Frequently Asked Questions – The Endothermic Generator

The endothermic generator has been used in heat treating for decades, first introduced into the heat treating market to produce consistency for a non-oxidizing, carbon rich source for a neutral or carburizing atmosphere. As delivery of natural gas to manufacturing facilities became reliable with a consistent chemistry, the appeal for endothermic gas gained momentum. The ability to continuously provide multiple furnaces with a gas composition allowing for a controllable and predictable gas led to higher quality.

The endothermic generator takes a carbon rich gas (typically Methane in North America) mixed with air at a specific ratio using heat and a chemical catalyst to produce a “carrier” gas that can be stabilized and delivered to an atmosphere furnace requiring a non-oxidizing, neutral or carbon rich gas.

Based on this introduction, there are a number of potential questions:

- What should the gas composition look like?
- How does one control variations in supply gasses?
- What is the proper ratio of gases?
- What are the common issues involved?

What should the gas chemistry look like?

In an ideal scenario with the reacted gas at 40°F (4.44°C) dewpoint, the gas chemistry should be roughly 40% H₂, 40% N₂, 20% CO, with trace amounts of CH₄ and CO₂ (Figure 1). As the mixture of gas and air is heated, a catalyst is used to help the reaction of the gas achieve the desired chemistry. Assuming the correct mixture, the right temperature to facilitate the reaction, and a good catalyst, the gas composition can be measured using a non-dispersive infrared analyzer to ensure the right chemistry. It
is important that the generator gas gets cooled preventing a reverse reaction; otherwise excessive sooting of the outlet piping and poor chemistry will result.

Using natural gas, the ideal ratio of air to gas is 2.7:1. However, due to many variables - Ambient Temperature, Relative Humidity, Atmospheric Pressure, Elevation, composition of the natural gas supply, condition of the catalyst, temperature uniformity of the generator, gas cooler efficiency, etc. - this chemistry will vary. Ratios as low as 2.4:1 and as high as 3.6:1 are possible given these sometimes uncontrollable factors.

The reaction to create the endothermic gas can occur as low as 1700°F (927°C); However, ideal operating temperature is recommended at 1900°F (1038°C). The chemistry of the gas changes depending on the temperature of the catalyst; good temperature control with accurate measurement of the retort and catalyst is required. If the operating temperature of the generator is going to change more than 50°F (10°C), a change in the ratio of air to gas may be required to obtain good endothermic gas chemistry.

\[ \text{CH}_4 \] – if the percentage of \( \text{CH}_4 \) is greater than 0, there is a portion of the reaction not occurring. This could be caused from;

1) **Temperature of generator retort not high enough to facilitate the reaction.** Typical endothermic generators operate between 1850°F and 1950°F (1010°C and 1065°C).
2) **Gas ratio not set properly.** If the gas mixture is too rich, it may not have enough air to allow for the reaction, leaving \( \text{CH}_4 \) residual in the reacted gas.
3) **Nickel in catalyst depleted.** The catalyst is made up of refractory infused with nickel. The nickel can become depleted not allowing the reaction to occur. This requires the catalyst to be replaced.
4) **Catalyst has become sooted.** If the generator was being run too rich or too long between burnouts, carbon can deposit on the catalyst rendering the Nickel ineffective. This requires a burnout.

Insufficient CO in the reacted gas indicates there is not enough hydrocarbon in the mixture. Check the ratio of the air and gas, and verify that the dewpoint control is working properly. Keep in mind, the air/gas ratio may be different for different outputs of endothermic gas. For example, the ratio of air to gas for the low end of the total endo flow for a generator may be less than that when you are approaching the maximum endo flow for the generator (or more specifically for the particular retort).

In a typical 40°F (4.44°C) dewpoint, the CO\(_2\) averages about 0.200%, with typical ranges between 0.175-0.25%. Low CO\(_2\) indicates that the endo gas dewpoint is low, and a change is needed in the ratio of air to gas. Conversely, a high CO\(_2\) indicates that the dewpoint of the endo gas is high, and the air to gas ratio needs to be adjusted lower.

Other culprits for gas chemistry inaccuracy may involve the cooler. As previously mentioned, the reacted endo gas requires cooling prior to delivery to the furnaces. If the gas is not cooled, the hot gases may start to reverse the reaction, lowering the CO value. If water cooled chillers are used, a leak in the chiller can cause the water to react with the gas, creating a high CO\(_2\) level. When this occurs, the controls will begin to provide a rich air gas ratio potentially leading to soot on the catalyst and even in
the endo lines. Periodic pressure checks of water cooled chillers are required, and maintaining cleanliness of water and air coolers is required to maintain proper cooling of reacted endo gas.

