Bay Area
Air Quality
Management
District

PRELIMINARY STAFF REPORT REGULATION 13: CLIMATE POLLUTANTS, RULE 5: PETROLEUM REFINERY HYDROGEN PLANTS

Source: https://chemicalparks.eu/news/2015-4-17-air-liquide-starts-up-a-large-hydrogen-production-unit-in-germany

September 2020

Prepared By

William Thomas Saltz
Senior Air Quality Specialist

(This page was intentionally left blank)

ACKNOWLEDGEMENTS

Air District staff members who also greatly contributed to the development of this report and draft rule proposal:

Art Valla, Principal Engineer: Engineering Division
Azibuike Akaba, Public Information Officer II: Community Engagement and Policy Division
Brian Butler, Senior Air Quality Engineer: Community Engagement and Policy Division
Linda Duca, Supervising Air Quality Specialist: Compliance and Enforcement Division
Jerry Bovee, Manager: Meteorology and Measurements Division
Madeline Stone, Assistant Counsel: Legal Division
Marco Hernandez, Acting Manager: Meteorology and Measurements Division
Victor Douglas, Manager: Community Engagement and Policy Division

PRELIMINARY STAFF REPORT

Regulation 13, Rule 5: Petroleum Refinery Hydrogen Systems

TABLE OF CONTENTS

I. INTRODUCTION

This Workshop Report provides preliminary information regarding development of a new rule by the staff of the Bay Area Air Quality Management District (BAAQMD or Air District), draft Regulation 13: Climate Pollutants, Rule 5: Petroleum Refinery Hydrogen Plants (Rule 13-5). Draft Rule 13-5 would limit vented emissions of total organic compounds from petroleum refineries' hydrogen production, hydrogen carrying systems, and hydrogen end users such as process units. Total organic compounds include organic compounds and methane.

The State of California made the reduction of greenhouse gas emissions a priority. In September 2016, Governor Brown signed Senate Bill 32 (Chapter 249, Statutes of 2016), which mandated a greenhouse gas emissions reduction target of 40 percent below 1990 emission levels by 2030. Senate Bill 605 (Chapter 523, Statutes of 2014) requires the California Air Resources Board to develop a plan to reduce emissions of short-lived climate pollutants, and Senate Bill 1383 (Chapter 249, Statutes of 2016) requires the California Air Resources Board to approve and implement a plan by January 2018 to achieve these reductions. Senate Bill 1383 also sets a target for the reduction of methane emissions of 40 percent below 2013 levels by 2030. Pursuant to Senate Bill 605 and Senate Bill 1383, the California Air Resources Board subsequently developed the Short-Lived Climate Pollutant Reduction Strategy, adopted in March 2017.

The Air District has a policy goal of reducing Bay Area greenhouse gas emissions to 40 percent below 1990 levels by 2030, and 80 percent below 1990 levels by 2050. Methane is a potent and short-lived climate pollutant; its global warming potential is 86 times greater than that of carbon dioxide, when compared on a 20-year time horizon.[1,2] Methane represents the second largest emissions of greenhouse gases in the region, after carbon dioxide. In 2015, all methane sources located within the Air District emitted an estimated 10 million metric tons of carbon dioxide equivalent, about 10 percent of the Bay Area's greenhouse gas inventory. The sources of methane emissions include stationary sources such as landfills, wastewater treatment facilities, refineries, natural gas production and distribution systems; mobile sources such as cars and trucks; and natural sources such as wetlands. Reducing emissions of short-lived climate pollutants, including methane, can have a dramatic effect on climate change in the near term as their atmospheric lifetime is much less than longer-lived greenhouse gases, such as carbon dioxide. These climate pollutants are estimated to be responsible for roughly 40 percent of the current net climate forcing effect.[a] Given the importance of controlling methane, the Air District developed a comprehensive Basin-wide Methane Strategy as part of its 2017 Clean Air Plan. The Methane Strategy is an agency-wide effort to better quantify and reduce the region's methane emissions. Draft Rule 13-5 is one of the first rules developed as part of this Strategy. Other source-specific methane rules are under development to address emissions from specific operations.

Petroleum refineries are a large source of methane emissions in the Bay Area. Draft Rule 13-5 would address one of the largest sources of methane emissions from Bay Area petroleum refineries—hydrogen production plants and systems. There are currently nine permitted hydrogen plants associated with five petroleum refineries within the Air District's jurisdiction.

[1] Based on the 20-year global warming potential reported for methane in the Intergovernmental Panel on Climate Change Fifth Assessment Report.

[2] Unless otherwise stated, this report uses the 20-year global warming potential GWP of 86 when calculating the carbon dioxide equivalent of methane emissions since the emission reduction actions being considered are within that time frame.

Petroleum refinery hydrogen plants vent hydrogen gas that can contain methane and other hydrocarbons under a variety of circumstances including normal operating conditions as well as startups, shutdowns, malfunctions, upsets and emergencies. Air District staff estimates that methane emissions from all petroleum hydrogen plant sources average approximately 2,300 tons per year for calendar years 2016 through 2018; this is based on an Air District emissions inventory resulting from hydrogen plant operators' responses to a fall 2019 questionnaire and emissions data reported to the California Air Resources Board. The intent of draft Rule 13-5 is to minimize both methane and other organic compound emissions which are defined as "total organic compound" emissions, normally vented from atmospheric vents located at petroleum refinery hydrogen plants during normal operating conditions, startups, shutdowns, malfunctions, upsets and emergencies. The reduction in total organic compound emissions would be achieved by providing hydrogen system operators the flexibility to use any gas control technology that is appropriate for minimizing total organic compound emissions in accordance with the requirements in Rule 13-5. Typically, hydrogen plant operations either capture and reuse hydrogen gases containing methane and other constituents, including organic compounds, for incorporation into refinery gas fuel systems or they use flares to burn the mixture of hydrogen gas, methane, and other constituents. Capturing hydrogen and other gases and reusing them in the refinery system could control total organic compound emissions up to nearly 100 percent; routing these gases to an abatement device would result in a lower control efficiency. If flares are used to control total organic compound emissions from hydrogen plants, the hydrogen gases containing total organic compounds routed directly to a flare would have to meet a 98 percent control efficiency to comply with federal standards for refinery flares.

