

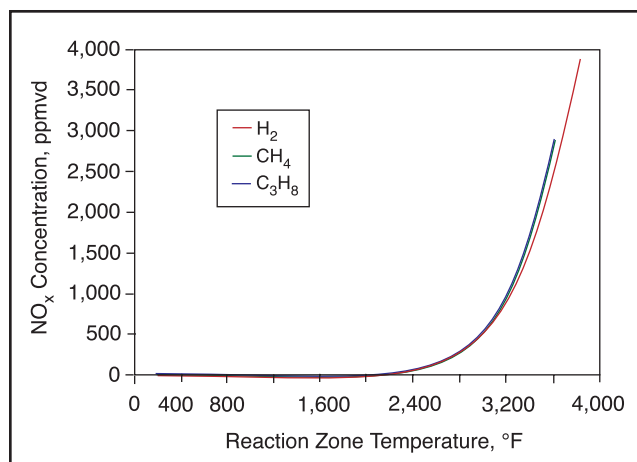
Controlling Emissions During Cold Furnace Startup

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High carbon monoxide emissions from a furnace while its temperature is being ramped up can exceed permit limits if appropriate measures are not taken. Here are a few suggestions.

Environmental regulations continue to reduce the allowable nitrogen oxides (NO_x) emissions from process heaters (1). This has led to the development of ultra-low- NO_x burners (2, 3).

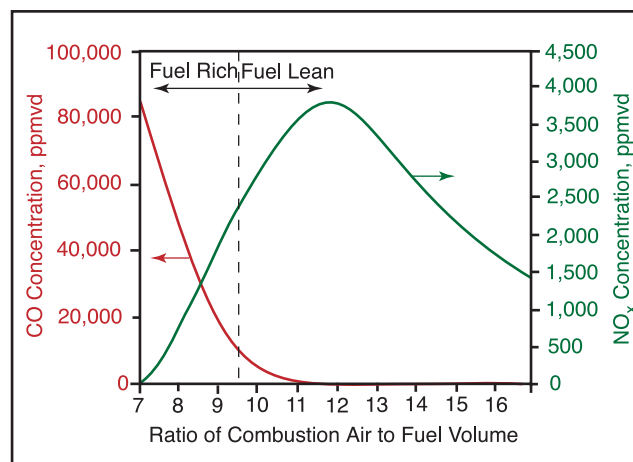
Thermal NO_x emissions are strongly dependent on temperature (Figure 1). Although equilibrium conditions are not attained in the flame, the figure shows the correlation between NO_x emissions and the reaction zone (flame) temperature.



■ Figure 1. Equilibrium calculations of NO_x concentration (parts per million, volumetric dry) as a function of reaction zone temperature for various fuels combusted with air at stoichiometric conditions.

Therefore, most NO_x -reduction techniques try to reduce the temperature of the flame and minimize the peak temperatures in the flame. Some of these techniques include steam or water injection into the flame, air and/or fuel staging, flue gas recirculation, ultra-lean premixing, and eliminating preheating of the fuel and/or combustion air.

It is also important to minimize emissions of carbon monoxide (CO), which is a regulated pollutant. CO and



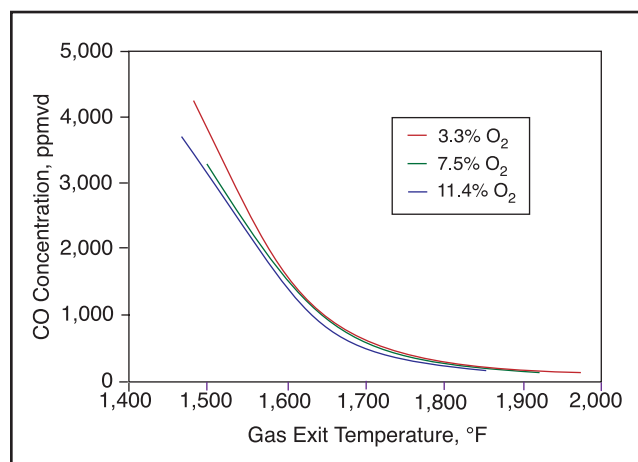
■ Figure 2. Calculated NO_x and CO concentrations as a function of air/fuel ratio at adiabatic equilibrium conditions for CH_4 combustion with air.

