UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

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MEMORANDUM

FROM: Sims Roy
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TO: Docket A-95-51

SUBJECT: Hazardous Air Pollutant (HAP) Emission Control Technology for New Stationary Combustion Turbines

The purpose of this memorandum is to summarize the HAP emission control technology for new stationary combustion turbines and to provide emission factors which may be used to estimate HAP emissions from combustion turbines. Two types of control technologies are discussed in this memorandum: oxidation catalyst systems and lean premix combustion.

Oxidation Catalyst Systems

There are about 200 combustion turbines in the United States that have installed oxidation catalysts primarily for controlling CO emissions but also for VOC and hydrocarbon emission control. These oxidation catalyst systems also reduce HAP emissions such as formaldehyde, acetaldehyde, and benzene from all types of combustion turbines, including simple cycle, combined cycle, cogeneration, and baseline and peaking units. Oxidation catalyst systems have been installed only on diffusion flame combustion turbines. In a diffusion flame combustor, the fuel and air are injected at the combustor and are mixed only by diffusion prior to ignition.

The performance of these oxidation catalyst systems on diffusion flame combustion turbines results in 90-plus percent control of CO and about 85 to 90 percent control of formaldehyde. Similar emission reductions are also achieved on other HAP pollutants. This determination is based primarily on an evaluation of a technology called SCONOx, which is a comparable technology to CO oxidation catalysts. It employs a precious metal catalyst for the removal of CO via catalytic oxidation, just as a CO oxidation catalyst does. A correlation was therefore made between the efficiencies of the SCONOx system and CO oxidation catalysts. The difference is that the SCONOx system uses a chemically modified catalyst so that the catalyst also removes NOX. These chemical modifications are not believed to affect the oxidation catalyst performance. For more information on this topic, refer to Attachment A.

Formaldehyde is the most significant HAP emitted from combustion turbines and accounts for about two-thirds of the HAP emissions. Carbon monoxide is a good surrogate for formaldehyde and other HAPs. Therefore, assuring that the oxidation catalyst system is achieving 90-plus percent reduction of CO assures that the same catalyst system is effective in reducing formaldehyde and other HAP emissions. Carbon monoxide concentrations can also be readily monitored continuously, whereas formaldehyde and other HAPs are difficult to monitor continuously. It may also be possible to establish a concentration limit for CO or HAPs, but a percent reduction is a sound performance check of the oxidation catalyst system.

Oxidation catalyst systems can be used on combustion turbines which combust all types of gaseous and liquid fuels except for landfill and digester gases, which foul the catalyst very quickly because of a compound called siloxane contained in these fuels. Siloxanes are difficult and very costly to remove from these fuels. Therefore, the application of oxidation catalyst systems to combustion turbines that burn landfill or digester gas does not appear to be feasible. Also there are no known installations of oxidation catalysts on combustion turbines burning landfill or digester gases.

Emission Factor Tables

Appendix A includes uncontrolled emission factors for diffusion flame combustion turbines combusting natural gas and diesel fuel at high loads and also at various load conditions. The emission factors were calculated from turbine test reports summarized in the EPA Combustion Turbine Emissions Database (see http://www.epa.gov/ttn/atw/combust/turbine/turbpg.html - Combustion Turbine Emissions Database v.4). As the combustion turbine load decreases, CO and HAP emissions typically increase. The emission factors for high loads (Tables 1 and 2) should therefore not be used to estimate emissions of turbines operating at low loads. The emission factor tables can be used to determine the emission potential of uncontrolled HAP emissions for combustion turbines. Controlled emissions can then be estimated by using the appropriate emission reduction of the control technology.

These emission factors are based on HAP emission tests that were performed between 1988 and the early 1990s and represent diffusion flame combustor technology. More recently lean premix combustor technology turbines have replaced diffusion flame combustor technology turbines, and virtually all new combustion turbines sold are lean premix combustor technology turbines. These turbines are discussed in the following section.

Lean Premix Combustion

There are an estimated 800 or more existing lean premix stationary combustion turbines in the United States. Lean premix technology, introduced in the 1990s, was developed to reduce NOx emissions without the use of add on controls. In a staged lean premix combustion, the air and fuel are thoroughly mixed to form a lean mixture before delivery to the combustor. The premixing of fuel and air and staged entry limits the flame temperature and the residence time at the peak flame temperature. Lean premix combustors emit lower levels of NOx, CO, formaldehyde, and other HAP than diffusion flame combustion turbines. This technology can only be used for natural gas-fired sources.