This Preliminary Staff Report discusses the purpose of draft Rule 13-5, its emission standards, and how emissions would be monitored and compliance with the rule would be determined. Staff continues to gather information to estimate the associated costs of compliance with the requirements of the draft rule.

The Air District initially published this report in December of 2019 to explain draft Rule 13-5 to members of the public, affected industry, and other interested parties. Draft regulatory language for Rule 13-5 was developed and was made available for review as well. The Air District held a public workshop on January 27, 2020 to discuss the draft Rule and invited stakeholder input on all aspects of the draft rule. Refinery representatives and hydrogen plant third-party operators provided feedback to Air District staff that resulted in significant changes to draft Rule 13-5. This updated version of draft Rule 13-5 will be submitted to hydrogen plant operators and other interested stakeholders for their review and comments. Following this Request for Comments, staff will prepare a Public Hearing package – containing the proposed regulatory version of Rule 13-5, a draft staff report, a socioeconomic analysis, and a California Environmental Quality Act environmental analysis – that will be presented to the Air District's Board of Directors for its consideration.

II. BACKGROUND

A. Refinery Hydrogen Use

Hydrogen, the most abundant substance in the universe, is a colorless, odorless, tasteless and non-toxic gas at standard temperature and pressure (normal conditions). Hydrogen gas is highly flammable, is considered to be an energy carrier—similar to electricity and natural gas, and is used in an extensive range of industrial applications.[b] While this report references the production and consumption of hydrogen in petroleum refineries, the purpose of this Rule is to reduce the emissions of total organic compounds—which includes methane—that is often a component of the hydrogen gas stream vented to atmosphere under various operational conditions. For example, venting may occur during normal operational conditions or during startups and shutdowns. Reducing hydrogen gas emissions results in the reduction of methane and other emissions.

In the petroleum refining industry, hydrogen is used extensively in the processing of crude oil into refined fuels such as gasoline and diesel. Hydrogen is consumed in desulfurization units to remove contaminants from fuels and feedstocks. Additionally, hydrogen is used in the refinery fuel system. As petroleum refinery product specifications become more stringent to meet environmental requirements, refinery demand for hydrogen has continually increased to supply the refinery hydrogen consumers (process units). The two primary hydrogen consumers in Bay Area petroleum refineries are processes known as hydrotreating and hydrocracking.

1. Hydrotreating

Hydrotreating is a process whereby hydrogen is added to a hydrocarbon gas (often referred to as a feedstock) stream over a bed of catalysts typically containing molybdenum with nickel or cobalt, at an intermediate temperature and pressure, as well as other process-specific operating conditions. The purpose of hydrotreating is to remove sulfur and other undesirable compounds, such as unsaturated hydrocarbons and nitrogen, from the hydrocarbon stream.[c] Sulfur will poison (shorten the lifespan of) catalysts used in hydrocarbon processing applications so refineries take measures to protect catalysts to extend their operating longevity as long as possible. During hydrotreating, sulfur compounds react with hydrogen to form hydrogen sulfide, while nitrogen compounds react to form ammonia. Aromatics and olefins are saturated by the hydrogen and lighter products are created. The final result of the hydrotreating process is the substantial reduction of sulfur and other contaminants from the original feedstock.

2. Hydrocracking

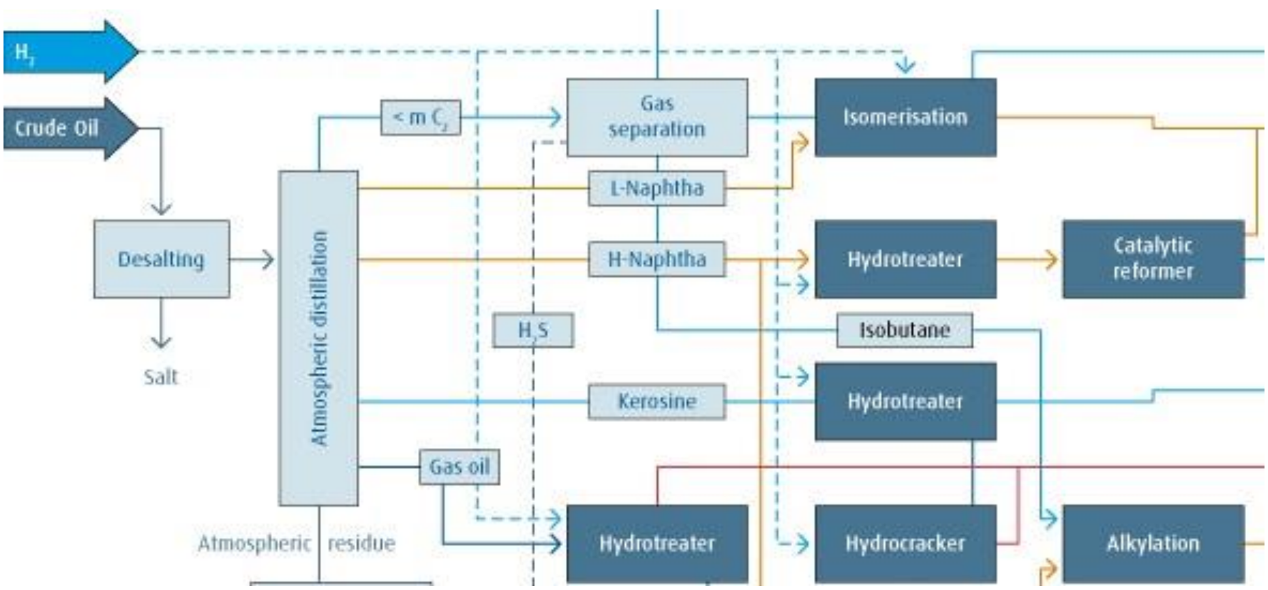
Hydrocracking is a refinery process that produces lighter hydrocarbon molecules with higher value for diesel, aviation fuel and petrol fuel from long-chain hydrocarbons. In this process, heavy gas oils, heavy residues or similar boiling-range heavy distillates are reacted with hydrogen in the presence of a catalyst at high temperature and pressure. The heavy feedstocks molecules are broken (or “cracked”) into light or middle distillate products—for example, naphtha, kerosene and diesel—or base stocks for lubricants. For some refineries, the hydrocracker unit is the top hydrogen consumer. Hydrogen is the key component that enables the hydrocracking process to reduce the product boiling range appreciably by converting the majority of the feedstock to lower-boiling, more desirable products.[d]

