

# AN OVERVIEW OF ENDOTHERMIC GENERATORS

## Technical Data

The endothermic generator creates an atmosphere to provide a positive pressure in a heat treating furnace, and a platform on which a carburizing or decarburizing environment can be formulated, by addition of enriching gas or dilution air. Generator maintenance scheduling, operation, and control are discussed.

## INTRODUCTION

Endothermic atmosphere, commonly called endo, carrier gas or RX\* gas, is synthesized in the catalytic retort(s) of endo generators. This gas, combined with an additive gas such as natural gas or propane, or air, is used in heat-treating furnaces to modify the surface chemistry of work positioned in the furnace. Other carrier gases such as exothermic gas, dissociated ammonia and other nitrogen-based atmospheres are found in many heat treating facilities, but endo is most common. Because endo can have a profound impact on the quality of processing, it is important to establish a preventive maintenance program for the generator, and then follow the program religiously.

The most common source of endo is the reaction product of air and natural gas in ratios between about 2.5 to 1 to 5.5 to 1. Since the reaction is not spontaneous below ratios of 6 to 1, it is necessary to supply heat to the generator---hence the term endothermic, meaning heat absorbing. Typical endogas generators produce an atmosphere of approximately 20% carbon monoxide, 40% hydrogen and 40% nitrogen, trace amounts of carbon dioxide and other gases originating in the natural gas or created by the reaction. The application of heat is not sufficient to create the desired products rapidly, so the reacting gases must be exposed to a catalytic agent to accelerate the reaction.

Principal components of an endogas generator are: a heating chamber to supply heat by combustion or electric heating elements, one or more cylindrical retorts (usually vertical) in the heating chamber with numerous small, porous ceramic pieces, impregnated with nickel as a catalyst for the reaction. Also included as part of the generator is a heat exchanger to rapidly cool the reaction products to a temperature that will not allow the reaction to proceed further. One of the most critical parts of the system is the control system that maintains the reaction temperature and adjusts the gas/air ratio to provide the desired dew point.

\*NOTE: RX is a trademark of Surface Combustion

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### MAINTENANCE SCHEDULE

Note: The maintenance schedule suggested in the following paragraphs has been culled from numerous "industry standards" as well as over twenty years of application experience of SSI staff working with the equipment. Because of the make and design of your equipment, and your routine maintenance procedures, not all of these recommendations may apply.

#### Daily:

Visually examine all instrumentation to assure that operation is normal...without incident. Determine that control outputs are within the expected range of operation. Check temperature of water discharged from heat exchanger.

#### Weekly:

Regenerate (burn out) carbon in generator using air (preferred method), exothermic gas, or lean endothermic gas. After regeneration and readjustment of generator to proper dew point, check the gas analysis (including CH<sub>4</sub> content) with an infrared analyzer if possible. Clean the air filter.

#### Monthly:

Clean air-gas mixing valve (carburetor) thoroughly. Check calibration of gas analysis and control equipment such as automatic dew point

controllers, manual dew point indicators, CO/CO<sub>2</sub> analyzers and oxygen probe carbon potential control systems. The primary standard for carbon analyzers is shim stock tests. Alnor or equivalent dew point testing gives a reasonable indication of correct operation. Inspect thermocouples and protection tubes and replace every 3 to 4 months. Check natural gas pressure after the regulator to maintenance balance to the carburetor. Verify correct operation of over temperature controls.

#### Semi-annually:

Replace heat exchanger with standby, clean and refurbish for next service. Inspect catalyst in retort and fill to proper level or replace. Inspect and clean all burners. Clean endo delivery lines to furnaces. Inspect cooling water thermostats, solenoids. Perform complete instrument calibration and service, including safety controls. Have oxygen probe (carbon sensor) refurbished, inspected and certified.

#### Annually:

Check compressor blades. Check motor and compressor bearings.

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### Additional Troubleshooting Considerations

Problems at the furnace can alter an otherwise correct endo atmosphere due to air or water incursion. Therefore both the atmosphere manifold and the furnace should be checked carefully, when a problem is encountered, before attempting any corrective changes in the generator atmosphere control system.

#### Air Maintenance

One of the major sources of difficulty, and hence a nagging maintenance problem, is poor quality air. Contaminants in the air can include dust, fumes from acid cleaning tanks and oil quenching systems. Airborne dust has been linked to failure of pumps and flowmeters, and poor electrical contact in relays. Combustible vapors can cause a carbon sensor to read low, resulting in over carburization.

