ENDOTHERMIC GAS PRODUCTION OVERVIEW

Written by

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Introduction

This document is intended as an introduction to endothermic gas production with the purpose of providing heat treatment personnel with a basic understanding of the gas generation process and some important rules-of-thumb when trying to identify gas generation problems.

What is Endothermic Gas?

"Endothermic Gas" is a common atmosphere used in many heat-treatment furnaces for applications that require a strong oxygen reducing atmosphere. The most common heat treatment applications include gas carburizing and carbonitriding. It is important to understand that endothermic gas is not actually one gas but a mixture of different gasses. To begin, let us examine what Endothermic Gas is made of.

Endothermic Gas produced from natural gas (CH_4) is primarily composed of:

Hydrogen Gas (H_2)....................................40%
Nitrogen Gas (N_2)......................................40%
Carbon Monoxide Gas (CO)............ 19.5 – 19.8%
Carbon Dioxide (CO_2) .... 0.2 - 0.5%
Water Vapor (H_2O) ....< 0.1%
Methane (CH_4) ....< 0.1%

Endothermic Gas produced from LPG or Propane (C_3H_8) is primarily composed of:

Hydrogen Gas (H_2)....................................31%
Nitrogen Gas (N_2)......................................46%
Carbon Monoxide Gas (CO)............ 22.5 - 22.8%
Carbon Dioxide (CO_2) .... 0.2 - 0.5%
Water Vapor (H_2O) ....< 0.1%
Propane (C_3H_8).......................................< 0.1%

Endothermic Gas Production

The most common and economical method of producing this mixture of gasses is with the use of an endothermic gas generator. Endothermic gas generators are comprised of an air-gas mixing system that supplies a mixture of air and natural gas (or propane) through a heated retort that contains a nickel coated ceramic catalyst. The retort and catalyst are heated to 1900'F where the natural gas (or propane) does not burn but actually decomposes and reacts with oxygen in the air to create the endothermic gas components noted above.

The final critical step in gas generation is the cooling of the gas from the reaction temperature of 1900'F to less than 300'F as quickly as possible to "freeze" the gas and prevent a reverse reaction from occurring.

In addition, there is usually a closed loop control scheme in place that will sample the endothermic gas water vapor or carbon dioxide content and make small mixture adjustments to create the desired endothermic gas quality.

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Gas Reactions and Ratio Control

Inside the 1900'F retort within the endothermic gas generator there are a number of critical reactions occurring. Once again, it is useful to recall that the mixture of air and gas being pumped into the retort is not actually burning and there is no heat being created within the retort itself. The heat is being provided by the combustion burners or electric heating elements surrounding the retort assembly. This heat is being absorbed by the mixture of air and gas and provides the energy required to make the chemical reactions shown below.

Predominant Natural Gas (CH_4) Reaction

$$\mathbf{2}CH_4 + \mathbf{4}N_2 + O_2 + \text{HEAT} \Rightarrow \mathbf{2}CO + \mathbf{4}H_2 + \mathbf{4}N_2$$

Predominant LPG or Propane (C_3H_8) Reaction

$$\mathbf{2}C_3H_8 + \mathbf{12}N_2 + \mathbf{3}O_2 + \text{HEAT} \Rightarrow \mathbf{6}CO + \mathbf{8}H_2 + \mathbf{12}N_2$$

The difference in %CO when endothermic gas is produced with different hydrocarbons is important to note because carbon controllers at the furnace are preset to make certain assumptions. One of those parameters is known as the "CO Factor". This value should be changed to represent the actual %CO of the endothermic gas being introduced into the furnace atmosphere since this value will directly effect the carbon potential (%C) calculation made inside the carbon controller.

For generator operators looking at the flow meters on the gas generator, the above equations can also be described in terms of the Air/Gas Ratio.

