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A White Paper

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Analysis of CO_2 Emissions, Reductions, and Capture for Large-Scale Hydrogen Production Plants

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Abstract

Hydrogen (H_2) production, when used for making ultra-low sulfur diesel (ULSD), results in cleaner air. Over 95 percent of global hydrogen production is through steam methane reforming (SMR) *(1)*. When used to make ULSD, a ton of H_2 avoids the emission of 2.75 tons of sulfur dioxide (SO_2) and 144 tons of equivalent carbon dioxide (CO_2) from the truck tailpipe when particulate filters are used *(2)*.

SMR plants are safe, reliable and efficient. Process and equipment improvements made over the past 25 years have reduced the CO_2 intensity of hydrogen plants by more than 20 percent, to the point where emissions are within 13 percent of the theoretical minimum. Over the next five years, process, equipment, and operational improvements to modern, large-scale hydrogen plants can potentially bring CO_2 emissions down to within 9 percent of the theoretical minimum. Improvements to hydrogen pipeline networks have also led to additional CO_2 reductions.

The SMR process emits CO_2 as a byproduct, thereby raising the question of whether electrolysis could be used to produce hydrogen and avoid this emission. This paper shows that electrolysis, when powered by fossil-fuel sources of electricity, has an indirect energy use that is over three times greater than the direct CO_2 emissions from SMR.

Hydrogen Plant Process Description

Modern, large-scale hydrogen plants that use natural gas as a feedstock are the primary means of meeting the growing demand for hydrogen from the refining sector. A modern SMR-based hydrogen plant consists of four primary subsystems (see Figure 1).

Natural gas is used as both feed and fuel. The natural gas stream is split, and the majority is used as process feed, which is compressed and desulfurized before entering the reformer reactor tubes. The natural gas used as fuel is mixed with pressure swing adsorption (PSA) tail gas and combusted within the reformer furnace to provide the energy required to drive the reforming reactions. Gas leaving the reformer enters a high-temperature shift reactor, where carbon monoxide (CO) is reacted with steam to produce additional hydrogen. After cooling, hydrogen-rich gas from the shift reactor is processed by a PSA unit for purification to product hydrogen specifications. The PSA tail gas, consisting of unreacted methane, CO, nitrogen, and unrecovered hydrogen, is recycled for mixing with natural gas and used as fuel in the reformer furnace. Additional information for each subsystem is provided in Table 1.

To efficiently manage energy flows within the hydrogen plant, a complex heat exchanger network is integrated within and around the reformer furnace. See Figure 2.
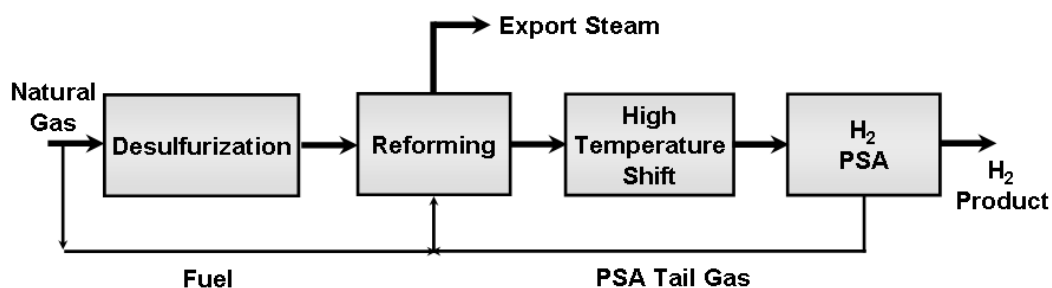
Figure 1: Hydrogen Plant Block Flow Diagram

Table 1
Hydrogen Plant Subsystems

Desulfurization	
Function	Remove all sulfur compounds to less than 0.1 ppmw.
Typical Operating Temperature	650°F to 750°F

Processing Steps	1. Hydrotreating reactor: Converts sulfur compounds to H_2S and saturates any olefins.
	  a. Catalyst: Co-Mo or Ni-Mo
	  b. Typical catalyst life: 7 years
	2. Sulfur removal reactor: Removes H_2S.
	  a. Catalyst: ZnO
	  b. Reaction: $H_2S + ZnO \rightarrow ZnS + H_2O$
	  c. Typical catalyst life: 1 to 2 years (depends on natural gas sulfur content).

