# TECHNICAL SUPPORT DOCUMENT FOR HYDROGEN PRODUCTION: PROPOSED RULE FOR MANDATORY REPORTING OF GREENHOUSE GASES

Office of Air and Radiation U.S. Environmental Protection Agency

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#### 1. Source Description

In 2007, roughly 9 million metric tons per year of hydrogen was produced in the U.S.¹ in a variety of ways. This production results in about 60 million metric tons of CO₂ emissions each year. Table H1 provides estimates of U.S. hydrogen production for the various business sectors. Merchant hydrogen is consumed at sites other than where it is produced. Captive hydrogen (e.g., hydrogen produced at oil refineries, ammonia, and methanol plants) is consumed at the site where it is produced. This technical support document assumes that CO₂ emissions associated with captive hydrogen production facilities are included as part of the GHG emissions from the industry producing those other chemical products (e.g., ammonia, petroleum products, and methanol), and therefore this document is focused on merchant hydrogen production.

Table H1. Estimated Hydrogen Production by Business Sector

| <b>Business Sector</b> | Annual Hydrogen Production<br>(million metric tons per year) | Estimated CO <sub>2</sub> Emissions (million metric tons per year) |
|------------------------|--|--|
| Merchant hydrogen      | 2.0  | 17   |
| Oil refineries         | 2.6  | ~ 25   |
| Ammonia plants         | 2.1  | 18   |
| Methanol plants        | 1.5  | None   |
| Chlorine plants        | 0.4  | None   |
| Other                  | 0.3  | < 1  |
| Total                  | 8.9  | ~ 60   |

At present, merchant hydrogen is produced commercially primarily from natural gas, but also from naphtha and coal<sup>2</sup>. In 2003, The Innovation Group<sup>3</sup> reported U.S. merchant hydrogen production capacity to be 1.5 million metric tons per year. This same report forecast a 10% annual growth rate for merchant hydrogen production from 2003 to 2006. EPA assumed 8% annual growth rate from 2003 to 2007 to arrive at an estimate of 2.0 million metric tons per year for merchant production in 2007. The estimated CO<sub>2</sub> emissions shown in the right column is calculated using the ratio of 8.62 tons of CO<sub>2</sub> emissions per ton of hydrogen production based on a 2001 NREL report<sup>4</sup>.

Oil refineries mainly use steam methane reforming for hydrogen production, but they also use steam naphtha reforming when naphtha is available at less cost. Steam naphtha reforming

<sup>&</sup>lt;sup>1</sup> U.S. DOE – Fossil Energy. *Today's Hydrogen Production Industry*. http://www.fossil.energy.gov/programs/fuels/hydrogen/currenttechnology.html.

<sup>&</sup>lt;sup>2</sup> S. Czernik, R. French, C. Feik, and E. Chornet (2001). *Production of Hydrogen from Biomass-Derived Liquids*. Proceedings of the 2001 DOE Hydrogen Program Review, NREL/CP-570-30535. <a href="http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/30535i.pdf">http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/30535i.pdf</a>, National Renewable Energy Laboratory, Golden, CO.

<sup>&</sup>lt;sup>3</sup> http://www.the-innovation-group.com/chemprofile.htm, dated February 24, 2003.

<sup>&</sup>lt;sup>4</sup> Spath, P. L. and M. K. Mann. *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming*. Report No. NREL/TP-570-27637, National Renewable Energy Laboratory, Golden, CO, February 2001.

produces roughly 10.5 tons of CO<sub>2</sub> per ton of H<sub>2</sub>. In 2003, The Innovation Group<sup>5</sup> reported the total captive hydrogen production capacity at 145 locations to be 2,995 million standard cubic feet (scf) per day, which translated to an annual capacity of 2.6 million metric tons per year. This same report did not anticipate a growth rate for captive hydrogen production from 2003 to 2006. The proportions of natural gas and naphtha reforming vary from year to year; assuming an equal split, CO<sub>2</sub> emissions from oil refineries due to hydrogen production is around 25 million metric tons per year.

Ammonia plants use steam methane reforming to produce hydrogen as an intermediate. U.S. ammonia production is currently about 12 million metric tons per year, which requires the production of 2.1 (12 million metric tons x 3.02 g per mole of  $H_3$  / 17.02 g per mole of  $NH_3$ ) million metric tons of hydrogen per year. Assuming 8.62 tons of  $CO_2$  emissions per ton of hydrogen as above, the corresponding  $CO_2$  emissions are 18 million metric tons per year.

Methanol plants also use steam methane reforming to produce hydrogen as an intermediate, but, unlike ammonia plants, the carbon leaves the methanol plant bound in the methanol. U.S. hydrogen production at methanol plants is currently about 1.5 million metric tons per year, with no CO<sub>2</sub> emissions.

Chlorine is produced by electrolysis of sodium chloride brine, which results in production of sodium hydroxide, chlorine, and hydrogen. U.S. production of chlorine results in the production of about 0.4 million metric tons of hydrogen, but no CO<sub>2</sub>. Some of this hydrogen may simply be released to the atmosphere.

The "Other" category is primarily electrolysis, but it may include petrochemical plants which use dehydrogenation (a catalytic process to form organic compounds with hydrogen as a byproduct but not CO<sub>2</sub>) or coal (or petroleum coke) gasification to produce hydrogen. The "Other" category may also include various small plants using steam reforming, partial oxidation, or autothermal reforming of natural gas, ethane, propane, and liquid hydrocarbon fuels to produce hydrogen.

Table H2 groups hydrogen production processes by development stage and CO<sub>2</sub> emissions, including those hydrogen production methods under development by the U.S. Department of Energy and other organizations. These processes include a wide range of technologies to produce hydrogen economically from a variety of resources in environmentally friendly ways<sup>6</sup>. About 95% of all hydrogen (not just merchant hydrogen) produced in the U.S. today is made from natural gas via steam methane reforming<sup>7</sup>. Numerous other processes are used to produce the other 5% of hydrogen produced in the U.S. today. Some of these other processes do not produce GHG emissions<sup>8</sup>.

<sup>6</sup> U.S. DOE Hydrogen Program (2006). *Hydrogen Production Fact Sheet*. October. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/doe h2\_production.pdf. Washington, DC.

<sup>&</sup>lt;sup>5</sup> http://www.the-innovation-group.com/chemprofile.htm, dated February 24, 2003.

<sup>&</sup>lt;sup>7</sup> U.S. DOE – Energy Efficiency and Renewable Energy Hydrogen, Fuel Cells, and Infrastructure Technology Program, Natural Gas Reforming, <a href="http://www1.eere.energy.gov/hydrogenandfuelcells/production/natural\_gas.html/">http://www1.eere.energy.gov/hydrogenandfuelcells/production/natural\_gas.html/</a>. Washington, DC.

<sup>&</sup>lt;sup>8</sup> U.S. DOE Hydrogen Program (2007). *Hydrogen and Our Energy Future*. Report No. DOE/EE-0320. <a href="http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/hydrogenenergyfuture\_web.pdf">http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/hydrogenenergyfuture\_web.pdf</a>. Washington, DC.

