San Joaquin Valley Air Pollution Control District

Best Available Control Technology (BACT) Guideline 1.8.Y

Emission Unit:Hydrogen Production - Steam HydrocarbonIndustry Type:HydrogenReformer:Process HeaterProduction

Last Update: March 1, 2024

Equipment Rating: Up to 60 tons of hydrogen production per day, 184 MMBtu/hr Process Heater

Pollutant	Achieved in Practice or contained in SIP	Technologically Feasible	Alternate Basic Equipment	
NOx	Process heater meeting a limit of 2.7 ppmv @ 3% O2	Process Heater meeting 2.5 ppmv @ 3% O ₂	1) Hydrogen production via electrolysis	
SOx	Process heater firing on a fuel meeting the District Rule 4320 fuel sulfur requirement of 5 grains S/100 dscf		 2) Hydrogen production via partial oxidation process (¹), autothermal reforming 	
PM10	Process heater meeting a limit of 0.0039 lb/MMBtu		or gasification	

(¹) Partial oxidation includes the Grannus Process[™] (2023)

BACT is the most stringent control technique for the emissions unit and class of source. Control techniques that are not achieved in practice or contained in a state implementation plan must be cost effective as well as feasible. Economic analysis to demonstrate cost effectiveness is required for all determinations that are not achieved in practice or contained in an EPA approved State Implementation Plan.

*This is a Summary Page for this Class of Source – Permit Specific BACT Determinations on Next Page(s)

New BACT ANALYSIS Hydrogen Production – Steam Hydrocarbon Reformer: Process Heater

Facility Name: Aemetis Advanced Products Riverbank

Engineer: James Harader Lead Engineer: Nick Peirce

Project #: N-9742, N-1224324

I. PROPOSAL

The proposed hydrogen production plant steam-naphtha reformer includes an 184 MMBtu/hr process heater fired on off-gas from the pressure swing adsorber. The process heater creates the steam uses in the steam-naphtha reformer. This new-BACT analysis will address the hydrogen production plant and the main emission unit associated with the hydrogen production process, the 184 MMBtu/hr process heater.

II. PROCESS DESCRIPTION

Hydrogen Production Background:

Hydrogen is a common raw material for many types of products. It is used in processes like energy storage, thermal heating, industrial processes (e.g., manufacture of polymers, methanol), transportation, electricity production, synthesis of synthetic fuels, upgrading oil, and ammonia/fertilizer production. However, to be of use in the proposed process, it first must be separated into pure H2 in order for it to be used as a building block for the proposed sustainable aviation fuel and renewable diesel products.

Proposed Hydrogen Production Method:

Most hydrogen produced today in the United States is performed via steam-methane reforming, a mature production process in which high-temperature steam (700°C– 1,000°C) is used to produce hydrogen from a methane source, such as natural gas. In steam-methane reforming, methane reacts with steam in the presence of a catalyst to produce hydrogen, CO, and a relatively small amount of CO2. This method is endothermic (i.e., heat must be supplied to the process for the reaction to proceed).

In a subsequent process called the "water-gas shift reaction," the carbon monoxide (CO) and steam are reacted using a catalyst to produce CO2 and more hydrogen. In a final process step called "pressure-swing adsorption" process, the CO2 and other impurities are removed from the gas stream leaving essentially pure hydrogen.

Steam-methane reforming reaction CH4 + H2O (+ heat) \rightarrow CO + 3H2

Water-gas shift reaction CO + H2O \rightarrow CO2 + H2 (+ small amount of heat)

Alternatively, other hydrocarbons, such as naphtha, may be used as feedstock rather than methane using a similar steam reforming process. For the proposed hydrogen plant, waste naphtha generated by the proposed HydroFlex fuel production operation will be reformed into hydrogen to be used to hydrogenate the feedstocks such as vegetable oils and animal fats.

Steam-hydrocarbon reforming is an endothermic process, meaning it requires heat to be input into the process. For this type of process, heat is input in the form of steam. The steam for the steam-hydrocarbon reforming reaction is generated by the 184 MMBtu/hr process heater that is fired on off-gas from the pressure swing adsorber. The "off gas" is a mixture of unreacted hydrocarbons (naptha, methane, etc.) from the Hydrogen production operation.

BACT is triggered for NOx, SOx and PM₁₀ from the process heater that generates steam for the steam-hydrocarbon reforming process.

III. Top-Down BACT Analysis

BACT analysis for NOx Emissions

Step 1 - Identify All Possible NOx Control Technologies

The following BACT clearinghouse references were reviewed to determine the control technologies that have been required for NOx from hydrogen plant process heaters.

- EPA RACT/BACT/LAER (RBLC) clearinghouse
- CARB BACT clearinghouse
- South Coast AQMD (SCAQMD) BACT clearinghouse
- Bay Area AQMD (BAAQMD) BACT clearinghouse
- Sacramento Metro AQMD (SMAQMD) BACT clearinghouse
- San Joaquin Valley APCD (SJVAPCD) BACT clearinghouse
- Monterey Bay Air Resources District (MBARD) BACT clearinghouse
- Santa Barbara County APCD (SBAPCD) BACT clearinghouse

The following table shows the results of the search of the EPA RBLC:

Hydrogen Production – Process Heaters > 20 MMBtu/hr from EPA RBLC				
RBLC ID Facility Name	Fuel Equipment Rating	NOx Limit		
TX-0865 Equistar Chemicals	Natural Gas and Process Gas 202 MMBtu/hr	5 ppmvd @ 3% O ₂ (0.006 lb/MMBtu)		
AR-0162 Energy Security Partners	Fuel Gas 391.5 MMBtu/hr	0.03 lb/MMBtu		
TX-0933 Nacero Penwell	Natural Gas and Fuel Gas Not Provided	0.015 lb/MMBtu		
LA-0346 IGP Methanol	Not Identified 522 MMBtu/hr	0.017 lb/MMBtu		
SC-0182 Fiber Industries	Not Identified Not Provided	0.05 lb/MMBtu		
LA-0291 Sasol Chemicals Unit #1	Process Gas 73.8 MMBtu/hr	0.038 lb/MMBtu		
LA-0291 Sasol Chemicals Unit #2	Process Gas 424.8 MMBtu/hr	0.1 lb/MMBtu		
AR-0173 Big River Steel LLC	Process Gas 75 MMBtu/hr	0.1 lb/MMBtu		

The CARB BACT Clearinghouse was searched and applicable BACT Guidelines/Determinations were found from SCAQMD and BAAQMD. The requirements of these guidelines are discussed below.

South Coast BACT Requirements				
Category/Determination	BACT Requirement for NOx			
Process Heater – Non Refinery BACT Guideline for Non-Major Pollution Facilities (page 104 of BACT Guidelines Part D)	Compliance with South Coast Rule 1146			
Application #326118	2.7 ppmv @ 3% O ₂			
Hydrogen Reforming Furnace	(0.0032 lb/MMBtu)			
Application #337979	5 ppmv @ 3% O ₂			
Hydrogen Reforming Furnace	(0.006 lb/MMBtu)			
Application #411357	5 ppmv @ 3% O ₂			
Hydrogen Reforming Furnace	(0.006 lb/MMBtu)			
Application #389926	5 ppmv @ 3% O ₂			
Hydrogen Reforming Furnace	(0.006 lb/MMBtu)			

Bay Area AQMD BACT Requirements*				
Category/Determination	BACT Requirement for NOx			
Heater – Refinery Process ≥ 50 MMBtu/hr	 5 ppmvd NOx @ 3% O₂ (Achieved in Practice, 0.006 lb/MMBtu) 			
Heater – Refinery Process, Natural or Induced Draft 5 MMBtu/hr to < 50 MMBtu/hr	 25 ppmvd NOx @ 3% O₂ (Achieved in Practice, 0.030 lb/MMbtu) 10 ppmvd NOx @ 3% O₂ (Technologically Feasible, 0.012 lb/MMBtu) 			
Heater – Refinery Process, Forced Draft 5 MMBtu/hr to < 50 MMBtu/hr	 20 ppmvd NOx @ 3% O₂ (Achieved in Practice, 0.024 lb/MMBtu) 10 ppmvd NOx @ 3% O₂ (Technologically Feasible, 0.012 lb/MMBtu) 			

*Bay Area AQMD only has BACT Guidelines listed for process heaters at Refineries. Although this BACT Guideline is not applicable to refinery units, refinery process heaters operate similarly to non-refinery process heaters. Therefore, the requirements have been included as a reference point for the emission levels that have been achieved in similar units to those being evaluated in this project.

