CALIFORNIA
AIR RESOURCES BOARD

Verifier Accreditation Training for Mandatory GHG Reporting

Oil and Gas Systems Specialty – Course 3.3

Hydrogen Production

Verifier Accreditation Training for Mandatory Greenhouse Gas Reporting

Course 3: Oil and Gas Systems Specialty

- 3.1 Upstream Extraction and Processing - Petroleum and Natural Gas (PNG) Systems
- 3.2 Petroleum Refineries
- **3.3 Hydrogen Production**

Course 3.3 Hydrogen Production

1. **Overview**
   - **Hydrogen production**
   - **Emissions data**
   - **MRR relation to EPA Subpart P**
   - **Calculating emissions**
   - **Verifying emissions**
2. Monitoring Requirements
3. Covered Product Data
4. Nonconformances and Verification Tips

Section 95114 Hydrogen Production

- Reporting guidance for hydrogen producers is available at: https://www.arb.ca.gov/cc/reporting/ghg-rep/guidance/hydrogen-producers.pdf
- Source definition
  - Operators that produce hydrogen gas sold as a product to other entities
  - Includes hydrogen facilities located within another facility if they are under separate ownership (Merchant Hydrogen Facilities)
  - Refineries that have a hydrogen production unit (integrated hydrogen plant) report emissions under Subpart P / §95114
- Processes include - reforming, gasification, oxidation, reaction, or other transforming of carbon feedstocks
- Covered product data
  - Mass of “on-purpose” hydrogen gas produced (MT)
  - Liquid hydrogen sold (MT)

Hydrogen Production

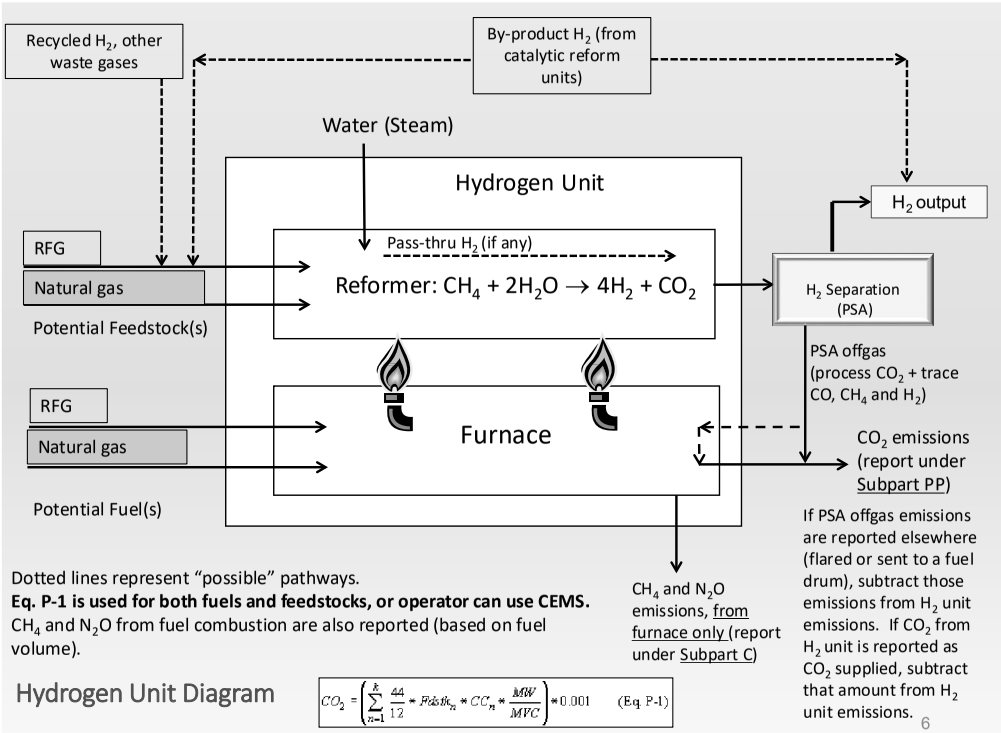
- Steam Methane Reforming (SMR)
  - Hydrogen is usually produced by the steam reforming of methane (CH_4) or natural gas. In the first stage, steam reacts with methane at 700-1100 °C to yield syngas

    $CH_4 + H_2O$ (+heat) $\longrightarrow CO + 3H_2$

    In the second stage, additional hydrogen is generated by the water-gas shift reaction performed at about 130 °C

    $CO + H_2O \longrightarrow CO_2 + H_2$ (+ small amount of heat)
- Partial Oxidation
  - Partial oxidation creates syngas by partially combusting a fuel-rich hydrocarbon mixture in a reformer

    $CH_4 + \frac{1}{2} O_2 \longrightarrow CO + 2\ H_2$ (+ heat)



Hydrogen Unit Diagram

Pressure-Swing Adsorption (PSA) (1 of 2)

- In a final process step called "Pressure-Swing Adsorption" unreacted CO, CO_2 and other impurities such as unreacted CH_4 are removed from the gas stream, leaving essentially pure hydrogen. The resulting H_2 stream can achieve purities of 99.999%.
- The PSA unit utilizes a timed cycle of steps of adsorption, pressure equalization, depressurization, blowdown, purge, and repressurization across multiple beds loaded with various types of adsorbent (activated alumina, silica gel, activated carbon, mol sieves).

