NOxRx®

A wet-scrubbing solution for NOx and SOx emissions from stationary biogas engines.

A White Paper

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**Introduction / Background**

Biogas & Electric has developed NOxRx® with funding from USDA-NIFA SBIR Phase 1 and 2 grants in addition to seed funding from Waste Management, Inc. NOxRx® is a patented (US8,012,746 and other patents pending) air pollution control technology for biogas engines operating at both agricultural and municipal wastewater treatment based anaerobic digestion facilities. NOxRx® is a wet scrubbing technology that reduces NOx and SOx emissions from the exhaust stream of a biogas fired internal combustion engine. Efficacy of NOxRx® was demonstrated at the bench scale in December of 2010. Additionally, a full scale project demonstrated efficacy by significantly reducing targeted emissions (NO, NO₂, SO₂) in the exhaust stream of a 300 kW Guascor lean burn biogas engine operating at a dairy in California.

**Biogas Market**

According to the American Biogas Council, there are an estimated 12,000 sites in the United States available for biogas project development. There are 8,200 farms with a potential for 1,700 MW and 3,899 wastewater treatment plants with a potential for 750 MW. Additionally, there are over 300 biogas projects currently being developed in the US. Presently, there are more than 2,000 biogas producing sites that are operational in the United States, 192 digesters on farms and 1,238 anaerobic digesters at wastewater treatment plants. However, only 860 wastewater treatment plants use the biogas they produce. Emissions regulations governing stationary biogas engines in EPA designated ozone non-attainment areas are very stringent, effectively stopping biogas project development.

**Problem Statement**

The US EPA has designated many regions as “Ground Level Ozone Non-Attainment,” meaning the air quality is poor, negatively impacting those living and working in the area. Ground-level ozone is not a pollutant emitted by combustion engines directly into the air, but is created through photochemical reactions between oxides of nitrogen (or NOx), volatile organic compounds (or VOCs) and sunlight. NOx is emitted by internal combustion engines, and VOC’s are generated from gasoline vapors, and chemical solvents. Together, NOx and VOC’s combine in the atmosphere creating damaging ground level ozone that is a major health and economic concern.

Currently available SOx and NOx reduction systems have high installation and operational costs, and are not capable of complying with the California Air Resource Board’s (CARB) NOx standard of 0.07 lbs. of NOx per Megawatt Hour (roughly 2-3 ppm of NOx at 15% O₂ levels). NOxRx® enables a biogas project to use a low cost and highly efficient internal combustion engine to produce both electrical and thermal energy instead of other technologies such as fuel cells, micro-turbines, upgrading biogas for the pipeline, or gasification which have certain shortcomings as illustrated in Figure 1 below.
There are two approaches to reducing NOx emissions, the first is through optimizing the combustion process, and the second is through post-combustion emissions reductions solutions. Post-combustion reduction solutions for lean burn biogas engines include:

1.) Selective Catalytic Reduction or SCR
2.) Selective Non-Catalytic Reduction or SNCR
3.) Wet-scrubbing – which is the base technology for NOxRx®

Selective Catalytic Reduction or SCR is currently the leading technology for lean burn biogas engines, and is the same system that operates on many diesel trucks on the road today. As illustrated in Figure 2 below, the exhaust exits the engine, cools slightly to 500° F, some liquid urea is injected into the exhaust stream and a rare-earth metal catalyst helps reduce NOx into elemental nitrogen and water.

The reduction rate for SCR systems is good; however, SCR systems will not function in even low sulfur or siloxane environments. Sulfur and siloxanes in the exhaust stream precipitate out over the catalytic bed, coating or “poisoning” the catalyst, destroying the system’s NOx reduction capability. Thus, SCR systems require highly effective H₂S and siloxane removal systems to treat the biogas stream prior to combustion. Additionally, SCR has many variable operating costs including: continual urea purchases, catalyst replacement, in addition to maintenance and operating costs associated with the required H₂S and siloxane reduction component.

SCR systems are capable of reducing NOx to the 9-11 ppm level in an exhaust stream from a lean burn biogas engine. However, SCR has not been proven capable of meeting the California Air Resource Board (CARB) standard of 2-3 ppm.

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**Table 1**

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**Figure 2 - SCR System**

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Selective Non-Catalytic Reduction or SNCR does not require a catalyst, and thus there is no need for H₂S and siloxane reduction prior to combustion as illustrated in Figure 3 below.

![Figure 3 - SNCR System](image)

However, SNCR does not work unless the exhaust stream is heated up to 1450° F for the chemical reactions to occur. The energy required to heat an exhaust stream from approximately 700° F to 1450° F makes SNCR prohibitively expensive for most biogas projects.