NO_x emissions are both strong functions of the air/fuel ratio (Figure 2). At near stoichiometric conditions for the particular fuel being burned (approximately 9.5 for air/ CH_4 combustion), as the air/fuel ratio increases, CO decreases while NO_x increases.

In normal practice, most burners are operated with about 3% excess oxygen (approximately 15% excess air) to ensure low CO emissions and high combustion efficiency. This excess O_2 helps compensate for the imperfect mixing that occurs in real burners. It also allows for any variations in operating conditions that may occur during normal operation, such as daily and seasonal changes in ambient air temperature and humidity, and minor variations in the fuel gas composition.

At equilibrium conditions, there is enough time for all of the reactions to go to completion, so chemical kinetics are not important. However, most real combustion processes are not equilibrium processes, and kinetics usually are important. In most low- NO_x burner designs, mixing is deliberately delayed to stretch out the reactions and reduce the peak temperatures in the flame. The fuel and air are not perfectly mixed and do not have an unlimited amount of time to react.

Chemical kinetics calculations made using CHEMKIN (4, 5) demonstrate how CO generation is affected by various parameters. Figure 3 presents the predicted CO levels as a function of the reaction zone exit temperature for CH_4 combusted with various amounts of excess air, for a baseline (100%) residence time in a perfectly stirred reactor (PSR). These temperatures represent the gas temperature exiting the combustion reaction zone (which was controlled by varying the amount of heat loss from the PSR reactor model). CO emissions are very high at lower temperatures



■ Figure 3. Calculated CO concentration as a function of reaction zone exit temperature and excess O_2 for CH_4 combustion and a baseline (100%) residence time.

and rapidly decrease as the gas temperature increases. At startup conditions, levels of excess O_2 are often high, because the burner air dampers are usually set for normal firing-rate conditions. Since the actual firing rate is typically low at startup, excess air levels are high until the firing rate is gradually increased up to normal operating conditions. In Figure 3, the CO concentration decreases with excess air level because of the dilution effect.

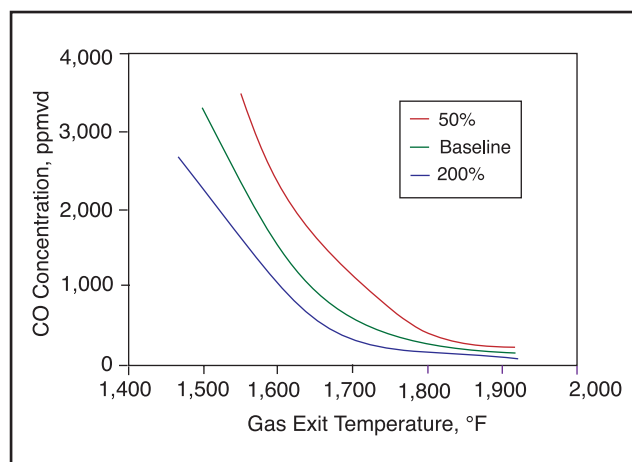
Figure 4 plots predicted CO emissions as a function of reaction zone exit temperature for various residence times in the flame zone with 7.5% excess O_2 . A relatively high level of excess O_2 has been used because this condition is common at startup. Figure 4 shows that the longer the residence time, the less CO is produced, because there is more time for the CO to be converted to CO_2 .

Figures 3 and 4 demonstrate the importance of chemical kinetics in CO formation.

Startup conditions

Many factors make startup conditions significantly different from normal operating conditions. The first and most obvious is that the furnace is cold. This means the furnace walls absorb a much higher proportion of radiant energy than they do when they are hot. This higher radiant absorption during startup removes heat from the flame at a higher rate and reduces the flame temperature, compared to normal operations.

