CALIFORNIA
AIR RESOURCES BOARD

Verifier Accreditation Training for Mandatory GHG Reporting

Oil and Gas Systems Specialty – Course 3.2

Petroleum Refineries

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 3.2 Petroleum Refineries

1. **Overview**
   - **Refineries**
   - **Beginning verification**
2. Emissions Data Reported by Refineries
3. Monitoring Requirements
4. Product Data
5. Nonconformances and Verification Tips

Oil and Gas Systems Specialist

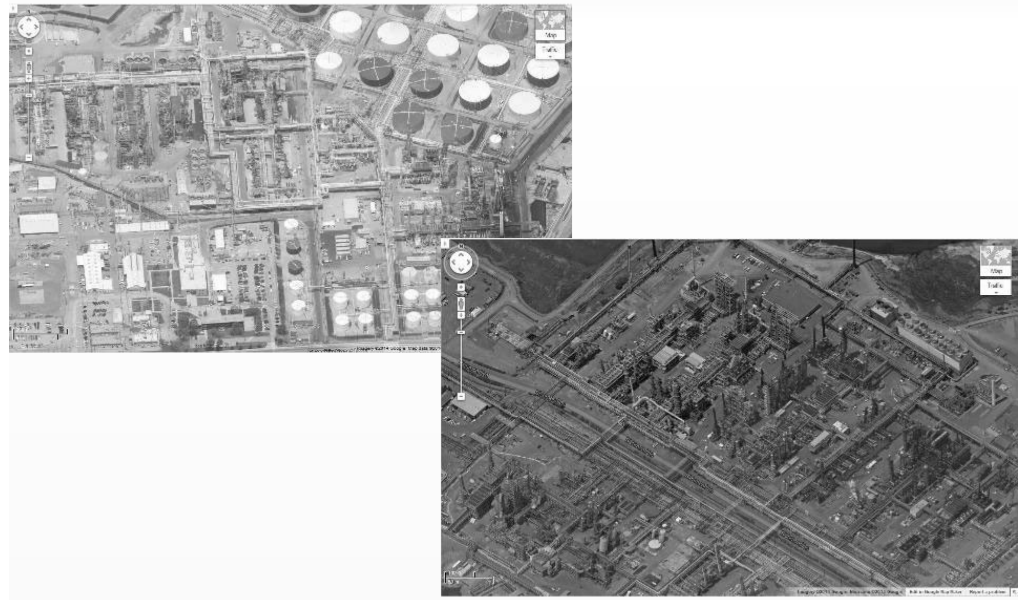
Provides verification services to operators of

- §95113 - Petroleum refineries
- §95114 - Hydrogen production units or facilities
- §95150 - 95158 Petroleum and natural gas systems listed in §95101(e)
  - Includes onshore production of crude oil and natural gas, natural gas processing facilities, natural gas distribution facilities, and others.

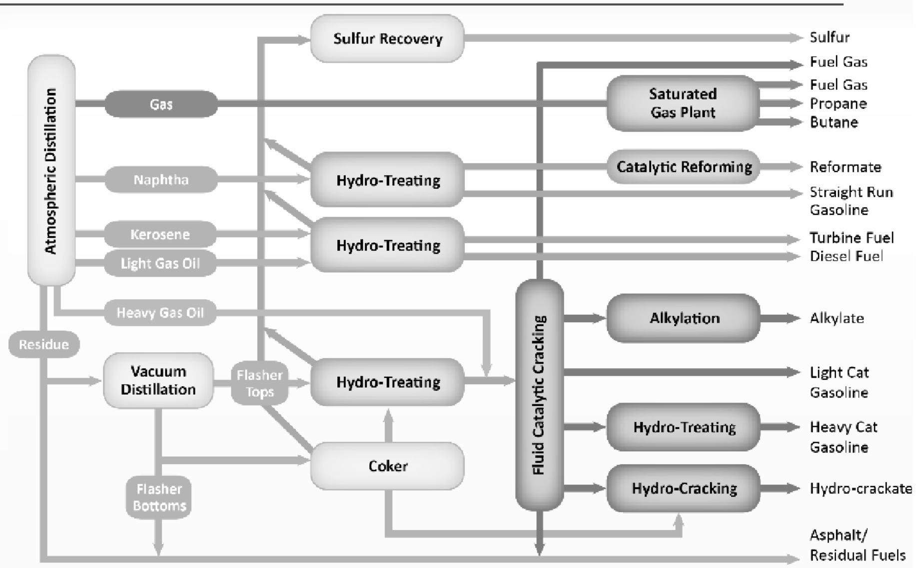
§95113 Petroleum Refineries
(Defined in §95102(a))

- Any facility that uses petroleum to produce
  - Gasoline
  - Gasoline blending stocks
  - Naphtha
  - Kerosene
  - Distillate fuel oils
  - Residual fuel oils
  - Lubricants
  - Asphalt (bitumen) by distillation of petroleum or re-distillation, cracking, or reforming of unfinished petroleum derivatives
- Not included: facilities that distill only pipeline transmix (off-spec material created when different specification products mix during pipeline transportation)

Refineries! Pretty Simple?