In order to maintain a good air quality, it is necessary to establish a routine for cleaning filters. In some cases it may be necessary to install ductwork to bring outside, contaminant free air to the equipment. Dust-tight electrical housings are sometimes necessary to eliminate dust and fume problems.

#### Cooler Maintenance

The design objective of coolers is to cool the generated atmosphere as quickly as possible to below about 2600F in order to stabilize the composition before being delivered to the furnace. Two problems impact on operation of the water-cooled heat exchanger. First, dissolved and suspended solids in the water will deposit and coat the tube walls, thereby reducing the heat transfer rate. Further, dissolved oxygen in the water can promote oxidation of the tubes resulting in premature failure.

Water-cooled heat exchangers should be cleaned and pressure tested for leaks during catalyst replacement. Air-cooled exchangers should be blown out with air or rodded as necessary also during catalyst replacement.

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### Gas Supply

For the successful operation of any gas generator, an adequate supply of gas of the proper composition is required at all times.

Dirt, scale and water vapor can cause plugging and failure of regulators and control valves. Flowmeters are especially susceptible to dirt build-up on the float and walls. Gummy deposits from a poor gas mixture can also cause sticking of valve parts and carburetors.

One of the most troublesome problems is the inconsistent analysis of the supply fuel. Propane-air additives to natural gas supplies ('peak shaving') alter effective generator ratios. Unsaturated hydrocarbons such as ethylene and propylene break down quickly into oily soot or coke. Unfortunately, there is little choice when using utility-supplied natural gas. In some instances, propane is selected to avoid these problems, but is not always an economical solution.

Sulfur, both naturally occurring and as additive mercaptans, can cause poisoning of the nickel catalyst and an ultimate failure of the generator to crack gas properly.

It is therefore essential that the gas supply system be kept under close observation, and that all critical components of the system, such as those previously mentioned, be inspected and cleaned as required on a programmed basis. It may be advisable to inform your gas/utility supplier of your special concerns should they, at their discretion opt to alter your feedstock supply by "dosing" or "spiking" (i.e. peak shaving) your gas. We find, in many instances, that the gas utility companies will not advise you of this practice and are reluctant to discuss it.

### Maintenance of the Combustion System

The maintenance of the combustion system of a gas fired endothermic generator is not different from other combustion systems; that is, it should be kept clean and adjusted. Most such systems are relatively simple.

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### Electrical Maintenance

A reliable, uniform supply of regulated power is necessary to operate relays and solenoid valves.

Electrical problems are usually easy to spot, since maintenance personnel are well trained and have sufficient test equipment and wiring diagrams for trouble shooting

### Thermocouples and Protection Tubes

In most atmosphere generators, we recommend the use of type S thermocouples. Because of the relatively high temperatures maintained in atmosphere generators (1850oF to 1950oF), thermocouples should be inspected every three to four months, and replaced if found faulty.

Protection tubes and seal rings should be checked each time the thermocouples are replaced; a broken or leaking tube will greatly shorten the life of the thermocouple. If there is a substantial difference in indicated temperature between the control and overtemp instruments, it can very well be caused by deterioration of one of the protection tubes, causing early failure of the couple. If this should happen, check, and replace as necessary. It is often standard practice to replace the protection tubes when the thermocouple is replaced.

### Maintenance of Temperature Controls

In addition to temperature controls, most atmosphere generators have an over temperature (high limit) instrument to shut the system down in the event of a runaway temperature.

Because of the great variety of recorders, recorder/controllers and controllers, it is difficult to discuss exact inspection, calibration and repair procedures, but general rules of thumb apply. Pens, ink and charts should be checked daily. This ensures a quick look at the instrument to determine if it is operating properly. Manufacturers recommendations for routine maintenance should be scheduled. Temperature calibration is usually fairly stable, but should be checked every six months, at the same time as the thermocouples. The over temperature instrument requires little service, but it does require a monthly check for proper function, and semi-annual calibration.

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### Installation of Catalyst

Catalyst specialists recommend a layer of untreated (no nickel) alumina substrate on the diffuser block extending 2" to 4" into the combustion chamber, to act as a buffer zone. This material can be recovered and reused when changing catalyst.

Slowly pour catalyst into the retort, avoiding dust that may have resulted from shipping. A good rule to follow is to fill the retort to a point just below the top of the combustion chamber. On most generators, this is about 8" below the top plate. Do not overfill. Catalyst in the cooler area above the combustion zone will create sooting due to a reversible reaction in this temperature transition zone. Replace the retort cover plate, using a new gasket.