Monterey Bay ARD, Sacramento Metro AQMD, Santa Barbara County APCD, and San Joaquin Valley APCD Clearinghouses do not include Guidelines that would apply to process heaters > 20 MMBtu/hr.

A review of District, State and Federal rules revealed the following requirements:

Rule	Requirements for NOx
	≥ 20 MMBtu/hr and ≤ 75 MMBtu/hr
SCAQMD Rule 1146	5 ppmvd @ 3% O ₂ (0.006 lb/MMBtu)
Emissions of Oxides of Nitrogen from Industrial, Institutional, and Commercial Boilers, Steam	<u>> 75 MMBtu/hr</u>
Generators, and Process Heaters	5 ppmvd @ 3% O ₂ (0.006 lb/MMBtu)
	≥ 20 MMBtu/hr and ≤ 75 MMBtu/hr
BAAQMD Regulation 9 Rule 7	
	9 ppmvd @ 3% O ₂
Nitrogen Oxides and Carbon Monoxide from Industrial,	(0.011 lb/MMBtu)
Institutional, and Commercial	<u>> 75 MMBtu/hr</u>
Boilers, Steam Generators, and	
Process Heaters	5 ppmvd @ 3% O ₂
	(0.006 lb/MMBtu)
SMAQMD Rule 411	<u>≥ 20 MMBtu/hr</u>

NOx from Boilers, Process	30 ppmvd @ 3% O ₂
Heaters, and Steam Generators	(0.036 lb/MMBtu)
SBCAPCD Rule 342	<u>> 20 MMBtu/hr</u>
Boilers, Steam Generators, and	7 ppmvd @ 3% O ₂
Process Heaters	(0.0084 lb/MMBtu)
MBARD Rule 441	<u>≥ 20 MMBtu/hr</u>
Boilers, Steam Generators, and Process Heaters	9 ppmvd @ 3% O ₂ (0.011 lb/MMBtu)
	> 20 MMBtu/hr and ≤ 75 MMBtu/hr
SJVAPCD Rule 4306 Boilers, Steam Generators and	7 ppmvd @ 3% O ₂ (0.0084 lb/MMBtu)
	> 75 MMBtu/hr
Process Heaters – Phase 3	
	5 ppmvd @ 3% O ₂
	(0.006 lb/MMBtu)
	> 20 MMBtu/hr and \leq 75 MMBtu/hr
SJVAPCD Rule 4320	2.5 ppmvd @ 3% O ₂ (0.003 lb/MMBtu) or pay Fees Pursuant to Section 5.3 of Rule 4320
Advanced Emission Reduction	
Options for Boilers, Steam	> 75 MMBtu/hr
Generators, and Process Heaters	<u> </u>
	2.5 ppmvd @ 3% O ₂ (0.003 lb/MMBtu) or pay Fees Pursuant to Section 5.3 of Rule 4320

A review of District permits for process heaters equal to or greater than 20 MMBtu/hr revealed the following operations:

Facility Permit	Permit Limit for NOx
Alon Bakersfield Refining S-33-53-22 Two 65 MMBtu/hr process gas- fired heaters, a 34.7 MMBtu/hr process gas-fired heater, a 22.7 MMBtu/hr process gas-fired heater, and a 25 MMBtu/hr process gas-fired heater	30 ppmv @ 3% O₂ (0.036 lb/MMBtu)
Alon Bakersfield Refining S-33-55-23	5 ppmv @ 3% O ₂ (0.006 lb/MMBtu)

233	MMBtu/hr	process	gas-fired
heat	ter		

The following control options were identified based on the above information:

Option 1: 2.7 ppmv NOx @ 3% O₂ for units rated > 20 MMBtu/hr

South Coast AQMD has permitted a unit with a NOx limit of 2.7 ppmvd @ 3% O₂ (Howe Baker Engineers, Application #326118). Furthermore, the heater was operated using pressure swing adsorber off-gas, similar to the proposed unit. This level of control is therefore considered to be achieved in practice.

Option 2: 5 ppmvd NOx @ 3% O₂ for units rated > 20 MMBtu/hr

This control option is based upon South Coast AQMD Rule 1146 Requirements. Additionally, multiple units were identified above, throughout the size range, that are currently limited to and have demonstrated compliance with 5 ppmvd NOx. However, this option is less stringent than option #1, which is achieved in practice; therefore, this option has been eliminated from consideration.

Option 3: 2.5 ppmvd NOx @ 3% O₂ for units rated > 20 MMBtu/hr

This control option is based upon San Joaquin Valley Air Pollution Control District Rule 4320 requirements. No units were identified that are currently limited to or complying with this emission level.

In addition to the above control options, alternate methods of hydrogen do not require the use of a process heater. These methods are considered to be alternate basic equipment. These options are described below:

Alternate Methods of Producing Hydrogen

• <u>Autothermal Reforming (ATR)</u>: This process uses oxygen and CO2 or steam in a reaction with methane, or other hydrocarbons, to form synthetic gas, also known as syngas. The reaction takes place in a single chamber where the methane/hydrocarbon is partially oxidized. The reaction is exothermic (i.e., heat is released) due to the oxidation.

The key difference between steam reforming and autothermal reforming is that steam reforming uses the reaction of hydrocarbons with water, whereas autothermal reforming uses the reaction of methane with oxygen and CO2 or steam to form synthetic gas. Moreover, steam reforming is an endothermic reaction while autothermal reforming is an exothermic reaction. The reactions can be described in the following equations, using CO2:

 $2 \text{ CH4} + \text{O2} + \text{CO2} \rightarrow 3 \text{ H2} + 3 \text{ CO} + \text{H2O}$

And using steam:

 $4 \text{ CH4} + \text{O2} + 2 \text{ H2O} \rightarrow 10 \text{ H2} + 4 \text{ CO}$

Since this process is exothermic, a process heater is not required. Therefore, combustion emissions are not generated by the autothermal reforming process.

 <u>Partial Oxidation</u>: This method is a type of chemical reaction in which methane and other hydrocarbons in natural gas react with a limited amount of oxygen that is not enough to completely oxidize the hydrocarbons to CO2 and water. With less than the stoichiometric amount of oxygen available, the reaction products contain primarily hydrogen and CO (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a relatively small amount of CO2 and other compounds. In a subsequent water-gas shift reaction, the CO reacts with water to form CO2 and more hydrogen.

Partial oxidation is an exothermic process that is typically much faster than steam reforming and requires a smaller reactor vessel. As can be seen in chemical reactions of partial oxidation, this process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel.

Partial oxidation of methane reaction

 $CH4 + \frac{1}{2}O2 \rightarrow CO + 2H2 \text{ (+ heat)}$

Water-gas shift reaction

 $CO + H2O \rightarrow CO2 + H2$ (+ small amount of heat)

This process is exothermic; therefore, a process heater is not required and combustion emissions are not expected from this process.

 <u>Grannus Process</u>: Another process to be considered is the Grannus Process[™], a patented exothermic chemical process that integrates a partial oxidation gas boiler with the water gas shift process to make hydrogen synthetic gas as described in its website at: <u>https://grannusllc.com/technology/</u> and in SJVAPCD project S-8943/S-1163737. Although the above-mentioned SJVAPCD project issued only an Authority to Construct permit for the installation of a 7.9 MW (nominal ISO rating) electric power generation system (combined cycle configuration) consisting of a natural gas-fired gas turbine engine with heat recovery steam generator (HRSG), that same project determined that the other ammonia plant equipment did not require permits because the plant's emissions units qualified as Low-Emitting Units. The electric power generation system was to provide electrical power and steam to the proposed anhydrous ammonia manufacturing equipment located at the same site at the South Kern Industrial Center in Kern County. However, it should be noted that the facility was not built and the ATC has expired. As proposed in this project, the turbine listed above provided the power; however, the plant can be operated on standard industrial power supplied by the electrical grid.