Refinery Schematic



Emissions Data Reported by Refineries

CO_2, CH_4 and N_2O emissions from the following sources:

- Fuel gas combustion
- Natural gas combustion
- Flares
- Fluid catalytic cracking (FCC) and fluid coking
- Coking
- Catalytic reforming
- Sulfur recovery
- Coke calcining*
- Asphalt blowing
- Delayed coking
- Process vents
- Uncontrolled blowdown
- Equipment leaks
- Storage tanks
- Product loading
- H_2 production

*Not included in definition of petroleum refinery, but included in Subpart Y, referenced in §95113

Refinery Sources Reported Under Other Parts of the MRR

- Electricity Generation and Cogeneration §95112
- Hydrogen Production §95114
- Stationary Combustion §95115
- Fuel Suppliers §95121 (for LPG only; other fuels are reported in separate emissions data report)
- Suppliers of Carbon Dioxide §95123 (combined with refinery report or with fuel supplier report)

Source Contributions to Refinery Emissions

Source	Contribution to Total Emissions (%) [a]
SFC (refinery gas/still gas)[b]	30 – 75
SFC (natural gas, if used)[b]	0 – 25
FCC and cokers	10 – 35
Hydrogen plant (combustion and process)	0 – 20
Sulfur recovery unit	0 – 5
Catalyst regeneration (other than FCC)	0 – 5
Flares and thermal oxidizers	0 – 2
Pilots	0 – 1
Misc. sources combined [c]	0 – 1

[a] Relative contribution for California refineries
[b] SFC is stationary fuel combustion, primarily boilers and heaters
[c] Miscellaneous sources include chemical plant, gasoline and diesel powered equipment, misc. vents, blowdowns, and fugitive emissions from storage tanks and leaks

Preparation for Site Visit

- Verifiers should review GHG Monitoring Plan and conduct data checks before site visit
- Issues log must be very detailed with audit trail for complicated issues
- Systems analysis is appropriate
  - Consider reviewing data recorded on the day of the site visit as a test of the data acquisition system
- Identify risks of data handling early in the verification to inform sampling plan and data checks
- Clearly communicate which staff that oversee metering and lab analysis must be present for site visit

Evidence to Review in GHG Monitoring Plan (1 of 2)

- Refinery schematic and a list of all emissions sources and process units at the facility, with explanations as necessary
- Flow diagram(s) for fuel gas movement with fuel meters, sampling locations and process units identified on the diagram
- All off-line calculations used to pre-process inputs to Cal e-GGRT

Evidence to Review in GHG Monitoring Plan
(2 of 2)

- Printout of all Cal e-GGRT inputs
- Missing data procedures and records used by the reporter
- Meter calibration documentation, as applicable
- Copies of Title V permits, if applicable
- Aerial photograph with references

Characteristics of Good GHG Emissions Data

- All data are well-documented
  - Especially standard temperature and pressure adjustments (STP)
- Emissions were calculated for all applicable sources in sections 95113, 95114, 95115, and 95123
- The correct Cal e-GGRT functions were used for each source
- Pre-processing of input data for Cal e-GGRT was accurate
- Cal e-GGRT inputs were entered accurately (including correct units of measure)
- Appropriate procedures were followed for missing data and for reporting volumes at STP

Procedures for Substituting Missing Emissions Data (§95113(k))

- Capture rate ≥ 90% - substitute the best available estimate of the parameter using available process data
- Capture rate ≥ 80% and <90% - substitute highest value recorded during the year and two previous years
- Capture rate <80% - substitute highest value recorded in all records kept according to §95105(a)
- Stationary combustion units and CEMS follow §95129

Case Study #4 - Meter and Instrumentation Data Analysis

- The GHG Monitoring Plan and refinery fuel gas flow data files were provided in advance of the site visit
- Using the example fuel flow data table below, what questions would you ask about the data and what additional evidence would you request?
- Consider the following issues:
  - Data completeness
  - Data inconsistencies
  - Invalid or suspect data
  - Process offline or instrumentation failure
  - Calibration adjustments

Case Study #4 -Data Set

Refinery ABC			STP= 68F			
Meter Tag #	ARB 2013 FCCU					
Units	mmscft					
	January	February	March	April	May	June
1	0.24	0.03	113.75	97.85	23.65	43.85
2	0.24	23.60	113.66	93.80	23.60	42.41
3	0.23	23.38	113.80	91.59	23.38	42.15
4	0.23	23.92	113.76	93.35	23.92	43.51
5	0.23	22.55	13.73	102.93	22.55	43.47
6	0.23	18.85	13.76	93.73	18.85	38.96
7	0.22	16.03	13.74	95.61	16.03	33.49
8	0.23	11.76	13.69	96.96	11.76	27.35
9	0.22	9.70	13.78	104.85	9.70	22.17
10	0.22	0.03	13.73	109.00	10.79	25.34
11	0.22	0.03	13.76	114.00	15.55	33.55
12	0.11	0.03	13.64	112.00	19.73	39.94
13	0.00	0.02	13.51	110.00	22.65	44.45
14		0.02	13.69	114.00	24.25	45.83
15		0.02	13.62	114.00	22.80	
16		0.02	13.62	114.00	19.38	
17		0.02	13.65	114.00	0.02	31.16
18		0.02	13.71	111.25	0.02	
19		0.02	13.75	111.11	0.02	
20		0.02	13.76	106.74	0.02	30.32
21		0.02	13.74	104.76	0.02	26.28
22	55.20	0.02	-13.71	107.71	0.02	27.11
23	107.67	107.67	0.00	107.67	0.02	28.56
24	109.89	109.89	-13.52	109.89	13.31	27.78
25	111.59	111.59	-13.33	111.59	13.55	27.89
26	110.07	110.07	-1.99	110.07	13.84	29.33
27	112.59	112.59	-0.30	112.59	13.18	28.10
28	110.81	110.81	-0.30	110.81	13.59	28.52
29	113.30	113.30	-0.46	113.30	14.63	29.35
30	107.73	107.73	133.50	107.73	14.00	28.37
31	109.52	109.52	133.50	109.52	14.56	29.58
TOTAL	**1051.00**	**1143.25**	**911.22**	**3306.42**	**419.37**	**898.85**

