Principles and Use of Endothermic Gas Generators

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Basic Principles

The purpose of a heat treating atmosphere varies with the desired end result of the heat treating process. The atmospheres used in the heat treating industry have one of two common purposes:

- To protect the material being processed from surface reactions; that is to be *chemically inert*.
- To allow the surface of the material being processed to change; that is, to be *chemically reactive*.

Endothermic gas, or "Endo" is quite commonly used for "neutral" hardening and as a carrier gas for gas carburizing and carbonitriding. The endothermic reaction requires heat to be supplied and this is accomplished in an Endothermic Gas Generator. These units, as illustrated in Figure 1 are the most widely used, simple, and time proven pieces of equipment available in the industry.

Endothermic Generator Operation

Endothermic atmosphere is prepared by reacting a mixture of hydrocarbon gas, typically methane or propane and air, metered in a proportion such that there is just enough oxygen to form carbon monoxide and hydrogen without excess carbon dioxide or water vapor. A nickel impregnated catalyst, usually porous refractory cubes or alumina spheres are commonly used to help promote the chemical reaction.

After the air-gas mixture is compressed to about 1-2 psig, the mixture is passed over a heated catalyst contained in a pressure tight retort which is externally heated using either gas burners or electric heating elements. The temperature of the catalyst is extremely important to assure that the gas is completely reacted so as to yield a consistent composition. The ratio of the diameter of the retort to its length, for any given capacity, is extremely important in producing a completely reacted gas (<0.5% CH_4). The percentage of nickel, typically 5% in the catalyst is an important consideration.

Since the efficiency of the endothermic reaction is thermally dependent it is critical that most catalyst in the retort reach a temperature of at least 925°C (1700°F), preferably 1040°C (1900°F). Surprisingly, the effective depth of catalyst need not be very great, as little as 6" has been found to be effective, provided that all of the atmosphere reaches temperature. In order to achieve this temperature, the heating chamber outside an alloy retort is typically run at 1095°C (2000°F) while a ceramic retort requires temperatures as high as 1200°C (2200°F).

After the passage of the air-gas mixture over the catalyst, the reaction is "frozen" by chilling the gas rapidly to 315°C (600°F) in either a water cooled or air cooled heat exchanger. This prevents a "carbon reversal" reaction from occurring in which carbon and carbon dioxide are formed from the carbon monoxide present in the endothermic gas. This reaction is as follows:

$$(1) \qquad CO \rightarrow C + CO_2$$
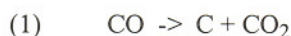
The reaction proceeds to the right, or produces soot in the temperature range between 700°C (1300°F) and 500°C (900°F) so the gas must be cooled rapidly through this transition temperature.

Key Components

The basic construction of an Endothermic Gas Generator are shown in Figure 2 and consists of these basic components:

- Heated reaction retort with catalyst
- Air-gas proportioning control (carburetor)
- Compressor to pass the air-gas mixture through the retort
- Gas cooler, air or water cooled
- Firecheck valve to prevent backfire
- Burnoff vent
- Heating source, gas burners or electric heating elements
- Thermocouples

Optional items include:
- Control device(s)
  - Dew point instrument
  - Oxygen/carbon probe
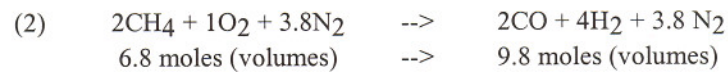 - Infrared (CO) analyzer
- Automatic turndown capability

The Chemistry of Endothermic Gas Generation

A typical endothermic gas composition based on natural gas as a feedstock is:

N_2	45.1 % (by volume)
CO	19.6 % (by volume)
CO_2	0.4 % (by volume)
H_2	34.6 % (by volume)
CH_4	0.3 % (by volume)

Dewpoint   +20/+50

(Air/Gas) Ratio   2.6:1

The chemical reaction with natural gas (assuming 100% CH_4) can be expressed as:

$$(2) \quad 2CH_4 + 1O_2 + 3.8N_2 \quad \rightarrow \quad 2CO + 4H_2 + 3.8\,N_2$$
$$6.8 \text{ moles (volumes)} \quad \rightarrow \quad 9.8 \text{ moles (volumes)}$$

Therefore, using natural gas, the output of an endothermic generator can be calculated as:

9.8 / 6.8 = 1.42* times greater than the total air/gas input.

> * Since natural gas is not 100% methane (typically between 93 - 95% in the US), the ratio is actually closer to 1.42 x 94 ÷ 100 ≈ 1.34.

Note that the theoretical air/gas ratio is 4.8 ÷ 2 = 2.4:1. Actual practice finds this number to be in the range of 2.5:1 to 3.5:1.