B. Refinery Hydrogen Production

1. Refinery Hydrogen Source

With the increase in demand for hydrogen use at petroleum refineries, producing their own hydrogen, instead of purchasing it, is economically advantageous for refineries. In some instances, refineries pay an independent, third party to produce hydrogen in a facility that is either contiguous to or located within the refinery property. The production, distribution and use of hydrogen within petroleum refineries is all part of an integrated system that is referred to as a "Refinery Hydrogen Plant" for the purposes of this report and the development of draft Rule 13-5. A petroleum refinery may incorporate one or more hydrogen plants into its hydrogen distribution network that delivers hydrogen to processes (or "consumers" covered in the previous section of this report) that use hydrogen. A secondary method of producing hydrogen in petroleum refineries is known as "catalytic reforming" or "naphtha reforming units." However, the majority of hydrogen is produced in hydrogen plant steam methane reforming processes. The heart of the plant consists of a steam methane reformer and additional hydrogen purification steps that are integrated with all the processes in need of hydrogen throughout the refinery.

Figure 1: Basic diagram of hydrogen distribution to petroleum refinery consumers

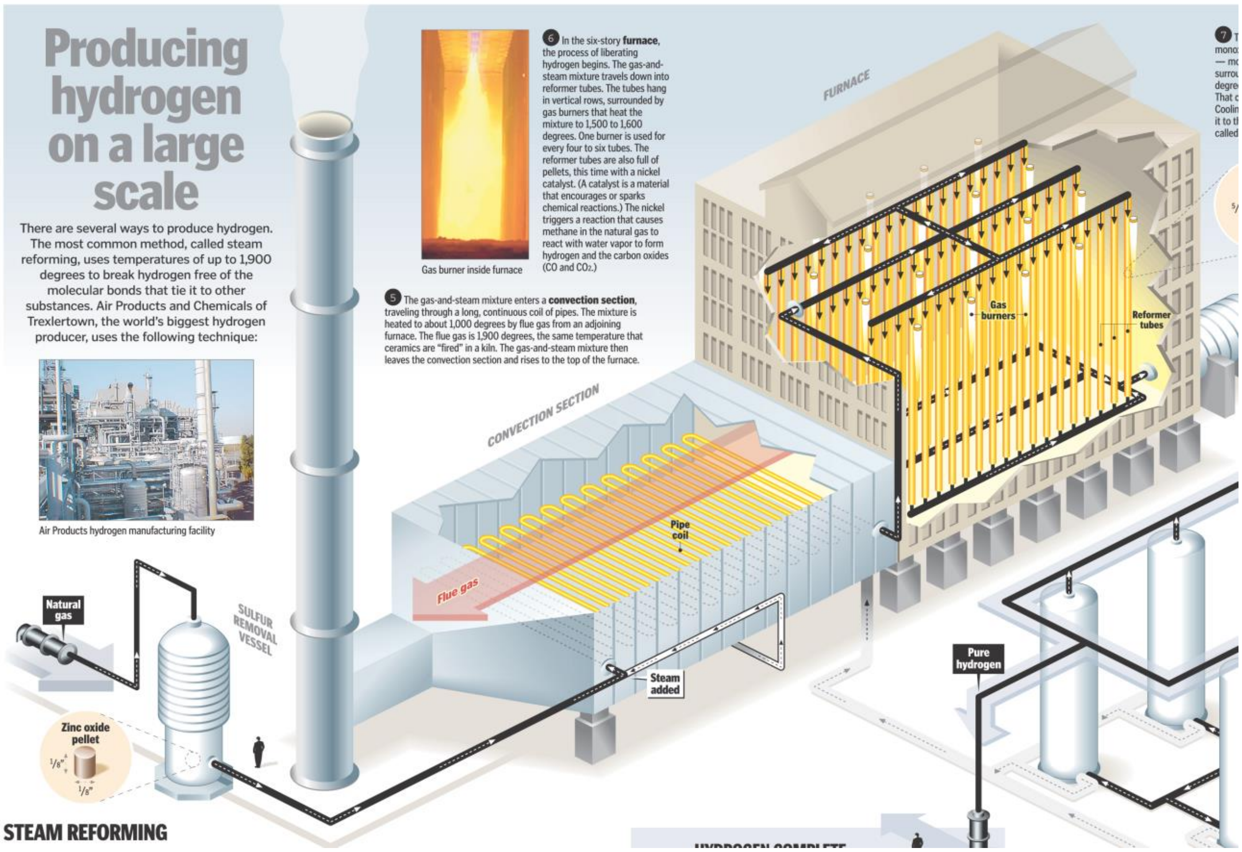


Source:https://www.linde-gas.com/en/processes/petrochemical-processing-and-refining/hydrogen_applications_refineries/index.html

Hydrogen production via steam methane reforming generally includes four steps: 1) the purification of the feed gas (usually natural gas or refinery fuel gas, although other gases may be used depending on economic conditions); 2) steam and methane are reformed in the box to convert most of the methane gas to hydrogen via the chemical reaction $CH_4 + H_2O \rightleftharpoons CO + 3\ H_2$; 3) temperature shift reaction to convert some of the remaining methane to hydrogen; and 4) final product purification step.

"Hydrogen plants" often refer to a process unit that converts natural gas or other feedstocks to hydrogen. However, because hydrogen gas containing total organic compounds can be vented to atmosphere at locations other than the specific location where hydrogen production occurs, for the purposes of Rule 13-5, a hydrogen plant is defined as a comprehensive operation that includes all forms of petroleum refinery hydrogen production, hydrogen compression operations, hydrogen consumers, hydrogen delivery and hydrogen distribution systems.