Case Study #4 - Solution

H OVERALL DATA SET

Refinery ABC STP= 68F
Meter Tag # ARB 2013
Units: mmscft

DAY OR MEASUREMENT	MONTH					
	January	February	March	April	May G	June
1	0.24	0.03	113.75	97.85	23.65	43.85
2	0.24	23.60	113.66	93.80	23.60	42.41
3	0.23	23.38	113.80	91.59	23.38	42.15
4	0.23	23.92	113.76 E	93.35	23.92	43.51
5	0.23	22.55	13.73	102.93	22.55	43.47
6	0.23	18.85	13.76	93.73	18.85	38.96
7	0.22	16.03	13.74	95.61	16.03	33.49
8	0.23	11.76	13.69	96.96	11.76	27.35
9	0.22	9.70	13.78	104.85	9.70	22.17
10	0.22	0.03	13.73	109.00	10.79	25.34
11	0.22	0.03	13.76	114.00	15.55	33.55
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13	0.00	0.02	13.51	110.00	22.65	44.45
14	A	0.02	13.69	114.00	24.25	45.83
15		0.02	13.62	114.00	22.80	
16		0.02	13.62	114.00	19.38	
17		0.02	13.65	114.00	0.02	31.16 A
18		0.02	13.71	111.25	0.02	
19		0.02	13.75	111.11	0.02	
20		0.02	13.76	106.74	0.02	30.32
21		0.02	13.74	104.76	0.02	26.28
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TOTAL	1051.00	1143.25	911.22	3306.42	419.37	898.85

B

- A MISSING DATA
- B DATA ON NON-EXISTENT DAYS
- C EXACT DATA MATCH
- D NEGATIVE DATA
- E RECALIBRATION?
- ROUNDED OFF DATA - MAYBE HAND ENTERED?
- G DRAMATIC DROP OFF OR CHANGE STARTING MONTH
- H DOES UNIT HAVE RANGE TO OPERATE? (E.G. 13-15 --> 115?)
- I METER MALFUNCTION

Course 3.2: Refineries

- Overview
- Emissions Data Reported by Refineries
  - **Fuel gas combustion**
  - **Natural gas combustion**
  - **Flares**
  - Fluid catalytic cracking (FCC) and fluid coking
  - Coking
  - Catalytic reforming
  - Sulfur recovery
  - Coke calcining
  - Asphalt blowing
  - Delayed coking
  - Process vents
  - Uncontrolled blowdown
  - Equipment leaks
  - Storage tanks
  - Product loading
  - H_2 production

Calculation Methods for Fuel Gas Combustion Emissions

- CO_2 emissions - 40 CFR §98.33 combustion Tier 3 (CC) and Tier 4 (CEMS) methodology
- CH_4 and N_2O emissions - 40 CFR §98.33 combustion methodology for same Tier as CO_2 (EF from Table C-2, 40 CFR Subpart C, "Petroleum")
  - Eq. C-8, C-8a, or C-8b for Tier 3
  - Eq. C-10 for Tier 4

Fuel Gas Monitoring Requirements

- Fuel gas systems at refineries are major emissions sources and can be very complex
- Verifiers should gain a clear understanding of fuel movement from sources to combustion units, flow meter locations, sampling locations, and aggregated emission sources
- Reporters must properly adjust to STP
- Daily sampling and analysis of carbon content and molecular weight is required for Tier 3 (the most common calculation method for RFG)

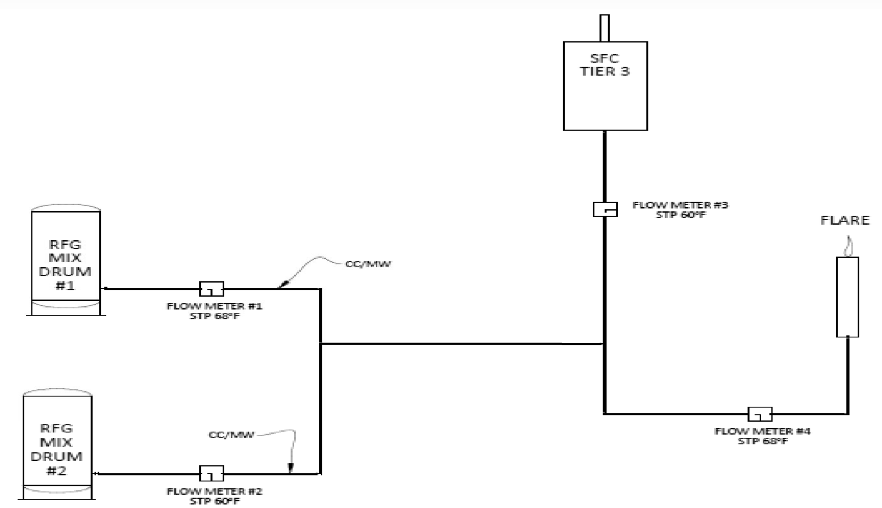
Calculation Methods for Flare Emissions

- For CO_2 emissions
  - If gas composition is measured, 40 CFR §98.253 Eq. Y-1a or Eq. Y-1b
  - If gas heating value is measured, 40 CFR §98.253 Eq. Y-2
  - For flare startups, shutdowns and malfunctions (SSM), use above equations, or use Eq. in §95113(d) if the composition or heating value of flare gas is not measured at least weekly
  - For flare emissions, §95113(d) excludes use of Eq. Y-3 and provides an alternative equation for SSM
- For CH_4 emissions, 40 CFR §98.253 Eq. Y-4
- For N_2O emissions, 40 CFR §98.253 Eq. Y-5

Case Study #5 - Refinery Fuel Gas Combustion and Flare Emissions (1 of 2)

- A facility has two refinery fuel gas (RFG) mixing drums, each with a flow meter, known fuel gas carbon content (CC), molecular weight (MW), and heating value (HHV)
- The RFG (at 60 ºF) is combusted in a boiler equipped with an RFG flow meter, and RFG also flows to a flare stack with a flow meter (at 68 ºF)
- The operator reports 1,375 MMscf/yr RFG combined through the two mixing drum meters
- The boiler RFG flow is reported at 1,110 MMscf/yr and the flow to the flare is reported at 215 MMscf/yr
- MW = 20 kg/kg-mole (daily average); CC = 0.60 kg C/kg RFG (daily average); RFG HHV at combined mixing drums is 550 Btu/scf (monthly average).
  - Calculate the CO_2 emissions from each process
  - Calculate the CO_2 emissions if the flare flow line had a RFG recovery system with a 96.7% recovery rate
  - What concerns would you address with the reported data?