Typical Applications of Endothermic Gas Generators

A. Annealing
    1. Iron and Steel [1]
B. Brazing
    1. Copper [2]

2. Silver [2]

    C. Carbon Restoration
        1. Iron and Steel

    D. Carrier Gas
        1. Carburizing
        2. Carbonitriding
        3. Nitrocarburizing

    E. "Neutral " Hardening
        1. Low, medium, and high alloy carbon steels

    F. Normalizing
        1. Iron and Steel [1]

    G. Sintering
        1. Powder Metals [3]

Notes:
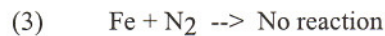
(1) Without scale, decarburization or carburization
(2) Without fear of decarburization
(3) Strongly reducing atmosphere

Gas Chemistry Reactions in the Furnace

The principal gases in an Endothermic Gas Atmosphere, react at elevated temperatures in the following manner:

Nitrogen reactions:

(3) $Fe + N_2 \longrightarrow$ No reaction

(4) $Fe + N \longrightarrow Fe_xN_y$ (e.g. Fe_2N. Fe_4N, $Fe_{16}N_2$)

Atomic nitrogen (N) does not normally occur in a generated furnace atmosphere unless it is purposely introduced by the addition of ammonia (NH_3). Then we have the additional reaction:

(5) $2NH_3 \xrightarrow{\ (*)\ } 2N + 6H = N_2 + 3H_2$
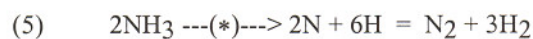
(∗) When this reaction occurs at the surface of the steel being heat treated atomic nitrogen is available to react with the iron as shown in Equation (4) above.

Equation (4) helps explain the carbonitriding reaction as well as being the basic gas reaction of gas nitriding.

Oxygen reactions:

(6) $2Fe + O_2 = 2FeO$
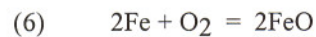
Oxidation of iron occurs in the presence of oxygen as shown by reaction (6).

Oxygen will also **decarburize steel**, therefore, if steel is to be kept bright during heat treatment and free of decarburization, oxygen should be avoided.

Carbon dioxide reactions:

$$(7) \qquad Fe + CO_2 = FeO + CO$$

Carbon dioxide (CO_2) is one of the reaction products when a fuel is burned in air. Carbon dioxide oxidizes iron at elevated temperatures as shown in equation (7). **To prevent oxidation, it is necessary to have an excess of carbon monoxide** (CO) to force the reaction in the reverse (<--) direction. Therefore, to prevent oxidation, CO is a desirable constituent.

$$(8) \qquad Fe_3C + CO_2 = 3Fe + 2CO$$

Carbon dioxide (CO_2) is not only oxidizing to steel but it is extremely decarburizing as shown in equation (8.). To prevent decarburization, CO_2 must be controlled very closely. The actual amount depends upon the CO content, temperature and the carbon content of the steel.
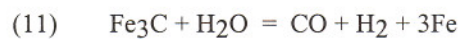
Water vapor reactions:

$$(9) \qquad CO + H_2O = CO_2 + H_2 \quad \text{(Water Gas Reaction)}$$
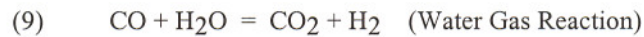
Not only does CO_2 react with iron to cause oxidation and decarburization, but it also reacts with any H_2 present in the furnace atmosphere. This reaction is shown by equation (9) and is referred to as the water-gas reaction. **This equation represents the balancing reaction for gas atmospheres.**

Water vapor (H_2O) is a strongly decarburizing gas and, therefore, any constituent such as CO_2 will have a tendency to form water vapor and thus CO_2 must also be closely controlled.

$$(10) \qquad Fe + H_2O = FeO + H_2$$
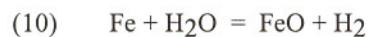
Water vapor (H_2O) and carbon dioxide (CO_2) oxidize and decarburize steel. The oxidation reaction is shown in equation (10). Note, that H_2 is formed when water vapor oxidized iron. Therefore, **to prevent oxidation and to keep iron bright, a definite excess of H_2 over H_2O vapor is required** for each temperature.

$$(11) \qquad Fe_3C + H_2O = CO + H_2 + 3Fe$$

Water vapor (H_2O) like CO_2 is strongly decarburizing as is shown in Equation (11). The reactive products are CO, H_2 and decarburized iron. To prevent decarburization by water vapor, CO and H_2 must be present in amounts to satisfy the equilibrium condition at each temperature. The water vapor constituent, like CO_2, must be very closely controlled.

Since water vapor (H_2O) and CO_2 are in the same reaction, Equation (9), these two constituents run hand-in-hand with the ability to control the carbon potential of an atmosphere. Dew point of a furnace atmosphere looks at the H_2/ H_2O ratio of Equation (9). Similarly, oxygen probes or infrared (CO analyzers look at the CO_2/CO ratio of Equation (9).