Figure 2: Depiction of the interior of a typical steam methane reformer

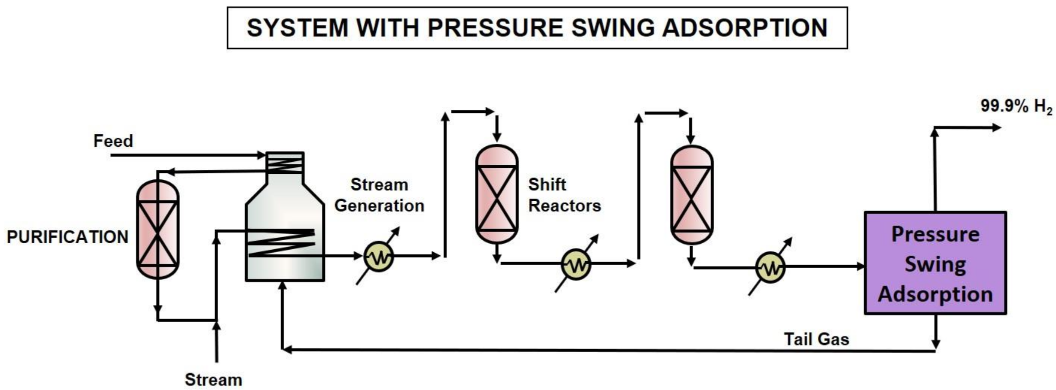


Source: Air Products

Refinery hydrogen plants consist of two types, those with pressure swing adsorption and those without. Pressure swing absorption produces a purer form of hydrogen required by certain refinery applications.

Prior to distributing hydrogen into the refinery hydrogen network, most hydrogen plants use a pressure swing adsorption process for the final purification step at the back end of the steam methane reforming operation to produce an ultra-pure hydrogen with a minimum purity of 99.99 percent concentration in the gas stream from what was previously a concentration ranging between 95 percent to 97 percent. A byproduct of the pressure swing adsorption process, referred to as "tail gas" is impure hydrogen gas that does not meet specifications for refinery hydrogen consumers and is routed back to the steam methane reformer as fuel and can contain methane concentrations ranging between 15 percent and 20 percent.

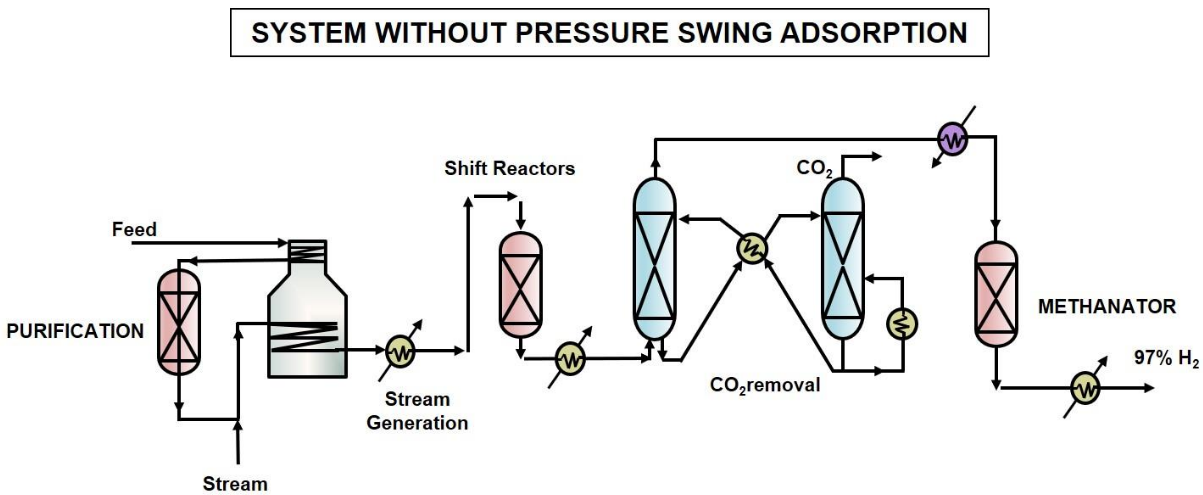
Figure 3: Flow diagram of a hydrogen plant with pressure swing adsorption purification



Source: Air District Staff

By contrast, a hydrogen plant that does not use a pressure swing adsorption process produces a less pure hydrogen stream that contains a higher amount of total organic compounds, including methane—generally between four and six percent.

Figure 4: Diagram of a hydrogen plant without pressure swing absorption purification



