

Use of SCR in a Hydrogen Plant Integrated with a Stationary Gas Turbine - Case Study: The Port Arthur Steam-Methane Reformer

Paper # 70093

Robert G. Kunz

Cormetech, Inc.
Environmental Technologies
Durham, North Carolina

David C. Hefele

Air Products and Chemicals, Inc.
Port Arthur, Texas

Ronald L. Jordan

Air Products and Chemicals, Inc.
Houston, Texas

Frederick W. Lash

Air Products and Chemicals, Inc.
Allentown, Pennsylvania

ABSTRACT

An “across-the-fence” steam-methane reforming (SMR) hydrogen plant integrated with gas-turbine technology was started up within the past three years at the Premcor refinery in Port Arthur, Texas. This plant, owned and operated by Air Products and Chemicals, Inc., is one of only a handful of SMRs containing an integrated gas turbine. The facility design typifies a growing trend among refiners to outsource their utility needs (i.e., hydrogen, steam, power). It is also one of a very few large industrial combustion sources in the U.S. outside California operating with selective catalytic reduction (SCR) for abatement of nitrogen oxides (NO_x). This paper presents a case study of the cooperative effort to apply Best Available Control Technology (BACT) to satisfy increasingly stringent environmental controls in this part of Texas, along with confirming test results.

The following issues are addressed: (1) The hydrogen from this plant enables Premcor to process sour crudes into a slate of environmentally friendly refined products. (2) Integration results in more efficient energy utilization and reduced NO_x and carbon monoxide (CO) emissions, even without post-combustion controls. (3) Stack testing and the continuous emissions monitoring system (CEMS) confirm that the flue gas from the SMR/gas-turbine combination is successfully being treated using SCR, with provision for continued compliance when either unit is out of service. (4) SCR design incorporates experience from previous SMR cases, where chromium-oxide species deposit on the catalyst to cause activity loss, a phenomenon also affecting SCRs in ethylene plants.

INTRODUCTION -- PROJECT OVERVIEW

The case study of this presentation follows the project from the conceptual stage, engineering, and permitting through start-up, commissioning, and nearly three years of service. As with all projects of this type, the need starts with the customer, in this case units of Premcor Inc. in Port Arthur, Texas. With hydrogen, steam, electricity, and the associated infrastructure provided by the Air Products plant, Premcor can concentrate on their core business of refining crude oil into finished products. Conversely, Air Products and its team are able to bring to bear their core competencies, expertise, distribution network, and economies of scale in producing hydrogen and co-products.

The project was jointly developed, engineered, and built by Air Products and Technip-Coflexip (formerly KTI). It is the latest in a series of over-the-fence hydrogen plants constructed to supply hydrogen for refining applications, the first of which was commissioned in 1993.¹ The plant employs Technip's reformer design, Air Products' pressure-swing-adsorption (PSA) system for hydrogen purification, and a commercial gas-turbine generator. SCR catalyst was supplied by Cormetech, Inc., and the reformer burners by the Callidus Company. Suppliers of other components not directly related to atmospheric emissions are too numerous to mention here.

Environmental permitting requirements were ascertained early at a Pre-Application Meeting with the Texas Natural Resource Conservation Commission (TNRCC), now known as the Texas Commission on Environmental Quality (TCEQ). At that time, TNRCC assigned an experienced permit engineer familiar with steam-methane reforming, and a cooperative, streamlined permitting process was set in motion. The permit application was submitted two weeks later, and the air quality construction permit was issued in another 14 weeks; to ensure such rapid service, the applicant must be prepared to respond immediately to the agency's questions during the review process. Because of the fast-track nature of this and other such projects and the necessary lead-time for environmental permitting before construction may begin, it is extremely helpful to be able to rely on proven elements of past jobs, rather than having to wait for the results of first-time engineering.

Plant start-up and commissioning went smoothly and on schedule to meet the customer's needs. Ongoing operation is also smooth. Stack testing and certification of the plant's continuous emissions monitoring system (CEMS) confirmed compliance with permit conditions. Here, too, it is important to have an experience base from which to predict flue-gas emissions.²⁻⁷

Highlights of what made this project a success are discussed below.

The Customer

The Premcor⁸ Port Arthur refinery is located on a 4000-acre site in Port Arthur, Texas, about 90 miles east of Houston.⁹ The refinery has a crude oil distillation capacity of

approximately 250,000 barrels per day (BPD), with the ability to process 100 % sour crude.⁹⁻¹³ Products include jet fuel, low-sulfur diesel fuel, petrochemical feedstocks, and fuel coke, as well as conventional and reformulated gasoline.¹² Additional information and a photograph of the Port Arthur refinery can be found on the Premcor web site.⁸

In late 2000, operation of a new 417-long tons per day sulfur complex and an 80,000-BPD delayed coker began at the refinery, followed by start-up of a 35,000-BPD hydrocracker shortly thereafter.¹⁴⁻¹⁶ These new additions, built and operated by the Port Arthur Coker Company,⁹ a Premcor subsidiary, enable up to 80 % lower-cost heavy sour crude to be processed.¹⁶