The anhydrous ammonia fertilizer manufacturing facility that was proposed in that project would have had a capacity of producing 250 tons of anhydrous ammonia fertilizer per day (or the equivalent of approximately 46 tons of hydrogen per day). This plant would have been the first demonstration plant for the Grannus Process[™], a process that makes anhydrous ammonia from pipeline natural gas (methane) and water. A detailed description and process flow diagrams are found in the file for project S-1163737. As proposed, the operation relies on certain streams being sent to a gas turbine's heat recovery steam generator for disposal as is explained in the project evaluation.

The Grannus Process includes additional equipment such as an Air Separation Unit and its storage. This equipment requires a footprint of one-half of an acre.

For this BACT Analysis, the Grannus Process will be included in the Partial Oxidation category, since the Grannus Process uses a nearly identical process to produce hydrogen.

 <u>Gasification</u>: This process produces a synthetic gas by reacting coal, petroleum coke, or biomass with high-temperature steam and oxygen in a pressurized gasifier. The resulting synthetic gas contains hydrogen and CO, which is reacted with steam to separate the hydrogen. Using coal gasification with a water gas shift approach produces a pure hydrogen fuel which can be combusted in gas turbines, in fuel cells, and in other applications. In current practice, large-scale coal gasification installations are primarily for electricity generation, or for production of chemical feedstocks. The hydrogen obtained from coal gasification can be used for various purposes such as making ammonia, powering a hydrogen economy, or upgrading fossil fuels.

This process requires high-temperature steam, similar to the steam methane reforming process. Therefore, a reduction in combustion emissions is not expected.

• <u>Electrolysis</u>: An electric current splits water into hydrogen and oxygen. If the electricity is produced by renewable sources, such as solar or wind, the resulting hydrogen will be considered renewable as well, and has numerous emissions benefits. Power-to-hydrogen projects are becoming more common, using excess renewable electricity, when available, to make hydrogen through electrolysis.

This process does not require high temperature steam and uses renewable energy, such as solar or wind, to generate the electricity necessary for the electrolysis process. Therefore, a process heater is not required and combustion emissions are not expected.

Several hydrogen production methods are in development, so their potential use in a large commercial project is still not known. Those methods include the following:

- <u>High-Temperature Water Splitting</u>: High temperatures generated by solar concentrators or nuclear reactors drive chemical reactions that split water to produce hydrogen.
- <u>Photobiological Water Splitting</u>: Microbes, such as green algae, consume water in the presence of sunlight and produce hydrogen as a byproduct.
- <u>Photoelectrochemical Water Splitting</u>: Photoelectrochemical systems produce hydrogen from water using special semiconductors and energy from sunlight.
- <u>Pyrolysis</u>: Pyrolysis of natural gas is an endothermic process that occurs in the absence of oxygen to form hydrogen and a solid carbon product. It is thought to be a good method for production of carbon black, but the potential as a source of hydrogen production with low CO2 emissions is still in the development stages. It is believed that more work is needed to better understand its market applications and limitations for commercial projects.

- <u>Photolytic Processes</u>: These processes use light energy to split water into H2 and O2. These processes are currently in the early stages of development and currently are not viable for large-scale production.
- <u>Renewable Liquid Reforming</u>: Renewable liquid fuels, such as ethanol, are reacted with high-temperature steam to produce hydrogen near the point of end use.
- <u>Fermentation</u>: Biomass is converted into sugar-rich feedstocks that can be fermented to produce hydrogen.

Step 2 - Eliminate Technologically Infeasible Options

In the second step, the technological feasibility of the control options identified in Step 1 is evaluated with respect to the source-specific or emissions unit-specific factors. To exclude a control option, a demonstration of technical infeasibility must be clearly documented and should show, based on physical, chemical, and engineering principles, the technical difficulties would preclude the successful use of the control option for the emissions unit under review.

High-temperature Water Splitting, Photobiological Water Splitting, Photoelectrochemical Water Splitting, Pyrolysis, Photolytic Processes, Renewable Liquid Reforming, and Fermentation are experimental technologies that are not yet commercialized. Therefore, these technologies will be removed from consideration.

Gasification is a commercial technology; however, it would require coal feedstock to be delivered to the facility and will not displace the proposed feedstock used in the proposed production of the biofuels. Furthermore, gasification also requires high-temperature steam which would be generated from combustion; therefore, gasification isn't believed to currently reduce criteria pollutant emissions from the proposed levels for the steam-hydrocarbon reforming operation. Therefore, this technology will be removed from consideration.

Rank	Capture and Control Efficiency	Status
1. Electrolysis	N/A	Alternate Basic Equipment
2. Autothermal Reforming	N/A	Alternate Basic Equipment
3. Partial Oxidation/Grannis Process	N/A	Alternate Basic Equipment
4. 2.5 ppmvd NOx @ 3% O ₂	N/A	Technologically Feasible
5. 2.7 ppmvd NOx @ 3% O ₂	N/A	Achieved in Practice

Step 3 - Rank Remaining Control Technologies by Control effectiveness

Step 4 - Cost Effectiveness Analysis

Cost Analyses for Alternate Basic Equipment Options

Electrolysis, Autothermal Reforming, and Partial Oxidation are considered to be alternate basic equipment, since these are alternative processes for producing hydrogen. District Policy APR 1305, *Best Available Control Technology (BACT)*, provides guidance for determining whether alternate basic equipment or processes are cost effective. The following formula is typically used:

CE_{alt} = (Cost_{alt} - Cost_{Basic}) / (Emission_{Basic} - Emission_{alt})

Where,

 CE_{alt} = cost effectiveness of alternate basic equipment expressed as dollars per ton of emission reduced.

Cost_{alt} = The equivalent annual capital cost of the alternate basic equipment plus its annual operating cost

Cost_{Basic} = The equivalent annual capital cost of the basic equipment, without BACT, plus its annual operating cost

 ${\sf Emission}_{{\sf Basic}}$ = the emissions from the proposed basic equipment, without BACT

Emission_{alt} = the emissions from the alternate basic equipment

The CE_{alt} (\$/ton) is then compared to the cost effectiveness threshold for the pollutant to determine whether the alternate basic equipment is cost effective.

In cases where multiple pollutants are controlled, a traditional cost effectiveness threshold in \$/ton is not typically used. Rather, a multi-pollutant cost effectiveness threshold (MCET) is calculated using the following formula

 $MCET = \sum (ton of emission reduction pollutant_i) x (cost effectiveness threshold pollutant_i),$

Only pollutants that are triggered for BACT are included in calculations to determine the MCET. This method establishes a \$/year cost effectiveness threshold, rather than a \$/ton threshold.

While the District's BACT Policy doesn't specifically provide guidance on using the MCET for alternate basic equipment, use of the MCET is the most conservative approach; therefore, the MCET will be used to determine the cost effectiveness threshold, and the annual cost will be determined by subtracting $Cost_{Basic}$ from $Cost_{alt}$.