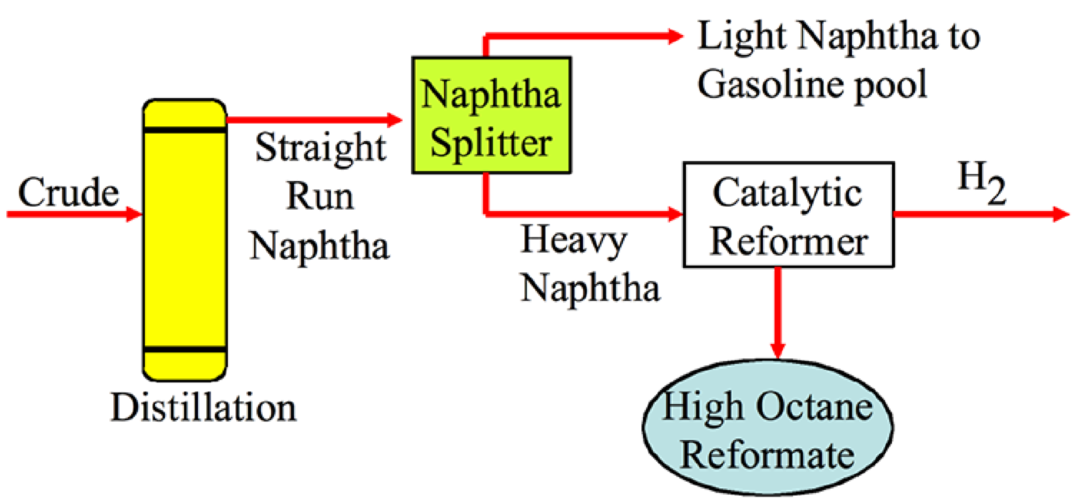
Source: Air District Staff

Methane emissions occur when impure hydrogen gases containing total organic compounds are purposely vented from atmospheric vents (sometimes referred to as process vents) located at various junctures throughout the hydrogen plant. With one exception, most atmospheric venting of impure hydrogen gas in Bay Area refineries occurs within the hydrogen plant steam methane reforming processes described in Figure 3 and Figure 4 above. For most facilities, hydrogen gas is not vented to atmosphere as a matter of course, it is only vented when necessary, usually for safety-related reasons such as refinery startups, shutdowns, emergencies, malfunctions, trips or process upsets.[e] A total of nine operational hydrogen plants are associated with Bay Area refineries; two of the hydrogen plants—one at the Valero refinery and the other at the PBF refinery—regularly vent hydrogen gas from certain atmospheric vents during normal operations. Most hydrogen plants typically have three to four atmospheric vents located in the steam methane reforming process unit. Each vent is used to release impure hydrogen gas under specific operational conditions. For example, one vent is used only during startups while another vent is used only during shutdowns.

2. Catalytic Reforming Units

Catalytic reforming units, sometimes referred to as naphtha reforming units, function as part of a petroleum refinery's secondary method of producing hydrogen. The primary purpose of the catalytic reforming process is to convert heavy naphthas distilled from crude oil into lighter components. During this chemical process, heavy naphthas that typically have low octane ratings are reformed into lighter naphthas with higher octane ratings. Often referred to as reformates, light naphthas are a product used as blending stocks for high-octane gasoline. As a byproduct of the naphtha reforming process, hydrogen is produced and is used in nearby hydrogen consumers. Although naphtha reforming unit gases vented to atmosphere contain a greater concentration of total organic compounds than that of hydrogen gas vented during hydrogen plant steam methane reforming operations, the relative amount of total organic compound mass emissions from naphtha reforming units are less than the amount emitted from hydrogen plants due to the difference in volumes and flowrates. For example, hydrogen plants sometimes vent total organic compounds in amounts ranging between 2,000 pounds pounds per day to 40,000 pounds per day, wheras total organic compound emissions from a naptha reforming unit will typically range between 600 pounds per day to 700 pounds per day.

Figure 5: Flow diagram schematic of a refinery catalytic reforming process



Source: Dr. Semih Eser via https://www.e-education.psu.edu/fsc432/content/catalytic-reforming.

C. Regulatory History

1. Air District Rules/Regulations

Currently, the Air District does not have a rule that specifically addresses vented total organic compound emissions from refinery hydrogen production operations and associated distribution systems. Air District Regulation 8, Rule 18: Equipment Leaks limits the emissions of total organic compounds from leaks from a wide variety of equipment such as valves, connectors, pumps, compressors, and other equipment located at petroleum refineries, chemical plants, bulk plants and bulk terminals. Because total organic compounds include methane, Regulation 8, Rule 18 addresses methane to a certain extent.[f]

2. Rules from other Air Districts

The South Coast Air Quality Management District has a hydrogen plant rule, Rule 1189: Emissions from Hydrogen Plant Process Vents, that regulates volatile organic compounds from hydrogen plant process vents as a method of limiting methanol emissions but does not specifically address methane, other organic compounds or any other greenhouse gas emissions.[g] No California air districts currently regulate total organic compound emissions, which includes methane, from hydrogen plant operations via source-specific rules.

3. State Regulations

At the State level, the Mandatory Reporting of Greenhouse Gas Emissions program requires petroleum refineries to report annual greenhouse gas emissions generated by various refining operations to the California Air Resources Board.[h] Although California regulates greenhouse gas emissions from large facilities such as petroleum refineries via California's Cap-and-Trade program, methane-specific emission reductions are not required.[i]

4. Federal Regulations

There are no substantive federal air quality regulations that address methane emissions from petroleum refining hydrogen plants. Refineries report annual greenhouse gas emissions to the United States Environmental Protection Agency as required by the Greenhouse Gas Reporting Program.[j]

5. Other Air District Rule Development Efforts

Concurrent with the development of Rule 13-5, the Air District is also developing Regulation 13, Rule 4: Sewage Treatment Plants and Anaerobic Digesters to minimize emissions of greenhouse gases and volatile organic compounds from anaerobic digesters and sewage treatment plants. Draft Rule 13-4 would implement portions of the 2017 Clean Air Plan and is intended to create a consistent regulatory framework for these operations. In addition, the Air District is working on amendments to Regulation 8, Rule 34: Solid Waste Disposal Sites to better address emissions of methane and non-methane volatile organic compounds from solid waste disposal facilities and improve compliance and permitting for these facilities.

III. TECHNICAL REVIEW

A. Emissions

Based upon results from a comprehensive questionnaire submitted to hydrogen plant owners and operators, staff created an emissions inventory for methane emissions from the venting of hydrogen gas produced, distributed and used in petroleum refinery hydrogen plants. According to this data, the average total yearly methane emissions for each of the past six calendar years (2013 through 2018) from all hydrogen plants is approximately 2,300 tons per year; this is equivalent to about 170,000 metric tons of carbon dioxide based on 20-year time horizon. However, this value does not include methane emissions from deaerator vents or from carbon dioxide scrubbing vents because most hydrogen plant operators do not know the extent of methane emissions from these particular types of atmospheric vents. Occasional source tests performed in past years on deaerator and carbon dioxide scrubbing vents did not focus on methane emissions because, at the time, these source types were not known to emit methane. Thus, the actual amount of methane emissions from hydrogen plants is not fully known and is likely to be higher.

Table I: Hydrogen Plant Methane Emissions from Bay Area Petroleum Refineries

Facility	**2016 Methane Emissions** (tons per year)	**2017 Methane Emissions** (tons per year)	**2018 Methane Emissions** (tons per year)
Air Liquide [P66]*	0	0	0
Air Products [Marathon]*	0	0	0
Air Products [Shell]	17	4	84
Chevron Refinery*	0	0	0
Marathon Refinery*	0	0	0
P66 Refinery*	0	0	0
PBF Refinery [Shell]	995	1,677	649
Valero Refinery	708	2,060	608
TOTAL	**1,720**	**3,737**	**1,341**
Average annual emissions for methane = 2,266 tons per year for 2016, 2017 and 2018			

Source: Emissions reported in tons per year by hydrogen plant owners/operators in response to Air District hydrogen plant emissions questionnaire.