The Air Products Hydrogen Plant

The adjacent 100-million standard cubic feet per day (MMSCFD) Port Arthur hydrogen plant (Figure 1) with an integrated gas turbine (Figure 2) is owned and operated by Air Products and Chemicals, Inc.,¹⁷ referred to by Premcor as a partner in this project.^{14,16} It provides the necessary hydrogen under a long-term supply agreement, plus steam and power to the refinery.¹⁷ This arrangement typifies a growing trend among refiners to outsource their utility needs.¹⁸⁻²⁰ The majority of the hydrogen product from the Air Products facility is supplied to Premcor, and the balance is distributed through the Air Products pipeline system to over 40 other customers between the Houston Ship Channel and the Texas/Louisiana border.¹⁷

Figure 1: Photograph of the Air Products Port Arthur Hydrogen Plant



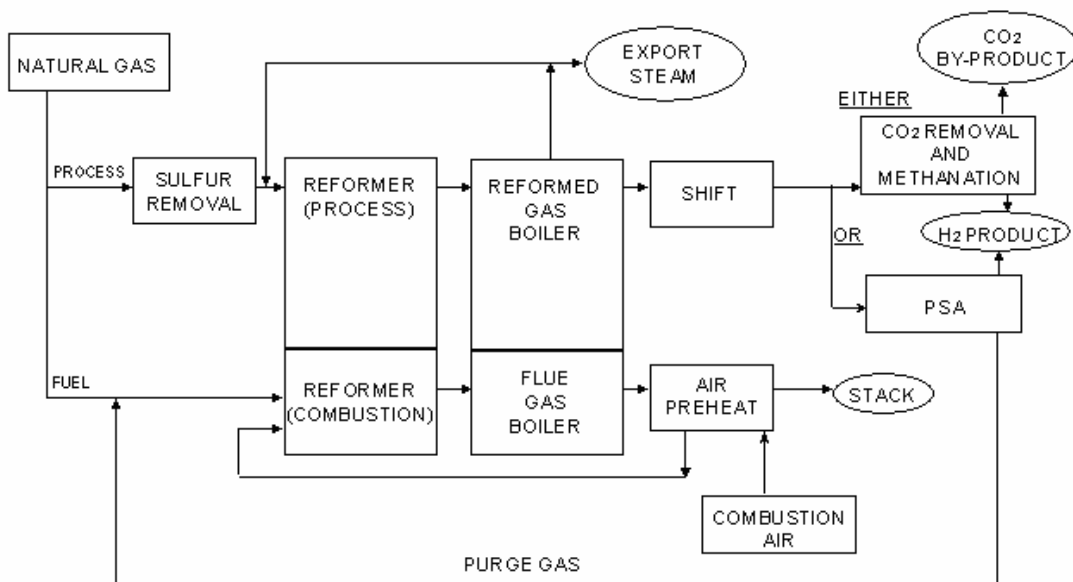
Figure 2: Photograph of Gas Turbine at the Air Products Port Arthur Plant



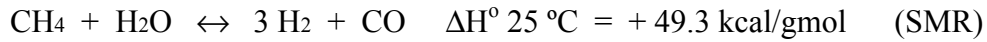
H₂ PROCESS DESCRIPTION

The steam-methane reforming (SMR) process (Figure 3) reacts a hydrocarbon with steam (H₂O) over a nickel-based catalyst to produce a mixture of hydrogen (H₂) and carbon monoxide (CO), generically known as synthesis gas (syngas). Major process steps consist of sulfur removal, reforming, water-gas shift (WGS), and H₂ product purification.

Figure 3: Process Flow Diagram for SMR Hydrogen Plant

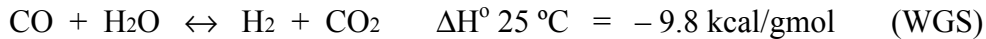


Following sulfur removal from the feed to protect process catalysts, the highly endothermic SMR reaction, shown below for methane (CH₄), occurs at high temperature and pressure in catalyst-filled tubes suspended in the radiant section of a furnace¹⁸



Heat for the reaction is supplied by gas-fired burners in the furnace.

The mildly exothermic WGS reaction¹⁸



also occurs to some extent in the reformer tubes and produces carbon dioxide (CO₂). Other components present in the syngas include unreacted methane, an excess of steam, and impurities such as nitrogen (N₂) from the feed. To maximize H₂ production, the WGS reaction is continued downstream of the furnace in a high-temperature shift (HTS) converter containing a different type of catalyst.

After shift conversion, the hydrogen is separated from the syngas in a pressure-swing-adsorption (PSA) unit capable of producing a hydrogen purity of 99.9 % to 99.999 %.^{2,18} (Older hydrogen plants, built before the mid 1970s, typically used amine absorption, carbon dioxide removal, and methanation steps instead of PSA to make a final hydrogen product 90 to 98 % pure.)² The other components in the PSA feed plus some hydrogen end up in the so-called PSA purge gas, a low-Btu gas which is recycled as the bulk of the fuel to the reformer-furnace burners. Combustible components in the PSA purge gas include hydrogen, carbon monoxide, and methane. This is supplemented typically by natural gas or refinery fuel gas as auxiliary, or trim, fuel. Some product hydrogen may also be fired, when necessary. Oxides of nitrogen (NO_x), CO, and other atmospheric contaminants are generated in the combustion process.

Waste heat is recovered by indirect heat exchange, lowering the temperature of both the process gas and the combustion gas as they proceed separately downstream, one to produce hydrogen and the other for discharge to the atmosphere. There is no physical contact between the process gas stream and the combustion flue gas. In general, heat can be recovered by heating combustion air, feed, fuel, and boiler feed water, and/or by making and superheating steam. Steam produced in excess of process requirements is exported. Low-level heat from gas compression and the like is rejected against cooling water.