**Table H2. Hydrogen Production Methods** 

| <b>Development Stage</b> | Without CO <sub>2</sub> Emissions   | With CO <sub>2</sub> Emissions   |
|--------------------------|---|--|
| Current                  | <ul> <li>Electrolysis of water;</li> <li>Chlorine production;</li> <li>Dehydrogenation of organic compounds (including catalytic reforming of naphthas and naphthenes)</li> </ul>   | <ul> <li>Steam methane reforming;</li> <li>Steam naphtha reforming;</li> <li>Coal gasification;</li> <li>Petroleum coke gasification</li> </ul>  |
| Under Development        | <ul> <li>Biomass gasification;</li> <li>Reforming of renewable liquid biofuels (e.g., ethanol, bio-oils);</li> <li>Nuclear high-temperature electrolysis;</li> <li>High-temperature thermochemical water splitting;</li> <li>Photo-biological water splitting;</li> <li>Photo-electro-chemical water splitting</li> </ul> | <ul> <li>Partial oxidation of methane and other hydrocarbon gases;</li> <li>Partial oxidation of naphtha and other hydrocarbon liquids;</li> <li>Autothermal reforming of gas and liquid hydrocarbons</li> </ul> |

Merchant hydrogen is primarily sold to refineries and chemical plants<sup>9</sup>. Including captive and other hydrogen production, hydrogen is mostly used for industrial applications such as petroleum refining, treating metals, and food processing (See Table H3 for additional applications and uses). According to a 2001 NREL report<sup>10</sup>, "Hydrogen is used in a number of industrial applications, with today's largest consumers being ammonia production facilities (40.3%), oil refineries (37.3%), and methanol production facilities (10.0%). Its main use as a fuel is in the NASA space program, where liquid hydrogen is a rocket fuel and hydrogen fuel cells power onboard electrical systems." The Innovation Group (2003) provides a more recent but different breakout<sup>11</sup> of hydrogen applications:

- Petroleum refining (66.8%)
- Petrochemicals (26.2%)
- Other (7%) -- includes metals (2.7%), electronics (1.5%), government (NASA) (1.2%), edible fats and oils (0.7%), float glass (0.3%), utility power generation (0.2%), miscellaneous (0.4%)

Table H3. Hydrogen Applications and Uses

| Application Uses |
|------------------|
|------------------|

<sup>&</sup>lt;sup>9</sup> U.S. DOE – Fossil Energy (2008). *Today's Hydrogen Production Industry*. http://www.fossil.energy.gov/programs/fuels/hydrogen/currenttechnology.html. Washington, DC.

<sup>&</sup>lt;sup>10</sup> Spath, P. L. and M. K. Mann. *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming*. Report No. NREL/TP-570-27637, National Renewable Energy Laboratory, Golden, CO, February 2001.

<sup>11 &</sup>lt;a href="http://www.the-innovation-group.com/chemprofile.htm">http://www.the-innovation-group.com/chemprofile.htm</a>, dated February 24, 2003.

| Metals   | Hydrogen is mixed with inert gases to obtain a reducing atmosphere, which is required for many applications in the metallurgical industry, such as heat treating steel and welding. It is often used in annealing stainless steel alloys, magnetic steel alloys, sintering and copper brazing.  Hydrogen can be produced by dissociation of ammonia at about 1800°F with the aid of a catalyst - which results in a mix of 75% hydrogen and 25% mononuclear nitrogen (N rather than N <sub>2</sub> ). The mix is used as a protective atmosphere for applications such as brazing or bright annealing.   |
|--|--|
| Chemicals,<br>Pharmaceuticals and<br>Petroleum | Hydrogen is used in large quantities as a raw material in the chemical synthesis of ammonia, methanol, hydrogen peroxide, polymers, and solvents.  In refineries, it is used to remove the sulfur and nitrogen that is contained in crude oil. Hydrogen is catalytically combined with various intermediate processing streams and is used, in conjunction with catalytic cracking operations, to convert heavy and unsaturated compounds to lighter and more stable compounds.  The pharmaceutical industry uses hydrogen to manufacture vitamins and other pharmaceutical products.  Large quantities of hydrogen are used to purify gases (e.g. argon) that contain trace amounts of oxygen, using catalytic combination of the oxygen and hydrogen followed by removal of the resulting water. |
| Glass and Ceramics                             | In float glass manufacturing, hydrogen is required to prevent oxidation of the large tin bath.   |
| Food and Beverages                             | It is used to hydrogenate unsaturated fatty acids in animal and vegetable oils, producing solid fats for margarine and other food products.  |
| Electronics                                    | Hydrogen is used as a carrier gas for such active trace elements as arsine and phospine, in the manufacture of semi-conducting layers in integrated circuits.  |
| Miscellaneous                                  | Generators in large power facilities are often cooled with hydrogen, since the gas processes high thermal conductivity and offers low friction resistance.  Liquid hydrogen is used as a rocket fuel.  The nuclear fuel industry uses hydrogen as a protective atmosphere in the fabrication of fuel rods.   |

Source: Universal Industrial Gases, Inc. (2008). *Hydrogen* (*H*<sub>2</sub>) *Properties, Uses, Applications, Hydrogen Gas and Liquid Hydrogen*. http://www.uigi.com/hydrogen.html. Easton, PA.

Instead of releasing the carbon dioxide generated by steam methane reforming to the atmosphere, a portion of it may be captured and diverted to other industrial uses. Common uses of the captured and diverted carbon dioxide include:

- Pure CO<sub>2</sub> used for the carbonation of beverages;
- Pure CO<sub>2</sub> used to produce dry ice;
- Pure CO<sub>2</sub> used as a fire extinguishing agent, refrigerant, or laboratory gas; and
- Pure CO<sub>2</sub> used for grain disinfestation.

# a. Total Emissions (based on Inventory)

Table H4 lists the U.S. inventory of 73 active liquid and gaseous merchant hydrogen production facilities in 2003 from The Innovation Group data<sup>12</sup>, along with 4 more facilities listed as planned for new construction in the 2004-2006 timeframe. The Innovation Group reported the merchant hydrogen facility capacity data in thousand standard cubic feet (scf) per day.

 $\frac{12}{\text{http://www.the-innovation-group.com/chemprofile.htm}}$ , dated 2003 (Four Canadian facilities were removed from the original list)

Additional merchant hydrogen production facilities or additional production capacity may have been constructed since, but more recent data are not available.

Table H4. Merchant Hydrogen Production Facilities in the U.S.

| Producer                           | H <sub>2</sub> Facility Capacity (thousand scf per day) | H <sub>2</sub> Facility<br>Capacity<br>(metric<br>tons/yr) | CO <sub>2</sub> Emissions at Full Facility Capacity <sup>a</sup> (metric tons/yr) |
|------------------------------------|---|--|---|
| Merchant Cryogenic Liquid Hydrogen | 1 0/  | • •  | ,   |
| Facility 1                         | 26,800  | 23,645   | 203,850   |
| Facility 2                         | 11,500  | 10,146   | 87,473  |
| Facility 3                         | 2,300   | 2,029  | 17,495  |
| Facility 4                         | 11,500  | 10,146   | 87,473  |
| Facility 5.                        | 11,500  | 10,146   | 87,473  |
| Facility 6                         | 15,000  | 13,234   | 114,095   |
| Facility 7                         | 8,500   | 7,499  | 64,654  |
| Total Merchant Cryogenic Liquid    | 87,100  | 76,847   |   |
| Merchant Compressed Hydrogen Gas   |   |  |   |
| Facility 8.                        | 830   | 732  | 6,313   |
| Facility 9                         | 15,000  | 13,234   | 114,095   |
| Facility 10                        | 7   | 6  | 53  |
| Facility 11                        | 50  | 44   | 380   |
| Facility 12                        | 165   | 146  | 1,255   |
| Facility 13                        | 200   | 176  | 1,521   |
| Facility 14                        | 200   | 170  | 1,321   |
| Facility 14a                       | 50,000  | 44,115   | 380,318   |
| Facility 14b                       | 700   | 618  | 5,324   |
| Facility 14c                       | 1,000   | 882  | 7,606   |
| Facility 15                        | 1,800   | 1,588  | 13,691  |
| Facility 16                        | 100,000   | 88,229   | 760,635   |
| Facility 17                        | 2,300   | 2,029  | 17,495  |
| Facility 18                        | 1,500   | 1,323  | 11,410  |
| Facility 19                        | 750   | 662  | 5,705   |
| Facility 20                        | 960   | 847  | 7,302   |
| Facility 21                        | 125,000   | 110,286  | 950,794   |
| Facility 22                        | 750   | 662  | 5,705   |
| Facility 23                        | 60,000  | 52,937   | 456,381   |
| Facility 24                        | 40,000  | 35,292   | 304,254   |
| Facility 25                        | 100,000   | 88,229   | 760,635   |
| Facility 26                        | 3,600   | 3,176  | 27,383  |
| Facility 27                        | 750   | 662  | 5,705   |
| Facility 28                        | 160,000   | 141,166  | 1,217,017   |
| Facility 29                        |   |  |   |
| Facility 29a                       | n.a.  | n.a.   | n.a.  |
| Facility 29b.                      | 35,000  | 30,880   | 266,222   |