Reforming	
Function	Converts methane and light hydrocarbons to hydrogen and carbon monoxide.

Reactions	1. Reforming: $CH_4 + H_2O + Heat \rightarrow 3H_2 + CO$
	  a. Highly endothermic reaction.
	  b. Reaction favored by high temperature, low pressure, and excess steam.
	2. Water gas shift: $CO + H_2O \rightarrow CO_2 + H_2 + Heat$
	  a. Mildly exothermic reaction.
	  b. Reaction favored by mild temperature and excess steam.

Characteristics	1. Ni-based catalyst poisoned by sulfur and chloride compounds. 2. Excess steam suppresses carbon formation. 3. 90 to 95 percent of the hydrocarbons are reacted. 4. Catalyst life: 5 years.

Table 1 Hydrogen Plant Subsystems	
Typical Operating Conditions	1. Process gas outlet temperature: 1400°F to 1700°F. 2. Pressure: 200 psig to 450 psig.
Equipment	1. Catalyst size: 5/8-in. x 5/8-in. rings, Ni-based. 2. Reformer tubes: 4-in. to 5-in. diameter by 40 ft to 45 ft long. 3. Reformer tube life: 10 years. 4. Furnace type: Round (can) or box.
High Temperature Shift	
Function	Convert carbon monoxide to hydrogen.
Reaction	Water gas shift: $CO + H_2O \rightarrow CO_2 + H_2 + Heat$ 1. Mildly exothermic reaction. 2. Reaction favored by mild temperature and excess steam. 3. Converts about 70 to 75 percent of carbon monoxide.
Catalyst	Iron/chrome
Catalyst Life	5 to 7 years
Typical Operating Temperature	650°F to 700°F
Typical Temperature Rise	125°F
H2 PSA	
Function	Purifies hydrogen-rich gas (purity hydrogen product >99.99 percent).
Adsorbents	Molecular sieve, activated carbon, alumina, and silica gel.
Typical Operating Conditions	1. Feed pressure: 200 to 900 psig. 2. Feed H_2 composition: 50 to 95 percent. 3. Tail gas pressure: 5 to 70 psig. 4. H_2 recovery: 65 to 90 percent.
Typical Operating Equipment	1. Adsorber vessels: 4 to 12. 2. Surge tank: 1 to 2 (12 to 13 ft diameter). 3. Valve skid and controls.

CO₂ Production and Emissions in Hydrogen Manufacture

Natural gas is the source of all carbon that is ultimately emitted in the reformer flue gas as CO_2. The CO_2 is formed by reaction of CO with steam in the reforming and shift processes and during combustion of natural gas, CO, and unreacted methane in the reformer furnace. Total CO_2 emissions can be determined by measuring the flow and composition of the natural gas entering the reformer as feed and fuel with conversion to CO_2 according to the following hypothetical reaction:

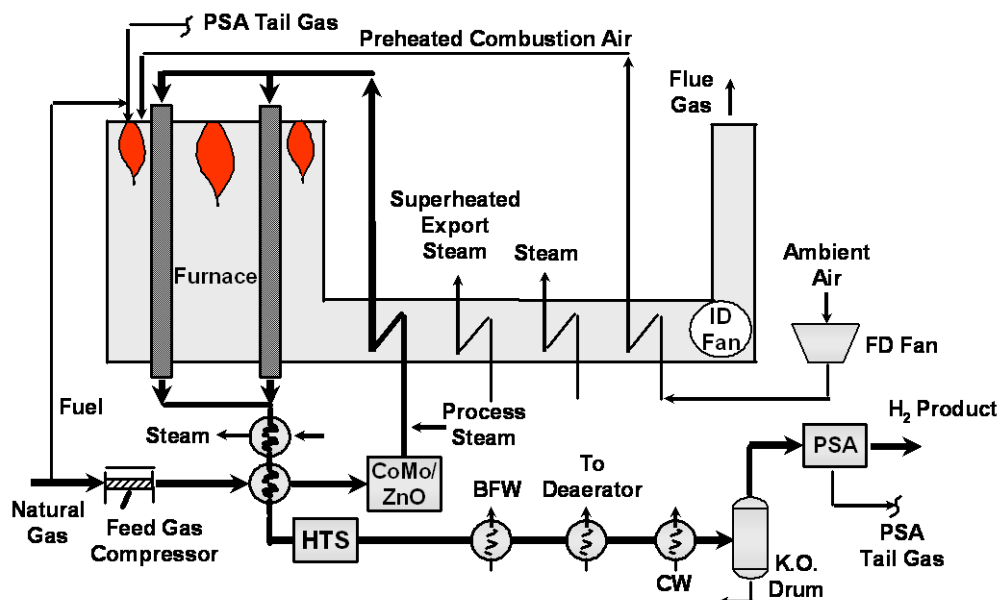$$C_XH_Y + (X+Y/4)O_2 \rightarrow (X)CO_2 + (Y/2)H_2O$$
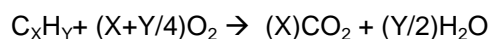
Figure 2: Steam Methane Reformer – Minimum Steam Case

For a typical natural gas composition approximated as 90 percent methane and 10 percent ethane, X equals 1.10 and Y equals 4.2.

Hydrogen Plant CO_2 Emissions: Modern versus Historical

In this paper, a modern hydrogen plant consists of an SMR followed by high temperature shift with PSA purification. A historical hydrogen plant consists of an SMR followed by high temperature and low temperature shifts, and an monoethanolamine (MEA) unit for CO_2 removal followed by methanation (chemical reaction to form methane) to remove residual CO and CO_2. Practically all large hydrogen plants operated by industrial gas firms and refineries built since the mid-1980s are the modern type. Figures 3 and 4 show CO_2 generation and emission from modern and historical hydrogen plants respectively for the same quantity of hydrogen product: 100 million standard cubic feet per day (100 MMscfd) of hydrogen contained in the product stream.

Note that the modern hydrogen plant's CO_2 intensity, short tons per day of CO_2 per 1 MMscfd of hydrogen, is 12 percent less than its historical counterpart (25 versus 28.5). This does not tell the complete story since the modern plant is exporting 150,000 lb/hour of steam that is efficiently used by the refinery.

Crediting the modern hydrogen plant for steam production, the CO_2 intensity drops to 22.1 short tons per day of CO_2 per 1 MMscfd of hydrogen, or 22 percent less that the historical plant. Table 2 summarizes the comparison between the modern and historical hydrogen plant CO_2 emissions. Note that the modern plant is at 113 percent of minimum theoretical CO_2 emissions.

Further Reductions in Hydrogen Plant CO_2 Emissions: 2009 to 2014

Not withstanding the close approach of modern large-scale hydrogen plants to the theoretical minimum CO_2 emission rate, improvements scheduled for implementation by Praxair over the next five years will lead to further reductions. The primary motivation for these improvements is cost savings from reduced natural gas consumption, which leads to higher profitability. The actual natural gas consumption rate is dependent on several parameters, including export steam flow, hydrogen product pressure, and ambient conditions, but a value of 370 btu/scf of H_2 is typical. Refer to Table 3.