GAS-TURBINE OPERATION

Natural gas fired in a gas turbine generates electricity and results in a hot exhaust stream containing about 15 % oxygen (O₂) on a moisture-free, or dry, basis and about 13 % O₂ on a wet basis, i.e., including the combustion moisture. This exhaust gas is normally sent

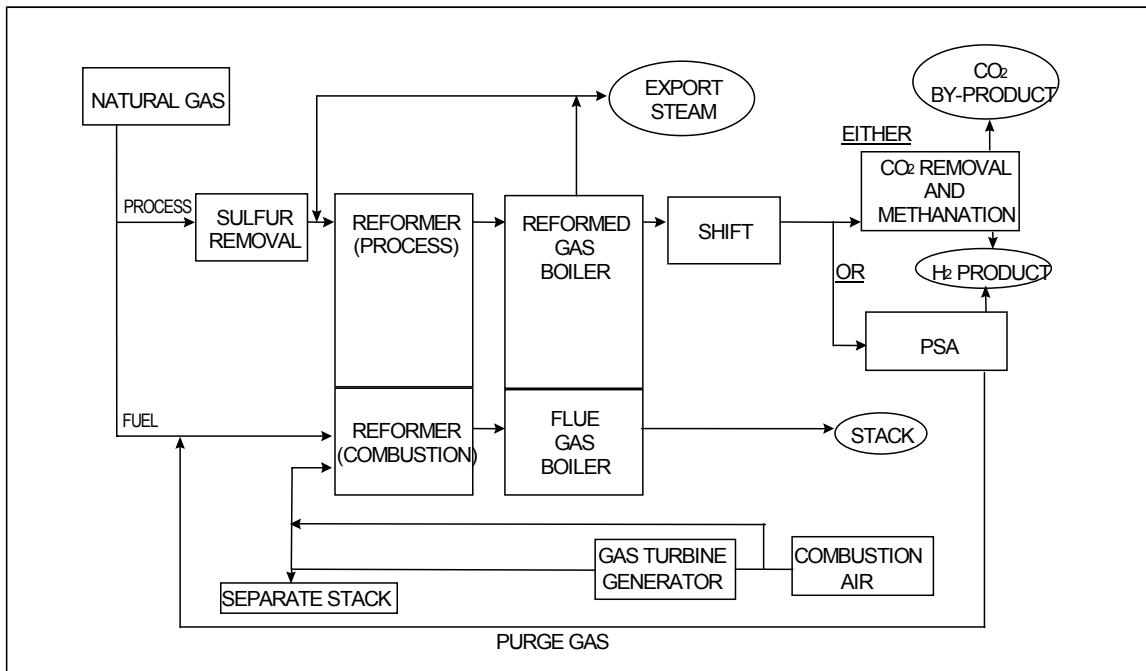
to a second device known as a heat recovery steam generator (HRSG), where the gas is cooled by making steam before discharge to the atmosphere. This is known as combined cycle operation.¹⁹

When a hydrogen plant is integrated with a gas turbine (Figure 4), all or part of the furnace combustion air is replaced by heated gas-turbine exhaust, and the reformer furnace flue-gas heat recovery train fulfills the role of HRSG.^{20,21} Use of this heated “combustion air” increases thermal efficiency.

The furnace flue gas at Port Arthur, during either normal integrated operation or a gas-turbine shutdown, is treated by SCR for NO_x abatement before exiting to atmosphere through the SMR furnace stack. With the gas turbine shut down, ambient air is used for combustion in the furnace, and more fuel must be fired to make up for the absence of air preheat.

For short periods of SMR downtime, the gas turbine can operate in the less efficient simple-cycle mode¹⁹ without heat recovery, and discharge directly through its own local stack upstream of the SCR. This allows the hot turbine flue gas to be isolated from the furnace for safety during unscheduled, emergency maintenance on the SMR.

Figure 4: Process Flow Diagram for SMR Integrated with Gas Turbine



REGULATORY BACKGROUND

Permitting of this project had to address the following considerations, among others:

- Nonattainment New Source Review (NNSR) for Ozone in Jefferson County
- Prevention of Significant Deterioration (PSD)
- Best Available Control Technology (BACT)
- 40 CFR 60 Subpart GG
- Title V Permitting

Choice of environmental control equipment is dictated by having to comply with or seeking to avoid triggering the above requirements.

Classification of the Port Arthur area (Jefferson County) is Moderate,²² with a major source significance threshold of 100 tons/year of ozone precursors; i.e., NO_x and volatile organic compounds (VOCs). Although not as stringent as the Severe Classification of the Houston/Galveston area (25 tons/year), this still limits allowable emissions from an SMR/gas-turbine combination (primarily NO_x), if one wishes to be considered a minor source.

PSD applies to criteria pollutants that are in attainment with the national ambient air quality standards (NAAQS). The most important of these from this plant is CO. Since elements of this facility (chemical process plant and gas turbine) are included among the 28 named source categories found in 40 CFR 52.21(b)(1), the applicable major source threshold is also 100 tons/year. Furthermore, there are no defined hazardous air pollutant (HAP) emissions that exceed allowable limits.

BACT for NO_x is satisfied by properly chosen emission control technology for both the SMR and gas turbine; by good combustion practices with an excess of O₂ for CO, VOCs, and particulate matter (PM₁₀); and by burning clean, low-sulfur fuels for sulfur oxides (SO_x) and PM₁₀.