Pressure-Swing Adsorption (PSA) (2 of 2)

- When a PSA bed is on-line, the syngas flows upward through the bed where at normal operating pressure components are physically adsorbed while the preferred hydrogen flows through the unit.
- The bed is taken out of service and goes through a series of depressurizations where the adsorbed components are released. The released components are an off gas that is then typically used as a fuel in SMR units. The bed is then repressurized and returned to service.
- The CO_2 is often captured and transferred off site (sold). The CO_2 is reported under (Subpart PP)

Emissions Data for Hydrogen Production

- Under §95112: Electricity generation/cogeneration, report any electricity generation emissions
- Under §95114: Hydrogen production, report process and combustion CO_2 emissions from each hydrogen production unit
- Under §95115: Stationary fuel combustion, report SFC source emissions other than the H_2 furnace
- Under §95123: Suppliers of CO_2, report any commercial CO_2 production emissions, either under the same facility ID number or under a separate facility ID number

Section 95114 Requirements

- Section 95114 incorporates a majority of the requirements of Subpart P
- Section 95114 also requires
  - More frequent (daily) sampling of carbon content and molecular weight for non-standard fuels and feedstocks, including refinery fuel gas (monthly sampling is acceptable for standardized fuels, including natural gas)
  - Weighted averaging of fuel and feedstock contents when calculating emissions, as opposed to arithmetic averaging, if samples are collected more often than monthly
  - Reporting of CH_4 and N_2O emissions from fuel combustion in the hydrogen unit
  - Merchant hydrogen facilities to also report flare emissions under the flaring section of Subpart P in Cal e-GGRT
  - Reporting of covered product data (discussed later)

Reporting Feedstock Composition

Section 95114(e)(1) - Reporting Feedstock Composition

- All facilities must measure and report carbon, atomic hydrogen and molecular hydrogen content of feedstocks
  - Monthly carbon content (daily for RFG)
  - Monthly atomic H content
  - Monthly molecular H_2 content
- Verify correct reporting of data from gas constituent analysis of gaseous feedstocks (excluding steam)
  - Monthly atomic C and H content mass percent total (e.g., 0.24%)
    - Include H contribution from methane, other hydrocarbons, and H_2, but not steam
  - Monthly molecular H_2 content mass percent (e.g., 0.03%)
    - For pipeline natural gas supplied by a utility, OK to assume zero
- Verify atomic C and H content of liquid feedstocks
- Verify atomic C and H content of solid feedstocks

Calculating CO_2 Emissions from Hydrogen Production using CEMS

- CO_2 emissions can be calculated using a qualifying CEMS or via material balance
- For a qualifying CEMS, follow Tier 4 Method
- Refer to general verification training course covering fuel combustion and CEMS
- If combustion and process emissions are combined in the CEMS measurement, facilities must also report CH_4 and N_2O combustion emissions and the carbon and hydrogen content of the feedstock

Calculating CO_2 Emissions from Hydrogen Production using Material Balance (1 of 2)

- For each hydrogen unit, calculate the annual CO_2 emissions from the fuel and feedstock using Eq. P-1, P-2, or P-3 depending on whether the fuel or feedstock is gaseous, liquid, or solid

$$CO_2 = (\sum_{n=1}^{k} \frac{44}{12} * Fdstk_n * CC_n * \frac{MW}{MVC}) * 0.001 \quad \text{(Eq. P-1)}$$

  - Hydrogen production facilities in California historically only use gaseous feedstocks, and report using CEMS (Tier 4) or Eq. P-1

Calculating CO_2 Emissions from Hydrogen Production using Material Balance (2 of 2)

- The equations use **weighted** averages for carbon content and gaseous molecular weight if measured more often than monthly.
- Measurement of carbon content and gaseous molecular weight is required:
  - Monthly for standardized fuels (e.g., natural gas)
  - Daily for non-standardized gas and liquid fuels, and all solid fuels
- Any carbon exiting the hydrogen unit and reported elsewhere (i.e. waste gas diverted to a fuel gas system or flare) must be reported in the "S" factor for the hydrogen unit, which adjusts emissions to avoid double counting
  - Total emissions must be correct, but emissions disaggregated by subpart are required only to be "reasonable"