Variations in the supply gas, volume and chemistry

Many different factors can be considered changes in the gas being supplied to the mixing system: composition of the natural gas supply, drop in supply pressure, inconsistent supply pressure, etc... All of these variables can have large and negative effects in the generator performance and the endo gas reaction.

“Gas spiking” or peak shaving, is a common issue that occurs during heavy demand. Typically an issue in northern parts of the US during winter, the natural gas supply has additives which can cause poor endo gas chemistry, excess soot, and premature nickel depletion. Unfortunately, little can be done to remedy this beyond monitoring and making adjustments to the ratio of air to gas as required.

Most generators have regulators to reduce the supplied gas pressure to a lower pressure that the equipment is readily available to use. However, large changes in pressure can affect the outlet pressures of these regulators, reducing the flow rate of the natural gas, thus requiring a change in air to gas ratio to obtain the desired endo gas chemistry. This could be due to additional equipment being added to the facility without thought to the existing natural gas plumbing, or low delivery pressure from the supplier. Additionally, older and unmaintained gas regulators may not control outlet pressure as precisely, leading to fluctuations. Improperly sized gas supply feeds to endothermic generators with powerful heating systems can cause pressure fluctuations every time the heating system demands gas. Properly sizing gas supply feeds with known plant pressures, and periodic checks and maintenance is imperative to creating a consistent ratio of air to gas.

Although there are multiple sensor types used for measurement, most automatically controlled endothermic generators rely primarily on dewpoint. The lower the dewpoint, the richer the endothermic gas (richer defined as having higher levels of carbon from the endothermic gas). It is common to operate the endo generator using a control variable for dewpoint of 35 to 45˚F (1.67 to 4.44˚C). A dewpoint that is too low runs the risk of sooting the catalyst and the endo lines. When the dewpoint is too high, the furnaces become more difficult to control and may lack the ability to achieve higher carbon potential.

Dewpoint control is typically achieved with a valve adding small amounts of air or gas to the mixture of gas entering the catalyst, controlled by a PID loop. Dewpoint control valves are designed to maintain the chemistry of the endo gas during day to day variations. However, large interruptions in normal use may require a change in the ratio of the air to gas. These interruptions can include large changes in demand and/or changes in atmospheric conditions affecting the chemistry of the air used for the reaction.

When to Change Ratio and How to Make Adjustments

While periodic checks of the endo gas chemistry should be taken daily or even per shift, changes to the ratio of air to gas should not be as frequent. However, when it is necessary, it should be performed by someone well trained in the proper method of making the adjustments. Additionally, utilizing a portable
A dewpoint analyzer and a multi-gas analyzer are critical to ensuring that the proper adjustments are being made. There are two common issues when making adjustments:

1) Changes to the ratio should be minimal. A small change, even as much as .01-.02, can affect the dewpoint as much as 5°F (2.78°C).
2) When making the adjustments, PATIENCE IS KEY! Make a small change and wait at least 30 minutes before making another adjustment. This is especially critical when the generator is producing a lower flow rate of gas.

Using a multi-gas analyzer (Figure 2), the result of these changes may be visible quicker than with a dewpoint sensor. The CO₂ may start to change quickly, providing feedback that the adjustment is working. Note that the CO and CO₂ will not completely settle and may oscillate. However, getting it to a steady state oscillation is key. If the CH₄ is high, reducing the CH₄ may take much longer. Increasing the ratio may change the CO, CO₂, and dewpoint quickly, however the change in CH₄ may take hours.

Common Issues

If the generator has kicked out, it’s often critical to get it making gas again. This is where a good understanding of equipment operation and its safety devices is critical in keeping the equipment operating. Reaction gas pressure switches, mixture pump and retort pressure switches, and firecheck valves are all critical devices to monitor the equipment and its operation. Periodic checks of pressure points on the generator should be taken and verified against original documentation to ensure that maintenance is not required.

Reaction gas pressure switches: These monitor the pressure of the natural gas feeding the mixing system. As previously mentioned, constant delivery pressure is critical to ensure the reaction of endo gas remains constant.

- A low gas pressure switch ensures that there is enough gas available for the reaction to occur. If the pressure of gas gets too low, the ratio of air to gas can become lean and cause premature ignition of the gas, firing back into the reaction piping tripping the firecheck valve.
- A high gas pressure switch ensures that there is not too much gas for the reaction, and that the pressure does not exceed rated pressure of safety devices. If the pressure of the gas gets too high, the ratio of the air to gas can become rich and will soot the catalyst.

Mixture Pump and Retort Pressure Switches are monitoring the outlet pressure of the mixture pump, and/or the outlet pressure of the coolers. These are both high and low pressure switches designed to keep the generator running safely.
• A Low pressure switch may be installed on the outlet of the mixture pump to ensure that it is running, thus allowing the shutoff valve of the natural gas to open to the mixture system. Additionally, this pressure switch ensures that there are not major issues, such as open/leaky pipes or broken gaskets, and that the mixture pump is able to create and supply the gas required to the system.