The EPA recently received and analyzed new emissions test data for 8 tests for formaldehyde on lean premix stationary combustion turbines. The tests were conducted on lean premix stationary combustion turbines ranging in size from 10 MW to 170 MW. The average formaldehyde emission factor for high (>80 percent) loads from these tests is 6.49E-05 lb/MMBtu. The 95^{th} upper percentile level is 2.02E-04 lb/MMBtu. The 95^{th} upper percentile emission factor may be more appropriate to use for determining whether a source is major since it considers the test result variability. Comparison of these emission factors to emission factors for diffusion flame stationary combustion turbines equipped with oxidation catalyst systems shows that HAP emissions from lean premix stationary combustion turbines are equivalent or lower than HAP emissions from diffusion flame stationary combustion turbines equipped with oxidation catalyst systems. Thus, lean premix combustion is a comparable technology to oxidation catalyst systems.

For purposes of monitoring HAP performance of lean premix combustor turbines, NOx emission levels characteristic of lean premix combustor technology could be used as an indicator of proper lean premix combustor performance, which in turn would assure proper operation and low HAP emissions.

Appendix A: Uncontrolled HAP Emission Factors for Diffusion Flame Combustion Turbines Combusting Natural Gas and Diesel Fuel at High Loads and Variable Loads

Table 1. HAP Emission Factors for Natural Gas-Fired Diffusion Flame Combustion Turbines for High Loads (>80%)

HAP	# Tests	Average Emission Factor (lb/MMBtu)	Range (Min - Max)
Acetaldehyde	6	3.95E-05	(1.10E-05 - 8.60E-05)
Benzene	11	1.00E-05	(6.78E-07 - 3.91E-05)
Formaldehyde	20	7.76E-04	(2.21E-06 - 5.61E-03)
POM	6	4.38E-06	(1.15E-06 - 1.06E-05)

Table 2. HAP Emission Factors for Distillate Oil-Fired Diffusion Flame Combustion Turbines for High Loads (>80%)

HAP	# Tests	Average Emission Factor (lb/MMBtu)	Range (Min - Max)
Benzene	3	8.30E-05	(1.40E-05 - 1.25E-04)
Cadmium	1	4.80E-06	---
Chromium	1[a]	1.08E-05	(1.02E-05 - 1.15E-05)
Formaldehyde	6	3.42E-04	(8.12E-05 - 1.01E-03)
Lead	1[a]	1.42E-05	(9.04E-06 - 1.93E-05)
Manganese	1	7.89E-04	---
Mercury	1	1.20E-06	---
POM	10	8.74E-05	(1.12E-05 - 3.10E-04)

[a]Two tests conducted on the same turbine using different test methods

Table 3. HAP Emission Factors for Natural Gas-Fired Diffusion Flame Combustion Turbines for All Loads

HAP	# Tests	Average Emission Factor (lb/MMBtu)	Range (Min - Max)
Acetaldehyde	7	4.51E-05	(1.10E-05 - 8.60E-05)
Benzene	18	1.45E-04	(6.78E-07 - 2.36E-03)
Formaldehyde	28	2.92E-03	(2.21E-06 - 2.54E-02)
POM	8	4.32E-06	(1.15E-06 - 1.06E-05)

Table 4. HAP Emission Factors for Distillate Oil-Fired Diffusion Flame Combustion Turbines for All Loads

HAP	# Tests	Average Emission Factor (lb/MMBtu)	Range (Min - Max)
Acetaldehyde	2	3.03E-05	(2.24E-05 - 3.82E-05)
Benzene	3	8.30E-05	(1.40E-05 - 1.25E-04)
Cadmium	1	4.80E-06	---
Chromium	1[a]	1.08E-05	(1.02E-05 - 1.15E-05)
Formaldehyde	8	2.81E-04	(8.12E-05 - 1.01E-03)
Lead	1[a]	1.42E-05	(9.04E-06 - 1.93E-05)
Manganese	1	7.89E-04	---
Mercury	1	1.20E-06	---
Nickel	1	5.20E-05	---
POM	10	8.74E-05	(1.12E-05 - 3.10E-04)

[a] Two tests conducted on the same turbine using different test methods

Attachment A

MEMORANDUM

DATE: August 19, 1999

SUBJECT: Comparison of CO Oxidation Catalysts with the SCONOx^{TM} System

Oxidation catalysts have been installed on stationary combustion turbines for the purpose of controlling emissions of carbon monoxide (CO) and some volatile organic compounds (VOC). These oxidation catalysts have the potential to oxidize organic hazardous air pollutants (HAPs) as well. Therefore, they are being considered as potential MACT control devices for combustion turbines.

The purpose of this memorandum is to document the achievable emissions reduction levels for CO emissions from gas turbines with CO oxidation catalysts. It is unknown if source tests have been performed on CO catalysts; however, emission testing documentation of a comparable system which includes CO oxidation was obtained. This system is known as the SCONOx^{TM} system.

SCONOx^{TM} is a comparable technology to CO oxidation catalysts. It employs a precious metal catalyst for the removal of CO via catalytic oxidation, just as a CO oxidation catalyst does. A correlation can therefore be made for the efficiencies of the SCONOx^{TM} system and CO catalysts. The difference in the catalytic oxidation technology is that the SCONOx^{TM} system uses a chemically modified catalyst so that the catalyst also removes NOX. These chemical modifications are not believed to affect the oxidation catalyst performance. The following sections describe each technology in greater detail.