### Breaking in New Catalyst

Heat the generator slowly to 1500 °F and hold for one hour. This is intended to avoid too rapid expansion of the retort and refractory lining of the combustion chamber. Then raise to normal operating temperature and hold for two hours before attempting to crack gas.

The new catalyst can be broken in by operating at your normal air/gas ratio. Considerable moisture is formed at this point due to reaction with the air in the retort and the pores of the catalyst substrate. This moisture will normally collect at the cold end of the heat exchanger, and should be drained out at the petcocks in the cold gas manifold. Allow sufficient time to dry out the pipes before taking dew point readings and adjusting the ratio for dew point control. Once the catalyst is broken in and reduced, it is not necessary to repeat this operation if "burnout" or reactivation is properly conducted.

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### Catalyst Maintenance

With any specific gas generator, the manufacturer provides recommendations regarding the catalyst--the kind used and its care. Maintenance of the catalyst is vital, and cannot be overemphasized.

The catalyst will last longer if a dew point above 35 °F is maintained. Generally speaking, operation at lower dew points will cause a buildup of carbon, which will appreciably shorten catalyst life. When the catalyst breaks down, it is difficult to achieve maximum gas flow. At that point, new catalyst must be charged. To avert such breakdown, carbon should be burned out of the catalyst bed every week. This is achieved by halting gas production, establishing a temperature of 1600 °F, and then establishing the recommended flow of air as indicated here:

Generator Size	Recommended Air Flow
500 CFH	
750CFH	25CFH 35CFH 50CFH
1000CFH	75CFH 75CFH/per
1500CFH	retort
Multiple Retorts	

If carbon is present on the catalyst, a blue flame will appear at the generator burnoff can or pipe. As soon as the flame disappears, stop the airflow. This is important. Do not continue airflow after the flame disappears. This indicates that all carbon has been removed. If air is continued, the nickel catalyst will become oxidized, and then must be reduced by the procedure outlined for breaking in new catalyst. The generator can be idled during weekends at 1500° F to 1600° F without cracking gas. The amount of time to burn off soot should not take more than a few minutes if the generator has been operated properly above 35° F. Operating generators at low dew points will require more time to burn off the carbon accumulation. It is important for good, efficient gas cracking to remove any carbon. It is also important to obtain the maximum catalyst life. The high refractory catalyst base resists disintegration by carbon, but even the best of catalysts will deteriorate with time in the presence of a heavy carbon deposit. Remember that any catalyst loses its efficiency if the nickel is blanketed by a layer of carbon. Therefore, it is important to check your generator occasionally to see if it is being operated properly and to remove any carbon deposit.

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If, after the catalyst reactivation, the dew point or CO<sub>2</sub> control cannot be achieved, the catalyst will require changing.

### Application of Dew Point Controls

Numerous attempts have been made to apply automatic control to endo generators. At best, many would agree that most of these systems have not performed consistently up to user expectations. Since the early 80's, however, oxygen probe based control systems have provided a more reliable and meaningful approach to automatic dew point control. Surprisingly, they have been shown to minimize the impact of peak shaving.

Two of the early attempts involve insertion of the probe directly into the top of the retort.... either vertically, or at an angle, so that the probe is located 2 to 3" above the surface of the catalyst bed. By this sitting, the probe is exposed to the endogas flow at a temperature between 1550oF and 1750oF typically. While the primary objective of these techniques is to have "in situ" exposure, a number of operating and maintenance concerns have become evident.

Some of the most troubling features of the in situ mounting are:

- High ambient temperatures on the top of the generator;
- Difficult maintenance at this location;
- Concerns related to mounting in a single retort of a multi-retort unit -what's happening in the other retort(s)?
- Shortened probe life because of the high temperature exposure; and
- shortened probe life because of soot buildup in the probe sheath.

Note that burnoff is not an option in this location due to the pressure levels in the endo manifold and impact on the product by the burn off air.

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A third, more recent application using O<sub>2</sub> probes has shown the most promise compared to previously attempted methods. The overall system is shown in Fig. 1, with a close-up view of the sensor installation in Fig.2. We are convinced that the advantages of this system far outweigh the drawbacks. This method does not require accessing the probe into the retort or its exit piping. Instead, a small sample of cooled endogas from the generator exit manifold, or an individual retort in a multi-retort generator, is transported to the short probe which is fitted into a reheat well in the sidewall of the generator heating chamber.