| Facility 29c | 100,000 | 88,229  | 760,635 |
|--------------|---------|---------|---------|
| Facility 29d | 30,000  | 26,469  | 228,191 |
| Facility 29e | 21,000  | 18,528  | 159,733 |
| Facility 30  | ,       | - 7     |         |
| Facility 30a | 12,000  | 10,587  | 91,276  |
| Facility 30b | 27,000  | 23,822  | 205,372 |
| Facility 30c | 52,000  | 45,879  | 395,530 |
| Facility 30d | 29,000  | 25,586  | 220,584 |
| Facility 30e | 80,000  | 70,583  | 608,508 |
| Facility 31  | n.a.    | n.a.    | n.a.    |
| Facility 32  | 1,080   | 953     | 8,215   |
| Facility 33  | n.a.    | n.a.    | n.a.    |
| Facility 34  | 13,000  | 11,470  | 98,883  |
| Facility 35  | 1,500   | 1,323   | 11,410  |
| Facility 36  | 1,080   | 953     | 8,215   |
| Facility 37  | 150     | 132     | 1,141   |
| Facility 38  | 190     | 168     | 1,445   |
| Facility 39  | 120     | 106     | 913     |
| Facility 40  | 7       | 6       | 53      |
| Facility 41  | 500     | 441     | 3,803   |
| Facility 42  | 400     | 353     | 3,043   |
| Facility 43  | 1,500   | 1,323   | 11,410  |
| Facility 44  | 35,000  | 30,880  | 266,222 |
| Facility 45  | 35,000  | 30,880  | 266,222 |
| Facility 46  | 10,000  | 8,823   | 76,064  |
| Facility 47  | 80,000  | 70,583  | 608,508 |
| Facility 48  | 290     | 256     | 2,206   |
| Facility 49  | 720     | 635     | 5,477   |
| Facility 50  | 290     | 256     | 2,206   |
| Facility 51  | n.a.    | n.a.    | n.a.    |
| Facility 52  | 3,000   | 2,647   | 22,819  |
| Facility 53  | 430     | 379     | 3,271   |
| Facility 54  | 290     | 256     | 2,206   |
| Facility 55  | 6,000   | 5,294   | 45,638  |
| Facility 56  | 1,440   | 1,270   | 10,953  |
| Facility 57  | 1,920   | 1,694   | 14,604  |
| Facility 58  | 95,000  | 83,818  | 722,604 |
| Facility 59  | 126,000 | 111,169 | 958,401 |
| Facility 60  | 3,980   | 3,512   | 30,273  |
| Facility 61  | 760     | 671     | 5,781   |
| Facility 62  | 35,000  | 30,880  | 266,222 |
| Facility 63  | 1,920   | 1,694   | 14,604  |
| Facility 64  | 4,800   | 4,235   | 36,510  |
| Facility 65  |         |         |         |
| Facility 65a | 40,000  | 35,292  | 304,254 |
| Facility 65b | 25,000  | 22,057  | 190,159 |
| Facility 65c | 29,000  | 25,586  | 220,584 |
| Facility 65d | 75,400  | 66,525  | 573,519 |

| Facility 65e <sup>b</sup>     | 200,000   | 176,458   | 1,521,271  |
|-------------------------------|-----------|-----------|------------|
| Facility 66                   | 200       | 176       | 1,521      |
| Facility 67                   | n.a.      | n.a.      | n.a.       |
| Facility 68                   | 32,400    | 28,586    | 246,446    |
| Total Merchant Compressed Gas | 1,914,729 | 1,689,347 | 14,564,106 |
| Total Merchant Product        | 2,001,829 | 1,766,194 | 15,226,620 |

<sup>&</sup>lt;sup>a</sup> Includes both process and combustion related emissions estimated based on production capacity (i.e., facilities are assumed to operate at full production capacity).

Source of Capacity Data: The Innovation Group (2003). *Hydrogen*. <a href="http://www.the-innovation-group.com/chemprofile.htm">http://www.the-innovation-group.com/chemprofile.htm</a>. Morristown, NJ.

Annual merchant hydrogen facility production capacity in metric tons per year were calculated assuming 365 days of operation per year, 2,205 pounds per metric ton, and a standard density of hydrogen of 0.00533 lb/scf.

Annual CO<sub>2</sub> emissions at full facility capacity (in metric tons per year) were calculated from annual merchant hydrogen facility capacity using the process and combustion CO<sub>2</sub>-to-H<sub>2</sub> mass ratio of 8.62. Table H5 lists the analysis steps used to determine the CO<sub>2</sub> emissions from merchant steam methane reforming based on an NREL report by Spath and Mann <sup>13</sup>. Essentially all merchant hydrogen produced in the U.S. today is made from natural gas via steam methane reforming <sup>14</sup>. Spath and Mann describe a typical, large steam methane reforming facility in terms of hydrogen capacity and natural gas consumption. Note that their CO<sub>2</sub>-to-H<sub>2</sub> molar ratio of 0.395 is not equal to the ideal molar ratio for steam methane reforming of 0.25. The ratio is higher because not all of the available hydrogen is captured in the product stream. Some of the hydrogen and some unused methane are included in the tail gas, partly to provide heat to the boiler/reformer unit.

Table H5. Analysis of CO<sub>2</sub> Emissions from Steam Methane Reforming Merchant Hydrogen Production Facilities

| Parameter  | Value   | Comments   |  |  |
|--|---------|--|--|--|
| NREL hydrogen facility capacity                                | 1.5     | million Nm <sup>3</sup> of H <sub>2</sub> /day                           |  |  |
| NREL facility natural gas consumption (process and combustion) | 435     | Mg/day = metric ton/day  |  |  |
| Conversion scf per Nm <sup>3</sup>                             | 37.23   | scf/Nm³ (standard is 60 °F at 30 in. Hg) (Normal is 0°C at 101.325 N/m³) |  |  |
| Density of H <sub>2</sub>                                      | 0.00533 | lb/scf (calculated at standard conditions)                               |  |  |
| NREL facility capacity   | 135.0   | Calculated in metric ton/day   |  |  |
| Specific gravity of natural gas                                | 0.60    | Chemical Engineer's Handbook, 5th Ed., Table 9-15, typical value         |  |  |
| Density of natural gas   | 0.045   | lb/scf (calculated using air density of 0.075 lb/scf)                    |  |  |
| Natural gas heat content (HHV)                                 | 1,029   | Btu/scf (from U.S. Inventory)  |  |  |

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<sup>&</sup>lt;sup>b</sup> New construction planned in 2003 for the 2004-2006 timeframe.

<sup>&</sup>lt;sup>13</sup> Spath, P. L., and M. K. Mann (2001). *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming*. Report No. NREL/TP-570-27637, National Renewable Energy Laboratory, Golden, CO, February.