Wet-scrubbing is a technology that has been used in the air pollution control industry for decades. As illustrated in Figure 4 below, NOx scrubbers have an exhaust stream entering the bottom of an absorber containing a packed media bed. A caustic liquid with a pH of 12 to 14 would be injected into the top of the absorber and flow counter-current to the exhaust stream – sinking the targeted pollutants into the liquid phase.

![Figure 4 – Traditional Wet Scrubber](image)

Conventionally, chemicals are continually injected into the wet scrubbing system to maintain the pH of the caustic liquid which will flow in a closed loop. Typically, the liquid used to scrub the exhaust stream will create yet another waste stream that naturally needs to be managed as well.
**NOxRx® a Wet-Scrubbing Solution**

**Description of Demonstration Site:**

The full scale NOxRx® demonstration facility was installed at a 3,500 head flushed lane California based dairy as illustrated in **Figure 5**. The site was equipped with a stirred, covered lagoon type anaerobic digester of approximately 30 million gallons. An additional uncovered storage lagoon of identical size was installed adjacent to the digester and served as a storage location for AD effluent. Effluent from this storage lagoon was pumped into wastewater tanks located at the head of each feeding lane and then used to flush the lanes back into the digester two times per day.

**Figure 5 – Dairy**

A biogas stream of 75 - 150 scfm is produced by the digester in Figure 5 above. The biogas is passed through a coiled-loop chiller to condense and remove water prior to combustion. The gas has an average composition of approximately 71.3 mole % methane, 24.48% CO₂, 2.78% N₂, and 1.08% H₂S when sampled after the chiller. The H₂S concentration varies between 6,000 ppm and 15,000 ppm. No sulfide removal was employed prior to combustion.

The full biogas stream is used to power a 300 kW Guascor lean burn CHP biogas engine. The manufacturer’s engine specifications document lists 1948 acfm as the peak exhaust gas volume for this engine at 743° F. The raw untreated exhaust gas was measured by the authors to
have a pollutant profile of approximately 50 - 100 ppm NOx and 400 - 1000 ppm SOx. All exhaust gas composition data was acquired using a Testo 350XL portable hand held combustion gas analyzer.

**Description of Solution:**

Biogas & Electric’s solution, NOxRx®, as illustrated in Figure 6 below, incorporates an innovative, modular, multi-stage wet-scrubbing system that utilizes wastewater from the anaerobic digester with a unique NO oxidation strategy. The NOxRx® demonstration project is non-catalytic; and thus there is no need for biogas clean-up (siloxane and H2S removal) prior to combustion for effective emission reduction purposes.

The first stage of the NOxRx® system is the Quencher/Cooler, which simultaneously cools and saturates the exhaust with water. After the Quencher/Cooler the exhaust has been cooled to approximately 100°F, and is now suitably conditioned for rapid NO oxidation.

Following NO oxidation, the exhaust enters the Absorber Array. Within the first absorber, 50-75% of the NOx can be removed as the NO2 absorbs and reacts within the absorber with the anaerobic digester effluent. The NOx level in the exhaust stream is similarly reduced by each subsequent absorber stage before leaving the stack containing the targeted levels of SOx and NOx emissions.

**Results:**

Results from the demonstration project were very encouraging as NOx was reduced to levels below the current Best Available Control Technology (“BACT”) or BACT (Urea Injected Selective Catalytic Reduction) or (“SCR”) as designated by San Joaquin Valley Air Pollution Control District (Table 1). The current NOx BACT level is 9-11 ppm adjusted to 15% O2.

![Table 1 – Results Summary](attachment:image)

*NOx levels are adjusted to 15% O2 basis.*

**Description of Solution - Details:**

**Quencher and cooler Stages:**

Hot biogas engine exhaust must be saturated with water vapor and cooled prior to the oxidation and wet scrubbing steps. The exhaust can be saturated with either plant water or water from a primary/secondary clarifier within the quencher. Some initial cooling of the exhaust also takes place within the quencher. The saturated exhaust stream is then further cooled within the cooler. This can be accomplished through the use of either digester effluent or primary/secondary clarifier water within the cooler. All SO2 was effectively removed by the cooler as illustrated by Table 2 below.