CostBasic for Steam-hydrocarbon Reforming

The US Department of Energy National Energy Technology Laboratory publication, *Comparison of Commercial, State-of-the-Art, Fossil-Based Hydrogen Production Technologies (April 2022)*¹, includes a highly detailed cost analysis for steam-methane reforming. A levelized cost of hydrogen of \$1.06 per kilogram of hydrogen was derived from the cost analysis. The levelized cost of hydrogen includes capital costs, maintenance costs, owners' costs, and operating costs. However, the levelized cost of hydrogen assumes that methane is purchased and then processed into hydrogen. The proposed hydrogen plant is nearly 100% fueled from naphtha and hydrocarbon waste gases generated by the proposed HydroFlex plant (N-9742-20-0). Therefore, the cost of methane, \$0.77/kilogram of hydrogen, will be deducted from the total levelized cost of hydrogen produced in the publication; however, that value was based on an electricity cost of \$71.70/MWh of electricity used. The latest electricity cost for industrial usage in California is \$207.2/MWh of

https://www.netl.doe.gov/projects/files/ComparisonofCommercialStateofArtFossilBasedHydrogenProductionTechnologies_041222.pdf

electricity²; therefore, the electricity cost/kilogram of hydrogen produced was increased to 0.1302 ($0.04507/Kg H_2 \times 207.2/MWh \div 71.70/MWh$). Thus, the adjusted levelized cost of hydrogen (LCOH) is: LCOH_{adjusted} = $1.06/Kg H_2 - 0.77/Kg H_2 + (0.1302 - 0.04507)/Kg H_2$ LCOH_{adjusted} = $0.38/Kg H_2$

The hydrogen production plant has a rated output of 61,422 Kg H₂/day. Thus, the annualized cost is:

 $Cost_{Basic} = 61,422 \text{ Kg H}_2/day x 365 \text{ days/year } x \$0.38/\text{Kg H}_2$ $Cost_{Basic} = \$8,519,231/year$

Emissions Basic for Steam Methane/Organic Reforming

Emissions_{Basic} is the emissions from the proposed equipment, without BACT. Since the alternate basic equipment would potentially displace multiple emission units (process heater, process vents, and fugitive components), all of these emission units will be included in the analysis. However, only pollutants that trigger BACT from these emission units will be included.

The proposed basic equipment includes a process heater that triggers BACT for NOx, SOx, and PM_{10} emissions. The process heaters do not include addon controls for SOx and PM_{10} ; therefore, the proposed emission rates are "without BACT". The proposed NOx emission rate is based on the Rule 4320 emission limit; therefore, that emission rate is also "without BACT".

The plant also includes hydrogen vents that trigger BACT for VOC emissions. The hydrogen vents are controlled by a thermal oxidizer which is a BACT control. Therefore, the emission rate included below is based upon uncontrolled emissions from the hydrogen vents, without BACT controls.

Additionally, the steam reformer emits fugitive emissions that trigger BACT for VOC emissions. The proposed fugitive emission rate are without BACT.

	Annual Emissions: Permit Unit N-9742-21					
Pollutant	Process Heater W/O BACT (lb/year)Process Vent W/O BACT (lb/year)Fugitives (lb/year)Total (lb/year)Total (tons/year)					
NOx	9,720	0	0	9,720	4.86	
SOx	20,470	0	0	20,470	10.24	
PM10	6,125	0	0	6,125	3.06	

² <u>https://www.eia.gov/electricity/monthly/epm_table_grapher.php?t=epmt_5_6_a</u>

VOC	0 ³	36,900 ⁴	3,030	39,930	19 97
100	0	50,500	0,000	00,000	15.57

ABE Option 1: Electrolysis Cost Effectiveness

Costalt for Electrolysis

Pursuant to the DOE NETL website (<u>https://netl.doe.gov/research/carbon-management/energy-systems/gasification/gasifipedia/technologies-hydrogen</u>), the levelized cost of hydrogen from electrolysis ranges from \$4.15 to \$10.30 per kilogram of hydrogen produced. The \$4.15/kg H₂ value will be conservatively used, without any adjustments.

Cost_{alt} = 61,422 Kg H₂/day x 365 days/year x \$4.15/Kg H₂ Cost_{alt}= \$93,038,975/year

Emissionsalt for Electrolysis

 $Emissions_{alt} = 0$ for all pollutants

MCET for Electrolysis

Electrolysis reduces all emissions to zero. Therefore, all emissions from the steam reforming process are reduced by this technology.

- $MCET = \sum$ (ton of emission reduction pollutant_i) x (cost effectiveness threshold pollutant_i),
- MCET = 4.86 tons-NOx/year x \$35,300/ton +10.24 tons-SOx/year x \$20,400/ton + 3.06 tons-PM10 x \$12,800/ton + 19.97 tons-VOC x \$25,300/ton

MCET = \$924,863/year

Cost Effectiveness for Electrolysis

Cost Effectiveness = Cost_{alt} – Cost_{Basic} Cost Effectiveness = \$93,038,975/year -\$ 8,519,231/year Cost Effectiveness = \$84,519,744/year

Since this value is greater than the MCET of \$924,863/year, electrolysis is not cost effective.

³ The process heater did not trigger BACT for VOC emissions. Therefore, process heater emissions are equal to zero in this analysis.

⁴ District BACT Policy states that emission rates considered are prior to applying BACT. Thus, the control efficiency of the thermal oxidizer serving the hydrogen production vents was not considered when determining Emissions_{Basic} for the process vent.

ABE Option 2: Autothermal Reforming Cost Effectiveness

Costalt_for Autothermal Reforming

The US Department of Energy National Energy Technology Laboratory publication, Comparison of Commercial, State-of-the-Art, Fossil-Based Hydrogen Production Technologies (April 2022), includes a highly detailed cost analysis for autothermal reforming. A levelized cost of hydrogen of \$1.51 per kilogram of hydrogen was derived from the cost analysis, with no carbon sequestration. The levelized cost of hydrogen includes capital costs, maintenance costs, owners' costs, and operating costs. However, the levelized cost of hydrogen assumes that methane is purchased and then processed into hydrogen. The proposed hydrogen plant is nearly 100% fueled from naphtha and hydrocarbon waste gases generated by the proposed HydroFlex plant. Therefore, the cost of methane, \$0.77/kilogram of hydrogen, will be deducted from the total levelized cost of hydrogen. Additionally, electricity costs accounted for \$0.2121/kilogram of hydrogen produced in the publication (after excluding 25% of the power that was allocated towards carbon sequestration); however, that value was based on an electricity cost of \$71.70/MWh of electricity used. The latest electricity cost for industrial usage is \$207.2/MWh of electricity; therefore, the electricity cost/kilogram of hydrogen produced (without carbon sequestration) was increased to \$0.6129 (\$0.2121/Kg H₂ x \$207.2/MWh ÷ \$71.70/MWh). Thus, the adjusted levelized cost of hydrogen (LCOH) is:

 $LCOH_{adjusted} =$ \$1.51/Kg H₂ - \$0.77/Kg H₂ + (\$0.6129 - \$0.2121)/Kg H₂ $LCOH_{adjusted} =$ \$1.14/Kg H₂

The hydrogen production plant has a rated output of 61,422 Kg H₂/day. Thus, the annualized cost is:

Cost_{alt} = 61,422 Kg H₂/day x 365 days/year x \$1.14/Kg H₂ Cost_{alt} = \$25,557,694/year

Emissionsalt for Autothermal Reforming

Autothermal reforming is expected to eliminate combustion emissions and to significantly reduce process vent emissions; however, fugitive emissions are still expected. Thus, the emissions from the autothermal reforming process are conservatively calculated below using only the fugitive emission rate:

Emissions_{alt} = 3,030 lb-VOC/year x ton/2000 lb = 1.515 tons-VOC/year

MCET for Autothermal Reforming

- $MCET = \sum$ (ton of emission reduction pollutant_i) x (cost effectiveness threshold pollutant_i),
- MCET = 4.86 tons-NOx/year x \$35,300/ton +10.24 tons-SOx/year x \$20,400/ton + 3.06 tons-PM10 x \$12,800/ton + (19.97 tons-VOC -1.515 tons-VOC) x \$25,300/ton

MCET = \$886,534/year

Cost Effectiveness for Autothermal Reforming

Cost Effectiveness = Cost_{alt} – Cost_{Basic} Cost Effectiveness = \$25,557,694/year –\$ 8,519,231/year Cost Effectiveness = \$17,038,463/year

Since this value is greater than the MCET of \$886,534/year, autothermal reforming is not cost effective.