• A high pressure switch may be installed on the outlet of the mixture pump and/or on the outlet piping of the coolers to ensure that the retorts, coolers, and reaction piping pressure does not become too high. Additionally, it will prevent excess backpressure of the mixture pump (deadheading), which could cause damage. These pressure switches may open a relief type valve that allows gas to be directed to the burnoff vent in an attempt to reduce the reaction gas pressure.

Firecheck valves are installed to prohibit the flow of reaction gas to the retort inlet in the event of a backfire into the reaction gas piping. This is a major safety device that MUST be installed to prevent catastrophic failure. However, infrequent periodic checks and disregarded maintenance are common on these devices. A periodic check with a differential pressure manometer should be taken across the firecheck valve during normal operation to ensure that the pressure drop is not becoming too great. This could indicate that the unit has become contaminated (often with soot and oil) and can cause the mixture pump system to work harder to create the same amounts of endo gas. Additionally, periodic checks that the tripping mechanism and limit switch feedback should be taken to ensure that it can be tripped and reset properly, and that the feedback from the limit switch monitoring the firecheck valve does not allow the mixture pump system to start.

**Pressure Relieving and Low Flow Relief Systems**

As previously mentioned, a high pressure switch may be installed on the outlet of the mixture pump or coolers to ensure that the outlet pressure is not becoming too high. This can be used in conjunction with an electronic valve to relieve excess pressure to the burnoff vent. In addition, vent regulators perform the same function as the combination of the pressure switch and electronic valve, but by mechanical means.
The High pressure switch with an electronic valve offers the capability of being able to electronically monitor the pressure, alarm, and even shut down the equipment. The electronic valve can be used to relieve pressure in the event of a high pressure situation. Additionally, modern generator controls offer great turndown capability; however in the event of the demand being less than the turndown, the electronic valve can be used to allow excess gas to be burned off, so that minimum turndown is maintained. The downside of the electronic valve is that these are typically open or closed, which can result in an immediate change in demand. This can cause the dewpoint to change until the system can recover.

Relief regulator systems have been installed for decades, and have proven to be a reliable means for pressure relief. The relief regulator monitors the reaction gas pressure (either on the outlet of the mixture pump or on the outlet of the cooler), and relieves excess gas to the burnoff. When using a pressure relief regulator, electronic limits must be set to the mixture pump, allowing pressure to build in the reaction gas piping for the pressure relief regulator to open to maintain minimum turndown. Adjusting and dialing the pressure relief regulators may require multiple attempts of increasing and decreasing flow and pressure to ensure safe and reliable operation. However, when these devices do open, the flow is linear in proportion to the increase in pressure (i.e., as the pressure starts to build, the relief regulator will start to open; as the pressure continues to build, the relief regulator will continue to open more).
Modern Generator Control Packages

In recent years, systems have been implemented to help eliminate excess gas. These packages allow endothermic generators to turndown from traditional 2-3:1, to as high as 6-7:1 before any gas needs to be vented off. The more advanced systems do this without requiring any maintenance or operator input to make any manual adjustments to manual mixers, pressure control regulators, or dewpoint control loops.

These systems use the latest technologies to quickly measure and adjust the air and gas flows to maintain tight ratio and dewpoint control during large demand changes. Additionally, these systems automatically adjust the ratio of air to gas if the dewpoint control loop is all the way open or closed for an excessive amount of time - shifting the ratio so that the dewpoint control loop is out of the limits of its control and it can continue to control.
A common question when sizing an advanced turndown package is the demand is: What is the
generator maximum capacity vs. what is the actual maximum demand of the system? Often, the
generator is capable of supplying endothermic gas to all of the equipment without being at maximum
capacity. This is either due to standard offerings of the OEM supplier, or considerations of adding
additional equipment to the heat treating facility in the future. However, more often than not, the
actual maximum demand is much less than the actual maximum capacity of the equipment.

For example, a given generator may be rated for a maximum capacity of 5000 SCFH of endothermic gas.
However, actual maximum demand is 3600 SCFH of endothermic gas. If the turndown system is sized for
the generator maximum capacity, the turndown system control range is ~850-5000 SCFH. If the
turndown system is sized for the demand (with a little room to spare, so for example 4000 SCFH), the
turndown system control range is ~650-4000 SCFH. With the lower turndown, if the system demand is
reduced to minimal equipment, it may not require any excess gas being wasted. Additionally, if
additional capacity is required in the future, the modern systems can be resized and back into
production with minimal downtime.