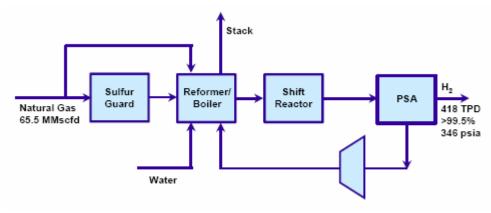
<sup>14</sup> U.S. DOE – Energy Efficiency and Renewable Energy Hydrogen, Fuel Cells, and Infrastructure Technology Program, Natural Gas Reforming, <a href="http://www1.eere.energy.gov/hydrogenandfuelcells/production/natural\_gas.html/">http://www1.eere.energy.gov/hydrogenandfuelcells/production/natural\_gas.html/</a>. Washington, DC.

| NREL facility natural gas<br>consumption (process and<br>combustion)                     | 21,933  | MMBtu/day (calculated)  |
|--|---------|---|
| GHG Emission Factors (process and combustion)  | 0.05306 | metric tons CO <sub>2</sub> / MMBtu (from U.S. Inventory)                     |
| Process and combustion CO <sub>2</sub> emissions from NREL facility                      | 1,164   | metric tons CO <sub>2</sub> /day (calculated)                                 |
| Mass ratio of process and combustion CO <sub>2</sub> to H <sub>2</sub> at NREL facility  | 8.62    | Calculated, including both process and combustion emissions                   |
| Molar ratio of process and combustion CO <sub>2</sub> to H <sub>2</sub> at NREL facility | 0.395   | Calculated using 2.016 g/mole H <sub>2</sub> and 44.01 g/mole CO <sub>2</sub> |

## b. Types of Emissions to Be Reported

The Total National Emissions estimates reported here include a mix of process and combustion emissions. Figure H1 is the block flow diagram for steam methane reforming without CO<sub>2</sub> removal, and Figure H2 is the block flow diagram for steam methane reforming with CO<sub>2</sub> capture by an amine process. Natural gas is used as the feedstock as well as a supplementary fuel to the steam boiler. Once the feedstock passes through a reactor bed to remove sulfur compounds, steam methane reforming consists of three steps<sup>15</sup>:

- Reformation of the feedstock to obtain a synthesis gas using high temperature steam supplied by burning tail gas from the hydrogen purification step;
- Using a water-gas shift reaction to form hydrogen and carbon dioxide from the carbon monoxide produced in the first step; and
- Pressure swing absorption to produce nearly pure hydrogen and a tail gas containing carbon dioxide, hydrogen, methane, carbon monoxide, water vapor, and other minor components.

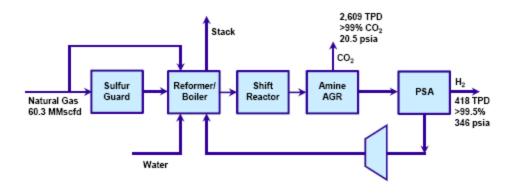


Source: National Energy Technology Center<sup>16</sup>

Figure H1. Block Flow Diagram for Steam Reforming of Natural Gas

15 U.S. Hydrogen Association fact sheet, <a href="http://nationalhydrogenassociation.org/general/factSheet\_production.pdf">http://nationalhydrogenassociation.org/general/factSheet\_production.pdf</a>.

<sup>&</sup>lt;sup>16</sup> Klett, M. G., J. S. White, R. L. Schoff, and T. L. Buchanan (2002). Hydrogen Production Facilities Facility Performance and Cost Comparisons. Parson Infrastructure and Technology Group, Final Report under Contract No. DE-AM26-99FT40465 between Concurrent Technologies Corporation and the National Energy Technology Center. Golden, CO, March.



Source: National Energy Technology Center<sup>17</sup>

Figure H2. Block Flow Diagram for Steam Reforming of Natural Gas for CO<sub>2</sub> Removal

#### i) Process Emissions

For steam methane reforming, the basic chemical reactions in the steam reformer and the watergas shift reactor are:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
  
 $CO + H_2O \rightarrow CO_2 + H_2$ 

These reactions result in a molar ratio of  $CO_2$  to  $H_2$  of 0.25. However, in an actual steam methane reforming process, the tail gas from the pressure swing absorption stage includes unreacted methane and some hydrogen. These fuel gases are used to fire the boiler in the reformer/boiler unit. According to the NREL report<sup>18</sup>, the molar ratio of  $CO_2$  to  $H_2$  product for typical steam methane reforming is 0.395.

For steam reforming of other gas and liquid hydrocarbons (including naphtha), the three process steps are the same as for steam methane reforming: reformer/boiler, water-gas shift, and pressure-swing absorption. Steam reforming of a generalized hydrocarbon and the water-gas shift reaction are:

$$\begin{aligned} C_n H_{2n+m} + n \ H_2 O &\rightarrow n \ CO + (2n+m/2) \ H_2 \\ CO + H_2 O &\rightarrow CO_2 + H_2 \end{aligned}$$

These ideal reactions result in a molar ratio of  $CO_2$  to  $H_2$  of 1/(3n + m/2) and a mass ratio of  $CO_2$  to  $H_2$  of 44.01/2.016/(3n + m/2).

<sup>17</sup> Klett, M. G., J. S. White, R. L. Schoff, and T. L. Buchanan (2002). *Hydrogen Production Facilities Facility Performance and Cost Comparisons*. Parson Infrastructure and Technology Group, Final Report under Contract No. DE-AM26-99FT40465 between Concurrent Technologies Corporation and the National Energy Technology Center. Golden, CO, March.

<sup>&</sup>lt;sup>18</sup> Spath, P. L. and M. K. Mann (2001). *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming*, Report No. NREL/TP-570-27637, National Renewable Energy Laboratory, Golden, CO, February 2001.

Partial oxidation can be carried out non-catalytically or catalytically (autothermal reaction). Partial oxidation is preferred when the raw material is a heavier fraction of petroleum while steam reforming is more convenient for lighter ones. In the partial oxidation process, air is used as oxidant and the use of air results in nitrogen being mixed with the hydrogen produced, reducing the partial pressure of the hydrogen entering the pressure swing absorption unit. Partial oxidation is accomplished by reacting a fuel with a restricted amount of oxygen:

$$\begin{aligned} C_n H_{2n+m} + n/2 & O_2 \rightarrow n & CO + (n+m/2) & H_2 \\ CO + H_2 O \rightarrow CO_2 + H_2 \end{aligned}$$

These reactions take advantage of oxygen having a greater affinity for carbon than for hydrogen. These ideal reactions result in a molar ratio of  $CO_2$  to  $H_2$  of 1/(2n + m/2), and a mass ratio of  $CO_2$  to  $H_2$  of 44.01/2.016/(2n + m/2).

For coal gasification, the process steps are:

- Air separation unit (to separate the oxygen from the air);
- Coal gasifier to produce raw synthetic gas;
- Steam mixer (to add process steam);
- Water-gas shift converter;
- Water removal:
- Amine unit (to remove sulfur compounds);
- Pressure swing absorption unit (to produce hydrogen and a tail gas); and
- Combustion of tail gas to make process steam.

The coal gasification reactions are roughly equivalent to:

$$CH_n + \frac{1}{2}O_2 + mH_2O \rightarrow mCO_2 + (m+n/2)H_2 + (1-m)CO + other species$$

Where "n" is typically around  $0.8^{19}$  and "m" is almost but less than one, depending on the success of the water-gas shift converter. These ideal reactions result in a molar ratio of  $CO_2$  to  $H_2$  of m/(m+n/2), and a mass ratio of  $CO_2$  to  $H_2$  of 44.01/2.016\*m/(m+n/2).

#### ii) Combustion Emissions

In steam methane reforming using natural gas, almost all of the natural gas is used as feedstock (resulting in process  $CO_2$  emissions). The plants are designed to allow the tail gas to make steam and maintain the temperature of the reformer/boiler unit. However, a small portion of the natural gas is used during plant startup to preheat the reformer/boiler unit and during normal plant operations to supplement the heat provided by the tail gas as needed to maintain the proper temperature of the reformer/boiler unit (resulting in minor combustion  $CO_2$  emissions). The process and combustion emissions go up the same stack from the boiler/reformer unit. Since the

<sup>&</sup>lt;sup>19</sup> U.S. DOE Hydrogen Program (2007). *Hydrogen and Our Energy Future*. Report No. DOE/EE-0320. <a href="http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/hydrogenenergyfuture\_web.pdf">http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/hydrogenenergyfuture\_web.pdf</a>. Washington, DC.

emissions are predominately process emissions and because the natural gas combustion products are emitted from the same stack, EPA has treated all the emissions as process emissions.

