INDUSTRIAL HEATING

The International Journal of Thermal Processing
AUGUST 2019

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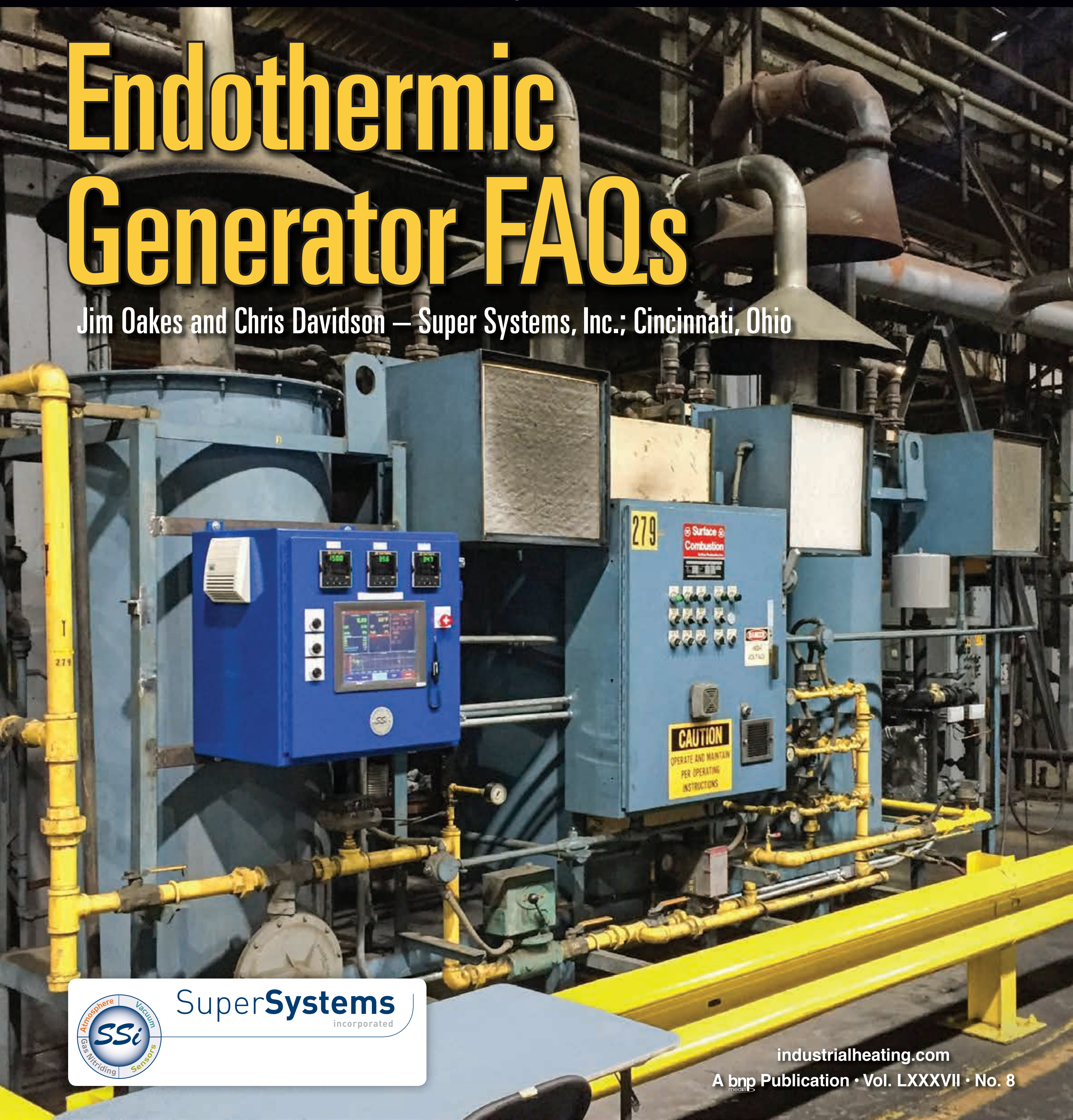

industrialheating.com
A bnp Publication • Vol. LXXXVII • No. 8

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The endothermic generator has been used in heat treating for decades. It was first introduced into the heat-treating market to produce consistency for a nonoxidizing, carbon-rich source for a neutral or carburizing atmosphere.

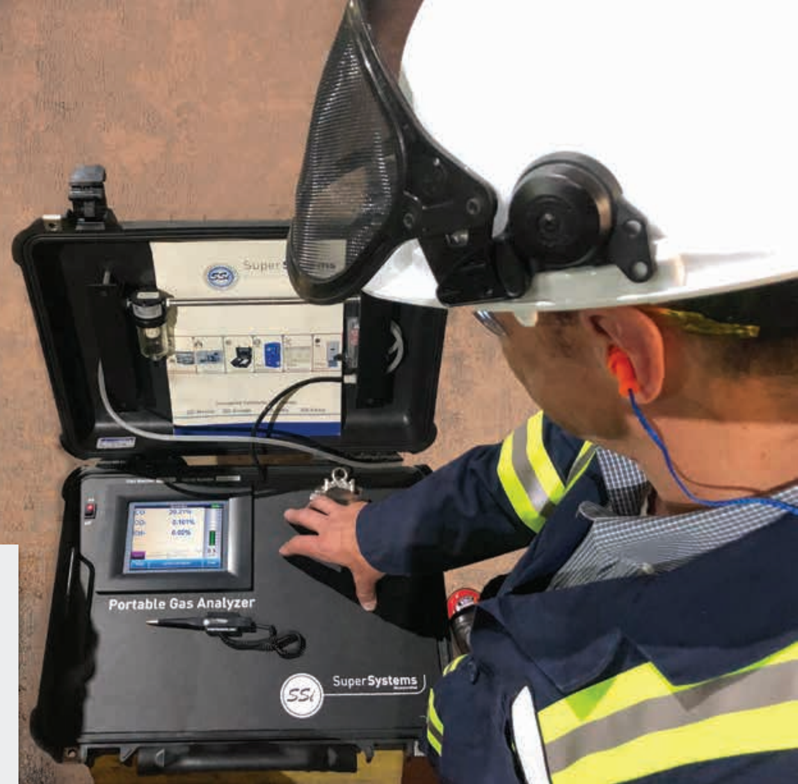

Fig. 1. A multi-gas analyzer

As delivery of natural gas to manufacturing facilities became reliable with a consistent chemistry, the appeal for endothermic (endo) 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 gases?
- What is the proper ratio of gases?
- What are some common issues?