The reheat well can be inserted to a point in the refractory wall that establishes a probe operating temperature between 1350 °F and 1550 °F, preferably 1400 °F. The thermal well provides a thermal shock barrier and a transition buffer between the sample and the combustion atmosphere. This arrangement also allows for a convenient burnoff of the sensor with absolutely no impact on the generated atmosphere quality. Trouble shooting is comfortably conducted at ground level without the extreme discomfort encountered when working with retort mounted probes. High probe temperature/ short life expectancy concerns are eliminated. The proximity of endogas sampling ports for both the O<sub>2</sub> probe and conventional dew point devices (Anor or equivalent) provide greater surety and confidence. There is a valid argument for concerns relating to sampling problems, equilibrium shifts and removal from the "in situ" environment, but we believe the advantages of the reheat well/O<sub>2</sub> probe measuring system overwhelmingly outweigh the disadvantages.

Closing the loop for endo generator control is accomplished by connection to a state-of-the-art microprocessor analyzer/ controller. This device should calculate and display dew point, control output, probe millivolt output and temperature. It should regulate the addition of enriching gas or dilution air for control. If you choose a programmable controller, you can write a "watchdog" program that will sound an alarm if the control output is nearing its maximum. An alarm display might state or infer, for example, that "you are adding over 90% of the maximum trim gas available.....adjust your carburetor (mixing valve) to a richer ratio that allows control gas flow to approach zero". Because the problem has been immediately alarmed, corrective action can be taken to prevent serious malfunction. If programmability is not available, frequent (daily) visual inspection of the control output will determine if you are approaching the limit of control so that you may take steps to adjust the mixing valve.

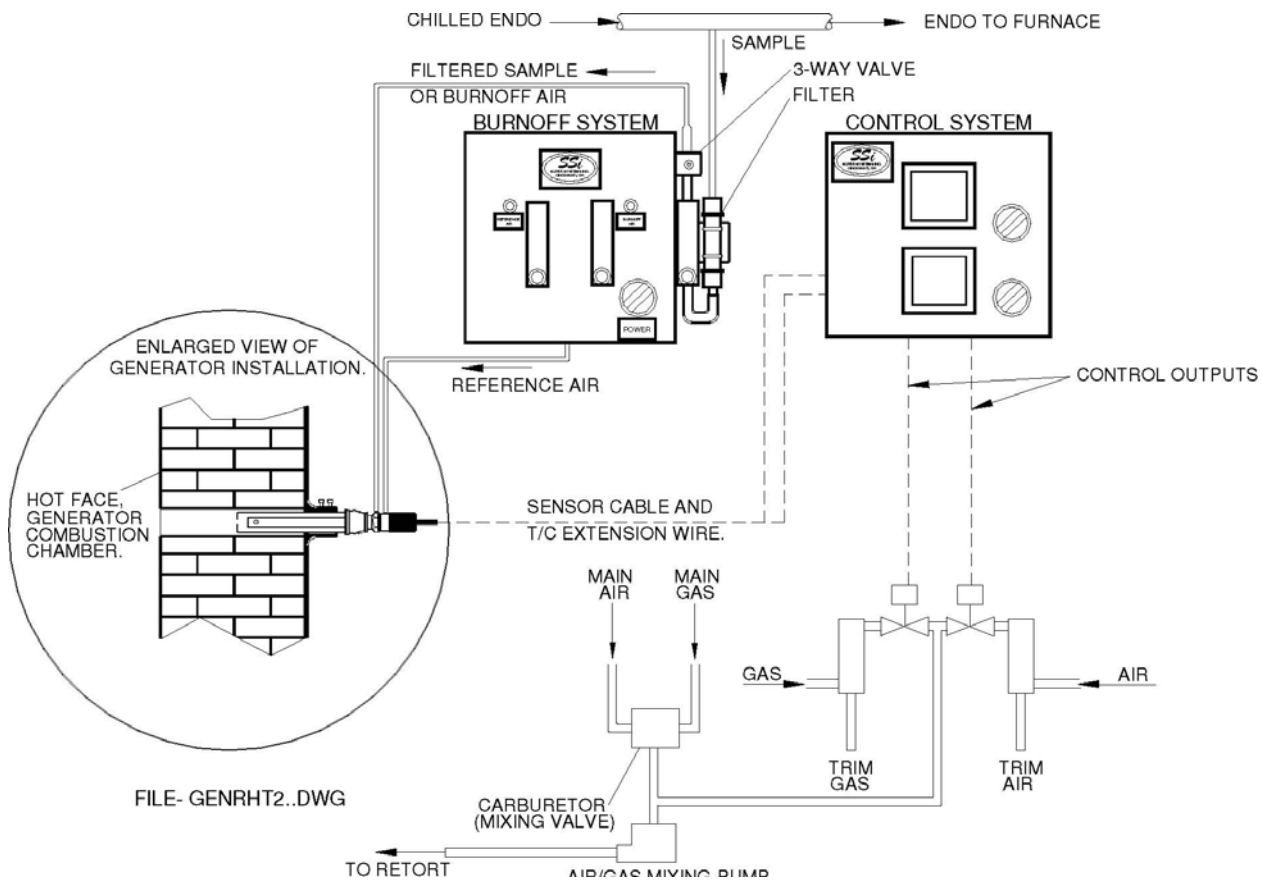
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Fig. 2 shows the control components of Fig.1 and details of the combination reference air/probe burn off system complete with timers, flowmeters and a sample filter to remove carbon particulates. A probe/ well burn off cycle is initiated on a regular basis, usually 12 to 24 hours. As the burn off starts, a relay operates to disconnect power from the gas/air additive valves in order to maintain control while burn off proceeds. After the burn off period of 5 to 10 minutes is completed, power is restored to the additive valves and control operation is resumed. Because of the quick recovery of this system, virtually no deviation from set point can be noted.