Avoiding double counting – using the S Factor

- If the facility captures CO_2 from the hydrogen unit and correctly reports off-site CO_2 transfers as a CO_2 supplier under §95123, then reporters must subtract the mass of CO_2 transferred off-site from the H_2 unit emissions using the "S" Factor
- Reporters must also calculate and subtract from their facility emissions, using the "S" factor, any CH_4 and CO_2 emissions reported under other sections of the regulation (e.g., §95113, §95115, or *de minimis*)

Verifying CO_2 Emissions from Hydrogen Production (1 of 2)

Evidence to request

- Fuel and feedstock consumption records
- Carbon content records for fuels
- Carbon, atomic hydrogen, and molecular hydrogen content records for feedstocks
- Molecular weight records for gaseous fuels and feedstocks
- All inputs to Cal e-GGRT
- All off-line calculations
- Meter and instrument records, as applicable
- GHG Monitoring Plan

Verifying CO_2 Emissions from Hydrogen Production (2 of 2)

How to evaluate the evidence

- Verify that no data are missing; if data are missing verify that missing data provisions were applied correctly
- Verify that the data were collected at the appropriate frequency for the fuel type
- Verify that all data were entered correctly into Cal e-GGRT
- Verify that compatible units of measure were used for all variables
- Verify that gaseous fuel volumes were based on 68 °F and 1 atm
- Verify that any off-line calculations were accurate and appropriate (weighted average CC and MW)

Case Study #9 - Hydrogen Plant Weighted Average Carbon Content and Emissions (1 of 2)

Use O&G Case Studies Handout

- Using the fuel data in the table, calculate the weighted average carbon content
- Calculate the correct CO_2 emissions using Eq. P-1, and determine the percent error
- Does this error represent a material misstatement?
- Note that one measurement is missing
  - Has the facility used the appropriate missing data provisions?

Case Study #9 - Hydrogen Plant Weighted Average Carbon Content and Emissions (2 of 2)

Case Study: Weighted Average and Emissions Calculation

A hydrogen plant was offline for the start of the year, and begins operations January 16. For the month of January, the operator uses Equation P-1 to calculate CO2 process emissions, but incorrectly uses the arithmetic average of 0.659 for the measured carbon content of the refinery fuel gas feedstock. The weighted average molecular weight for the RFG is 26.18 kg/kg-mol and the volume of RFG for the month is 45,000,000 scf. The plant reports 3,353 MT of CO2 emissions for the month of January.

- Using the data in the table below, calculate the weighted average for carbon content.
- Calculate the correct CO2 emissions using Equation P-1, and determine the % error.
- Does this represent a material misstatement?
- Note that one measurement for carbon content is missing. Has the facility used the appropriate missing data provisions?

Date in January	RFG Carbon Content (kg C/kg gas)	MW (kg ga/kg-mol gas)	RFG Mass (kg) (= scf x MW/849.5)	Carbon Mass (= CC x Kg RFG)	RFG Volume (scf)
15-Jan	Plant offline, no emissions				
16	0.75	27	95,350	71,513	3,000,000
17	0.65	26	61,212	39,788	2,000,000
18	0.6	25	58,858	35,315	2,000,000
19	0.6	25	58,858	35,315	2,000,000
20	0.65 missing data substituted using best available estimate	26	91,819	59,682	3,000,000
21	0.7	27	127,134	88,994	4,000,000
22	0.75	27	95,350	71,513	3,000,000
23	0.65	26	61,212	39,788	2,000,000
24	0.6	25	58,858	35,315	2,000,000
25	0.65	26	91,819	59,682	3,000,000
26	0.7	27	127,134	88,994	4,000,000
27	0.75	27	127,134	95,350	4,000,000
28	0.65	26	91,819	59,682	3,000,000
29	0.6	25	58,858	35,315	2,000,000
30	0.65	26	91,819	59,682	3,000,000
31	0.6	25	88,287	52,972	3,000,000
	Arithemtic ave. = 0.659	Weighted ave. = 26.18	Total = 1,385,521	Total = 928,899	Total = 45,000,000

Case Study #9 - Solution

- Weighted average CC

  928,899/1,385,521 = 0.670 (§95114(f)(2))
- Emissions calculation

  Incorrect $= \frac{44}{12}$ x 45,000,000 scf x 0.659 x $\frac{26.18}{849.5}$ x 0.001 = 3,351 MT CO_2

  Correct $= \frac{44}{12}$ x 45,000,000 scf x 0.670 x $\frac{26.18}{849.5}$ x 0.001 = 3,407 MT CO_2

  Error = (3,351-3,407)/3,351 x 100 = -1.67% error

  No material misstatement (but a correctable error)
- Missing emissions data

  % Missing Data= $\frac{One\ missing\ day}{16\ Total\ days}$ x 100 = 6.25% missing data