## 2. Options for Reporting Threshold

The requirements of other emissions reporting programs were reviewed and the results are summarized below (see Table H6). The reporting programs reviewed included:

- 2006 IPCC guidelines<sup>20</sup>
- API Compendium<sup>21</sup>
- Department of Energy 1605(b) Voluntary Reporting Program<sup>22</sup>
- California Mandatory GHG Reporting Program Initial Statement of Reasons 10/16/07 version with 12/06/07 updates<sup>23</sup>
- New Mexico Green House Gas Mandatory Emissions Inventory (finalized 1/3/08)<sup>24</sup>
- European Union Emissions Trading System (EU-ETS)<sup>25</sup>

Table H6. Thresholds for Other Reporting Programs

|   | CO <sub>2</sub> Threshold Level<br>(Metric Tons CO <sub>2</sub> e/year)  | H <sub>2</sub> Production Capacity<br>(Tons H <sub>2</sub> /year) |
|---|--|---|
| 2006 IPCC guidelines  | N/A  | Not mentioned   |
| API Compendium  | None   | Not mentioned   |
| Department of Energy 1605(b)<br>Voluntary Reporting Program   | No minimum   | Not mentioned   |
| California Mandatory GHG Reporting<br>Program - Initial Statement of Reasons<br>- 10/16/07 version with 12/06/07<br>updates | Facility CO <sub>2</sub> emissions from combination of stationary combustion and process sources > 25,000 metric tons per year | Not mentioned   |
| New Mexico Green House Gas<br>Mandatory Emissions Inventory<br>(finalized 1/3/08)   | Simplified documentation for CO <sub>2</sub><br>emissions <5% of facility GHG<br>emissions (CO <sub>2</sub> equivalent)        | Not mentioned   |
| European Union Emissions Trading<br>System (EU-ETS)   | N/A  | Not mentioned   |

<sup>&</sup>lt;sup>20</sup> IPCC (2006) *2006 IPCC Guidelines for National Greenhouse Gas Inventories*. The National Greenhouse Gas Inventories Programme, The Intergovernmental Panel on Climate Change, H.S. Eggleston, L. Buenida, K. Miwa, T Ngara, and K. Tanabe (eds.). Hayama, Kanagawa, Japan.

<sup>&</sup>lt;sup>21</sup> API Compendium (2004). *Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry*. <a href="http://www.api.org/ehs/climate/response/index.cfm">http://www.api.org/ehs/climate/response/index.cfm</a>. Washington, DC, February.

<sup>&</sup>lt;sup>22</sup> DOE (2007). *Guidelines for Voluntary Greenhouse Gas Reporting*. Department of Energy 1605(b) Voluntary Reporting Program, 10 CFR Part 300, RIN 1901-AB11. <a href="http://www.eia.doe.gov/oiaf/1605/aboutcurrent.html">http://www.eia.doe.gov/oiaf/1605/aboutcurrent.html</a>. Washington, DC, April.

<sup>&</sup>lt;sup>23</sup> CARB (2007). *Mandatory Greenhouse Gas Emissions Reporting*. California Environmental Protection Agency Air Resources Board, Initial Statement of Reasons - 10/16/07 version with 12/06/07 updates. <a href="http://www.arb.ca.gov/cc/reporting/ghg-rep/ghg-rep.htm">http://www.arb.ca.gov/cc/reporting/ghg-rep/ghg-rep.htm</a>, Sacramento, California.

<sup>&</sup>lt;sup>24</sup> New Mexico (2008). *Green House Gas Mandatory Emissions Inventory (finalized 1/3/08)*. New Mexico Environment Department Air Quality Bureau. <a href="http://www.nmenv.state.nm.us/aqb/ghg/ghgrr\_index.html">http://www.nmenv.state.nm.us/aqb/ghg/ghgrr\_index.html</a>. Santa Fe, NM.

<sup>&</sup>lt;sup>25</sup> EU-ETS (2005). *Guide on Monitoring and Reporting*. European Union (EU) Emissions Trading Scheme (ETS) Manual No. 1, Version 1.0. <a href="http://www.euets.net/">http://www.euets.net/</a>. Uden, The Netherlands, October.

Most of these protocols have no reporting threshold, or simplified reporting requirements for CO<sub>2</sub> emissions below 5% of the facility total GHG emissions (CO<sub>2</sub> equivalent). The California threshold is for merchant hydrogen production facilities that emit greater than 25,000 metric tons per year of CO<sub>2</sub> from the combination of stationary combustion and process sources. If California facility operations result in emissions of less than 20,000 metric tons per year of CO<sub>2</sub> for three consecutive years, then the operator is exempt from reporting until the emissions exceeds 25,000 metric tons per year of CO<sub>2</sub>. This threshold is based on actual emissions and not on the facility capacity.

The European Union Emissions Trading System (EU-ETS) covers the following sectors: electric power, oil refineries, coke ovens, metal ore and steel, cement kilns, glass, ceramics, and paper and pulp, but not hydrogen production. The thresholds vary by sector and are expressed in terms of production. For example, the threshold for combustion for energy production is 20 MW, which roughly corresponds to 100,000 metric tons of CO<sub>2</sub> per year. This threshold is based on facility capacity (20 MW) and not on actual facility emissions.

Depending upon the facility, a considerable difference may exist between actual and potential capacity to emit. However, most industrial facilities operate at least 90% of the available 8,760 hours in a year (6 weeks of down time per year, at most), and operate at near full capacity during those hours, implying emissions that are at least 75% of operating at full capacity for 8,760 hours per year.

### a. Options Considered

Four options for reporting emissions thresholds were considered for the reporting of CO<sub>2</sub> emissions from merchant hydrogen production facilities: 1,000 metric tons, 10,000 metric tons, 25,000 metric tons, and 100,000 metric tons of process CO<sub>2</sub> emissions per year per facility (including the minor combustion emissions). Table H7 compares the effect of the threshold on reported emissions and number of reporting facilities in the U.S. For example, a threshold of 25,000 metric tons per year captures over 98% of CO<sub>2</sub> emissions from merchant hydrogen production facilities. For reference, the hydrogen production capacities corresponding to the CO<sub>2</sub> thresholds are listed (assuming steam methane reforming), based on the calculation methods discussed in Section 1a.

Table H7. Effect of Threshold on Reported Emissions from Merchant Hydrogen Production Facilities in the U.S.

| CO <sub>2</sub>   | $\mathbf{H}_{2}$   | Emissions Covered              |         | <b>Entities Covered</b> |         |
|---|--|--------------------------------|---------|-------------------------|---------|
| Threshold<br>Level<br>(Metric Tons<br>CO <sub>2</sub> e/year) | Production<br>Capacity<br>(Tons<br>H <sub>2</sub> /year) | Tons<br>CO <sub>2</sub> e/year | Percent | Number                  | Percent |
| 100,000   | 11,600   | 14,251,265                     | 93.6%   | 30                      | 39%     |
| 25,000  | 2,900  | 14,984,365                     | 98.4%   | 41                      | 53%     |
| 10,000  | 1,160  | 15,130,255                     | 99.4%   | 51                      | 66%     |
| 1,000   | 116  | 15,225,220                     | 100.0%  | 73                      | 95%     |
| No threshold  | 0  | 15,226,620                     | 100.0%  | 77                      | 100%    |

Capacity thresholds need to be provided.

## b. Emissions and Facilities Covered per Option

Table H8 lists the incremental emissions and facilities as the threshold decreases. For example, a threshold of 25,000 metric tons per year captures 4.8% more CO<sub>2</sub> emissions from merchant hydrogen production facilities than a threshold of 100,000 tons and includes 11 more facilities. As before, the hydrogen production capacities corresponding to the CO<sub>2</sub> thresholds are listed (assuming steam methane reforming), based on the calculation methods discussed in Section 1a.

Table H8. Effect of Threshold on Reported Emissions from Merchant Hydrogen Production Facilities in the U.S.

| CO <sub>2</sub>   | $\mathbf{H}_2$                                  | Emissions Covered              |         | Covered Entities Covered |         |
|---|---|--------------------------------|---------|--------------------------|---------|
| Threshold<br>Level<br>(Metric Tons<br>CO <sub>2</sub> e/year) | Production Capacity (Tons H <sub>2</sub> /year) | Tons<br>CO <sub>2</sub> e/year | Percent | Number                   | Percent |
| 100,000   | 11,600  | 14,251,265                     | 93.6%   | 30                       | 39%     |
| 25,000  | 2,900   | 733,100                        | 4.8%    | 11                       | 14%     |
| 10,000  | 1,160   | 145,890                        | 1.0%    | 10                       | 13%     |
| 1,000   | 116   | 94,965                         | 0.6%    | 22                       | 29%     |
| No threshold  | 0   | 1,400                          | 0.0%    | 4                        | 5%      |

## 3. Options for Monitoring Methods

#### a. Existing Relevant Reporting Programs/Methodologies

Monitoring methods required by the emissions reporting programs listed above were reviewed.