Proper Mixture Flow Rate with Natural Gas (Methane)
Air Flow / Gas Flow = 2.5
(Air Flow + Gas Flow) x 1.43 = Endothermic Gas Flow

Proper Mixture Flow Rate with Propane
Air Flow / Gas Flow = 7.5
(Air Flow + Propane Flow) x 1.53 = Endothermic Gas Flow

IMPORTANT NOTE FOR GENERATORS USING NATUAL GAS

While natural gas is primarily composed of methane gas (CH_4), to meet peek demand times a gas supplier will typically introduce a mixture of other hydrocarbons (i.e. propane) into the natural gas supply. When this occurs the gas supplier will dilute the additional propane gas with an inert gas (i.e. nitrogen) to maintain a consistent heat quantity per volume (BTU/CF) within the gas supply line.

The result of this "peak shaving" is that the combustion systems and burners throughout the heat treatment facility will not be greatly affected. However, as indicated above, the chemical reaction required to produce endothermic gas and the atmosphere inside a heat treating furnace will definitely be affected. A properly tuned fuel-injection mixing system will account for these changes automatically on an gas generator by introducing a larger amount of air flow to maintain the desired endothermic gas quality.

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Endothermic Gas Quality Control

While the amount of carbon dioxide and water vapor within endothermic gas is relatively small, the concentrations of these components are critical in determining the carbon potential (%C) of the endothermic gas being produced for a particular heat treatment application. Therefore, most generators will use either Dew Point or CO_2 as a process variable when controlling endothermic gas production.

The ideal endothermic gas dew point or %CO_2 is usually dictated by the temperature and desired carbon potential (%C) within the heat treating furnace where the endothermic gas will be introduced. As a guide, here a basic table that describes what carbon potential of endothermic gas when introduced into a heat treatment furnace operating at a particular temperature.

Dew Point vs. Carbon Potential Relationship

Endothermic Gas	%Carbon Potential in Furnace at Temperature		
Dew Point (‘F)	1500’F	1600’F	1700’F
30	1.10	0.80	0.55
40	0.85	0.60	0.40
50	0.60	0.40	0.25

Once the desired dew point is selected, the primary means of controlling this variable is by adjusting the air/gas ratio of the mixture being pumped into the retort(s) of the endothermic gas generator. This is typically controlled using either a carburetor/trim valve setup or more precisely with a fuel-injection ratio control system.

To better understand what the air/gas ratio adjustments are actually doing to the gas, we need to review the reactions associated with the production of carbon dioxide (CO_2) and water vapor inside the generator.

Methane Combustion

$$CH_4 + 2O_2 => CO_2 + 2H_2O$$

Water Vapor Production (Dew Point Control)

$$2H_2 + O_2 => 2H_2O$$

Carbon Dioxide Production (CO2 Analyzer Control)

$$2CO + O_2 => 2CO_2$$

According to these equations, the amount of CO_2 and water vapor being produced in the endothermic gas is primarily the result of additional air in the gas mixture. Therefore, more air (higher air/gas ratio) will produce more water vapor and result in the production of endothermic gas with a higher dew point. If there is not enough air in the mixture then carbon soot is created in the generator. This is discussed in more detail in the next section.

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In addition to the creation of water vapor the excess oxygen will also produce carbon dioxide. There is a direct relationship between the amount of carbon dioxide and water vapor created within endothermic gas that is described by the following equation:

Hydrogen Water Vapor Reaction

$$H_2 + CO_2 <=> H_2O + CO$$

However, a simple "rule-of-thumb" when trying to understand the relationship of dew point and carbon dioxide in endothermic gas is simply:

Typical Carbon Dioxide / Dew Point Relationship "Rule-of-Thumb"

$$\text{Dew Point ('F)} = \%CO_2 * 100$$

(for $\%CO_2$ values between 0.30 and 0.50)

The key point to remember is that more air (higher ratio) will produce a higher dew point and $\%CO_2$ in the endothermic gas being produced.