*Hydrogen plants reporting zero emissions control methane emissions by either recovering potential emissions and routing them to the refinery fuel gas system or they route methane gas to a flare where the gases are combusted.

Additionally, staff is reviewing reported emissions from hydrogen system operators and the emissions data measured from aerial flights conducted by NASA JPL to ensure consistency with results from the District's questionnaire.[k] Furthermore, staff is reviewing mass methane emissions reported by the hydrogen system operators and calculated mass emissions extrapolated from data collected during a recent investigation conducted by the Air District regarding petroleum refineries compliance with Regulation 8, Rule 2: Miscellaneous Operations to ensure consistency and accuracy.

Staff has yet to determine the extent of non-methane organic compounds vented from petroleum refinery hydrogen plants. Hydrogen plant operators do not monitor atmospheric vents for non-methane organic compound emissions. Normally, desulfurized natural gas is used as the feedstock during the steam methane reforming process. Very little non-methane organic compound emissions are vented from this process. However, when the feedstock includes desulfurized refinery fuel gas, emissions from atmospheric vents most likely include non-methane organic compounds because refinery fuel gas contains organic compounds other than methane. The amount of refinery fuel gas contained in steam methane reforming feedstock varies greatly depending on the percent makeup of refinery fuel gas in the feedstock. Therefore, the amount of non-methane organic compounds emitted to atmosphere from petroleum refinery hydrogen plant vents will vary substantially from one hydrogen plant to another.

B. Emission Control Methods

NOTE: Staff is currently seeking additional information on the methods, techniques and associated costs for controlling total organic compound emissions from hydrogen plants in general and specifically for deaerators and carbon dioxide scrubber vent controls. To acquire accurate emissions data, staff is proposing requirements for hydrogen plants to install flowrate meters and to perfrom total organic compound monitoring.

Because vented methane emissions from petroleum refinery hydrogen plants are not currently subject to emission limits, such emissions are usually uncontrolled unless the methane is a constituent of a gaseous stream that includes other air pollutants, such as volatile organic compounds, subject to emission limit requirements of another Air District regulation. However, not all volatile organic compound abatement technology will capture or control methane emissions. For example, activated carbon is commonly used to extract volatile organic compounds from gaseous streams via an adsorption process that traps volatile organic compound molecules onto the surface of carbon molecules while the remainder of the gaseous stream continues to flow through the carbon bed. However, methane is not typically captured by activated carbon so it flows through unabated.

One example of control technology that reduces methane as a co-benefit of reducing other air contaminants is a flare. Flares are used as a safety, not a control, device to reduce refinery gases that often may include a mixture of gases including volatile organic compounds, toxic air contaminants, oxides of nitrogen, sulfur oxides and methane. Nevertheless, one Bay Area refinery and one third-party operator use flares dedicated specifically to control hydrogen gas emissions, and thus, methane emissions and any associated organic compound emissions. These particular types of flares destroy total organic compound emissions at a minimum 98 percent control efficiency.

Thermal oxidizers are another example of control technology used to thermally destroy industrial vapor streams. They are commonly used in refineries and chemical plants to control hydrocarbon-based vapors. Typically, thermal oxidizers are available in four different types depending on a variety of operational factors. They include direct-fired, recuperative, catalytic and regenerative thermal oxidizers. Thermal oxidizers can be used for planned atmospheric venting occurrences such as startups and some shutdowns; however, they generally cannot be used for unplanned events such as malfunctions, upsets and emergencies.

A third method of controlling total organic compound emissions already employed at two local refineries is the use of a closed loop system, via flare headers, that captures hydrogen system gas streams, sometimes vented at other refineries, and reintroduces the captured gas into the refinery's fuel gas system. Only a small amount of captured total organic compound gas is vented to atmosphere because the gas recovery system only sends recovered gas to the flare for combustion for safety-related reasons such as emergencies, malfunctions, unplanned shutdowns, upsets and trips in the refinery system. The balance of captured gas is used in the gas recovery system. Less than two percent of flare header gas is emitted to the atmosphere post combustion. Flare headers, a collection system for refinery waste vapor streams, contains a mixture of refinery gases, including hydrogen gas.

Although not technically considered a control technology, use of pressure swing adsorption can significantly reduce methane and other organic compound emissions. Pressure swing adsorption purification is a method of separating one or more gas species from a gaseous stream containing additional (desirable) gas species. As mentioned earlier in this report, pressure swing adsorption is used in hydrogen production as a final purification step to separate hydrogen gas molecules from other (impure) gas molecules, such as methane, carbon monoxide and carbon dioxide. Under continuous pressure, an adsorbent material targets gas with dissimilar adsorption properties as an effective way of extracting very pure hydrogen.[i] As depicted in Figure 3 of this report, tail-gas, a byproduct of the pressure swing adsorption process containing the removed impurities, can then be sent back to the steam methane reformer as fuel for the steam methane reforming process. Normally, pressure swing adsorption purification removes methane molecules from the hydrogen gas stream only at the back end of the steam methane reforming process unit. Atmospheric venting prior to the pressure swing adsorption step contains methane and other air contaminants.

Figure 6: Image of several tanks containing the adsorbent material that comprise part of a pressure swing adsorption system

Source: https://www.petrosadid.com/fixed_equipment/process_package/pressure_swing_adsorption.php

Representatives from the Valero refinery and from Air Products, a third-party operator that recently purchased both hydrogen plants from the PBF refinery (formerly known as the Shell refinery), have indicated they are considering using refinery flare technology to control total organic compound emissions. Staff estimates control of total organic compound emissions with a flare system would result in a reduction of 2,221 tons of methane, assuming a flare control technology of 98 percent.[3] This methane reduction would be equivalent to a reduction of 173,322 metric tons of carbon dioxide equivalent using a global warming potential value of 86 based on a 20-year time horizon.[4]

[3] EPA 40 CFR § 63.670 are requirements for flare control devices to ensure refinery flares achieve a minimum 98 percent control efficiency.

[4] Carbon dioxide equivalent emissions calculated by converting 2,267 short tons to metric tons (2,056) then multiplied by global warming potential value of 86 expressed over 20 years.