These methods all coalesced around variants of two methods: direct measurement of  $CO_2$  emissions by continuous emissions monitoring system (CEMS), and the fuel and feedstock mass balance method. The CEMS method follows 40CFR Part 60 or 40CFR Part 75 Appendix F. The CEMS method employs instrument packages which continuously monitor stack flow rates and concentrations of selected gas species and particulate matter. The data is transferred to a data acquisition system that interprets the data and produces emissions reports on demand. Such systems are commonly used to measure  $NO_x$  emissions.

#### b. Monitoring Methods Considered

# i) Option 1: Direct Measurement (Annual Reporting)

An unknown number of merchant hydrogen production facilities currently employ direct measurement of emissions by continuous emissions monitoring system (CEMS). CEMS equipment may have been installed for other purposes, such as measuring  $NO_x$  emissions, but rarely for  $CO_2$  emissions. At plants with existing CEMS equipment for measuring emissions other than  $CO_2$ , a CEMS retrofit (e.g., to measure  $CO_2$  concentration and stack flow rate) would

be required to allow the CEMS equipment to measure CO<sub>2</sub> emissions. For plants with no existing CEMS equipment, a complete set of CEMS components (e.g., CO<sub>2</sub> gas monitor, volumetric flow monitor, data loggers or programmable logic controllers (PLCs), data acquisition and handling system (DAHS), and power and signal cables in conduits) would need to be installed on every stack at the merchant hydrogen production facility. In most cases, process CO<sub>2</sub> emissions are emitted via the same stack as combustion emissions. Where process or combustion CO<sub>2</sub> emissions are emitted via secondary stacks or vents, additional CEMS components will be needed.

Elements of a CEMS include a platform and sample probe within the stack to withdraw a sample of the stack gas, an analyzer to measure the concentration of the GHG (e.g., CO<sub>2</sub>) in the stack gas, and a flow meter within the stack to measure the flow rate of the stack gas. The emissions are calculated from the concentration of GHGs in the stack gas and the flow rate of the stack gas. The CEMS continuously withdraws and analyzes a sample of the stack gas and continuously measures the GHG concentration and flow rate of the stack gas.

For direct measurement using stack testing, sampling equipment would be periodically brought to the site and installed temporarily in the stack to withdraw a sample of the stack gas and measure the flow rate of the stack gas. Similar to CEMS, for stack testing the emissions are calculated from the concentration of GHGs in the stack gas and the flow rate of the stack gas. The difference between stack testing and continuous monitoring is that the CEMS data provide a continuous measurement of the emissions while a stack test provides a periodic measurement of the emissions.

Owners and operators of facilities should assess whether CEMS or stack testing is the most economical method for direct measurement given the configuration of their facility operations.

#### ii) Option 2: Hybrid (Annual Reporting)

This hybrid method combines direct measurement by CEMS, where CEMS components are currently employed for other purposes, and the fuel and feedstock mass balance approach at facilities where CEMS not currently employed or at facilities where combustion or process CO<sub>2</sub> emissions are emitted via secondary stacks or vents.

The fuel and feedstock mass balance method entails measurements of the quantity and carbon content of all fuel and feedstock delivered to the facility and of all products leaving the facility, with the assumption that all the carbon entering the facility in both the fuel and feedstock is converted to  $CO_2$ . To handle cases where a fraction of the carbon dioxide is diverted, the mass balance methodology includes a term to account for the diverted carbon dioxide to another industry to avoid the possibility of double counting these emissions. It is expected that the other industry will account for the carbon dioxide released to the atmosphere from their facility or from their products (e.g., dry ice or carbonated beverages).

The calculation methodology for process related  $CO_2$  emissions in metric tons per year is expressed as (Source: New Mexico Green House Gas Mandatory Emissions Inventory (finalized  $1/3/08)^{26}$ ):

```
CO_2 = \sum_{}^{} ((FSR \times CF) - S) \times 3.664 \times metric \ ton/1000 \ kg
0
Where:
CO_2 = emissions \ of \ CO_2 \ (metric \ tons/yr)
FSR = \text{fuel and feedstock supply rate (kg/day)}
CF = \text{carbon fraction in feedstock (kg C/kg feed stock)}
S = \text{carbon fraction diverted and accounted for elsewhere (kg C/day)}
3.664 = 44.01/12.01 = \text{conversion factor (carbon to carbon dioxide)}
n = \text{days of operation}
```

The "S" term is included to avoid double counting of some CO<sub>2</sub> process emissions associated with hydrogen production. For example, the CO<sub>2</sub> may be diverted for such uses as fire extinguishers. This "S" term would be non-zero in situations where CO<sub>2</sub> is delivered off-site and where CO<sub>2</sub> emissions are accounted for using other methodologies in the regulations. Including the "S" term provides net emissions. For gross emissions, where CO<sub>2</sub> sent offsite is accounted for separately, this term is removed.

This calculation methodology is equally applicable to steam methane reforming, steam reforming of other gas and liquid hydrocarbons, partial oxidation of liquid hydrocarbons, and coal gasification. The feedstock supply rate in all cases is currently measured for financial accounting purposes (e.g., using a conventional gas meter).

The carbon fraction in the fuel/feedstock may be provided as part of an ultimate analysis performed by the supplier (e.g., the local gas utility in the case of natural gas feedstock). If the fuel/feedstock supplier does not provide the gas composition or ultimate analysis data, the facility would be required to perform an ultimate analysis of the fuel/feedstock on a regular basis. Any of various appropriate ASTM standard test methods would be applied, such as D1945 Standard Test Method for Analysis of Natural Gas by Gas Chromatography and D3176 Standard Practice for Ultimate Analysis of Coal and Coke<sup>27</sup>. Applicable test methods need to be determined.

Similarly, the carbon fraction diverted and sold to others is currently measured for financial accounting purposes in terms of flow rate and composition. That is, if the facility sells  $CO_2$  over the fence, then the quantity of  $CO_2$  sold will always be known as part of the sales transaction. Normally the carbon fraction diverted is 99+% pure carbon dioxide, implying 12.01 kg of carbon per 44.01 kg of  $CO_2$  sold, as measured by a  $CO_2$  flow meter.

http://www.astm.org/CDSTAGE/Petro/TOC.htm. West Conshohocken, PA.

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New Mexico (2008). Green House Gas Mandatory Emissions Inventory § 95114 (finalized 1/3/08). New Mexico Environment Department Air Quality Bureau. <a href="http://www.nmenv.state.nm.us/aqb/ghg/ghgrr\_index.html">http://www.nmenv.state.nm.us/aqb/ghg/ghgrr\_index.html</a>. Santa Fe, NM. 27 ASTM (2008). ASTM Standards Source (Online and CD-ROM): Petroleum Collection.

# iii) Option 3: Simplified Emissions Calculation (Annual Reporting)

For the simplified emissions calculation method, the process and combustion related GHG emissions are based on the hydrogen production and a constant facility-specific proportionality factor, following IPCC Tier 1 guidelines<sup>28</sup>. The proportionality factor is based on historical data for the plant's consumption of fuel and feedstock and the plant's hydrogen production, assuming that the carbon content of the natural gas or other fuel/feedstock remains constant over time. This method was used to calculate CO<sub>2</sub> emissions in Section 1.a and for the threshold analysis as described in Section 2.a. This method has increased uncertainty but a relatively low incremental cost for implementation.