Case Study #5 - Refinery Fuel Gas Combustion and Flare Emissions (2 of 2)



Case Study #5 - Refinery Fuel Gas Combustion and Flare Emissions Solution (1 of 2)

- The boiler RFG meter is calibrated to STP at 60ºF., the flare RFG meter is calibrated to STP at 68ºF
- The MW and CC are given and used a daily arithmetic average
- CC and MW must either be collected downstream from where RFG mix 1 and mix 2 are combined, or the CC and MW of the mixture must be determined using the weighted average of the CC and MW of RFG mix 1 and mix 2:
- [(Flow1 x CC1) + (Flow2 x CC2)] / (Flow1 + Flow2) = CC of the mixture used to calculate combustion and flare emissions
- Boiler emissions - Eq. C-5 with MVC of 836.6 scf/kg-mole

  $= \frac{44}{12} \times$ 1,110 MMscf/yr × 1,000,000 scf/MMscf × 1/836.6 scf/kg-mole × 20 kg/kg-mole × 0.60kgC/kg of fuel × 0.001 MT/kg = 58,379.2 MT CO_2/yr

Case Study #5 - Refinery Fuel Gas Combustion and Flare Emissions Solution (2 of 2)

- Flare emissions - Eq. Y-1a with MVC of 849.5 scf/kg-mole

  $= 0.98 \times 0.001 \times \frac{44}{12} \times$ 215 MMscf/yr × 1,000,000 scf/MMscf ×

  1/849.5 scf/kg-mole × 20 kg/kg-mole × 0.60 kg C/kg of fuel = 10,913.24 MT CO_2/yr
- Flare recovery system capture rate of 96.7%
  - = 10,913.24 MT/yr × (1 - 0.967) = 360.14 MT CO_2/yr
- <u>Questions to ask</u>
  - RFG metering doesn't reconcile, any other user of RFG?
  - What would you do if CC and MW were different in RFG?
  - Why are meters calibrated at different conditions?
  - Why was Y-1a selected as most appropriate equation? How does HHV Eq. Y-2 compare?
  - Would you complete a secondary calculation using HHV?
  - Any start-up, shut-down, or malfunction conditions per §95113(d)?

Course 3.2: Refineries

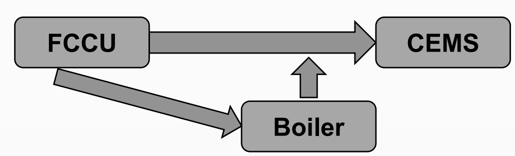
- Overview
- Emissions Data Reported by Refineries
  - Fuel gas combustion
  - Natural gas combustion
  - Flares
  - **Fluid catalytic cracking (FCC) and fluid coking**
  - **Coking**
  - **Catalytic reforming**
  - **Sulfur recovery**
  - **Coke calcining**
  - **Asphalt blowing**
  - **Delayed coking**
  - **Process vents**
  - **Uncontrolled blowdown**
  - Equipment leaks
  - Storage tanks
  - Product loading
  - H2 production

Calculation Methods for Fluid Catalytic Cracking (FCC) and Coking Emissions (1 of 2)

- If equipped with a qualifying CEMS, use Tier 4

If FCC and other combustion source are routed to the same stack, disaggregate the FCC emissions and "other" combustion emissions by solving for FCC:
FCC CO_2 = Total CEMS CO_2 – Boiler CO_2 (Tiers 1-3 for SFC)
[Note: Total CO_2 is accurate, so sum of FCC and boiler is also accurate]

- If not equipped with a CEMS, use Eq. Y-6, and Y-7a or Y-7b (do <u>not</u> use Y-8)



Calculation Methods for Fluid Catalytic Cracking (FCC) and Coking Emissions (2 of 2)

- For CH_4 and N_2O emissions, use either
  - Direct measurement (unit-specific measurement data)
  - Unit-specific source test emission factor
  - 40 CFR §98.253 Eq. Y-9 for CH_4 and Eq. Y-10 for N_2O
- For FCC and Fluid Coking, §95113(e) excludes use of Eq. Y-8 to calculate CO_2 emissions for units with rated capacities of 10,000 barrels per stream day or less.

Monitoring Requirements for Fluid Catalytic Cracking (FCC) and Coking

- Hourly or more frequent monitoring required
- Must monitor CO, CO_2, and O_2 in unit exhaust prior to combustion of other fuels when using 40 CFR §98.253 Eq. Y-6, Y-7a, or Y-7b

Case Study #6 - Fluid Catalytic Cracking Unit

- A fluid catalytic cracking unit (<10,000 bbl/day) sends flue gas to a boiler
- The boiler also receives supplemental fuel from natural gas
- The stack for the combined emissions does not have a CEMS.
- The refinery monitors the volume, and CO_2 and CO concentrations of the exhaust gas from the FCC
- The exhaust volume from the FCC for one hour is 10 MMscf at 68° F, the average %CO_2 is 20%, and the average %CO is 2%
  - Determine the calculation method for FCC emissions and resulting CO_2 emissions for one hour
  - How should the supplemental fuel emissions be calculated and reported?
  - How would the calculations be done differently if there were CEMS on the common stack and the FCC exhaust was not separately monitored?