ABE Option 3: Partial Oxidation/Grannus Process Cost Effectiveness

Costalt for Partial Oxidation/Grannus Process

The US Department of Energy National Energy Technology Laboratory publication, Comparison of Commercial, State-of-the-Art, Fossil-Based Hydrogen Production Technologies (April 2022), includes a highly detailed cost analysis for autothermal reforming. While this analysis was performed for autothermal reforming, several components of a partial oxidation process are identical to the components in an autothermal reforming process. Specifically, an air separation unit is needed to produce oxygen for the both processes. In the DOE study, electricity costs accounted for \$0.2121/kilogram of hydrogen produced in the publication (after excluding 25% of the power that was allocated towards carbon sequestration); however, that value was based on an electricity cost of \$71.70/MWh of electricity used. The latest electricity cost for industrial usage is \$207.2/MWh of electricity; therefore, the electricity cost/kilogram of hydrogen produced (without carbon sequestration) was increased to \$0.6129. Thus, the adjusted levelized cost of hydrogen (LCOH) for partial oxidation, using only the cost of electricity for the air separation unit, is:

LCOH_{adjusted} = \$0.6129/Kg H2

The hydrogen production plant has a rated output of $61,422 \text{ Kg H}_2/\text{day}$. Thus, the annualized cost is:

Cost_{alt} = 61,422 Kg H₂/day x 365 days/year x \$0.6129/Kg H₂ Cost_{alt}= \$13,740,623/year

Emissionsalt for Partial Oxidation/Grannus Process

Partial Oxidation eliminates combustion and significantly reduces process vent emissions; however, fugitive emissions are still expected. Therefore, only fugitive emissions are included for Emissions_{alt} for partial oxidation.

Emissions_{alt} = 3,030 lb-VOC/year x ton/2000 lb = 1.515 tons-VOC/year

MCET for Partial Oxidation/Grannus Process

- $MCET = \sum$ (ton of emission reduction pollutant_i) x (cost effectiveness threshold pollutant_i),
- MCET = 4.86 tons-NOx/year x \$35,300/ton +10.24 tons-SOx/year x \$20,400/ton + 3.06 tons-PM10 x \$12,800/ton + (19.97 tons-VOC - 1.515 tons-VOC) x \$25,300/ton
- MCET = \$886,534/year

Cost Effectiveness for Partial Oxidation/Grannus Process

Cost Effectiveness = Cost_{alt} – Cost_{Basic} Cost Effectiveness = \$13,740,623/year –\$ 8,519,231/year Cost Effectiveness = \$5,221,392year

Since this value is greater than the MCET of \$886,534/year, partial oxidation/Grannus Process is not cost effective. Furthermore, this analysis does not include the capital costs and other costs associated with a partial oxidization hydrogen plant, which would only make partial oxidation processes less cost effective. Therefore, the result of this analysis is very conservative.

Cost Analysis for Technologically Feasible Control Options

Option 4: Process Heater Meeting 2.5 ppmv NOx @ 3 % O2

A cost analysis is not required, since the applicant is proposing this level of control.

Step 5 - Select BACT

As shown above, alternate basic equipment hydrogen production technologies are not cost effective. BACT is a process heater meeting a NOx limit of 2.5 ppmv @ 3% O_2 , which the applicant is proposing. Thus, BACT for NOx is satisfied.

BACT analysis for SOx Emissions

Step 1 - Identify All Possible SOx Control Technologies

The following BACT clearinghouse references were reviewed to determine the control technologies that have been required for SOx from hydrogen plant process heaters.

- EPA RACT/BACT/LAER (RBLC) clearinghouse
- CARB BACT clearinghouse
- South Coast AQMD (SCAQMD) BACT clearinghouse
- Bay Area AQMD (BAAQMD) BACT clearinghouse
- Sacramento Metro AQMD (SMAQMD) BACT clearinghouse
- San Joaquin Valley APCD (SJVAPCD) BACT clearinghouse
- Monterey Bay Air Resources District (MBARD) BACT clearinghouse
- Santa Barbara County APCD (SBAPCD) BACT clearinghouse

The following table shows the results of the search of the EPA RBLC for SOx emissions from similar process heaters:

Non-Refinery Units from EPA RBLC				
RBLC ID	SOx Limit			
Facility Name	Equipment Rating	SOX Ellint		
AR-0162 Energy Security Partners	Fuel Gas 391.5 MMBtu/hr	0.0006 lb/MMBtu		

The CARB BACT Clearinghouse was searched and applicable BACT Guidelines/Determinations were found from SCAQMD and BAAQMD. The requirements of these guidelines are discussed below.

South Coast BACT Requirements			
Category/Determination	BACT Requirement for SOx		
Process Heater – Non Refinery BACT Guideline for Non-Major Pollution Facilities (page 104 of BACT Guidelines Part D)	Compliance with South Coast Rule 1146		

Bay Area AQMD BACT Requirements*			
Category/Determination	BACT Requirement for SOx		
Heater – Refinery Process ≥ 50 MMBtu/hr	 Natural Gas or Treated Refinery Gas Fuel with ≤ 100 ppmv Total Reduced Sulfur (Achieved in Practice) Natural Gas or Treated Refinery Gas 		
	Fuel with ≤ 50 ppmv Hydrogen Sulfide and ≤ 100 ppmv Total Reduced Sulfur (Technologically Feasible)		
Heater – Refinery Process, Natural or Induced Draft 5 MMBtu/hr to < 50 MMBtu/hr	 Natural Gas or Treated Refinery Gas Fuel with ≤ 100 ppmv Total Reduced Sulfur (Achieved in Practice) 		
	 Natural Gas or Treated Refinery Gas Fuel with ≤ 50 ppmv Hydrogen Sulfide and ≤ 100 ppmv Total Reduced Sulfur (Technologically Feasible) 		
Heater – Refinery Process, Forced Draft	 Natural Gas or Treated Refinery Gas Fuel with ≤ 100 ppmv Total Reduced Sulfur (Achieved in Practice) 		
5 MMBtu/hr to < 50 MMBtu/hr	 Natural Gas or Treated Refinery Gas Fuel with ≤ 50 ppmv Hydrogen Sulfide and ≤ 100 ppmv Total Reduced Sulfur (Technologically Feasible) 		

*Bay Area AQMD only has BACT Guidelines listed for process heaters at Refineries. Although this BACT Guideline is not applicable to refinery units, refinery process heaters operate similarly to non-refinery process heaters. Therefore, the requirements have been included as a reference point for the emission levels that have been achieved in similar units to those being evaluated in this project.

Monterey Bay ARD, Sacramento Metro AQMD, Santa Barbara County APCD, and San Joaquin Valley APCD Clearinghouses do not include Guidelines that would apply to process heaters > 20 MMBtu/hr.