This IPCC Tier 1 method uses hydrogen production to derive emissions as follows:

 $E_{CO2} = HP x FR x CCF x COF x 44.01/12.01 - R_{CO2}$ 

#### Where:

 $E_{CO2}$  = emissions of  $CO_2$  (metric tons/yr)

HP = hydrogen production (metric tons/yr)

FR = feedstock requirement per unit of output (tons of feedstock per ton of hydrogen)

CCF = carbon content factor of feedstock (weight fraction of carbon in feedstock)

COF = carbon oxidation factor of feedstock (fraction)

 $R_{CO2} = CO_2$  recovered for other uses (metric tons/yr)

Hydrogen production, emission factors, and  $CO_2$  recovered for other uses will be obtained from plant statistics. When a deduction is made for  $CO_2$  recovered for other uses, it is good practice to ensure that ultimate emissions are included elsewhere in the inventory. If data are not available, it is good practice to assume that  $CO_2$  recovered is zero.

## 4. Procedures for Estimating Missing Data

For the feedstock mass balance method, the likelihood of there being missing data for the option is small, since the natural gas meter and CO<sub>2</sub> meter data are needed for financial accounting purposes. If the local gas utility fails to provide the gas composition data, an interpolation of data from adjacent months should provide better than 1% accuracy for carbon content. Estimating CO<sub>2</sub> emissions from merchant hydrogen production data is a possibility, but only for backup purposes, since the ratio of CO<sub>2</sub> emissions to hydrogen production will vary somewhat from month to month. While valid under certain circumstances, this method would require significant modification and additional measurements to assure its applicability under operational scenarios commonly employed in merchant hydrogen production facilities.

#### **CEMS Data**

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<sup>&</sup>lt;sup>28</sup> IPCC (2006). 2006 IPCC Guidelines for National Greenhouse Gas Inventories. The National Greenhouse Gas Inventories Programme, The Intergovernmental Panel on Climate Change, H.S. Eggleston, L. Buenida, K. Miwa, T Ngara, and K. Tanabe (eds.). <a href="http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.html">http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.html</a>. Hayama, Kanagawa, Japan.

Procedures for management of missing data are established under Part 75 (Acid Rain Program.) These procedures would be applicable to direct measurement using CEMS for merchant hydrogen production, and are summarized in this section.

For options involving direct measurement of CO<sub>2</sub> flow rates or direct measurement of CO<sub>2</sub> emissions using CEMS, Part 75 establishes procedures for management of missing data. Procedures for management of missing data are described in Part 75.35(a), (b), and (d). In general, missing data from operation of the CEMS may be replaced with substitute data to determine the CO<sub>2</sub> flow rates or CO<sub>2</sub> emissions during the period in which CEMS data are missing.

Under Part 75.35(a), the owner or operator of a unit with a CO<sub>2</sub> continuous emission monitoring system for determining CO<sub>2</sub> mass emissions in accordance with Part 75.10 (or an O<sub>2</sub> monitor that is used to determine CO<sub>2</sub> concentration in accordance with appendix F to this part) shall substitute for missing CO<sub>2</sub> pollutant concentration data using the procedures of paragraphs (b) and (d) of this section. Subpart (b) covers operation of the system during the first 720 quality-assured operation hours for the CEMS. Subpart (d) covers operation of the system after the first 720 quality-assured operating hours are completed.

Under Part 75.35(b), during the first 720 quality assured monitor operating hours following initial certification at a particular unit or stack location (i.e., the date and time at which quality assured data begins to be recorded by a CEMS at that location), or (when implementing these procedures for a previously certified CO<sub>2</sub> monitoring system) during the 720 quality assured monitor operating hours preceding implementation of the standard missing data procedures in paragraph (d) of this section, the owner or operator shall provide substitute CO<sub>2</sub> pollutant concentration data or substitute CO<sub>2</sub> data for raw material input determination, as applicable, according to the procedures in Part 75.31(b).

Under Part 75.35(d), upon completion of 720 quality assured monitor operating hours using the initial missing data procedures of Part 75.31(b), the owner or operator shall provide substitute data for  $CO_2$  concentration or substitute  $CO_2$  data for raw material input determination, as applicable, in accordance with the procedures in Part 75.33(b) except that the term " $CO_2$  concentration" shall apply rather than " $SO_2$  concentration," the term " $CO_2$  pollutant concentration monitor" or " $CO_2$  diluent monitor" shall apply rather than " $SO_2$  pollutant concentration monitor," and the term "maximum potential  $CO_2$  concentration, as defined in section 2.1.3.1 of appendix A to this part" shall apply, rather than "maximum potential  $SO_2$  concentration."

## Stack Testing Data

For options involving direct measurement of CO<sub>2</sub> flow rates or direct measurement of CO<sub>2</sub> emissions using stack testing, "missing data" is not generally anticipated. Stack testing conducted for the purposes of compliance determination is subject to quality assurance guidelines and data quality objectives established by the U.S. EPA, including the Clean Air Act National Stack Testing Guidance published in 2005 (US EPA 2005). The 2005 EPA Guidance

Document indicates that stack tests should be conducted in accordance with a pre-approved site-specific test plan to ensure that a complete and representative test is conducted. Results of stack tests that do not meet pre-established quality assurance guidelines and data quality objectives would generally not be acceptable for use in emissions reporting, and any such stack test would need to be re-conducted to obtain acceptable data.

U.S. EPA regulations for performance testing under 40 CFR § 63.7(c)(2)(i) state that before conducting a required performance test, the owner/operator is required to develop a site-specific test plan and, if required, submit the test plan for approval. The test plan is required to include "a test program summary, the test schedule, data quality objectives, and both an internal and external quality assurance (QA) program" to be applied to the stack test. Data quality objectives are defined under 40 CFR § 63.7(c)(2)(i) as "the pre-test expectations of precision, accuracy, and completeness of data." Under 40 CFR § 63.7(c)(2)(ii), the internal QA program is required to include, "at a minimum, the activities planned by routine operators and analysts to provide an assessment of test data precision; an example of internal QA is the sampling and analysis of replicate samples." Under 40 CFR § 63.7(c)(2)(iii) the external QA program is required to include, "at a minimum, application of plans for a test method performance audit (PA) during the performance test." In addition, according to the 2005 Guidance Document, a site-specific test plan should generally include chain of custody documentation from sample collection through laboratory analysis including transport, and should recognize special sample transport, handling, and analysis instructions necessary for each set of field samples (US EPA 2005).

U.S. EPA anticipates that test plans for stack tests anticipated to be used to obtain data for the purposes of emissions reporting would be made available to EPA prior to the stack test and that the results of the stack test would be reviewed against the test plan prior to the data being deemed acceptable for the purposes of emissions reporting.

#### 5. QA/QC and Verification Requirements

#### Feedstock Mass Balance Method

For the feedstock mass balance method, QA/QC requirements are established for the utility gas meter and for the CO<sub>2</sub> meter. If the facility needs to install a dedicated gas meter for their hydrogen production operation, then they should follow the same QA/QC procedures as the local gas utility has in place. As for the measurement of the gas composition, the carbon content of natural gas is always within 1% of one mole of carbon per mole of natural gas. This is a more critical measurement for determining the heat content of the natural gas than it is for carbon content. Therefore, the local utility QA/QC requirements should be more than adequate. Similarly, the CO<sub>2</sub> concentration in the CO<sub>2</sub> stream delivered over the fence is normally 99+%, implying again that the quality control on the product exceeds the accuracy required for GHG emissions accounting.

#### Units using CEMS

For units using CEMS to measure CO<sub>2</sub> flow rates or CO<sub>2</sub> emissions, the equipment should be tested for accuracy and calibrated as necessary by a certified third party vendor. These

procedures should be consistent in stringency and data reporting and documentation adequacy with the QA/QC procedures for CEMS described in Part 75 of the Acid Rain Program.

## **Equipment Maintenance**

For units using flow meters to directly measure the flow rate of fuels, raw materials, products, or process byproducts, flow meters should be calibrated on a scheduled basis in accordance with equipment manufacturer specifications and standards. Flow meter calibration is generally conducted at least annually. A written record of procedures needed to maintain the flow meters in proper operating condition and a schedule for those procedures should be part of the QAQC plan for the capture or production unit. Measurement devices used to directly measure the emissions from equipment (e.g., hand-held devices used to measure fugitive emissions from valves and flanges) should also be calibrated on a scheduled basis.