At initial burner light-off, the furnace is full of ambient air. Burners with high furnace-gas entrainment produce cooler flames at startup, where large amounts of ambient air are entrained into the flame. Levels of excess O_2 are higher, both because of the air in the furnace and because the burners are operated with dampers at or near wide open, even



■ Figure 4. Calculated CO concentration as a function of reaction zone exit temperature and residence time for CH_4 combustion with 7.5% excess O_2 .

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though the fuel flowrates are initially lower at startup. As shown in Figure 2, higher excess air levels combined with lower gas temperatures produce higher CO levels.

During startup, the burner firing rate is initially low and it is gradually ramped up to the design firing rate as the heater warms up. This is done to prevent thermally shocking the materials in the heater, which could result in damage. When the firing rate is low during startup, the gas velocities exiting the burner are lower, and the furnace draft is also generally low until the heater warms up. The lower firing rate and lower furnace draft decrease the gas velocities in the heater, which increases the residence time. As shown in Figure 4, increased residence time normally reduces CO emissions. However, the slower gas velocities exiting the burner also lead to poorer mixing of the fuel and combustion air, which generally increases CO emissions.

NO_x emissions generally tend to be lower during cold-furnace startups because of the initially lower furnace gas temperatures. However, CO emissions tend to be higher during cold-furnace startups because of the incomplete combustion caused by the entrainment of cold furnace gases into the flame, as well as higher heat loss to the cold furnace walls. This problem is particularly prevalent in ultra-low-NO_x burners that incorporate large amounts of furnace gas entrainment into the flames. As furnace gas temperatures increase, CO emissions rapidly decrease.

Unfortunately, the short CO spike during cold startup can be problematic for a plant with an air permit based on, for example, hourly averages for a given pollutant. This brief but high CO spike can put a furnace out of compliance — even though it may only occur for a relatively short time during a startup, which may only occur once every year or even less often.

Numerous dynamics take place during heater startup. The fuel composition may be changing. It is not uncommon to start a heater on a fuel such as natural gas, until the processes in the plant are operational and refinery gas is available for use in the burners. The firing rate is being ramped up and the heater is warming up. The amount of

excess O₂ decreases as the firing rate increases. The furnace draft is normally increasing as the heater warms up. It takes time until normal operating conditions are reached — when the firing rate, heater draft and temperature and excess O₂ are at their design values.

The table summarizes the effects of various parameters at startup conditions on NO_x and CO emissions. The flame temperature is lower because of high heat-transfer rates to colder furnace walls. The furnace gas temperature is important because of high entrainment in ultra-low-NO_x burners. The residence time is lower because of reduced firing rates and lower draft levels. Most of the effects at startup tend to reduce NO_x and increase CO. The actual effects depend on the particular application and conditions.

Quantifying the effects

One burner. Figure 5 illustrates the NO_x and CO emissions during the startup of a pilot-scale test furnace with a single ultra-low-NO_x natural-draft burner firing vertically upward. The fuel composition was 15% hydrogen and 85% natural gas (>90% CH₄). Initially, the furnace was at approximately ambient conditions and the burner was at a relatively low firing rate with fairly high levels of excess O₂. The furnace draft was low, so the amount of air pulled into the burner was less than the amount pulled in at design conditions.

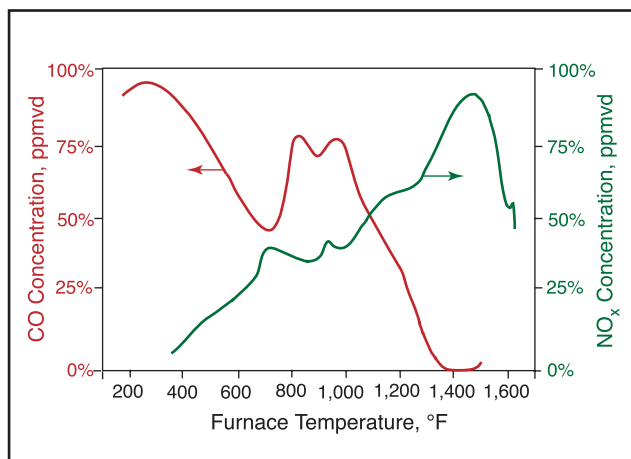
The figure shows that initially NO_x emissions were low and CO emissions were relatively high. After startup, the firing rate was gradually increased. The furnace temperature and the draft increased. The NO_x emissions gradually increased while CO decreased.