It has become an unfortunate fact that oxygen probe control of generators has been so successful that routine manual dew point analysis becomes less and less frequent, in some cases abandoned altogether. This is a dangerous precedent. We strongly advise that dew point be checked at least once a shift, both to avoid catastrophic losses in the event of malfunction, and to maintain operator proficiency in operation of the dewpointer.

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GENERATOR MANIFOLD

AIR/GAS MIXING PUMP ENDOTHERMIC GENERATOR REHEAT WELL SAMPLING, CONDITIONING AND CONTROL SYSTEM

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### Dew point versus %C control?

A frequent question from owners of control instruments that do not provide the option of dew point control is, "why can't I control my generator using carbon potential?" To answer this question, let's first discuss the merits of using the oxygen probe signal to calculate and control an endo generator using dew point as the control variable. Any dew point reading displayed by the control instrument can be immediately verified by cross checking with a conventional dew point instrument, such as the Alnor. A similar verification when %C is the controlled variable could require several hours by a trained technician using shim stock analysis.....just not practical.

Further, most heat treat personnel are familiar with the dew point scale for endo generators and are comfortable working with this control variable.

Finally, dew point is independent of atmosphere temperature. If we were to feed a 40 °F dew point endo into three tight furnaces which were individually controlled at 1500 °F, 1600 °F and 1700 °F, a manual dew pointer would show that each furnace atmosphere was exactly 40 °F. But each would display carbon potentials of 0.85%, 0.59% and 0.40% respectively (see Table 1). To demonstrate why it is not practical to control a generator using %C as the controlled variable, consider the fact that most endo generators typically supply several furnaces. Because the flow from a generator can vary significantly, the probe temperature will correspondingly change. Refer again to Table 1. An instrument set to control at 0.6%C at a sensor temperature of 1600 °F would provide 39 °F dew point gas. A change of temperature to 1550F at the same set point would deliver 45 °F dew point gas. A probe temperature of 1650F would result in a 34 °F dew point. Therefore, *you cannot expect to control a generator using carbon potential as the control variable and expect the dew point to remain constant.*

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**TABLE 1-DEW POINT VS % CARBON, 20%CO, 40%H<sub>2</sub>**

<b>%C</b>	<b>1500F</b>	<b>1550 F</b>	<b>1600 F</b>	<b>1650 F</b>	<b>1700 F</b>	<b>1750 F</b>	<b>1800 F</b>	<b>1900 F</b>	<b>2000 F</b>
<b>0.30</b>	73	66	60	54	48	43	38	30	22
<b>0.35</b>	68	61	55	49	44	39	34	26	18
<b>0.40</b>	64	57	51	45	40	35	31	22	15
<b>0.45</b>	60	54	48	42	37	32	27	19	11
<b>0.50</b>	57	50	44	39	34	29	24	16	9
<b>0.55</b>	54	47	42	36	31	26	22	14	6
<b>0.60</b>	51	45	39	34	28	24	19	11	4
<b>0.65</b>	48	42	37	31	26	21	17	9	2
<b>0.70</b>	46	40	34	29	24	19	15	7	0
<b>0.75</b>	44	38	32	27	22	17	13	5	-2
<b>0.80</b>	42	36	30	25	20	15	11	3	-4
<b>0.85</b>	40	34	28	23	18	14	9	2	-5
<b>0.90</b>	38	32	26	21	16	12	8	0	-7
<b>0.95</b>	36	30	25	20	15	10	6	-2	-8
<b>1.00</b>	34	28	23	18	13	9	5	-3	-10

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