Subpart GG contains emission and testing requirements for the gas turbine.

If each of the criteria pollutants does not exceed 100 tons/year during operation, the requirements of Title V are not triggered.

PROCESS AIR EMISSIONS –PERMIT LIMITS

The plant was permitted not only for the normal integrated operation, but also for atypical operations with each unit operating separately on a standalone basis (Table 1). A number of turndown cases were also considered. Only the combustion flue gas will be discussed here since this constitutes the principal source of air emissions from an SMR hydrogen plant.

Table 1. Concentration-Based Permit Limits for Various Cases.

Contaminant	SMR with Integrated Gas Turbine or SMR Standalone (Cases 1 and 3)^a	Gas Turbine Only (Case 2)^b
CO	10	25
NO _x	8 (annual average)	9
NH ₃ slip	25	–

a. Allowable flue-gas concentrations expressed as ppmvd @ 3 % O₂ (dry).

b. Allowable flue-gas concentrations expressed as ppmvd @ 15 % O₂ (dry).

Integrated Operation

In the normal integrated operation (Case 1), the hot gas-turbine exhaust enters the reformer furnace, where further combustion occurs. The resulting flue gas is then reacted with ammonia (NH₃) in an SCR unit to comply with the permitted NO_x limit before exiting to atmosphere through the SMR furnace stack. This NO_x limit avoids triggering of NNSR and is significantly below 0.06 lb NO_x/MMBtu(HHV), Texas BACT for natural-gas fired boilers and heaters without preheat.²³ Permit limit for unreacted ammonia leaving the SCR unit, the so-called ammonia slip, is 25 ppmvd @ 3 % O₂ (dry).

Carbon monoxide emissions are permitted at 10 ppmvd @ 3 % O₂ (dry), along with lesser amounts of other criteria pollutants. EPA Publication AP-42²⁴ now predicts a CO concentration in the vicinity of 100 ppmvd @ 3 % O₂ (dry) for natural-gas combustion in various types of boilers; previous editions estimated about 50 ppm CO from industrial boilers with over 100 MMBtu/hr heat input. The TNRCC guideline for boilers and heaters firing natural gas with no preheat is 100 ppmvd @ 3 % O₂ (dry).²³ These figures would ordinarily serve to define the permit limit. Acceptance here of a lower limit for CO based on previous experience and a vendor guarantee precludes triggering of PSD.

Gas Turbine Only

For short periods of gas-turbine operation without the SMR (Case 2), hot turbine exhaust is discharged through its own stack upstream of the SCR. This mode of operation is thermally inefficient and is minimized for economic reasons. Permissible emissions @ 15 % O₂ (dry) for NO_x and CO are in accordance with TNRCC Draft Guidance for

BACT (NO_x for simple cycle operation and CO regardless of type of service).²⁵ These levels are achieved with natural gas and the technology provided by the gas-turbine manufacturer.

SMR Only

With the gas turbine out of service and the SMR operating (Case 3), ambient air is used for combustion, and the reformer flue gas is treated by SCR as in Case 1. Permitted NO_x, NH₃, and CO emissions are the same.

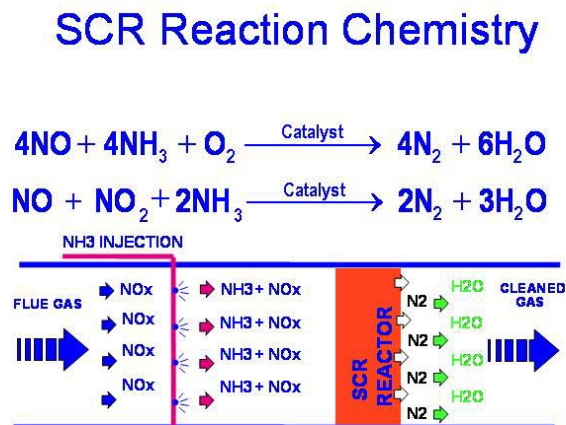
“Voluntary” Use of SCR

In summary, the key to maintaining NO_x emissions below the NNSR trigger point is the “voluntary” use of SCR on the flue gas from the reformer furnace. If NNSR were to be triggered by NO_x emissions in excess of 100 tons/year, SCR would be required as lowest achievable emission rate (LAER) technology, along with costly and perhaps hard to find emission offsets. However, SCR brings NO_x emissions below the NNSR trigger point, eliminating the need for NNSR and offsets. By whichever line of reasoning one chooses, SCR is required. The SCR process is discussed in the next section.

THE SCR PROCESS

In this process (Figure 5), the oxides of nitrogen NO and NO₂, commonly known as NO_x, are reacted with ammonia (NH₃) in the presence of a flow-through honeycomb catalyst to give nitrogen (N₂) and water vapor (H₂O).^{26,27}

Figure 5: NH₃ Reacts with NO_x in SCR Unit



Reaction stoichiometry with ammonia, injected upstream, depends on the relative amount of each oxide and whether or not oxygen (O₂) is present. For fired-heater combustion applications containing excess oxygen and parts-per-million (ppm) concentrations of NO_x with the typical 95 % NO and 5 % NO₂ split, the equations given in Figure 5 apply. The equations are also applicable to gas-turbine combustion, where the proportion of NO₂ is slightly higher. In the absence of competing side reactions, the theoretical molar ratio of NH₃ reacted to NO_x destroyed is 1.0.