IV. DRAFT RULE

A. Purpose

Draft Rule 13-5 is being developed to ensure that vented organic compounds, such as methane, volatile organic compounds, and toxic air contaminants are minimized from petroleum refinery hydrogen plants. Methane and organic compound emissions would be minimized during the production of hydrogen, the distribution of hydrogen and hydrogen consumption at various refinery process units.

B. Applicability

Draft Rule 13-5 would apply to petroleum refinery hydrogen plants, including third-party operators that produce hydrogen in hydrogen plants and other parts of the refinery that integrate the hydrogen into refinery processes. Recently, Air Products, a third-party operator, purchased two hydrogen plants from PBF Energy, a petroleum company that recently purchased the Shell petroleum refinery in the City of Martinez. Therefore, the PBF refinery will be the only Bay Area refinery that does not own and operate at least one hydrogen plant.

C. Exemptions

The requirements in draft Rule 13-5 are not intended to apply to methane, organic compound or total organic compound emissions already subject to other Air District rules. For example, fugitive total organic compound leaks from hydrogen plant equipment are already subject to the emission requirements in Rule 8-18: Equipment Leaks which addresses total organic compounds. Therefore, Rule 13-5 will not apply to emissions subject to Rule 8-18.

1. Exemption from Rule 8, Organic Compounds, Rule 2: Miscellaneous Operations

In addition, because Regulation 8, Rule 2: Miscellaneous Operations currently regulates non-methane organic compound emissions from miscellaneous sources, to avoid potential regulatory overlap with Rule 13-5, staff will propose the following language in Rule 8-2-118:

8-2-118 Exemption, Petroleum Refinery Hydrogen Plants: Organic compound emissions from petroleum refinery hydrogen plants are exempt from this rule provided they are subject to emission limits in Regulation 13, Rule 5.

Hydrogen plant operations that are currently subject to Rule 8-2 emission limits for non-methane emissions will continue to be until the TOC emission requirements are applicable.

2. Carbon Dioxide Scrubber Vents

Lastly, draft Rule 13-5 includes a limited exemption for atmospheric vents for both deaerators and carbon dioxide scrubbers. These two types of vents appear to emit methane and possibly other total organic compounds, however more investigation is required to ascertain the extent of emissions. Thus, deaerator vents and carbon dioxide scrubbing vents will be exempted from the emission limits in Rule 13-5. However, the owners/operators of these two source types will be required to install flowmeters and to monitor the total organic compound emissions on a periodic basis to verify total organic compound emission rates. If after monitoring for TOC emissions for a period one year, as required in Section 13-5-502, the data reflects that a deaerator vent or a carbon dioxide vent does not comply with the TOC emission requirements in Section 13-5-301, then Section 13-5-303 specifies that such vents will be subject to the emission requirements in Section 13-5-303.

D. Definitions

Because draft Rule 13-5 would be a new rule that limits emissions of a new contaminant, definitions are provided to clarify exemptions, standards and administrative requirements including monitoring and recordkeeping. The key definitions are new terms such as atmospheric vent, carbon dioxide scrubbing vent, gas recovery system, hydrogen plant and petroleum refinery hydrogen system, naphtha reforming unit and total organic compound. These and other definitions that reference existing regulations help to distinguish the applicability of this Rule from the applicability of other Air District Rules such as Regulation 8, Rule 18: Equipment Leaks; and Regulation 8, Rule 28: Episodic Releases from Pressure Relief Devices at Petroleum Refineries and Chemical Plants.

E. Standards

Draft Rule 13-5 would address methane and other organic compound emissions, in the form of total organic compounds emitted from refinery hydrogen plants as follows:

Section 13-5-301, Emission Limits for Existing Petroleum Refinery Hydrogen Plants, would prohibit the owner or operator of petroleum refinery hydrogen plants from venting to atmosphere hydrogen waste streams containing total organic compounds in excess of 15 pounds per day and containing a concentration of more of than 300 parts per million on a dry basis.

Section 13-5-302, Emission Limits for New Petroleum Refinery Hydrogen Plants, would prohibit the owner or operator of a new petroleum refinery hydrogen plant from venting to atmosphere hydrogen waste streams containing more than 0.01 percent (100 parts per million volume) total organic compounds by volume on a dry basis.

Section 13-5-303, Emission Limits for Deaerator Vents and Carbon Dioxide Scrubbing Vents, would prohibit the owner or operator of petroleum refinery hydrogen plants from venting to atmosphere hydrogen waste streams containing total organic compounds in excess of 15 pounds per day and containing a concentration of more of than 300 parts per million on a dry basis.

F. Administrative Requirements

Upon adoption of draft Rule 13-5 the owner or operator of an existing petroleum refinery hydrogen plant not already in compliance with the emission requirements in Rule 13-5 must apply for a permit to operate equipment to control total organic compound emissions. The owner or operator will have a total of five calendar years to design, purchase, apply for permits, install and operate total organic compound control equipment to comply with the requirements of Section 13-5-301.

Draft Rule 13-5 includes reporting requirements for owners or operators to notify the Air District of hydrogen plant atmospheric venting occurrences when total organic compound emissions exceed 15 pounds and the concentrations exceed 300 parts per million volume measured as methane on a dry basis. Within ten business days, a report of the event must be submitted to the Air District and include all parameters relating to emissions as well as the make and model of the control device. Any hydrogen plant built after Rule 13-5 is adopted must comply with the same notification requirements if total organic compound emissions from atmospheric venting exceed 0.01 percent (100 parts per million volume) methane by volume on a dry basis.

G. Monitoring and Records

The operator of a petroleum refinery hydrogen plant subject to the draft rule would have to monitor and record all parameters necessary to demonstrate compliance with the provisions contained in the standards section of draft Rule 13-5. Hydrogen plant atmospheric vents would be required to have flowrate meters installed. Operators of hydrogen plant deaerator vents and carbon dioxide scrubbing vents would have to install flowrate meters, recorders, sampling ports and must monitor total organic compound emissions. Because atmospheric venting from a pressure swing absorption unit that is properly maintained and operated should never exceed the total organic compound emission standards in Section 300 of Rule 13-5, the owner or operator of a hydrogen plant with a pressure swing absorption vent would not be required to maintain emission records unless the pressure swing absorption unit malfunctions, which would likely lead to an exceedance of the emissions standards in Section 13-5-300.