А	review	of	District,	State	and	Federal	rules	revealed	the	following
reo	quiremer	nts:								

Rule	Requirements for SOx
South Coast Rule 1146	•
Emissions of Oxides of Nitrogen from Industrial, Institutional, and	None
Commercial Boilers, Steam Generators, and Process Heaters	
BAAQMD Regulation 9 Rule 7	
Nitrogen Oxides and Carbon Monoxide from Industrial, Institutional, and Commercial Boilers, Steam Generators, and Process Heaters	None
SMAQMD Rule 411	
NOx from Boilers, Process Heaters, and Steam Generators	None
SBCAPCD Rule 342	
Boilers, Steam Generators, and Process Heaters	None
MBARD Rule 441	
Boilers, Steam Generators, and Process Heaters	None
SJVAPCD Rule 4306	
Boilers, Steam Generators and Process Heaters – Phase 3	None
	 Fire exclusively on PUC-quality natural gas, commercial propane, butane, or liquefied petroleum gas, or a combination
SJVAPCD Rule 4320	 of such gases; or Limit fuel sulfur content to no more than 5
Advanced Emission Reduction	grains of total sulfur per 100 scf; or
Options for Boilers, Steam Generators, and Process Heaters	 Install and properly operate an emission control system that reduces SO₂ emissions by at least 95% by weight or limits exhaust SO₂ to less than or equal to 9 ppmv @ 3% O₂

A review of District permits for hydrogen process heaters equal to or greater than 20 MMBtu/hr revealed the following operations:

Facility Permit	Permit Limit for SOx
Alon Bakersfield Refining S-33-53-22 Two 65 MMBtu/hr process gas- fired heaters, a 34.7 MMBtu/hr process gas-fired heater, a 22.7 MMBtu/hr process gas-fired heater, and a 25 MMBtu/hr process gas-fired heater	0.0286 lb/MMBtu
Alon Bakersfield Refining S-33-55-23 233 MMBtu/hr process gas-fired heater	0.0286 lb/MMBtu

The following control options were identified based on the above information:

Option 1: Fuel Sulfur Content Meeting District Rule 4320 Requirements

District Rule 4320 requires operations to meet a fuel sulfur content of 5 grains of total Sulfur per 100 scf of gas. This level is achieved in practice. Furthermore, this level of control is expected to be more stringent than a permit limit of 0.0286 lb-SOx/MMBtu or a fuel sulfur content permit limit of 100 ppm (as H_2S).

Alternate Methods of Producing Hydrogen

• <u>Autothermal Reforming (ATR)</u>: This process uses oxygen and CO2 or steam in a reaction with methane, or other hydrocarbons, to form synthetic gas, also known as syngas. The reaction takes place in a single chamber where the methane/hydrocarbon is partially oxidized. The reaction is exothermic (i.e., heat is released) due to the oxidation.

The key difference between steam reforming and autothermal reforming is that steam reforming uses the reaction of hydrocarbons with water, whereas autothermal reforming uses the reaction of methane with oxygen and CO2 or steam to form synthetic gas. Moreover, steam reforming is an endothermic reaction while autothermal reforming is an exothermic reaction. The reactions can be described in the following equations, using CO2:

 $2 \text{ CH4} + \text{O2} + \text{CO2} \rightarrow 3 \text{ H2} + 3 \text{ CO} + \text{H2O}$

And using steam:

 $4 \text{ CH4} + \text{O2} + 2 \text{ H2O} \rightarrow 10 \text{ H2} + 4 \text{ CO}$

Since this process is exothermic, a process heater is not required. Therefore, combustion emissions are not generated by the autothermal reforming process.

 <u>Partial Oxidation</u>: This method is a type of chemical reaction in which methane and other hydrocarbons in natural gas react with a limited amount of oxygen that is not enough to completely oxidize the hydrocarbons to CO2 and water. With less than the stoichiometric amount of oxygen available, the reaction products contain primarily hydrogen and CO (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a relatively small amount of CO2 and other compounds. In a subsequent water-gas shift reaction, the CO reacts with water to form CO2 and more hydrogen.

Partial oxidation is an exothermic process that is typically much faster than steam reforming and requires a smaller reactor vessel. As can be seen in chemical reactions of partial oxidation, this process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel.

Partial oxidation of methane reaction

 $CH4 + \frac{1}{2}O2 \rightarrow CO + 2H2 \text{ (+ heat)}$

Water-gas shift reaction

 $CO + H2O \rightarrow CO2 + H2$ (+ small amount of heat)

This process is exothermic; therefore, a process heater is not required and combustion emissions are not expected from this process.

 <u>Grannus Process</u>: Another process to be considered is the Grannus Process[™], a patented exothermic chemical process that integrates a partial oxidation gas boiler with the water gas shift process to make hydrogen synthetic gas as described in its website at: <u>https://grannusllc.com/technology/</u> and in SJVAPCD project S-8943/S-1163737. Although the above-mentioned SJVAPCD project issued only an Authority to Construct permit for the installation of a 7.9 MW (nominal ISO rating) electric power generation system (combined cycle configuration) consisting of a natural gas-fired gas turbine engine with heat recovery steam generator (HRSG), that same project determined that the other ammonia plant equipment did not require permits because the plant's emissions units qualified as Low-Emitting Units. The electric power generation system was to provide electrical power and steam to the proposed anhydrous ammonia manufacturing equipment located at the same site at the South Kern Industrial Center in Kern County. However, it should be noted that the facility was not built and the ATC has expired. As proposed in this project, the turbine listed above provided the power; however, the plant can be operated on standard industrial power supplied by the electrical grid.

The anhydrous ammonia fertilizer manufacturing facility that was proposed in that project would have had a capacity of producing 250 tons of anhydrous ammonia fertilizer per day (or the equivalent of approximately 46 tons of hydrogen per day). This plant would have been the first demonstration plant for the Grannus Process[™], a process that makes anhydrous ammonia from pipeline natural gas (methane) and water. A detailed description and process flow diagrams are found in the file for project S-1163737. As proposed, the operation relies on certain streams being sent to a gas turbine's heat recovery steam generator for disposal as is explained in the project evaluation.

The Grannus Process includes additional equipment such as an Air Separation Unit and its storage. This equipment requires a footprint of one-half of an acre.

For this BACT Analysis, the Grannus Process will be included in the Partial Oxidation category, since the Grannus Process uses a nearly identical process to produce hydrogen.

 <u>Gasification</u>: This process produces a synthetic gas by reacting coal, petroleum coke, or biomass with high-temperature steam and oxygen in a pressurized gasifier. The resulting synthetic gas contains hydrogen and CO, which is reacted with steam to separate the hydrogen. Using coal gasification with a water gas shift approach produces a pure hydrogen fuel which can be combusted in gas turbines, in fuel cells, and in other applications.

In current practice, large-scale coal gasification installations are primarily for electricity generation, or for production of chemical feedstocks. The hydrogen obtained from coal gasification can be used for various purposes such as making ammonia, powering a hydrogen economy, or upgrading fossil fuels.

This process requires high-temperature steam, similar to the steam methane reforming process. Therefore, a reduction in combustion emissions is not expected.

• <u>Electrolysis</u>: An electric current splits water into hydrogen and oxygen. If the electricity is produced by renewable sources, such as solar or wind, the resulting hydrogen will be considered renewable as well, and has numerous emissions benefits. Power-to-hydrogen projects are becoming more common, using excess renewable electricity, when available, to make hydrogen through electrolysis.

This process does not require high temperature steam and uses renewable energy, such as solar or wind, to generate the electricity necessary for the electrolysis process. Therefore, a process heater is not required and combustion emissions are not expected.

Several hydrogen production methods are in development, so their potential use in a large commercial project is still not known. Those methods include the following:

- <u>High-Temperature Water Splitting</u>: High temperatures generated by solar concentrators or nuclear reactors drive chemical reactions that split water to produce hydrogen.
- <u>Photobiological Water Splitting</u>: Microbes, such as green algae, consume water in the presence of sunlight and produce hydrogen as a byproduct.
- <u>Photoelectrochemical Water Splitting</u>: Photoelectrochemical systems produce hydrogen from water using special semiconductors and energy from sunlight.
- <u>Pyrolysis</u>: Pyrolysis of natural gas is an endothermic process that occurs in the absence of oxygen to form hydrogen and a solid carbon product. It is thought to be a good method for production of carbon black, but the potential as a source of hydrogen production with low CO2 emissions is still in the development stages. It is believed that more work is needed to better understand its market applications and limitations for commercial projects.

- <u>Photolytic Processes</u>: These processes use light energy to split water into H2 and O2. These processes are currently in the early stages of development and currently are not viable for large-scale production.
- <u>Renewable Liquid Reforming</u>: Renewable liquid fuels, such as ethanol, are reacted with high-temperature steam to produce hydrogen near the point of end use.
- <u>Fermentation</u>: Biomass is converted into sugar-rich feedstocks that can be fermented to produce hydrogen.