CO Oxidation Catalysts

The CO oxidation catalyst is an add-on device that is placed in the turbine exhaust duct. It promotes the oxidation of hydrocarbon compounds to carbon dioxide (CO_2) and water (H_2O) as the emission stream passes through the catalyst bed. The catalyst is usually a precious metal such as platinum, palladium, or rhodium. Other formulations, such as metal oxides for emission streams containing chlorinated compounds, are also used. The oxidation process takes place spontaneously, without the requirement for introducing reactants. The performance of a CO oxidation catalyst is affected by factors such as operating temperature and the presence of poisons in the emission stream.

Oxidation catalysts are typically used on turbines to achieve control of CO emissions, especially turbines that use steam injection, which can increase the concentrations of CO and unburned hydrocarbons in the exhaust. They are also being used to reduce VOC emissions. It is expected that existing catalysts similar to those in use for CO and VOC also oxidize organic HAPs.

SCONOx™

The SCONOx™ Catalytic Absorption System is a proprietary catalyst developed by Goal Line Environmental Technologies LLC. The system design is based on catalytic oxidation and absorption technologies. The catalytic functions of the system are the oxidation of CO to CO_2 and NO to NO_2. The CO_2 passes through the system and exits with the exhaust. The NOX (primarily in the oxidized form of NO_2) is subsequently absorbed on the treated surface of the catalyst. The NOX is eventually released from the catalyst as N_2 via a series of louvers that open and close over each section of the catalyst for short periods. The catalyst is periodically regenerated once it is saturated with NOX by passing a controlled mixture of Aregeneration gases@ over sections of the catalyst for short periods. These gases are non-hazardous.

The chemistry involved in each of the processes that occur in the SCONOx™ catalyst is as follows:

Oxidation & Absorption Cycle

$CO + 1/2O_2 \text{ ---> } CO_2$
$NO + 1/2O_2 \text{ ---> } NO_2$

$2NO_2 + K_2CO_3 \text{ ---> } CO_2 + KNO_3 + KNO_2$

Regeneration Cycle

$KNO_3 + KNO_2 + 4H_2 + CO_2 \text{ ---> } K_2CO_3 + 4\ H_2O + N_2$

Production of Regeneration Gas

$CH_4 + 1/2O_2 + 1.88N_2 \text{ ---> } CO + 2H_2 + 1.88N_2$
$CO + 2H_2 + H_2O + 1.88N_2 \text{ ---> } CO_2 + 3H_2 + 1.88N_2$

The SCONOx™ system was determined Lowest Achievable Emission Rate (LAER) by the U.S. EPA in July of 1997, and Best Available Control Technology (BACT) by the South Coast Air Quality Management District of California in September of 1997. The system is designed to reduce both CO and NOX emissions from natural gas-fired power plants to levels below ambient concentrations. CO emissions of 1 ppm and NOX emissions of 2 ppm are guaranteed by the manufacturer. However, the system has also proven to be effective in removing VOCs and HAPs.

Testing Oxidation Catalyst for HAP Reduction

A combustion turbine equipped with a SCONOx™ catalyst system was tested on March 14, 1997, by Delta Air Quality Services. Samples were collected at the inlet to the catalyst and at the exhaust from the cogeneration unit (turbine exhaust stack) and analyzed for formaldehyde, acetaldehyde, and benzene. The test revealed inlet and outlet concentrations of formaldehyde of 358 ppb and 10 ppb, respectively. Acetaldehyde was reduced from 13.6 ppb down to 0.8 ppb.

Formaldehyde and acetaldehyde reportedly were reduced by 97% and 94%, respectively. No conclusion regarding the control efficiency for benzene could be drawn since the levels before and after the catalyst were both very low and within 0.05 parts per billion of each other. CO was reduced from 50-75 ppm to below 2 ppm (96-97% efficiency) during the testing period.

The main practical limitation of SCONOx™ over CO oxidation catalysts is the maximum operating temperature (700°F) at which SCONOx™ can operate. This temperature limitation is caused by the chemical modification of the catalyst for NOX control and is not a limitation of the oxidation catalyst. The use of the SCONOx™ catalyst for simple cycle installations may be limited due to the temperature limitation. In addition, SCONOx™ has only been proven effective on natural gas-fired installations. Additional research on liquid and coal fuel combustion is currently in progress. Standard CO oxidation catalysts are currently being used on both natural gas and liquid fuel-fired units.

Conclusion

Since the oxidation process that occurs in the SCONOx™ catalyst is identical to that of CO catalysts, the efficiencies of a CO catalyst can be expected to be similar to that of a SCONOx™ catalyst. The removal efficiencies of the SCONOx™ catalysts have been demonstrated through testing to be at least 90% for formaldehyde and acetaldehyde.