion, chemical and catalytic conversion).

The relative competitiveness of different options depends on scale of production, H₂ purity requirement, and energy sources available. In order for hydrogen energy to penetrate widely into transportation and stationary applications, the costs of H₂ production and separation need to be reduced significantly from the current technology, e.g., by a factor of 2.

Development of H₂-based energy system require multi-faceted studies on hydrogen sources, hydrogen production, hydrogen separation, hydrogen storage, H₂ utilization and fuel cells, H₂ sensor and safety aspects, as well as infrastructure and technical standardization. Production of H₂ is an important part of the whole picture. The technical community also needs to explore the global questions related to hydrogen as energy carrier in the future. It is important to think about these questions in the context of sustainable energy development.

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