Step 2 - Eliminate Technologically Infeasible Options

In the second step, the technological feasibility of the control options identified in Step 1 is evaluated with respect to the source-specific or emissions unit-specific factors. To exclude a control option, a demonstration of technical infeasibility must be clearly documented and should show, based on physical, chemical, and engineering principles, the technical difficulties would preclude the successful use of the control option for the emissions unit under review.

High-temperature Water Splitting, Photobiological Water Splitting, Photoelectrochemical Water Splitting, Pyrolysis, Photolytic Processes, Renewable Liquid Reforming, and Fermentation are experimental technologies that are not yet commercialized. Therefore, these technologies will be removed from consideration.

Gasification is a commercial technology; however, it would require coal feedstock to be delivered to the facility and will not displace any feedstock necessary for the production of the biofuels. Furthermore, gasification also requires hightemperature steam which would be generated from combustion; therefore, gasification isn't believed to currently reduce criteria pollutant emissions from the proposed levels for the steam-hydrocarbon reforming operation. Therefore, this technology will be removed from consideration.

Rank	Capture and Control Efficiency	Status
1. Electrolysis	N/A	Alternate Basic Equipment
2. Autothermal Reforming	N/A	Alternate Basic Equipment

Step 3 - Rank Remaining Control Technologies by Control effectiveness

3. Partial Oxidation/Grannus Process	N/A	Alternate Basic Equipment
4. Meet District Rule 4320 Fuel Sulfur Content Requirements	N/A	Achieved in Practice

Step 4 - Cost Effectiveness Analysis

Cost Analyses for Alternate Basic Equipment Options

The cost analysis for ABE options was conducted in the NOx portion of this analysis. The ABE options were determined to not be cost effective.

Step 5 - Select BACT

As shown above, alternate basic equipment hydrogen production technologies are not cost effective. BACT for SOx from the process heater is meeting District Rule 4320 fuel sulfur content requirements.

BACT analysis for PM₁₀ Emissions

Step 1 - Identify All Possible PM₁₀ Control Technologies

The following BACT clearinghouse references were reviewed to determine the control technologies that have been required for PM₁₀ from hydrogen plant process heaters.

- EPA RACT/BACT/LAER (RBLC) clearinghouse
- CARB BACT clearinghouse
- South Coast AQMD (SCAQMD) BACT clearinghouse
- Bay Area AQMD (BAAQMD) BACT clearinghouse
- Sacramento Metro AQMD (SMAQMD) BACT clearinghouse
- San Joaquin Valley APCD (SJVAPCD) BACT clearinghouse
- Monterey Bay Air Resources District (MBARD) BACT clearinghouse
- Santa Barbara County APCD (SBAPCD) BACT clearinghouse

The following table shows the results of the search of the EPA RBLC:

Non-Refinery Units from EPA RBLC			
	Fuel	PM ₁₀ Limit	
Facility Name	Equipment Rating		
AR-0162 Energy Security Partners	Fuel Gas 391.5 MMBtu/hr	0.0039 lb/MMBtu	
TX-0933 Nacero Penwell	Natural Gas and Fuel Gas Not Provided	0.0075 lb/MMBtu	
LA-0346 IGP Methanol	Not Identified 522 MMBtu/hr	0.0075 lb/MMBtu	
SC-0182 Fiber Industries	Not Identified Not Provided	0.0076 lb/MMBtu	

The CARB BACT Clearinghouse was searched and applicable BACT Guidelines/Determinations were found from SCAQMD and BAAQMD. The requirements of these guidelines are discussed below.

South Coast AQMD BACT Requirements			
Category/Determination	BACT Requirement for PM ₁₀		
Process Heater – Non Refinery BACT Guideline for Non-Major Pollution Facilities (page 104 of BACT Guidelines Part D)	Natural Gas		

Bay Area AQMD BACT Requirements*				
Category/Determination	BACT Requirement for PM ₁₀			
Heater – Refinery Process ≥ 50 MMBtu/hr	 Natural Gas or Treated Refinery Gas Fuel 			
Heater – Refinery Process, Natural or Induced Draft 5 MMBtu/hr to < 50 MMBtu/hr	 Natural Gas or Treated Refinery Gas Fuel 			
Heater – Refinery Process, Forced Draft 5 MMBtu/hr to < 50 MMBtu/hr	 Natural Gas or Treated Refinery Gas Fuel 			

*Bay Area AQMD only has BACT Guidelines listed for process heaters at Refineries. Although this BACT Guideline is not applicable to refinery units, refinery process heaters operate similarly to non-refinery process heaters. Therefore, the requirements have been included as a reference point for the emission levels that have been achieved in similar units to those being evaluated in this project.

Monterey Bay ARD, Sacramento Metro AQMD, Santa Barbara County APCD, and San Joaquin Valley APCD Clearinghouses do not include Guidelines that would apply to process heaters > 20 MMBtu/hr.

A review of District, State and Federal rules revealed the following requirements:

Rule	Requirements for PM ₁₀
South Coast Rule 1146	
Emissions of Oxides of Nitrogen from Industrial, Institutional, and Commercial Boilers, Steam Generators, and Process Heaters	None
BAAQMD Regulation 9 Rule 7	
Nitrogen Oxides and Carbon Monoxide from Industrial, Institutional, and Commercial Boilers, Steam Generators, and Process Heaters	None
SMAQMD Rule 411	
NOx from Boilers, Process Heaters, and Steam Generators	None
SBCAPCD Rule 342 Boilers, Steam Generators, and Process Heaters	None
MBARD Rule 441	
Boilers, Steam Generators, and Process Heaters	None
SJVAPCD Rule 4306	
Boilers, Steam Generators and Process Heaters – Phase 3	None
SJVAPCD Rule 4320 Advanced Emission Reduction Options for Boilers, Steam Generators, and Process Heaters	 Fire exclusively on PUC-quality natural gas, commercial propane, butane, or liquefied petroleum gas, or a combination of such gases; or Limit fuel sulfur content to no more than 5 grains of total sulfur per 100 scf; or Install and properly operate an emission control system that reduces SO₂ emissions by at least 95% by weight or limits exhaust SO₂ to less than or equal to 9 ppmv @ 3% O₂

A review of District permits for process heaters (non-refinery) equal to or greater than 20 MMBtu/hr revealed the following operations:

Facility Permit	Permit Limit for SOx
Alon Bakersfield Refining S-33-53-22 Two 65 MMBtu/hr process gas- fired heaters, a 34.7 MMBtu/hr process gas-fired heater, a 22.7 MMBtu/hr process gas-fired heater, and a 25 MMBtu/hr process gas-fired heater	0.0076 lb/MMBtu
Alon Bakersfield Refining S-33-55-23 233 MMBtu/hr process gas-fired heater	0.003 lb/MMBtu*

*While this unit is permitted at 0.003 lb/MMBtu, no source testing was required for this permit unit. Therefore, this limit cannot be verified and will not be considered in establishing BACT for PM_{10} .

The following control options were identified based on the above information:

Option 1: 0.0039 lb-PM₁₀/MMBtu

This level of control has been achieved at Energy Security Partners, listed in the EPA RBLC. Therefore, this level of control is Achieved in Practice.

Option 2: 0.0076 lb-PM₁₀/MMBtu

This is the default AP-42 emission factor for natural gas. However, a lower level of control has been achieved; therefore, this option will be removed from consideration.

Alternate Methods of Producing Hydrogen

• <u>Autothermal Reforming (ATR)</u>: This process uses oxygen and CO2 or steam in a reaction with methane, or other hydrocarbons, to form synthetic gas, also known as syngas. The reaction takes place in a single chamber where the methane/hydrocarbon is partially oxidized. The reaction is exothermic (i.e., heat is released) due to the oxidation.

The key difference between steam reforming and autothermal reforming is that steam reforming uses the reaction of hydrocarbons with water, whereas autothermal reforming uses the reaction of methane with oxygen and CO2 or steam to form synthetic gas. Moreover, steam reforming is an endothermic reaction while autothermal reforming is an exothermic reaction.