Case Study #6 - Fluid Catalytic Cracking Unit
Solution

- The appropriate methods are from 40 CFR §98.253(c)
- Eq. Y-8 is not allowed under the MRR. If there are no CEMS, Eq. Y-6 is used
  - 10,000,000 scf/hr × $\frac{(20+2)}{100}$× 44kg/kg-mole × $\frac{1}{849.5}$ scf/kg-mole × 0.001 MT/kg = 113.9 MT CO_2 per hour
- **Hourly results for the data year are summed to report annual emissions from the unit**
- The emissions from the supplementary fuel are calculated separately according to Subpart C

Calculation Methods for Flexicokers

- Emissions from combustion of low value fuel gas must be accounted for only once
- Typically, reporters use the general SFC methods in 40 CFR §98.33
- Alternatively, reporters may use the methods for fluid coking provided that reporter does not otherwise account for the subsequent combustion of this low value fuel gas

Calculation Methods for Catalytic Reforming Emissions

- For CO_2 emissions
  - If equipped with a qualifying CEMS, use 40 CFR §98.33(a)(4)
  - If O_2, CO_2, and CO are measured daily or more frequently prior to combustion of other fuels, must follow the procedures for FCC units using 40 CFR §98.253 Eq. Y-6, and Y-7a or Y-7b
  - Otherwise use 40 CFR §98.253 Eq. Y-11
- For CH_4 and N_2O emissions, use
  - Unit-specific source test emission factor, or
  - 40 CFR §98.253 Eq. Y-9 for CH_4 and Eq. Y-10 for N_2O

Calculation Methods for Sulfur Recovery Plants

- Claus plants
  - CO_2, CH_4, and N_2O emissions from combustion of supplemental fuels in Claus or tail gas combustors, use Tiers 1-3 for SFC
    - The sour gas stream is not a supplemental fuel
  - If a qualifying CEMS is used
    - Follow the Tier 4 method of 40 CFR §98.33 for CO_2 emissions
    - If monitoring combined process and supplemental fuel emissions, calculate process emissions as the difference between CEMS and supplemental fuel emissions
  - Otherwise calculate CO_2 emissions using Eq. Y-12
- Non-Claus plants follow process vent procedures (slide 43)

Monitoring Requirements for Sulfur Recovery Plants

- Use continuous flow monitor, if available, to measure sour gas flow, otherwise use engineering estimates
- Use continuous gas composition monitor or sample data, if available, to measure carbon content of sour gas, otherwise use default carbon mole fraction of 0.20
- If tailgas is recycled and monitors are placed such that flow measurements overestimate emissions, engineering estimates or a default correction factor of 0.95 may be used with 40 CFR §98.253 Eq. Y-12

Case Study #7 - Sulfur Recovery Unit

- Calculate the CO_2 emissions from a Claus sulfur recovery unit, assuming 1,500 MMscf per year (68 °F) of sour gas feed, gas composition unavailable, and default mole fraction of carbon, without CEMS
- After completing the above calculation, it is discovered that a portion of the tailgas is recycled to the front of the sulfur recovery plant (upstream of meter) and that engineering estimates are used to perform the necessary correction
- 16,356 MT CO_2 were reported for this unit
  - Do you consider this to be a reasonable estimate? Why or why not?

Case Study #7 - Sulfur Recovery Unit Solution

- 40 CFR Part §98.253(f), Eq. Y-12
  - CO_2 = 1,500,000,000 scf x 44 g/kg-mole x 1/849.5 scf/kg mole x 0.20 kg-mole C/kg-mole gas x 0.001 MT/kg = 15,538.55 MT CO_2 (prior to the adjustment for tailgas recycling)
- Reported value does not appear to reasonably account for tailgas recycling
- The emissions, corrected for the recycling of tailgas, should be lower than the uncorrected value

Calculation Methods for Coke Calcining

- For CO_2 emissions
  - If qualifying CEMS is used, use Tier 4 method in 40 CFR §98.33 (Stationary Fuel Combustion)
  - If monitoring combined process and supplemental fuel emissions, calculate process emissions as the difference between CEMS and supplemental fuel emissions calculated based on 40 CFR §98.33
  - Otherwise, calculate CO_2 emissions using 40 CFR §98.253 Eq. Y-13
- For CH_4 and N_2O emissions, use either
  - Direct measurement
  - Unit-specific source test emission factor
  - 40 CFR §98.253 Eq. Y-9 for CH_4 and Eq. Y-10 for N_2O

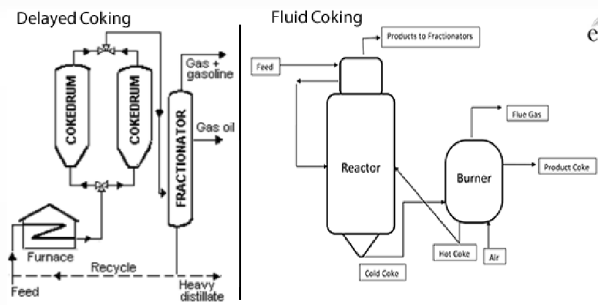
Calculation Methods for Asphalt Blowing

- Calculate CO_2 and CH_4 from uncontrolled and scrubbing-controlled units using 40 CFR §98.253 Eq. Y-14 and Y-15
- Units controlled with thermal oxidizer or flare for which emissions have not been included in flare or stationary fuel combustion emission calculations may use 40 CFR §98.253 Eq. Y-16a or Y-16b for CO_2 emissions and Y-17 for CH_4 emissions

Delayed Coking (Petroleum Coke Production)

Two types of **coking** processes exist—**delayed coking** and fluid **coking**.

With **delayed coking**, two or more large reactors, called coke drums, are used to hold, or **delay**, the heated feedstock while the cracking takes place. Coke is deposited in the coke drum as a solid.



Steam is added to prevent **coking** in the heater and the heated feed is introduced from the bottom of one of the coke drums. All of the heat necessary for **coking** is provided in the heater, whereas **coking** takes place in the coke drum; hence, the process is **called** "**delayed coking**."