Then the test furnace draft was adjusted to the target level. The combination of heat release and O₂ concentration changes produced a spike in CO and dip in NO_x

Table. Summary of effects on emissions during cold furnace startup.

Variable	Condition at Startup*	NO _x	CO
Flame Temperature	Lower	Lower	Higher
Excess Air	Higher	Lower	Higher
Furnace Gas Temperature	Lower	Lower	Higher
Residence Time	Higher	Higher	Lower

*relative to normal operating conditions



■ Figure 5. NO_x and CO emissions as a function of furnace temperature for an ultra-low-NO_x burner.

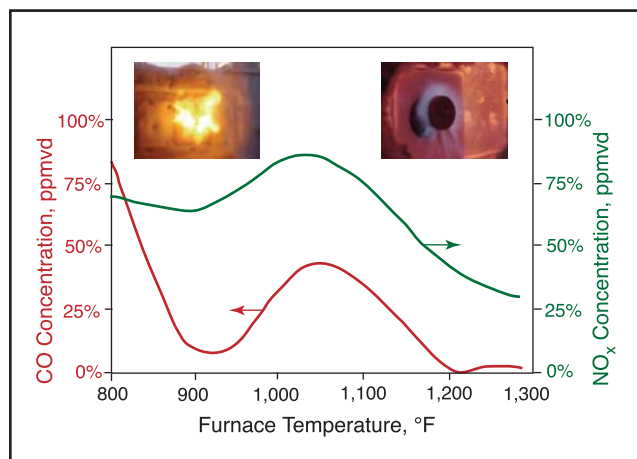
around 900°F. Further increases in temperature caused the NO_x to increase and CO to decrease.

The final reduction in NO_x beyond 1,400°F was caused by the reduction in excess O₂ toward the target of about 3%. Further increases in temperature, at the same excess O₂, would have caused NO_x to increase again.

Two premix burners. Figure 6 shows NO_x and CO emissions during the startup of two ultra-low-NO_x, pre-mix, radiant-wall burners firing in a pilot-scale test furnace. The fuel composition during startup was 100% natural gas (>90% CH₄). Here, too, the furnace was initially at approximately ambient conditions and the burners were at a relatively low firing rate with fairly high levels of excess O₂. The air doors on the burners were open to only about 10% to reduce the amount of air educted into the burner and provide a stable flame.

As the temperature of the refractory adjacent to the burners became hotter, the flame became more stable. This allowed the operator to gradually increase the heat release of the burners. As the burner heat release was increased, the air doors were further opened to allow more air through the burner. These steps were repeated several times during the startup process.

Figure 6 shows that the CO and NO_x emissions for the premix radiant-wall burners trend in a similar fashion, and are similar to those in Figure 5 above about 700°F. That is, both the CO and NO_x emissions from the premix burners decreased as the furnace box temperature increased during startup. The NO_x emissions from the premix burners decreased with temperature because as the tile temperature increased, the burner became more stable, so the operator could increase the amount of air going into the burner. By increasing the air flow, the fuel premixed with more air, resulting in a lower flame temperature.



■ Figure 6. NO_x and CO emissions as a function of furnace temperature for two ultra-low-NO_x radiant-wall burners.

The photographs in Figure 6 correspond to furnace temperatures of 800°F and 1,300°F. At 800°F, the flame appears bright yellow, which suggests that the flame was hot. At 1,300°F, the flame was light blue, significantly cooler than the bright yellow flame, which explains the lower NO_x emissions.