Application of SCR Technology To Hydrogen Production

Performance of SCR has been demonstrated on a number of SMR hydrogen plants.²⁸ The cited locations represent a joint accumulated operating experience for Air Products and Cormetech of over 30 years. The Port Arthur SCR design is based on this accumulated experience, along with Cormetech's extensive experience in gas-turbine applications. Cormetech has supplied SCR catalyst for other hydrogen-plant clients as well.

Direct experience with hydrogen-plant flue gas is important for initial catalyst sizing and prediction of run length since the presence of chromium-oxide species in the flue gas causes loss of SCR catalyst activity over time at a rate greater than normally expected for a clean-gas application. The loss of catalyst activity experienced has been attributed to a masking of active catalyst surface by an ongoing deposition of some form of chromium,²⁷ believed to have been evaporated at parts-per-billion (ppb) to ppm concentrations from the alloy metals in contact with hot flue gas.²⁹ This phenomenon has been reported previously in both an SMR hydrogen-plant reformer furnace²⁷ and in ethylene pyrolysis/cracking furnaces,^{30,31} where tube-metal temperatures are similar and the same family of chromium/nickel alloys are used.²⁹

This masking layer manifests itself as a discoloration of the SCR catalyst surface, heavy at the inlet and becoming gradually lighter approaching the outlet. The color deepens and spreads farther downstream with greater exposure time. The color varies from brownish to an iridescent black, possibly depending on the temperature of chromium oxide condensation on the catalyst.

The Port Arthur facility and its SCR have been in operation for nearly three years. Since the plant's SCR catalyst is not yet available for inspection, a photograph of an exposed sample removed from another SMR plant is shown in Figure 6, along with a fresh, unexposed sample for comparison.

The discoloration of the exposed sample (on the left) is dark brown at the inlet face and somewhat lighter brown at the outlet (not pictured). The fresh catalyst sample shown on the right in Figure 6 is a light tan, with a nominal pitch in the range of 2-4 mm, typical of clean-gas service.³²

Figure 6: Photograph of SCR Catalyst Samples
Left: Exposed Sample from SMR Service Right: Fresh Sample



A correlation of catalyst-activity decay with chromium concentration on catalyst, drawn from comprehensive follow-up testing in the laboratory of SCR catalyst samples exposed in the field at SMR plants is developed in a paper presented at the 2002 NPRA Environmental Conference.²⁸ Evidence presented there indicates that the chromium which ends up on the SCR catalyst comes predominantly from the reformer tubes.

STACK TEST AND MONITORING RESULTS

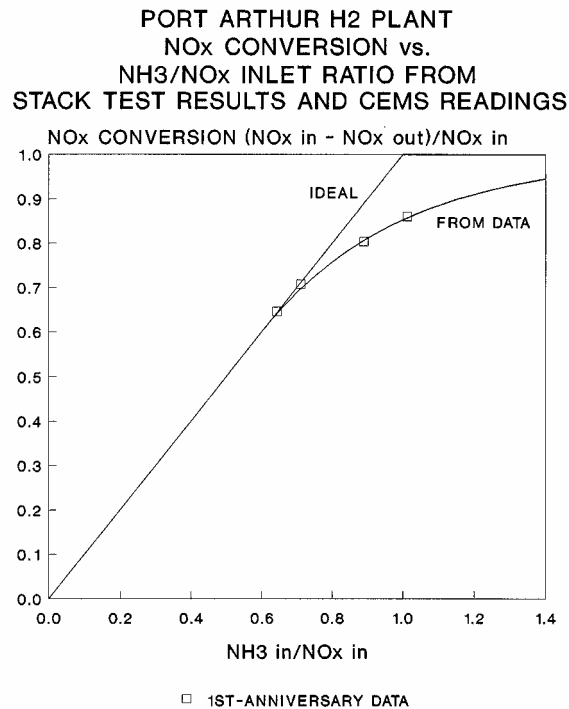
According to the TCEQ air quality permit, an initial stack sampling at maximum production must be conducted for NO_x, CO, VOC's, and NH₃ slip and must be repeated every five years. Measurement of NH₃ slip at maximum production must be repeated annually. SCR temperature, ammonia injection rate, and operating parameters indicative of production rate must also be recorded during stack emission testing.

An initial stack test during integrated operation (Case 1, as defined above) was conducted to verify permit compliance and to certify the continuous emissions monitoring system (CEMS); a plant performance test,³³ in which process variables were measured and simulated, was conducted at the same time. NH₃ slip during integrated operation was measured again a year later, almost to the day.

The plant met its permit conditions for all contaminants. NH₃ slip, measured in the 0.1- to 1-ppm range, increased marginally over the intervening year of operation, with no perceptible change in ammonia feed rate. NO_x conversion (η) is plotted against the

NH₃-to-NO_x ratio at the SCR inlet (α) in Figure 7. SCR catalyst activity (K/K_0), estimated from NO_x and ammonia data, is within the expected range for this type of operation.^{26,27}

Figure 7: NO_x Conversion (η) Varies with NH₃/NO_x Inlet Ratio (α)



Source testing of the gas-turbine exhaust duct (Case 2) was conducted on a separate occasion, in compliance with the permit and Subpart GG. Permit conditions were satisfied here also.