An equipment maintenance plan should be developed as part of the QA/QC plan. Elements of a maintenance plan for equipment include the following:

- Conduct regular maintenance of equipment, e.g. flow meters.
  - o Keep a written record of procedures needed to maintain the monitoring system in proper operating condition and a schedule for those procedures;
  - o Keep a record of all testing, maintenance, or repair activities performed on any monitoring system or component in a location and format suitable for inspection. A maintenance log may be used for this purpose. The following records should be maintained: date, time, and description of any testing, adjustment, repair, replacement, or preventive maintenance action performed on any monitoring system and records of any corrective actions associated with a monitor's outage period. Additionally, any adjustment that recharacterizes a system's ability to record and report emissions data must be recorded (e.g., changing of flow monitor or moisture monitoring system polynomial coefficients, K factors or mathematical algorithms, changing of temperature and pressure coefficients and dilution ratio settings), and a written explanation of the procedures used to make the adjustment(s) shall be kept.<sup>29</sup>

#### Data Management

QA/QC Plans generally include data management procedures Elements of data management procedures that are appropriate and could be included in a plan are as follows:

- For measurements of carbon content, assess representativeness of the carbon content measurement by comparing values received from supplier and/or laboratory analysis with IPCC default values.
- Conduct third party (off-site) or on-site sampling and analysis of material carbon contents to verify information provided by suppliers.

<sup>&</sup>lt;sup>29</sup> Part 75, Appendix B1, Available at <a href="http://www.epa.gov/airmarkt/spm/rule/001000000B.htm">http://www.epa.gov/airmarkt/spm/rule/001000000B.htm</a>.

- Check for temporal consistency in production data, carbon content data, and emission estimate. If outliers exist, can they be explained by changes in the facility's operations, etc.?
  - o A monitoring error is probable if differences between annual data cannot be explained by:
    - **§** Changes in activity levels;
    - **§** Changes concerning fuels or input material; or
    - **§** Changes concerning the emitting process (e.g. energy efficiency improvements).<sup>30</sup>
- Determine the "reasonableness" of the emission estimate by comparing it to previous year's estimates and relative to national emission estimate for the industry:
  - o Comparison of data on fuel or input material consumed by specific sources with fuel or input material purchasing data and data on stock changes,
  - o Comparison of fuel or input material consumption data with fuel or input material purchasing data and data on stock changes,
  - Comparison of emission factors that have been calculated or obtained from the fuel or input material supplier, to national or international reference emission factors of comparable fuels or input materials
  - o Comparison of emission factors based on fuel analyses to national or international reference emission factors of comparable fuels, or input materials,
  - o Comparison of measured and calculated emissions.<sup>31</sup>
- Maintain data documentation, including comprehensive documentation of data received through personal communication:
  - o Check that changes in data or methodology are documented

#### Calculation checks

Calculation checks should be performed for all reported calculations. Elements of calculation checks include:

Perform calculation checks by reproducing a representative sample of emissions calculations or building in automated checks such as computational checks for calculations:

- Check whether emission units, parameters, and conversion factors are appropriately labeled
- Check if units are properly labeled and correctly carried through from beginning to end of calculations
- Check that conversion factors are correct

<sup>30</sup> Official Journal of the European Union, August 31, 2007. Commission Decision of 18 July 2007, "Establishing guidelines for the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council. Available at <a href="http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:229:0001:0085:EN:PDF">http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:229:0001:0085:EN:PDF</a>.

<sup>&</sup>lt;sup>31</sup> Official Journal of the European Union, August 31, 2007. Commission Decision of 18 July 2007, "Establishing guidelines for the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council. Available at <a href="http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:229:0001:0085:EN:PDF">http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2007:229:0001:0085:EN:PDF</a>.

- Check the data processing steps (e.g., equations) in the spreadsheets
- Check that spreadsheet input data and calculated data are clearly differentiated
- Check a representative sample of calculations, by hand or electronically
- Check some calculations with abbreviated calculations (i.e., back of the envelope checks)
- Check the aggregation of data across source categories, business units, etc.
- When methods or data have changed, check consistency of time series inputs and calculations.<sup>32</sup>

As part of the data verification requirements, the owner or operator would submit a detailed explanation of how company records of measurements are used to quantify all sources of carbon input and output within 7 days of receipt of a written request from EPA or from the applicable State or local air pollution control agency (the use of electronic mail is acceptable).

#### **Data Verification**

As part of the data verification requirements, the owner or operator would submit a detailed explanation of how company records of measurements are used to quantify all sources of carbon input and output within 7 days of receipt of a written request from EPA or from the applicable State or local air pollution control agency (the use of electronic mail is acceptable)

## 6. Data to Be Reported

## a. Description for each method

#### i) Option 1: Direct Measurement

For options for which the monitoring method is based on direct measurement, either using a CEMS or through stack testing, the GHG emissions are directly measured at the point of emission.

#### a) Continuous Emission Monitoring System (CEMS)

For direct measurement using CEMS, the facility should report the GHG emissions measured by the CEMS for each monitored emission point and should also report the monitored GHG concentrations in the stack gas and the monitored stack gas flow rate for each monitored emission point. These data would illustrate how the monitoring data were used to estimate the GHG emissions.

The facility should report the following data for direct measurement of emissions using CEMS:

- The unit ID number (if applicable);
- A code representing the type of unit;

<sup>32</sup> U.S. EPA 2007. Climate Leaders, Inventory Guidance, Design Principles Guidance, Chapter 7 "Managing Inventory Quality". Available at <a href="http://www.epa.gov/climateleaders/documents/resources/design\_princ\_ch7.pdf">http://www.epa.gov/climateleaders/documents/resources/design\_princ\_ch7.pdf</a>.

- Maximum product production rate and maximum raw material input rate (in units of metric tons per hour);
- Each type of raw material used and each type of product produced in the unit during the report year;
- The calculated CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions for each type of raw material used and product produced, expressed in metric tons of each gas and in metric tons of CO<sub>2</sub>e;
- A code representing the method used to calculate the CO<sub>2</sub> emissions for each type of raw material used (e.g., part 75, Tier 1, Tier 2, etc.);
- If applicable, a code indicating which one of the monitoring and reporting methodologies in part 75 of this chapter was used to quantify the CO<sub>2</sub> emissions;
- The calculated CO<sub>2</sub> emissions from sorbent (if any), expressed in metric tons; and
- The total GHG emissions from the unit for the reporting year, i.e., the sum of the CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O emissions across all raw material and product types, expressed in metric tons of CO<sub>2</sub>e.

## b) Stack Testing

For direct measurement using stack testing, the facility should report the GHG emissions measured during the stack test, the measured GHG concentrations in the stack gas, the monitored stack gas flow rate fore each monitored emission point, and the time period during which the stack test was conducted. The facility should also report the process operating conditions (e.g., raw material feed rates) during the time period during which the test was conducted.

#### ii) Option 2: Hybrid

If CEMS data are taken, they will be reported as described above.

If the feedstock mass balance method is used, annual  $CO_2$  emissions will be reported, along with annual merchant hydrogen production, feedstock type, amount of feedstock used, carbon fraction in the feedstock, number of plant operating days during the year, amount of carbon-containing product (e.g., liquid  $CO_2$ ) diverted, and amount of carbon diverted. If the feedstock mass balance method is used, the  $CO_2$  data will be reported annually even if the feedstock metering data and feedstock composition data are recorded more frequently.

## iii) Option 3: Simplified Equation

If the simplified equation is used, annual CO<sub>2</sub> emissions will be reported, along with annual merchant hydrogen production, feedstock type, feedstock requirement per unit of hydrogen output, weight fraction of carbon in the feedstock, carbon oxidation factor, and amount of CO<sub>2</sub> diverted.

#### b. Description of additional recordkeeping

Additional data to be retained onsite (recordkeeping) will include monitoring plan for the facility, emissions data, emission factors, documentation of calculations, laboratory results, QA/QC plan, monthly fuel consumptions, specific gravity of feedstock, and purity of CO<sub>2</sub> diverted.

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