Assuming successful development and commercialization, the natural gas consumption rate of new hydrogen plants and existing modern plants retrofit with the above improvements could be reduced to 340 btu/scf of H_2. This would yield a CO_2 intensity of 23
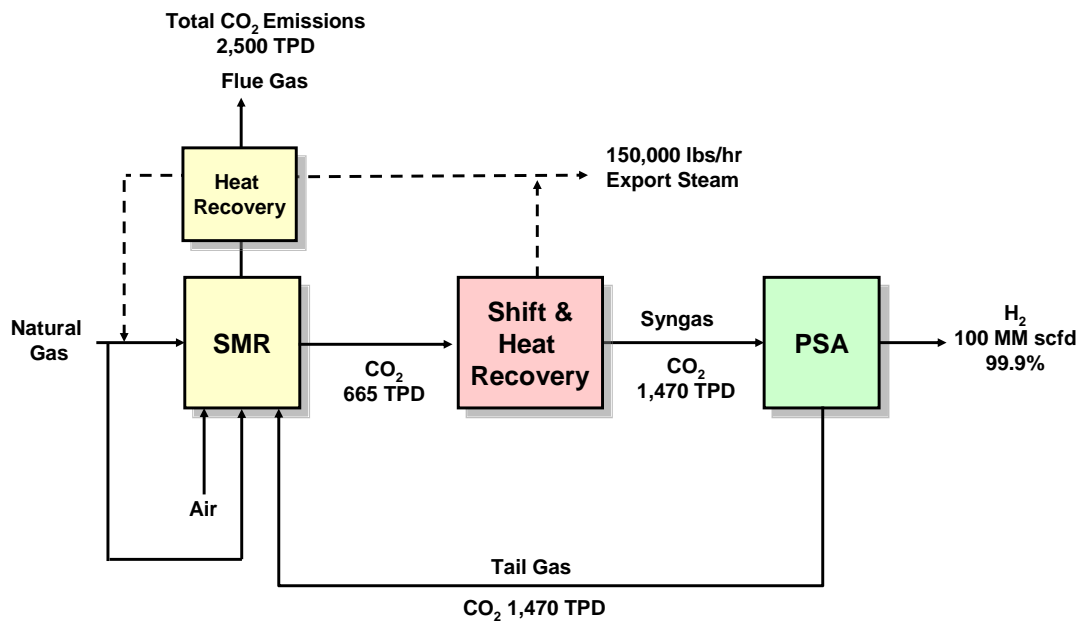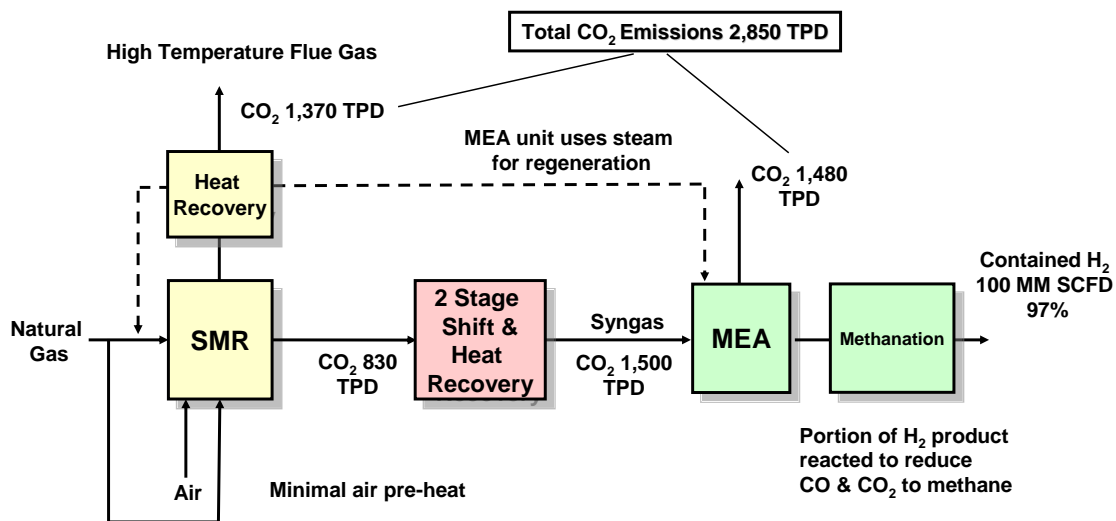
Figure 3: Modern Hydrogen Plant