Circumstances did not allow a voluntary testing of the SMR without the gas turbine (Case 3), but CEMS data are available to analyze this atypical operation. Further details for all three cases are provided below.

Integrated Operation

NO_x from the integrated operation is somewhat lower than expected for standalone hydrogen-plant operation, based on SCR-inlet NO_x for a similar plant, but without a gas turbine. Simultaneous outlet NO_x was below permit levels, making the calculated NO_x-removal efficiency within design range. This is not the worst case for SCR design, and the SCR with new catalyst is not being pushed very hard in Case 1.

The CO concentration was reported as less than 0.1 ppmvd @ 3 % O₂ (dry), based on the average of the required 3 compliance-test runs. In two of the runs, measured CO concentration was below the minimum detectable limit. Very low CO concentrations are typical for SMR plants without an integrated gas turbine. Carbon monoxide will be lower for the integrated case compared to standalone gas-turbine operation because of a combination of furnace firebox temperature and residence time.³⁴ It is this synergism that contributes to the low measured CO, rather than dilution of the higher gas-turbine CO into the SMR flue gas.

Gas Turbine Only

NO_x, O₂, and the unit load were measured at several different load conditions. The flow rate of the natural gas fuel, its sulfur content, and its heating value were also determined. NO_x tested under permit limits, with fairly constant average values under all load conditions.

CO was not measured. The vendor guarantee of 25 ppmvd @ 15 % O₂ (dry) falls within the range predicted from AP-42 gas-turbine emission factors³⁵ in conjunction with Method 19 of 40 CFR 60, Appendix A.³⁶ That range depends on the type of flue-gas treatment employed by the turbines in the EPA data sets.

SMR Only

The gas turbine was taken down for extended maintenance once during the period under discussion, while maintaining maximum H₂ production. For this condition, natural gas was used as trim fuel in the SMR, along with ambient air for combustion. In SMR standalone operation, more fuel must be fired at the same hydrogen production rate to compensate for the lack of air preheat. Since the amount of PSA purge gas available is fixed and limited by process conditions, the additional firing has to come from trim fuel.

Inlet NO_x @ 3 % O₂ (dry) concentrations from daily-average CEMS readings increased for the SMR-only condition and returned to expected levels for integrated operation with the gas turbine. Steady state in both directions was achieved with minimal transition time.

NO_x is higher on a ppm basis when the gas turbine is down because of a significantly higher adiabatic flame temperature (AFT) compared to integrated operation. Higher concentrations of inerts (N₂, CO₂, and water vapor) from the hot gas-turbine exhaust being substituted for ambient air in combustion lower the flame temperature in the integrated case, despite the elevated temperature of the turbine exhaust (~1000 °F). The AFT, and consequently NO_x, also increase somewhat because of the greater proportion of trim fuel in the mixture being fired.² NO_x is higher on a lb/hr basis as well.

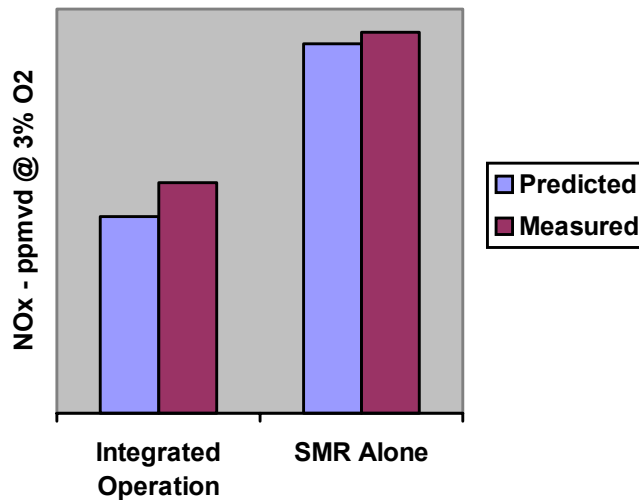
NO_x-removal efficiency is higher in this case, approaching 80 %, to meet the same outlet NO_x permit levels, and the SCR must be flexible enough to handle this condition. Also, the ammonia injection system must be capable of producing a higher inlet NH₃/NO_x ratio, compared to the 0.5-0.7 estimated for integrated operation.

CO is not measured in the CEMS at this plant. Where it is measured by CEMS^{26,27} and elsewhere, CO has not been found to be a problem in an SMR as long as one operates above the CO breakpoint.⁵

COMPARISON OF MEASURED AND PREDICTED SMR NO_x

It is possible to predict NO_x concentrations with and without gas-turbine integration from a correlation of NO_x data from other SMR plants.⁵ This relationship utilizes the theoretical adiabatic flame temperature calculated for the combustion products and the actual excess oxygen in the furnace firebox. Figure 8 compares measured and predicted values for both normal integrated operation (Case 1) and for the gas-turbine-down case (Case 3).

Figure 8: Predicted vs. Measured NO_x at SCR Inlet



Prediction for the integrated case uses information derived from the performance-test fuel- and turbine-exhaust-compositions and furnace excess O₂ to calculate the adiabatic flame temperature for each of three periods of extended operation. Although the composition of the refinery fuel gas used as trim fuel was highly variable, values of NO_x predicted from the design correlations⁵ compared well to the measured NO_x during the testing period.