  Best available estimate is allowed for data substitution
  - For example, estimate using the mean of the measurements taken immediately before and after missing measurement

Course 3.3: Hydrogen Production

1. Overview
2. **Monitoring Requirements**
   - **Monitoring and QA/QC requirements**
   - **Verifying measurement data**
   - **Missing emissions data procedures**
3. Covered Product Data
4. Nonconformances and Verification Tips

Monitoring and QA/QC Requirements under §95114

- CEMS must comply with QA/QC requirements specified in 40 CFR §98.34(c) (refer to Course 1)
- Calibrate gas flow meters according to Tier 3 methodologies in 40 CFR §98.34(b)(1)
- Measure carbon content and molecular weights by either:
  - Approved methods for measuring carbon content and molecular weight in 40 CFR §98.164(b)(5)(i)-(xviii)
  - A continuous gas chromatograph operated, maintained, and calibrated according to the manufacturer's instructions

Verifying Measurement Data from Hydrogen Units under §95114

- Evidence to request
  - Calibration records for all flow meters and other instruments
  - Manufacturer calibration requirements
  - Primary element inspection (orifice plate)
- How to evaluate evidence
  - Verify that acceptable monitors and instruments were used for each measurement
  - Verify that calibrations were performed according to manufacturer specifications with respect to frequency, tolerances, etc.
  - Verify that reporter adhered to their GHG monitoring plan

Missing Data Procedures for Emissions Data Reported under §95114(h)

- If using CEMS, follow the procedures of §95115 and §95129(b)
- Units not using CEMS to report emissions
  - If the data capture rate is ≥ 90%, substitute the best available estimate of the parameter based on all available process data
  - If the data capture rate is ≥ 80% but < 90%, substitute the highest quality-assured value recorded for the parameter during the given year and the two previous data years
  - If the data capture rate is < 80%, substitute the highest quality-assured value recorded for the parameter in all records kept according to §95105(a)

Questions

1. Overview
2. Monitoring Requirements
3. **Covered Product Data**
4. **Nonconformances and Verification Tips**

Verifying Covered Product Data Reported under §95114 (1 of 3)

- Covered product data reporting requirements
  - Annual metric tons of on-purpose hydrogen gas produced
    - On-purpose H2 is produced by a process dedicated to producing hydrogen (e.g., steam methane reforming)
    - Includes mass of H2 output from the unit excluding impurities
    - Must also report by-product H2 produced (not covered product data)
      - By-product H2 is any captured H2 not produced by a dedicated unit
  - Guidance is available at: https://ww2.arb.ca.gov/mrr-

OTHER FACILITY REPORTING INFO

Annual mass of on-purpose hydrogen gas produced (metric tons)	Annual mass of by-product hydrogen gas produced (metric tons)	Annual mass of liquid hydrogen sold (metric tons)	Annual mass of all CO_2 captured, transferred off-site, and reported by the hydrogen production facility as a supplier of CO_2 (metric tons)
10,000	175	0	0

Verifying Covered Product Data Reported under §95114 (2 of 3)

- How do I verify on-purpose H2 gas produced and liquid H2 sold?
  - Request invoice or meter records of gaseous hydrogen production, sales records for liquid hydrogen
  - Verify the calculations and underlying measurement records (volume to mass conversion @STP)
  - Request copies of the data entered into Cal e-GGRT
  - Compare the accounting records to the submitted data
  - Verify that on-purpose gas produced, by-product gas produced, and liquid sold are reported with no double-counting

Verifying Covered Product Data Reported under §95114 (3 of 3)

- All on-purpose hydrogen is covered product data
- If a portion of that hydrogen is sold or transferred to a petroleum refinery or hydrogen fueling station, the facility operator must separately report the quantity of hydrogen sold to each purchaser
  - The customer information is additional information for CARB review, and is not the basis for determining C&T allocation

Verification Tips

Example Operator Nonconformances Identified by Verifiers

- CH_4 and N_2O emissions from furnace not reported
- Flare emissions not reported
- Hydrogen unit Subpart P emissions double-counted in Subpart C
- Temperature correction for product data performed incorrectly
- Volume to mass conversion of hydrogen produced not well-documented
- Elemental H content of feedstocks not reported

Verification Tips

- Verify the calculations and underlying measurement records; ensure operator used correct temperature conversion factors for emissions and product data
- Ensure all unit level and Subpart P summary product data are accurate and consistent
- Ensure all H content, by-product H_2, and product data are reasonable and accurate

Course 3: Oil and Gas Systems Specialty

Complete

3.1 Upstream Extraction and Processing - Petroleum and Natural Gas (PNG) Systems

3.2 Petroleum Refineries

3.3 Hydrogen Production