Figure 4: Historical Hydrogen Plant

Table 2 Modern vs. Historical Hydrogen Plants		
Source	**CO$_2$ Formed/Emitted (tons per day)**	
	Modern Hydrogen Plant	**Historical Hydrogen Plant**
Complete conversion of feed to H$_2$	1485	1485
Combustion of fuel to provide reforming energy	420	420
Combustion of fuel to provide export steam	290	NA
Power for separation and compression	10	10
Total emissions (theoretical minimum)	2205	1915
Actual emissions	2500	2850
Tons of CO$_2$/1 MMscf of H$_2$ Product		
Intensity	25	28.5
Actual/Theoretical x 100	113%	149%
Notes:		
1. For 100 MMscfd of hydrogen contained in the product stream.		
2. Feed composition: 90 percent methane, 10 percent ethane.		
3. Power at 50 percent thermal efficiency.		

tons of CO$_2$ per 100 MMscfd of product H$_2$ or 104 percent of the theoretical CO$_2$ emissions.

Table 3 Hydrogen Plant Efficiency Improvements	
Improvement	**Btu/scf reduction**
Stack loss reduction	4 to 7
Fixed heat loss reduction	1 to 5
S:C ration reduction	2 to 3
Reformer temperature increase	2 to 4
Shift reactor optimization	1
PSA tail gas preheating	5 to 10
Compressor ISC unloaders	1
Total	**16 to 31**

CO$_2$ Reductions by Hydrogen Supply Management

Industrial gas firms such as Praxair have developed efficient networks of hydrogen plants interconnected by pipelines to reliably and economically supply hydrogen to refineries and other users. A map of Praxair's U.S. Gulf Coast hydrogen production and distribution system is shown in Figure 5.

As part of the development of such networks, lower-efficiency historical hydrogen plants have been acquired from refineries and replaced with modern plants. For example, Praxair acquired an 80 MMscfd historical hydrogen plant from a large Texas refinery, replacing it with a 100 MMscfd plant as part of a capacity expansion to meet the growing hydrogen demand of the U.S. refining industry. (This demand was driven by clean fuel specifications, product mix, and demand for motor fuels.) The difference in CO$_2$ intensity between the old and new facility is 3.5 tons per day of CO$_2$ per 1 MMscfd of H$_2$.
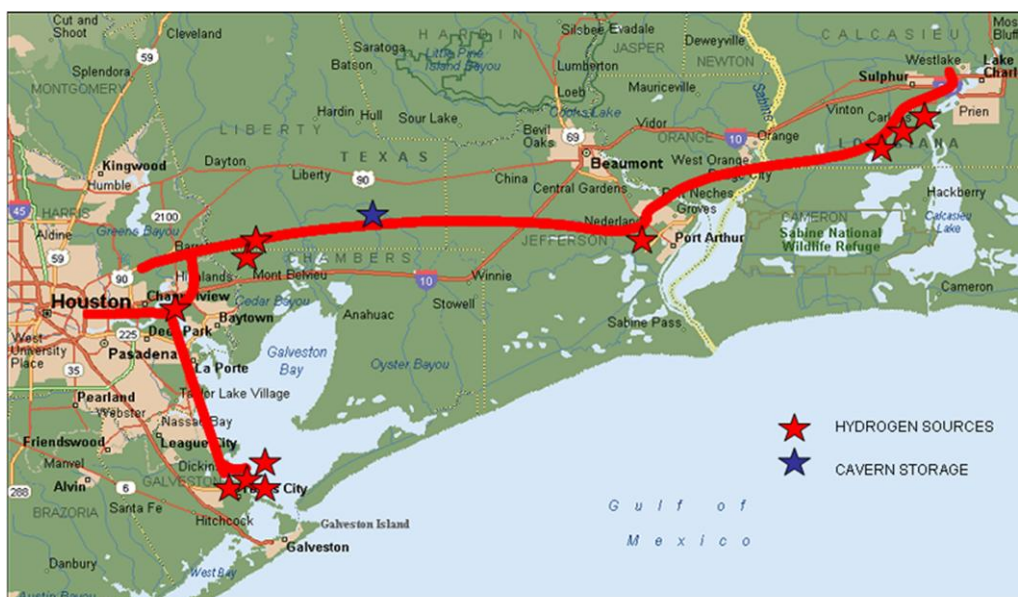
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Figure 5: U.S. Gulf Coast Hydrogen Production and Distribution System

Assuming an operating rate of 80 percent, this resulted in a net CO_2 reduction of 82,000 tons of CO_2 per year.