The reactions can be described in the following equations, using CO2:

 $2 \text{ CH4} + \text{O2} + \text{CO2} \rightarrow 3 \text{ H2} + 3 \text{ CO} + \text{H2O}$

And using steam:

4 CH4 + O2 + 2 H2O \rightarrow 10 H2 + 4 CO

Since this process is exothermic, a process heater is not required. Therefore, combustion emissions are not generated by the autothermal reforming process.

 <u>Partial Oxidation</u>: This method is a type of chemical reaction in which methane and other hydrocarbons in natural gas react with a limited amount of oxygen that is not enough to completely oxidize the hydrocarbons to CO2 and water. With less than the stoichiometric amount of oxygen available, the reaction products contain primarily hydrogen and CO (and nitrogen, if the reaction is carried out with air rather than pure oxygen), and a relatively small amount of CO2 and other compounds. In a subsequent water-gas shift reaction, the CO reacts with water to form CO2 and more hydrogen.

Partial oxidation is an exothermic process that is typically much faster than steam reforming and requires a smaller reactor vessel. As can be seen in chemical reactions of partial oxidation, this process initially produces less hydrogen per unit of the input fuel than is obtained by steam reforming of the same fuel.

Partial oxidation of methane reaction

 $CH4 + \frac{1}{2}O2 \rightarrow CO + 2H2$ (+ heat)

Water-gas shift reaction

 $CO + H2O \rightarrow CO2 + H2$ (+ small amount of heat)

This process is exothermic; therefore, a process heater is not required and combustion emissions are not expected from this process.

 <u>Grannus Process</u>: Another process to be considered is the Grannus Process[™], a patented exothermic chemical process that integrates a partial oxidation gas boiler with the water gas shift process to make hydrogen synthetic gas as described in its website at: <u>https://grannusllc.com/technology/</u> and in SJVAPCD project S-8943/S-1163737.

Although the above-mentioned SJVAPCD project issued only an Authority to Construct permit for the installation of a 7.9 MW (nominal ISO rating) electric power generation system (combined cycle configuration) consisting of a natural gas-fired gas turbine engine with heat recovery steam generator (HRSG), that same project determined that the other ammonia plant equipment did not require permits because the plant's emissions units qualified as Low-Emitting Units. The electric power generation system was to provide electrical power and steam to the proposed anhydrous ammonia manufacturing equipment located at the same site at the South Kern Industrial Center in Kern County. However, it should be noted that the facility was not built and the ATC has expired. As proposed in this project, the turbine listed above provided the power; however, the plant can be operated on standard industrial power supplied by the electrical grid.

The anhydrous ammonia fertilizer manufacturing facility that was proposed in that project would have had a capacity of producing 250 tons of anhydrous ammonia fertilizer per day (or the equivalent of approximately 46 tons of hydrogen per day). This plant would have been the first demonstration plant for the Grannus Process[™], a process that makes anhydrous ammonia from pipeline natural gas (methane) and water. A detailed description and process flow diagrams are found in the file for project S-1163737. As proposed, the operation relies on certain streams being sent to a gas turbine's heat recovery steam generator for disposal as is explained in the project evaluation.

The Grannus Process includes additional equipment such as an Air Separation Unit and its storage. This equipment requires a footprint of one-half of an acre.

For this BACT Analysis, the Grannus Process will be included in the Partial Oxidation category, since the Grannus Process uses a nearly identical process to produce hydrogen. <u>Gasification</u>: This process produces a synthetic gas by reacting coal, petroleum coke, or biomass with high-temperature steam and oxygen in a pressurized gasifier. The resulting synthetic gas contains hydrogen and CO, which is reacted with steam to separate the hydrogen. Using coal gasification with a water gas shift approach produces a pure hydrogen fuel which can be combusted in gas turbines, in fuel cells, and in other applications.

In current practice, large-scale coal gasification installations are primarily for electricity generation, or for production of chemical feedstocks. The hydrogen obtained from coal gasification can be used for various purposes such as making ammonia, powering a hydrogen economy, or upgrading fossil fuels.

This process requires high-temperature steam, similar to the steam methane reforming process. Therefore, a reduction in combustion emissions is not expected.

• <u>Electrolysis</u>: An electric current splits water into hydrogen and oxygen. If the electricity is produced by renewable sources, such as solar or wind, the resulting hydrogen will be considered renewable as well, and has numerous emissions benefits. Power-to-hydrogen projects are becoming more common, using excess renewable electricity, when available, to make hydrogen through electrolysis.

This process does not require high temperature steam and uses renewable energy, such as solar or wind, to generate the electricity necessary for the electrolysis process. Therefore, a process heater is not required and combustion emissions are not expected.

Several hydrogen production methods are in development, so their potential use in a large commercial project is still not known. Those methods include the following:

- <u>High-Temperature Water Splitting</u>: High temperatures generated by solar concentrators or nuclear reactors drive chemical reactions that split water to produce hydrogen.
- <u>Photobiological Water Splitting</u>: Microbes, such as green algae, consume water in the presence of sunlight and produce hydrogen as a byproduct.
- <u>Photoelectrochemical Water Splitting</u>: Photoelectrochemical systems produce hydrogen from water using special semiconductors and energy from sunlight.

- <u>Pyrolysis</u>: Pyrolysis of natural gas is an endothermic process that occurs in the absence of oxygen to form hydrogen and a solid carbon product. It is thought to be a good method for production of carbon black, but the potential as a source of hydrogen production with low CO2 emissions is still in the development stages. It is believed that more work is needed to better understand its market applications and limitations for commercial projects.
- <u>Photolytic Processes</u>: These processes use light energy to split water into H2 and O2. These processes are currently in the early stages of development and currently are not viable for large-scale production.
- <u>Renewable Liquid Reforming</u>: Renewable liquid fuels, such as ethanol, are reacted with high-temperature steam to produce hydrogen near the point of end use.
- <u>Fermentation</u>: Biomass is converted into sugar-rich feedstocks that can be fermented to produce hydrogen.

Step 2 - Eliminate Technologically Infeasible Options

In the second step, the technological feasibility of the control options identified in Step 1 is evaluated with respect to the source-specific or emissions unit-specific factors. To exclude a control option, a demonstration of technical infeasibility must be clearly documented and should show, based on physical, chemical, and engineering principles, the technical difficulties would preclude the successful use of the control option for the emissions unit under review.

High-temperature Water Splitting, Photobiological Water Splitting, Photoelectrochemical Water Splitting, Pyrolysis, Photolytic Processes, Renewable Liquid Reforming, and Fermentation are experimental technologies that are not yet commercialized. Therefore, these technologies will be removed from consideration.

Gasification is a commercial technology; however, it would require coal feedstock to be delivered to the facility and will not displace any feedstock necessary for the production of the biofuels. Furthermore, gasification also requires hightemperature steam which would be generated from combustion; therefore, gasification isn't believed to currently reduce criteria pollutant emissions from the proposed levels for the steam-hydrocarbon reforming operation. Therefore, this technology will be removed from consideration.

Rank	Capture and Control Efficiency	Status
1. Electrolysis	N/A	Alternate Basic Equipment
2. Autothermal Reforming	N/A	Alternate Basic Equipment
3. Partial Oxidation/Grannus Process	N/A	Alternate Basic Equipment
4. 0.0039 lb-PM10/MMBtu	N/A	Achieved in Practice

Step 3 - Rank Remaining Control Technologies by Control effectiveness

Step 4 - Cost Effectiveness Analysis

Cost Analyses for Alternate Basic Equipment Options

The cost analysis for ABE options was conducted in the NOx portion of this analysis. The ABE options were determined to not be cost effective.

Step 5 - Select BACT

As shown above, alternate basic equipment hydrogen production technologies are not cost effective. BACT for PM_{10} from the process heater is 0.0039 lb- $PM_{10}/MMBtu$. The facility is proposing a limit slightly lower than 0.0039 lb- $PM_{10}/MMBtu$; therefore, BACT is satisfied.