H. Manual of Procedures

Section 13-5-600, the Manual of Procedures section in Rule 13-5 would require petroleum refinery hydrogen system owners or operators to use one of the prescribed methods to determine total organic compound emissions either on a mass basis or a volumetric basis. A modification of South Coast Air Quality Management District Method 25.3 may be used, subject to Air District approval, to monitor methane mass emissions from deaerator vents or carbon dioxide scrubbing vents.[m]

V. RULE DEVELOPMENT / PUBLIC PARTICIPATION PROCESS

As part of the Rule 13-5 rule development process, staff reached out to petroleum refinery industry experts and environmental advocacy and community groups. Staff conducted a briefing with the Refinery Technical Workgroup community members on June 27, 2019, to familiarize them on the basic operations and primary processes of hydrogen plants, and thus, to better enable them to participate in Refinery Technical Workgroup discussions for the Rule 13-5 rule development project. Staff conducted the first Refinery Technical Workgroup meeting on July 17, 2019 to discuss the availability and feasibility of all potential vented methane emission controls for hydrogen production equipment/processes. Staff submitted a comprehensive questionnaire to all hydrogen plant operators requesting pertinent parametric and emissions data relating to all hydrogen venting occurrences during the past six years. The questionnaire was divided into two phases with a due date of November 18, 2019 for Phase I and a due date of January 10, 2020 for Phase II. In July and August of 2019, Air District staff visited all of the ten hydrogen plants, some of them twice, at all the refineries for a total of 15 visits spread among the five refineries within the Air District's jurisdiction. Staff typically had pre-meetings with refinery staff, including hydrogen plant operators, conducted tours of the hydrogen plants and, when necessary, held post-tour meetings to ask more questions and clarify information. A second round of tours were concluded in January 2020 to help staff identify possible controls for each hydrogen plant as each refinery is designed differently, and thus, may not be capable of using the same types of controls or install gas recovery systems in the same locations or with similar configurations as other refineries.

A workshop for draft Rule 13-5 was held in January 2020, at Air District headquarters. Staff met with Western States Petroleum Association and hydrogen system operators in March of this year to discuss the draft rule. As initially drafted, Rule 13-5 was based on the concept of controlling methane and organic compound emissions by requiring a minimum hydrogen gas purity when vented from hydrogen plant operations. Any control method currently used, including hydrogen gas recovery or hydrogen gas flaring would have resulted in the reduction of methane emissions and organic compound emissions based on control efficiency requirements.

Comments from industry included requests to change the emphasis in Rule 13-5 from controlling hydrogen gas purity to instead focus on addressing methane gas emissions. Furthermore, it was stressed that the four-year timeline to design, permit, purchase, and install controls for methane gas was not enough time, especially for the initial steps of designing and permitting controls. Other comments included concerns with potential duplication with existing Organic Rules; requests for exemptions for low-level methane emissions; and switching from percent weight standards to percent volume standards. The above concerns are addressed in the accompanying revision of draft Rule 13-5. The current version of draft Rule 13-5 addresses methane emissions in the form of “Total Organic Compounds,” which include both methane and other organic compounds. Modeled after the requirements in Regulation 8, Rule 2: Miscellaneous Operations, draft Rule 13-5 includes an emission limit of 15 pounds per day and 300 parts per million for total organic compounds.

Staff anticipates bringing this rule before the Board of Directors for consideration in December, 2020.

REFERENCES

[a] Forster P., et al. (2007) Changes in Atmospheric Constituents and in Radiative Forcing, in Solomon S. et al. (2007) Climate Change 2007: Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Figure 2.21.

[b] "Hydrogen: A Clean, Flexible Energy Carrier," Office of Energy Efficiency & Renewable Energy, February 21, 2017. https://www.energy.gov/eere/articles/hydrogen-clean-flexible-energy-carrier

[c] "The Hydrotreating Process Part 1," What-When-How, The Hydrotreating Process Part 1, http://what-when-how.com/petroleum-refining/the-hydrotreating-process-part-1/

[d] "Hydrogen - the key refinery enabler," Digital Refining, Processing, Operations & Maintenance, August 2012, https://www.digitalrefining.com/article/1000575,Hydrogen___the_key_refinery_enabler.html#.XaifCuhKgRk

[e] Compiled comments from representatives of several refineries and one independent third-party hydrogen plant operator during hydrogen plant tours by Air District staff in July 2019.

[f] BAAQMD Regulation 8, Rule 18: Equipment Leaks; http://www.baaqmd.gov/~/media/dotgov/files/rules/reg-8-rule-18-equipment-leaks/documents/rg0818.pdf?la=en

[g] South Coast Air Quality Management District, Rule 1189: Emissions from Hydrogen Plant Process Vents, http://www.aqmd.gov/docs/default-source/rule-book/reg-xi/rule-1189.pdf?sfvrsn=4

[h] Guha, A., Newman, S., Fairley, D., Dinh, T.H., Duca, L., Conley, S.C., Smith, M., Thorpe, A., Duren, R., Cusworth, D., Foster, K., Fischer M.L., and Martien, P.T., 2020, Assessment of regional methane emissions inventories through airborne quantification in the San Francisco bay area, in prep.

[i] Title 17, California Code of Regulations, section 95800 et seq.

[j] Greenhouse Gas Reporting Program (GHGRP), United States Environmental Protection Agency, https://www.epa.gov/ghgreporting

[k] "California's methane super-emitters," Nature, Novermber 6, 2019, https://www.nature.com/articles/s41586-019-1720-3

[l] "Hydrogen Recovery by Pressure Swing Adsorption," The Linde Group, https://www.linde-engineering.com/en/images/HA_H_1_1_e_09_150dpi_NB_tcm19-6130.pdf

[m] South Coast Air Quality Management District Methods & Procedures, Chapter VI, Method 25.3 – Low Concentration Non-Methane Non-Ethane Organic Compound from Clean Fueled Combustion Sources