Additional CO_2 reductions (not yet quantified) accrue from the development of efficient hydrogen supply systems shared among many customers. For example, Praxair has built a salt dome cavern for underground storage of hydrogen in eastern Texas (see Figure 6).
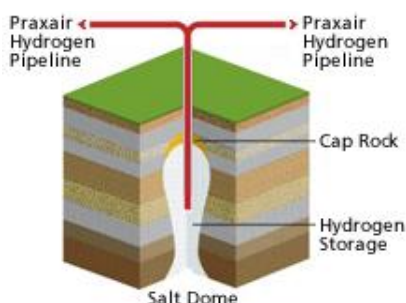

Figure 6: Hydrogen Storage Cavern

This facility has a working volume of 1.5 billion standard cubic feet (1.5 bscf) of hydrogen, allowing Praxair's hydrogen supply network to meet fluctuating customer demand without

rapidly modulating the capacity of hydrogen plants. As a result, the most efficient plants are used to the greatest extent.

CO₂ Capture from Hydrogen Plants

Several options are available for capture of 50 to 90 percent of the CO_2 normally emitted (see Figure 7). The option selected depends on the nature of future regulations, including allowance pricing. An allowance price or credit of $40 to $50/ton of CO_2 (2005 cost basis including compression to 2000 psig and pipeline transportation of 10 miles) should be adequate to trigger investment for capture at the 50 percent level.

Disposition of CO₂ Captured from Hydrogen Plants

CO_2 captured from a hydrogen plant is suitable for enhanced oil recovery (EOR) and underground storage in saline aquifers or depleted gas reservoirs. It is expected that levels of impurities such as water, nitrous oxide (NOx), sulfur oxide (SOx), and oxygen can be controlled to meet current and future specifications. Given the volume of CO_2 captured from SMR-based hydrogen plants, it will be necessary to aggregate with other
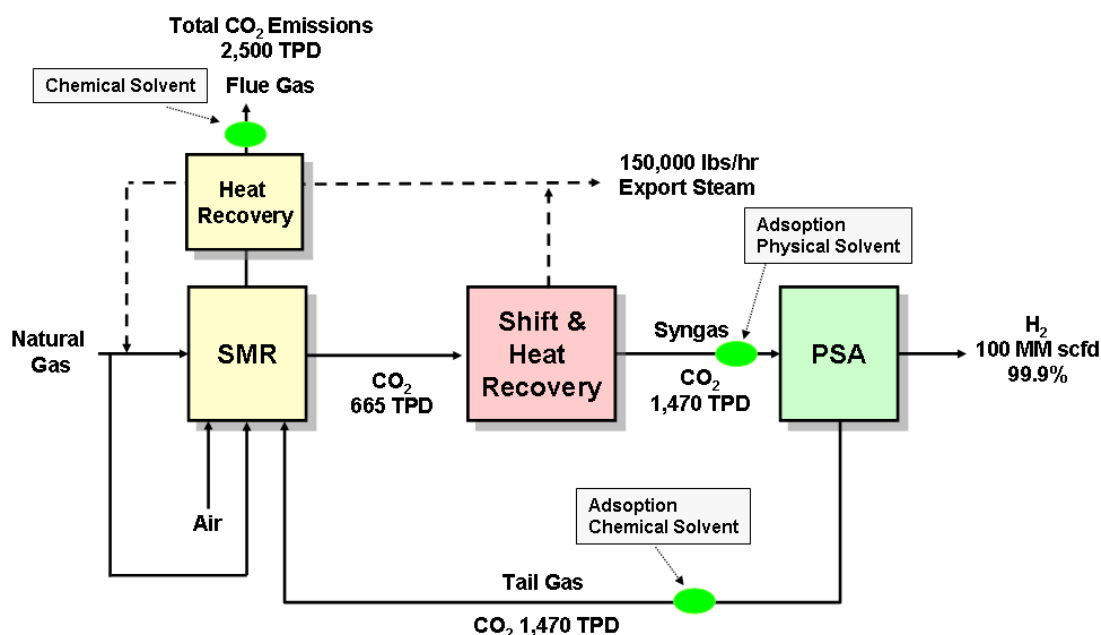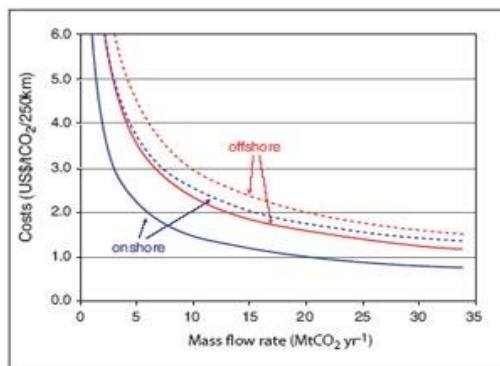
Figure 7: Hydrogen Plant CO$_2$ Capture Options