With no new performance-test data available, the same PSA purge-gas composition was assumed for SMR standalone. This purge gas and a typical natural gas were combined in

the ratio indicated by the CEMS and used as the fuel in combustion calculations. The prediction with ambient air is not sensitive to excess O₂.²⁻⁵

In summary, NO_x at the SCR inlet, whether measured or predicted, is different between Cases 1 and 3, and this difference is caused by a difference in the flame temperature for the two cases.

CONCLUSIONS

- Hydrogen is used for a variety of purposes in petroleum refining.
- Hydrogen allows sour crudes to be processed without exceeding sulfur specifications for refined products.
- The hydrogen itself must be manufactured in compliance with environmental regulations, and a cooperative permitting effort shortens lead time.
- Supply of hydrogen, steam, and electricity from an independently owned and operated industrial gas plant allows both the refiner and the gas supplier to focus expertise on individual core business.
- Integration of SMR and gas turbine enables more efficient energy utilization.
- Synergistic effects lower CO and NO_x generation during integrated operation.
- CO and related contaminants from incomplete combustion are controlled by excess O₂ and good combustion practices.
- SCR reduces NO_x to below regulatory thresholds.
- There is an experience factor in applying SCR to hydrogen (or ethylene) manufacturing because of deposition of chromium oxides on SCR catalyst; data are presented elsewhere.
- Chromium species originate predominantly from the alloy tubes in contact with hot flue gas.

ACKNOWLEDGEMENT

The authors are especially grateful to Mr. Bryan Huff of the Air Products Port Arthur plant staff for his help with CEMS issues and to Mr. George Wensell and Ms. Shirley Torain of Cormetech, Inc. and Ms. Justine McFarland of Air Products and Chemicals, Inc. for their assistance in preparing the manuscript and slides for presentation.

REFERENCES

1. Patel, N.M.; Davis, R.A.; Eaton, N.; Carlson, D.L.; Kessler, F.; Khurana, V. “‘Across-the-Fence’ Hydrogen Plant Starts up at California Refinery” *Oil & Gas Journal* **Oct. 3, 1994**, 92(40), 54-61.
2. Kunz, R.G.; Smith, D.D.; Patel, N.M.; Thompson, G.P.; Patrick, G.S. "Control NOx from Gas-Fired Hydrogen Reformer Furnaces" Paper AM-92-56 presented at the 1992 NPRA Annual Meeting, New Orleans, LA, Mar. 22-24, 1992.
3. Kunz, R.G.; Smith, D.D.; Patel, N.M.; Thompson, G.P.; Patrick, G.S. “Control NOx from Gas-Fired Hydrogen Reformer Furnaces,” In *Emission Inventory Issues - Proceedings of an International Specialty Conference*, Durham, NC, Oct. 19-22, 1992; VIP-27; Air & Waste Management Association: Pittsburgh, PA, 1993; pp. 381-392.
4. Kunz, R.G.; Smith, D.D.; Patel, N.M.; Thompson, G.P.; Patrick, G.S. “Control NOx from Furnaces” *Hydrocarbon Processing* **Aug. 1992**, 71(8), 57-62.
5. Kunz, R.G.; Smith, D.D.; Adamo, E.M. “Predict NOx from Gas-Fired Furnaces” *Hydrocarbon Processing* **Nov. 1996**, 75(11), 65-79.
6. Kunz, R.G.; Keck, B.R.; Repasky, J.M. “Mitigate NOx by Steam Injection” Paper ENV-97-15 presented at the 1997 NPRA Environmental Conference, New Orleans, LA, Sept. 28-30, 1997.
7. Kunz, R.G.; Keck, B.R.; Repasky, J.M. “Mitigate NOx by Steam Injection” *Hydrocarbon Processing* **Feb. 1998**, 77(2), 79-84.
8. Premcor Inc. News Release: “Premcor Selected as New Name for Clark,” May 10, 2000. This and the other cited Premcor News Releases are available on Premcor’s web site, <http://www.premcor.com>, formerly [clarkusa.com](http://www.clarkusa.com). (The parent company Premcor Inc. was formerly known as Clark Refining Holdings Inc., and its subsidiaries, Premcor USA Inc. and the Premcor Refining Group Inc., were formerly known as Clark USA, Inc. and Clark Refining & Marketing, Inc., respectively.)
9. Premcor Inc.: “Overview of Refineries,” available on Premcor Inc. web site, <http://www.clarkusa.com/refining.html>.
10. Anon. “Premcor Boosts Capacity at Port Arthur Plant” *The St. Louis Business Journal* **July 17, 2000**, available at <http://stlouis.bizjournals.com>.