Carbon monoxide reactions:

$$(12) \qquad 2CO = C + CO_2$$

The reversible reaction of CO to form carbon and CO_2 is of particular interest in a furnace atmosphere.

CO becomes increasingly more stable at elevated temperatures. It is only at lower temperatures (900°-1350°F.) that carbon monoxide will supply carbon as shown in Equation (12). Carbon in the form of soot is generated. We should think of CO as having a high enough carbon potential to maintain the equilibrium of reaction (11).

Methane reactions:

$$(13) \quad 3Fe + CH_4 \longrightarrow 2H_2 + Fe_3C$$

and

$$(14) \quad CH_4 \longrightarrow C + 2H_2$$
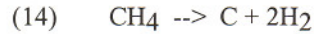
Methane and other hydrocarbons (propane/butane) are strong carburizing agents as shown in Equation (13). When these hydrocarbons dissociate, hydrogen (H_2) is the by-product. At elevated furnace temperatures, methane (CH_4) also breaks down, as shown in equation (14.). The higher the furnace temperature, the more tendency to form C and H_2. Because of this tendency, methane and other hydrocarbon gases supply carbon for gas carburizing.

When methane dissociates, nascent carbon is formed on the steel surface, and the steel absorbs the carbon supplied. **Free carbon, as soot, is not a good source of carbon for carburizing** and, therefore, Equation (12) must be controlled for best results. Free carbon or soot actually acts as an insulator or barrier through which other carbon must try to diffuse, thus, slowing the carburizing rate.

Three Common Generator Problems

Changes in Air-Gas Ratio

The air-gas ratio can be altered slightly to vary the dewpoint (moisture content) of the endothermic gas without appreciably affecting the carbon dioxide or residual methane levels. For example, for a +35°F dew point gas, there is typically <0.5% carbon dioxide in the atmosphere. The residual methane is also under 0.5% if the generator is operating efficiently. If the air-gas ratio "drifts", say above +35°F, the methane percentage will fall, but the carbon dioxide will steadily increase as more air is used until at +70°F there will be between 1.0 - 1.5% carbon dioxide.
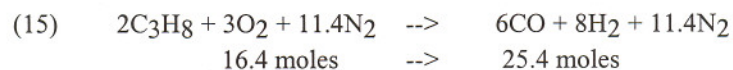
The air-gas ratio is normally set between 2.5:1 and 3.5:1 and monitored so as to avoid "drifting" and changes in gas chemistry.

Variations in Feed stock

"Peak shaving", or the addition of aerated propane into the natural gas supply causes the gas chemistry produced by an Endothermic gas generator to change.

As an example of feedstock variation, we will consider the influence of propane as opposed to methane.

The chemical reaction with propane containing 5% unsaturated hydrocarbons can be written n as:

$$(15) \quad 2C_3H_8 + 3O_2 + 11.4N_2 \longrightarrow 6CO + 8H_2 + 11.4N_2$$
$$16.4 \text{ moles} \longrightarrow 25.4 \text{ moles}$$

Therefore, using propane gas, the output of an endothermic generator will be $25.4 \div 16.4 = 1.54$ times the air/gas input.

Note that the theoretical air/gas ratio is $14.4 \div 2 = 7.2:1$. Actual practice finds this number at 7.5:1 to 8.0:1.

Sooting of the Catalyst Bed

The endothermic gas reaction takes place in two steps or stages. In the first stage, some of the methane burns with air creating an exothermic (heat generating) reaction. In the second stage, the surplus methane reacts with the carbon dioxide and water vapor produced in the first stage. This second stage is endothermic (heat absorbing).

Due to the nature of the chemical reactions taking place, a high temperature and sufficient catalyst bed are required to obtain a complete reaction, so that there is no carbon dioxide, excess methane, or excess water vapor in the final atmosphere. Chilling the gas suddenly prevents the carbon reversal reaction from occurring.

The importance of proper temperature and proper retort size cannot be over-emphasized to obtain a completely reacted gas. By completely reacted gas is meant one in which the amount of residual methane is less than 0.5%. If the temperature is not high enough and the gas not completely reacted, sooting of the catalyst bed will result. Once the catalyst starts to soot, it becomes ineffective, and the gas composition will drift, producing higher percentages of methane, carbon dioxide, and water vapor. Thus the process is not controllable and a specific carbon potential in the furnace atmosphere cannot be maintained. Furthermore, non-reacted methane will break down in the heat treating furnace to produce soot, which will cause high furnace maintenance. Clean, active catalyst is extremely important for responsive dew point or carbon potential control.

Similarly, if the gas coolers are not operating efficiently, sooting will occur due to the carbon reversal reaction. This typically takes place outside the retort causing a restriction in the outlet piping and the piping to the furnace causing back pressure to occur and a loss of flow.