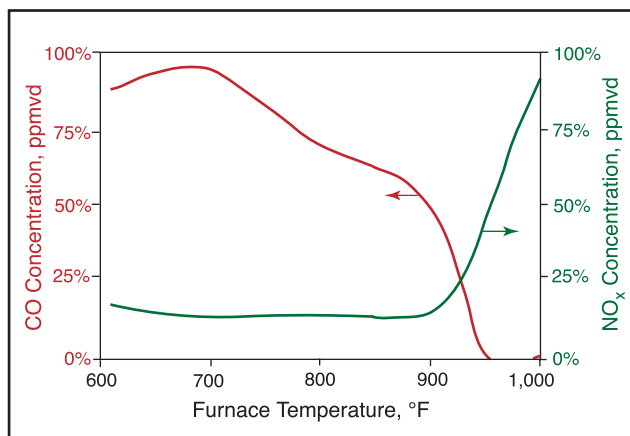
Figure 7 plots the emissions from an ultra-lean premix low-NO_x floor burner, which is commonly used in cracking furnaces. The fuel for these tests was approximately 51% natural gas (>90% CH₄) and 49% hydrogen. These data were collected during startup with excess O₂ levels of about 11% up to roughly 900°F, and then decreasing to about 8.6% excess O₂ near 1,000°F. This corresponded to increasing the fuel flowrate near 900°F while maintaining the same burner-air damper settings and draft conditions. Therefore, the fuel flowrate increased while the air flowrate remained about the same, causing the excess O₂ level to decrease. In this case, NO_x increased and CO decreased rapidly with temperature above about 900°F.

Recommendations

Theoretical analysis and experimental results show that CO emissions are often high during startup because of the flame quenching effect. The colder the furnace, the higher the heat transfer from the flames to the furnace. The increased transfer of energy out of the flame reduces its temperature, compared to operation at typical furnace operating temperatures. The reduced flame temperatures can increase CO emissions.

The flame-quenching problem is particularly exacerbated in many ultra-low-NO_x designs that incorporate furnace gas recirculation. Cold furnace gases are pulled into the flame and further reduce its temperature.

Increased CO emissions are often a problem because



■ Figure 7. NO_x and CO emissions as a function of furnace temperature for an ultra-low-NO_x premix floor burner operated with 3% excess O₂.

they can exceed permitted limits, which are usually based on normal operating conditions and not startup conditions. These temporary CO excursions can be dealt with in several ways.

A strategy that has been used in some ultra-low-NO_x burners in high-temperature cracking furnaces is the incorporation of a separate set of fuel injectors that are only used during startup. These so-called “startup tips” usually provide better mixing of the fuel and combustion air, and do not induce as much furnace gas recirculation as the fuel injectors used during normal operation. The startup tips would typically produce higher NO_x emissions during normal operation than normal tips would produce. However, at startup, the furnace and flame temperatures are much lower, and NO_x emissions are lower than at normal operation.

Once a certain furnace temperature has been reached, say about 1,200°F, then the fuel injection is switched from the startup tips to the regular tips. CO emissions are generally very low above that temperature, but NO_x emissions are beginning to rise on the startup tips. Switching over to the regular tips prevents the NO_x from increasing above target levels.

The drawbacks of startup tips are increased capital costs and more complicated operations. Some new advanced burner designs that produce lower CO emissions at startup, without the need for startup tips, are also available.

A more expensive solution is to use a lower-carbon fuel during startup, such as hydrogen or hydrocarbon fuels blended with hydrogen. The lower carbon content reduces CO emissions. However, the added cost associated with using a short-term supply of a fairly expensive fuel can be significant. In addition, the burners might need to be modified to handle high-hydrogen fuels because of the increased flame speed.

Another alternative to avoid exceeding permitted limits during startup is to work with the regulatory authorities and modify the air permits to account for the transient

increase in CO emissions. For example, the allowable limit for CO emissions might be higher when the furnace temperature is below a certain temperature, such as 1,000°F. The CO emissions would still be regulated, but with an allowance for the reduced furnace temperatures during startup.

In reality, furnaces are normally operated at considerably reduced firing rates during startup. This means that although the CO concentration in the flue gases might be significantly higher than during normal operation, the actual mass flowrate of CO might not be much higher because of the reduced firing rate. Giving operators more flexibility during startup regarding CO emissions could reduce the length of the startup, as it might be possible to start up even faster if the permissible CO limits were higher during that time.

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