Calculation Methods for Delayed Coking

- If water or steam is added to the vessel after venting to the atmosphere, must use option 1; otherwise, may use option 1 or option 2
- Option 1
  - Calculate CH_4 emissions from venting the coke drum using the process vent methods (described in next slide)
  - Calculate the CH_4 emissions from subsequent opening of the drum for coke cutting operations using 40 CFR §98.253, Eq. Y-18
- Option 2
  - Calculate CH_4 emissions for combined venting and opening of the coke drum using 40 CFR §98.253 Eq. Y-18
- Sum calculations for each drum to yield total delayed coking emissions

Calculation Methods for Process Vents

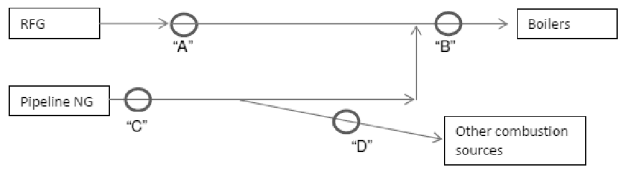
- Use Eq. Y-19 (40 CFR §98.253(j)) to calculate GHG emissions in the following cases:
  - Any process vent not covered in previous sections and expected to contain 2% or more CO_2, 0.5% or more CH_4, or 0.01% or more N_2O
  - Catalytic reforming unit depressurization and purge vents when CH_4 is used as purge gas
  - As an alternative method for calculating emissions from non-Claus sulfur removal processes, asphalt blowing operations and uncontrolled blowdown systems

Calculation Methods for Uncontrolled Blowdown Systems

- Calculate CH_4 emissions using procedures for process vents
- Procedure does not apply to systems routing uncondensed vapors to a flare or control device because this is considered to be controlled
- When calculating CH_4 emissions for uncontrolled blowdown systems as required by 40 CFR §98.253(k), the operator must use the methods for process vents in 40 CFR §98.253(j).

Case Study #8 - Multiple Fuel Gases and Metering

Case Study 3: Double-Counting and Metering



At point "A", the refinery measures weighted annual average CC (0.60) and MW (20 kg/kg-mole) of refinery fuel gas. The volume measurement is not +/-5% accurate and is not used.

Point "B" measures 1,500 MMscf of mixed refinery and natural gas.

At point "C", 2,000 MMscf of pipeline natural gas is purchased at 1,020 Btu/scf annual weighted average HHV.

At point "D", 1,500 MMscf is measured.

The refinery performs the following calculations:

For CO_2 emissions from boilers using equation C-5:

44/12 x 1500 MMscf x 1,000,000 scf/1MMscf x 1 kg-mole/849.5 scf x 20 kg/kg-mole x 0.60 kg/kg of fuel x 0.001 MT/kg = 77,693 MT CO_2

For CO_2 emissions from "other combustion sources" using equation C-2a:

1,500 MMscf x 1,020 Btu/scf x 53.02 kg CO2/MMBtu x .001 MT/kg = 81,120.6 MT CO_2

Total: 158,814 MTCO_2

Case Study #8 - Solution

- Reporter's calculation is incorrect because CC of RFG is applied to combined volume of pipeline NG and RFG
- The reporter would need to subtract the volume of pipeline NG (2000-1500 = 500 MMscf), and apply the CC to 1,000 MMscf of RFG
- To correctly calculate emissions from RFG using CC and MW from point "A" using Eq. C-5
  - 44/12 x 1,000 MMscf x 1,000,000 scf/1MMscf x 1/849.5 scf x 20 kg/kg-mole x 0.60 kg C/kg of fuel x 0.001 MT/kg = 51,795.17 MT CO_2
- To correctly calculate NG combustion emissions, separately calculate emissions from the 2 sources (1,500 MMscf to other combustion sources, and 500 MMscf to the boilers) use a Tier 2 method, or use the upstream meter information
  - 2,000 MMscf × 1,020 Btu/scf × 53.02 kg CO_2/MMBtu × 0.001 metric tons/kg = 108,160.8 MT CO_2
- Total: 159,956 MT CO_2

Course 3.2: Refineries

- Overview
- Emissions Data Reported by Refineries
  - Fuel gas combustion
  - Natural gas combustion
  - Flares
  - Fluid catalytic cracking (FCC) and fluid coking
  - Coking
  - Catalytic reforming
  - Sulfur recovery
  - Coke calcining
  - Asphalt blowing
  - Delayed coking
  - Process vents
  - Uncontrolled blowdown
  - **Equipment leaks**
  - **Storage tanks**
  - **Product loading**
  - H2 production

Calculation Methods for Equipment Leaks-Fugitive CH_4

- Two methods are available:
  - Simplified calculation using Eq. Y–21

    $CH_4 = (0.4 \times N_{CD} + 0.2 \times N_{PU1} + 0.1 \times N_{PU2} + 4.3 \times N_{H2} + 6 \times N_{FGS})$

  - Process-specific methane composition data (measurement data or process knowledge) and the Protocol for Equipment Leak Emissions Estimates (EPA-453/R-95-017, NTIS PB96-175401)

Calculation Methods for Storage Tanks Containing Stabilized Crude Oil - Fugitive CH_4

- If vapor-phase CH_4 concentration > 0.5 volume percent, use tank-specific methane composition data and the emission estimation methods in AP 42, Section 7.1
- If vapor-phase CH_4 concentration < 0.5 volume percent, use Eq. Y-22

Calculation Methods for Storage Tanks Containing Unstabilized Crude Oil - Fugitive CH_4

- Two methods are allowed
  - Tank-specific methane composition data and direct measurement of gas generation rate
  - 40 CFR §98.253 Eq. Y-23
- If routed to a flare, fugitive emissions are not reported for that source; they are reported instead as flare emissions
- If routed to a fuel gas system, fugitive emissions are not reported for that source; they are reported as stationary combustion emissions

Tanks for which Emissions Not Reported 40 CFR 98.253(m)

- Units permanently attached to conveyances such as trucks, trailers, rail cars, barges, or ships
- Pressure vessels designed to operate in excess of 204.9 kilopascals and without emissions to the atmosphere
- Bottoms receivers or sumps
- Vessels storing wastewater
- Reactor vessels associated with a manufacturing process unit

Calculation Methods for CH_4 from Crude Oil, Intermediate, and Product Loading Operations

- Operations for which the vapor-phase concentration of CH_4 is > 0.5 volume percent
  - Use vapor-phase methane composition data (from measurement data or process knowledge) and the procedures in AP-42, Section 5.2
- Operations for which the vapor-phase concentration of CH_4 is < 0.5 volume percent
  - Assume zero methane emissions