![Table 2 – Cooler results](attachment:image)
Multi-Stage Wet Scrubber (Absorber Array):

Three absorbers were constructed for the demonstration project as illustrated in Figure 6 below. The first absorber was three feet in diameter and contained 13.5 vertical feet of 2.3" LANPAC® polypropylene packed media. The second and third absorbers were each three feet in diameter and contained 8 vertical feet of 2.3" LANPAC® polypropylene packed media. Several types of packed media were tested including ceramic saddles, and larger LANPAC-XL® polypropylene media each with varying effective surface area, void fraction and pressure drop. Among all the packing media tested, 2.3" LANPAC® polypropylene was determined to have the best performance. AD effluent was introduced into the top of each absorber at a rate of 20-60 gallons per minute, and 50-75% of the NO₂ was absorbed into and reacted with the AD effluent at each stage.

![Figure 6 - Biogas Project Schematic with NOxRx® Installation](image)

Nitrogen in Wastewater

As NOxRx® sinks NOx into the wastewater the nitrogen concentration theoretically increases, but not by amounts that can be measured. For example, the added nitrogen for a typical 10mgd municipal wastewater treatment plant operating a 1 MW lean burn biogas engine can be calculated as follows. The untreated NOx level in a lean burn biogas engine is approximately 0.6 grams per bhp-hr (or 40ppm at 15% O₂), and the CARB standard is 0.07 lbs. per MW-hr (or 2-3ppm at 15% O₂). 0.6 grams per bhp-hr can be converted to 1.55 lbs. per MW-hr (as per CARB guidance: [http://www.arb.ca.gov/energy/dg/guidance/gappc.pdf](http://www.arb.ca.gov/energy/dg/guidance/gappc.pdf)) If NOxRx® were installed on a 1 MW lean burn biogas fired engine operating 24 hours per day, the total NOx produced would be 1.55 x 24 = 37.2 lbs. per day. The treated NOx level would be 0.07 x 24 = 1.68 lbs. per day.
Assuming the following:
- Molecular weight of nitrogen: 14
- Molecular weight of oxygen: 16
- Molecular weight of NOx (as NO2): 46
- Percent nitrogen in NOx (as NO2): 30%

\[30\% \times (37.2 - 1.68) = 11 \text{ lbs. of nitrogen per day}\]

Therefore, if NOxRx® were hypothetically installed on a 1 MW lean burn engine operating 24 hours per day, 11 lbs. of nitrogen per day would be introduced into the headworks of a 10 million gallon per day municipal wastewater treatment facility. One gallon of water weighs 8.34 lbs., and thus 11 lbs. of nitrogen would be added to approximately 83.4 million lbs. of sewage. The change in nitrogen concentration would be too small to be accurately measured.

**Conclusion**

Biogas projects in California and other regions have had difficulty obtaining air permits for operation due to NOx levels in the exhaust stream of the biogas engine. Existing NOx reduction solutions, (SCR and SNCR) are costly, and are not capable of meeting the CARB standard of 2-3 ppm. Furthermore, sulfur and siloxane levels in biogas hinder catalytic processes that reduce NOx emissions. NOxRx® is a patented, non-catalytic, wet scrubbing process that can be used at low temperatures to reduce the regulated pollutants NOx and SOx. Due to increasingly stringent NOx regulations, many biogas projects are using biogas upgrading technologies for pipeline injection or use in a fuel cell. NOxRx® reduces the air permitting risk around biogas projects, allowing debt financing for the project, in addition to enabling a low cost and efficient CHP lean burn engine to be used to monetize the methane rich biogas stream from the anaerobic digester.

The described research project has proven the technical feasibility of NOxRx® at full scale, as NOxRx® has now demonstrated efficacy at a dairy based biogas project in California. Both NOx and SOx emissions were reduced to CARB levels of 2-3 ppm, which is significantly below the current BACT technology, urea injected SCR, which has proven capabilities of reducing NOx to 9-11 ppm. Additionally, NOxRx® has flexibility to keep up with increasingly stringent regulations for reducing NOx emissions through retroactive incorporation of additional absorption stages. Existing NOx reduction solutions lack this flexibility. Furthermore, NOxRx® has proven to be highly sulfur tolerant, negating the need for expensive H2S removal technology to treat the biogas stream prior to combustion. However, if H2S and siloxane removal systems are part of an existing project, a catalytic stage that oxidizes approximately 50% of the NO to NO2 and approximately 95% of the CO to CO2 could be used in conjunction with the NOxRx® wet scrubbing system.

The next step in development of NOxRx® technology is to modify the system design to a more modular format that decreases both the footprint and the cost of the quencher, cooler and absorption stages while maintaining flexibility in both scale and performance.
Appendices

A. Pictures

Project site before construction (biogas flare with wastewater tank)

Steel building with exhaust line going into back of building
Quencher, cooler, first absorber, control panel and fan
Quencher, cooler, first and second absorber