11. Premcor Inc. News Release: "Premcor Increases Capacity at Port Arthur Refinery," July 17, 2000.
12. Premcor Inc. News Release: "Premcor Plans Temporary Shutdown of Port Arthur Refinery Crude Unit," July 6, 2001.
13. Premcor Inc. News Release: "Premcor Plans Maintenance at Port Arthur Refinery," July 6, 2001.
14. Premcor Inc. News Release: "Premcor USA Announces Third Quarter Results," Nov. 8, 2000.
15. Premcor Inc. News Release: "Premcor Starts New Coker Unit at Port Arthur Refinery," Dec. 12, 2000.
16. Premcor Inc. News Release: "Premcor Inc. Announces Fourth Quarter and Full Year 2000 Results," Feb. 13, 2001.
17. Air Products and Chemicals, Inc. News Release: "Air Products' New Port Arthur, Texas Hydrogen Plant Is Onstream: Facility to Supply Premcor Oil Refinery," June 26, 2001, available on the Air Products web site, <http://www.airproducts.com>.
18. Shahani, G.H.; Garodz, L.J.; Murphy, K.J.; Baade, W.F. "Hydrogen and Utility Supply Optimization" Paper AM-98-60 presented at the 1998 NPRA Annual Meeting, San Francisco, CA, Mar. 15-17, 1998.
19. 40 CFR 60, Subpart GG, U.S. Government Printing Office: Washington, D.C.
20. Terrible, J.; Shahani, G.; Gagliardi, C.; Baade, W.; Bredehoff, R.; Ralston, M. "Cogenerate Electricity from Hydrogen Plants" Paper AM-99-65 presented at the 1999 NPRA Annual Meeting, San Antonio, TX (March 21-23, 1999).
21. Terrible, J.; Shahani, G.; Gagliardi, C.; Baade, W.; Bredehoff, R.; Ralston, M. "Consider Using Hydrogen Plants to Cogenerate Power Needs" *Hydrocarbon Processing*, **Dec. 1999**, 78(12), 43-53.
22. Texas Natural Resource Conservation Commission (TNRCC) *General Guidance Document: Nonattainment New Source Review (NNSR)* (Draft), p.32 of 80, Austin, TX, Jan. 2002; RG-305.
23. Texas Natural Resource Conservation Commission (TNRCC) *Combustion Source Technical Guidance Package: Boilers & Heaters* (Draft), p.6 of 42, Austin, TX, Oct. 2001.

24. U.S. Environmental Protection Agency *Compilation of Air Pollution Emission Factors*, Fifth Edition, Volume I, Table 1.4-1 on p.1.4-5, "Emission Factors for Nitrogen Oxides (NO_x) and Carbon Monoxide (CO) from Natural Gas Combustion" U.S. Environmental Protection Agency: Research Triangle Park, NC, July 1998; AP-42.
25. Texas Natural Resource Conservation Commission (TNRCC), *Revised Draft of Best Available Control Technology (BACT) Guidance for Gas Turbines (GTs)*, pp.3,4,7 of 7, Austin, TX, Mar. 2000.
26. Kunz, R.G., "SCR Performance on a Hydrogen Reformer Furnace – A Comparison of Initial and First- and Second-Year Anniversary Emissions Data" Paper 96-RA 120.01 presented at the 89th Annual Meeting Air & Waste Management Association, Nashville, TN, June 23-28, 1996.
27. Kunz, R.G. "SCR Performance on a Hydrogen Reformer Furnace" *Journal of the Air & Waste Management Association* **1998**, 48, 26-34.
28. O'Leary, J.R.; Kunz, R.G; von Alten, T.R. "Selective Catalytic Reduction (SCR) Performance in Steam-Methane Reformer Service: The Chromium Problem" Paper ENV-02-178 presented at the 2002 NPRA Environmental Conference, New Orleans, LA, Sept. 9-10, 2002.
29. Kunz, R.G.; von Alten, T.R. "SCR Treatment of Ethylene Furnace Flue Gas (A Steam-Methane Reformer in Disguise)" Paper presented at Institute of Clean Air Companies (ICAC) Forum '02, Houston, TX, Feb. 2002.
30. Funahashi, K.; Kobayakawa, T.; Ishii, K.; H. Hata, H. "SCR DeNO_x in New Maruzen Ethylene Plant" In *Proceedings of the 13th Ethylene Producers' Conference*, Vol. 10; American Institute of Chemical Engineers, New York, NY, 2001; pp.741-755.
31. Suwa, A. "Operating Experiences of SCR DeNO_x Unit in Idemitsu Ethylene Plant," In *Proceedings of the 13th Ethylene Producers' Conference*, Vol. 10; American Institute of Chemical Engineers, New York, NY, 2001; pp.766-773.
32. Cormetech, Inc. Environmental Technologies Product Brochures: *Cormetech SCR Catalysts for Gas-Fired Generators* and *Cormetech SCR Catalysts for Coal-Fired Generators*: Durham, NC, 2002.
33. Wang, S.I., Smith, D.D.; Patel, N.M.; DiMartino, S.P. "Performance Tests for Steam Methane Reformers" *Hydrocarbon Processing* **Aug. 1982**, 61(8), 89-92.

34. Personal Communication from Mr. Greg Horne, Product Director, Burner Systems Group, John Zink Company, a division of Koch-Glitsch, Inc., Oct. 22, 1998.
35. U.S. Environmental Protection Agency *Compilation of Air Pollution Emission Factors*, Fifth Edition, Volume I, Table 3.1-1 on p.3.4-10, "Emission Factors for Nitrogen Oxides (NO_x) and Carbon Monoxide (CO) from Stationary Gas Turbines" U.S. Environmental Protection Agency: Research Triangle Park, NC, Apr. 2000; AP-42.
36. 40 CFR 60, Appendix A, Method 19, U.S. Government Printing Office: Washington, DC.

KEY WORDS

BACT, Best Available Control Technology, Air Pollution Control, Chromium-Oxide Deposition, Ethylene Manufacturing, Gas Turbine, Hydrogen Manufacturing, Integration of Steam-Methane Reforming and Stationary Gas Turbine, Nitrogen Oxides, NO_x, NO_x Control, NO_x Prediction, Petroleum Refining, SCR, SCR Catalyst, Selective Catalytic Reduction, SMR, Stationary Gas Turbine, Steam-Methane Reforming.