Gas Chemistry

In an ideal scenario with the reacted gas at 40˚F dew point, the gas chemistry should be roughly 40% H_2, 40% N_2, 20% CO, with trace amounts of CH_4 and CO_2 (Equation 1).

$$7.9N_2 + 2.1O_2 + 4CH_4 \rightarrow 7.9N_2 + 4CO + 8H_2$$

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 nondispersive infrared analyzer to ensure the right chemistry. It is important that the generator gas gets cooled to prevent 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 endo gas can occur as low as 1700˚F. However, ideal operating temperature is recommended at 1900˚F. The chemistry of the gas changes depending on the temperature of the catalyst, and 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), a change in the ratio of air to gas may be required to obtain good endo-gas chemistry.

If the percentage of CH_4 is greater than 0, a portion of the reaction is not occurring. Possible causes include:

1. Temperature of generator retort is not high enough to facilitate the reaction. Typical endothermic generators operate between 1850-1950˚F.
2. Gas ratio is not set properly. If the gas mixture is too rich, it may not have enough air to allow for the reaction, leaving CH_4 residual in the reacted gas.
3. Nickel in catalyst is depleted. The catalyst is made up of refractory infused with nickel. The nickel can become depleted, which doesn't allow 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. This renders the nickel ineffective and 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. Keep in mind, the air/gas ratio may be different for different outputs of endo gas. For example, the ratio of air to gas for the low end of the total endothermic flow for a generator may be less than when you are approaching the maximum flow for the generator (or more specifically for the particular retort).

In a typical 40˚F dew point, the CO_2 averages about 0.200%, with typical ranges of 0.175-0.25%. Low CO_2 indicates that the endo-gas dew point is low, and a change is needed in the ratio of air to gas. Conversely, a high CO_2 indicates that the dew point 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 on 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 U.S. during winter, the natural gas supply has additives that 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 adjust the supplied gas pressure to a lower pressure that the equipment is readily available to use. Large changes in pressure can affect the outlet pressures of these regulators, however, 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.

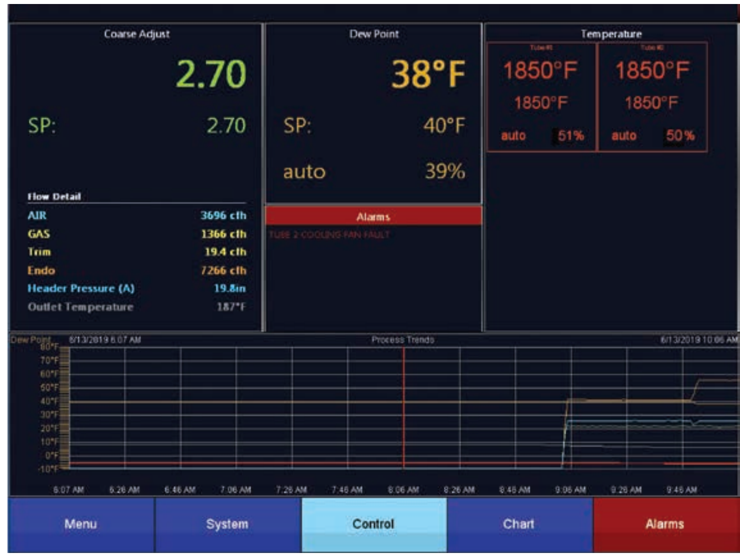

Fig. 2. Automatic adjustment the ratio of air to gas

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.

Dew-point 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. Dew-point 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. When it is necessary, however, it should be performed by someone well trained in the proper method of making the adjustments. Additionally, utilizing a portable dew-point 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:

- Changes to the ratio should be minimal. A small change, even as little as 0.01-0.02, can affect the dew point as much as 5˚F.
- 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 flowrate of gas.

Using a multi-gas analyzer, the result of these changes may be visible quicker than with a dew-point sensor. The CO_2 may start to change quickly, providing feedback that the adjustment is working (Fig. 1). Note that the CO and CO_2 will not completely settle and may oscillate. However, getting it to a steady-state oscillation is key. If the CH_4 is high, reducing the CH_4 may take much longer. Increasing the ratio may change the CO, CO_2 and dew point quickly. However, the change in CH_4 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 fire-check 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 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, which fires back into the reaction piping tripping the fire-check valve.
- A high-gas pressure switch ensures that there is not too much gas for the reaction and that the pressure does not exceed the 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 monitor 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 no 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 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 burn-off vent in an attempt to reduce the reaction gas pressure.

In recent years, systems have been implemented to help eliminate excess gas. These packages allow endothermic generators to turn-down 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 dew-point control loops.

These systems use the latest technologies to quickly measure and adjust the air and gas flows to maintain tight ratio and dew-point control during large demand changes. Additionally, these systems automatically adjust the ratio of air to gas if the dew-point control loop is all the way open or closed for an excessive amount of time (dew-point control loop is out of its control limits), and it can continue to control (Fig. 2).

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