Course 3.2: Refineries

1. Overview
2. Emissions Data Reported by Refineries
3. **Monitoring Requirements and Missing Data**
   - **Monitoring options**
   - **Recalibration requirements**
   - **Missing Data**
4. Product Data
5. Nonconformances and Verification Tips

Monitoring & QA/QC Options for Gas Flow, Gas Composition, and Heating Value Monitors (1 of 2)

- Equipment must be calibrated according to the procedures specified by the manufacturer (40 CFR §98.254(b))
- Flare or sour gas flow meters and process vent flow meters may use a calibration method published by a consensus-based standards organization (40 CFR §98.254(c))
- For gas composition and molecular weight, may use default values (if allowed) or chromatographic analysis if operated, maintained, and calibrated according to the manufacturer's instructions (40 CFR §98.254(d))

Monitoring & QA/QC Options for Gas Flow, Gas Composition, and Heating Value Monitors (2 of 2)

- Flare gas HHV - use results of chromatographic analysis if operated, maintained, and calibrated according to the manufacturer's instructions (40 CFR §98.254(e))
- Flow and gas composition monitoring equipment must be installed, operated, calibrated, and maintained consistent with the requirements of Part 98, or the applicable sections of Part 60 or 63 for catalytic cracking units (40 CFR §98.254(g))
  - Must be located to provide representative flow rates
  - Flow measurement must be continuous and reported at STP

Recalibration Requirements for Gas Flow, Gas Composition, and Heating Value Monitors

- Recalibrate each gas flow meter according to the following criteria (whichever provides the shortest time interval) (§95103(k)(4))
  - As specified in applicable subpart of 40 CFR Part 98
  - At the minimum frequency specified by the manufacturer
  - Once every 36 months
  - Upon replacement or repair
- Recalibrate each gas composition monitor and heating value monitor according to one of the following criteria (40 CFR §98.254(b)(2))
  - At the minimum frequency specified by the manufacturer
  - Annually
  - At the interval specified by standard industry practice

Other Monitoring and QA/QC Requirements for Refineries

- Procedures used to ensure the accuracy of the estimates of fuel usage, gas composition, and heating value must be documented (40 CFR §98.254(k))
  - The accuracy of measurements made with these devices must also be recorded, and the technical basis for these estimates must be provided
- Fuel flow meters, gas composition monitors, heating value monitors, and associated CEMS used to measure CO_2 from combustion sources must meet the applicable requirements in 40 CFR §98.33 (§95113(a) / 95115)
  - For refinery fuel gas combustion, §95113(a) requires daily fuel carbon content (CC) monitoring or CEMS (must use Tier 3 or 4 method)

Missing Data

- Capture rate ≥ 90% - substitute the best available estimate of the parameter using available process data
- Capture rate ≥ 80% and <90% - substitute highest value recorded during the year and two previous years
- Capture rate <80% - substitute highest value recorded in all records kept according to §95105(a)
- Stationary combustion units and CEMS follow §95129

Course 3.2: Refineries

1. Overview
2. Emissions Data Reported by Refineries
3. Monitoring Requirements and Product Data
4. Product Data
   - Product data
   - Verifying product data
5. Nonconformances and Verification Tips

Covered Product Data

There are 3 categories of refinery product data:

- Calcined coke produced (covered product data)
- On-purpose hydrogen gas produced (covered product data)
- Complexity Weighted Barrel (CWB) throughputs (covered product data)

- CWB, hydrogen, and calcined coke each receive a material misstatement assessment, and a single product data verification statement
  - Calcined coke is reported under separate facility ID numbers
  - Calcined coke is a purified form of coke and is used for industry (e.g., anodes for the Aluminum, steel and titanium smelting industry) and not as fuel

Verifying Refinery Product Data

- List of "Refinery Product Data" required to be reported is in Table 2-1 of section 95113
  - This is <u>not</u> covered product data, and is <u>not</u> subject to material misstatement
  - Production volumes reported based on amount produced during data year, which can be measured using sales with inventory adjustment (based on Form EIA-810)
- To calculate total Refinery Product volume, the volume of blendstocks and blending components produced elsewhere must be subtracted, unless the blend stock or blending component is used for purposes other than blending (e.g., as feed)
  - Annual volume of a material produced elsewhere and brought on-site is separately reported

Cost of Implementation Fee Regulation

- Facility must also report the volume of
  - Produced and imported CARBOB
  - Produced and imported finished California gasoline
  - Produced and imported California diesel
- Verify for reasonable assurance of conformance; not subject to material misstatement evaluation or product data verification statement
- COI fee reporting also includes the emissions from the combustion of refinery fuel gas only; there is a special field for this value in Cal e-GGRT
  - Not subject to verification.

Complexity Weighted Barrel (CWB) Calculation §95113(l)

- $CWB_{Total} = CWB_{Process} + CWB_{Off\text{-}sites} + CWB_{Non\text{-}Crude\ Sensible\ Heat}$
- Where CWB_{Total} is the total complexity weighted barrels for a petroleum refinery, and $CWB_{Process}$, $CWB_{Off\text{-}Sites}$, and $CWB_{Non\text{-}Crude\ Sensible\ Heat}$ must be calculated as follows:
- $CWB_{Process} = \Sigma(CWB_{Factor} \times \text{Throughput})$
- $CWB_{Off\text{-}Sites} = (0.327) \times (\text{Total Refinery Input}) + (0.0085) \times (CWB_{Process})$
- $CWB_{Non\text{-}Crude\ Sensible\ Heat} = (0.44) \times (\text{Non-Crude Input})$
- Each refinery reports Total Refinery Input, Non-Crude Input, and a Throughput value for each process. The reporting tool automatically calculates CWB_{Total} from these reported values