Figure 8: CO$_2$ Pipeline Costs *(3)*

sources to cost effectively transport the CO$_2$ to a sink. For example, the maximum CO$_2$ available from a 100 MMscfd hydrogen plant with a 95 percent operating rate is 780,000 short tons per year. Figure 8 shows that this quantity is far below the minimum economic threshold for pipeline transportation.

CO$_2$ Intensity of SMR-Based Hydrogen Plants vs. Water Electrolysis

Electrolysis of water is used on a small scale to supply hydrogen for applications where lower-cost sources are not available. From a CO$_2$ perspective, electrolysis has no direct emissions; however, the indirect emissions are large.

Table 4 provides information on the indirect CO$_2$ emissions from water-electrolysis-based hydrogen production.

Table 4 demonstrates that water electrolysis is not a viable means to lower CO$_2$ emissions attributable to hydrogen production. The theoretical minimum CO$_2$ intensity for electrolysis is greater than the actual for SMR-based hydrogen plants by a factor of 2. Even if a CO$_2$-free source of electric power, such as wind generation, is available, a better policy would be to use that power to reduce power produced at CO$_2$-emitting coal- and gas-fired power plants before considering hydrogen generation for large consumers currently served by natural-gas-based hydrogen plants.

Table 4 Analysis of CO$_2$ Emissions for Water Electrolysis Production of Hydrogen			
		kWh/kg of H$_2$	**kWh/1 MMscfd of H$_2$**
Electrolyzer power use	Theoretical minimum	33	83,970
	Large unit actual	50	127,000
Average U.S. power grid CO$_2$ intensity	1.3 lb of CO$_2$/kWh *(4)*		
		Tons of CO$_2$/1 MMscfd of H$_2$	
CO$_2$ intensity for electrolyzer	Theoretical minimum	54.6	
	Large unit actual	82.6	
CO$_2$ intensity for SMR-based H$_2$ plant	Theoretical minimum	22.1	
	Actual	25	
Notes: 1. 1 kg = 393 scf of H$_2$			

Conclusions

Process and equipment improvements made over the past 25 years have reduced the CO$_2$ intensity of hydrogen plants by more than 20 percent, to the point where emissions are within 13 percent of the theoretical minimum. Over the next 5 years, process, equipment, and operational improvements can potentially bring emissions down to within 9 percent of the theoretical minimum.

Additional CO$_2$ reductions have been achieved as industrial gas firms have developed sophisticated hydrogen pipeline networks in areas of concentrated demand, such as the Texas-Louisiana Gulf Coast. From 50 to 90 percent of the CO$_2$ emitted from hydrogen plants can be captured using technology currently available. Allowance prices of $50 per ton of CO$_2$ are needed to trigger investment *(5)*. The captured CO$_2$ will be suitable for EOR or geologic sequestration; however, the emissions from hydrogen plants must be aggregated with other sources to gain economies of scale for cost-effective pipeline transportation. Indirect emissions of CO$_2$ from electrolysis of water would be significantly higher than direct emissions from natural-gas-based hydrogen plants; therefore, electrolysis for hydrogen production is not an option for lowering CO$_2$ emissions.

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