SOOT and CARBON FALLOUT

Unfortunately, we have not covered the whole story for endothermic gas production. There are a number of hidden reactions that can occur with even the best ratio control system using the best dew point sensors.

The largest cause for problems in endothermic gas production typically revolves around the creation of carbon (or soot) in the gas being produced. Soot is a byproduct of a number of undesirable reactions that can take place in any endothermic gas generator. The easiest way for a generator to produce soot is when there is not enough air in the gas mixture being pumped into the retort(s) of the generator.

Too Much Natural Gas (CH_4) Reaction

$$\mathbf{3}CH_4 + \mathbf{4}N_2 + O_2 + HEAT => \mathbf{2}CO + \mathbf{5}H_2 + \mathbf{4}N_2 + (\%C_{(soot)} + \%CH_4)$$

This begins to occur when the dew point falls below 20'F and will continue to occur as long as the dew point of the gas remains low. During this time, the endothermic generator will not be very easily controlled and will not respond to ratio adjustments. A three gas analyzer is useful when identifying this reaction, because it will report a large amount of un-reacted methane (CH_4) in the endothermic gas.

"Leaning Out" a Generator

The easiest way to clean the catalyst of a small amount of soot build up is by manually increasing the air/gas ratio to 3.5+ parts air. This process introduces more oxygen into the retort which will react with the carbon on the catalyst in the following reaction. Once the carbon is gone, the normal reactions described above will take over and the dew point will rise quickly. This process can take anywhere between 5 to 15 minutes depending on the amount of soot resident inside the retort and catalyst.

Carbon Burning with Lean Air/Gas Mixture

$$2C_{(soot)} + O_2 => 2CO + HEAT$$

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"Burning Out" a Generator

If after 30 minutes of "leaning the generator" the dew point has not come up, it is usually advisable to perform a "burnout" on the generator. This is accomplished by stopping the air/gas mixture completely, reducing the generator temperature to 1500'F, and introducing a small amount of air flow (100 to 200_{CFH}) into the retort.

Carbon Burnout (100% Air)

$$C(soot) + O_2 \Rightarrow CO_2 + \ll\!+HEAT+\!\gg$$

Since this reaction creates a large amount of heat, it is important to keep watch on the temperature of the generator to ensure that there is no damage to the retort alloy. If the temperature rises by more than 50'F it is typically recommended that the burnout air flow is turned off until the temperature decreases back to the normal 1500'F. A three gas analyzer is useful when performing this procedure as it can identify when the CO and CO_2 concentrations fall to 0% which typically indicate that the carbon burnout is complete.

Carbon Fallout

The other primary cause for soot creation in endothermic gas usually involves the cooling system of the generator. The following reactions will occur quite quickly between the temperatures of 900 and 1300'F.

Water/Soot Precipitation

$$CO + H2 \Rightarrow C(soot) + H2O$$

Carbon Monoixide Decomposition (Carbon Fallout)

$$2CO \Rightarrow C(soot) + CO2$$

As mentioned, both of these reactions will produce a large amount of soot in the cooling system and pipeline downstream of the endothermic gas generator. Therefore, it is critical that endothermic gas be "frozen" as fast as possible from the reaction temperature of 1900'F to below 300'F to minimize any potential for carbon fallout to occur. When the gas temperature is below 300'F there is not enough energy in the gas for the above reactions to occur.

The use of a laser thermometer is useful when determining if there are any cooling problems with a particular generator.

Summary

Endothermic gas is a major component of the atmosphere inside most heat treating furnaces. Therefore, the precise control and documentation of the endothermic gas quality is critical in any facility seeking to provide a quality heat treating service.

Due to the significance of the endothermic gas in the heat treating process, it is highly recommended that any gas generator be equipped with a paperless chart recorder to document the historical performance of the generator at all times. In addition, the use of a three gas analyzer to regularly verify the endothermic gas quality is a good practice to identify any problems before they occur.

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