Complexity Weighted Barrel (CWB) Requirements

- CWB guidance for reporters and verifiers is available at: https://ww2.arb.ca.gov/mrr-guidance
- Measurement systems for unit throughputs must meet the accuracy requirements of §95103(k)
- Changes in methodology must follow §95103(m)

Verifying the Complexity Weighted Barrel (CWB) Calculation (1 of 4)

Complexity Weighted Barrel Worksheet

	A	B	C	D	E	F	G	H	I
4	CWB unit	EIA Number	Throughput Basis	CWB Factor	Coke-on-Catalyst CWB Factor	Coke-on-Catalyst % by Volume	Unit of Measure	Throughput	CWB (CWB/year)
5	Atmospheric Crude Distillation	401	Feed	1	0		thousands of barrels/year	80,000.00	80,000.00
6	Vacuum Distillation	402	Feed	0.91	0		thousands of barrels/year	40,000.00	36,400.00
7	Fluid Catalytic Cracking (FCC)	407	Feed	1.15	1.041	5.05%	thousands of barrels/year	17,000.00	108,919.85
8	Delayed Coker	405	Feed	2.55	0		thousands of barrels/year	12,507.00	31,892.85
9	Naphtha Hydrotreater	420/425/426	Feed	0.91	0		thousands of barrels/year	19,008.00	17,297.28
10	Kerosene Hydrotreater	421	Feed	0.75	0		thousands of barrels/year	9,000.00	6,750.00
11	Diesel/Selective Hydrotreater	422 / 423	Feed	0.9	0		thousands of barrels/year	11,200.00	10,080.00
12	Sulfur Recovery – Product Sulfur	435	Product Sulfur	140	0		thousands of long tons/year	175.00	24,500.00
13	Reformer – including AROMAX	430 / 431	Feed	3.5	0		thousands of barrels/year	7,250.00	25,375.00
14	Flare Gas Recovery	0	Feed	0.13	0		millions of standard cubic feet/year	2,000.00	260.00
15	Special Fractionation	0	Feed	0.8	0		thousands of barrels/year	15,602.00	12,481.60
16					0				
17					0				
18					0				
19					0				
20					0				
35					0				
36					0				
37					0				
38					0				
39					0				
40								CWB Process	353,956.58
41								Total Refinery Input (thousands of barrels per year)	85,000.00
42								Non-Crude Input (thousands of barrels per year)	3,507.00
43								CWB Offsites	30,803.63
44								CWB Non-Crude Sensible Heat	1,543.08
45									
46								TOTAL CWB for ALLOCATION = CWB Process + CWB Offsites + CWB Non-Crude Sensible Heat	386,303.29
47									

Verifying the Complexity Weighted Barrel (CWB) Calculation (2 of 4)

- Request to see the control room flow recorder records for each unit included in the CWB calculations and a diagram of the measurement location
- Verify that missing product data are not substituted
  - Any process unit with data deemed to be inaccurate must have a reported throughput equal to zero, and a best estimate of the missing value must be reported pursuant to §95103
  - Process units with inaccurate throughputs are excluded from material misstatement assessment

Verifying the Complexity Weighted Barrel (CWB) Calculation (3 of 4)

Verify that:

- Process units are classified into the correct CWB unit (see Appendix D in the Solomon CWB Report[1] and the definitions in section 95102(c))
- The correct throughput basis for the CWB unit was used (unit feed or output)
- Reported flow volumes match the flow recorder records
- Flow volumes are reported corrected to 60˚ F and 1 atm pressure
- CWB throughputs that are unit feeds include only the fresh feed volume and exclude any recycled material (except isomerization units may include recycled feed)
- Flow meters/measurement systems for CWB throughputs are calibrated and accurate to +/- 5% (or have a valid postponement request)

[1] http://www.arb.ca.gov/cc/capandtrade/meetings/081313/cwt-cwb_backgrounddocument.pdf

Verifying the Complexity Weighted Barrel (CWB) Calculation (4 of 4)

Verify that:

- The coke-on-catalyst volume percent (for FCC units) is determined by a reasonable and accurate method (refer to guidance)
- Units are correct —most throughputs, including non-crude input and total refinery input, are reported in “thousands of barrels”
- Hydrogen, natural gas, and any other inputs to a hydrogen production unit are excluded from non-crude input and total refinery input
- Total refinery input is in thousands of barrels, includes crude oil, feedstocks, blendstocks, additives, and excludes natural gas
- Non-crude input is in thousands of barrels, and includes only materials from off-site that are further processed on-site in a process unit, and excludes blendstocks, additives, and any materials that are not processed (heated) on-site in a process unit

Other Recommended Checks on CWB Throughputs

- Compare with refinery capacities filed with DOE-EIA
  - Available at http://www.eia.gov/petroleum/refinerycapacity/
  - Throughput reported to CARB should be below capacity reported to EIA
  - Exceptions in cases of differing definitions
  - Helpful cross-check, but doesn't take place of CWB assessment

Nonconformances and Verification Tips

Emissions Data

Example Errors Identified by Verifiers

- Inaccurate meter used to quantify fuel gas volume
- Missing data for fuel combustion parameters not substituted according to MRR requirements
- Revised data was not updated in Cal e-GGRT report

Verification Tips

- Focus on fuel gas systems: meter locations, flow data, sampling locations, gas analysis data - completeness, accuracy, representativeness
- Review fuel system block diagram or piping diagrams; spot check in field

Product Data

Example Errors Identified by Verifiers

- Hydrogen and natural gas included in Total Refinery Input
- Discrepancies in intermediate calculation spreadsheets
- Calibration postponement approved, but other meters not included in approval were not inspected

Verification Tips

- Verify accuracy of CWB measurement systems
- Ensure CWB throughputs are reported in correct units
- Verify correction of CWB throughputs to 60˚ F and 1 atm

Verifier Accreditation Training for Mandatory Greenhouse Gas Reporting

Course 3: Oil and Gas Systems Specialty

Complete:

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

Next:

- 3.3 Hydrogen Production