Oxyfuel Combustion – Possibilities for NO\textsubscript{x} Reduction

**Authors:** D. Spoljaric (Messer Austria GmbH); B. Holleis (Messer Austria GmbH); M. Potesser (Messer Austria GmbH); M. Demuth (Messer Austria GmbH); J. Ferda (Messer Polska)

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**Abstract:** A number of technologies are available to reduce NO\textsubscript{x} emissions. These technologies can be divided into two major classes, primary and secondary. Primary technologies minimise or prevent NO\textsubscript{x} formation in the combustion zone by controlling the combustion process. Secondary use chemicals to reduce NO\textsubscript{x} formed in the combustion zone to molecular nitrogen. Oxygen combustion is a primary technology able to reduce NO\textsubscript{x} concentrations for up to 90%.

**Introduction**

If oxygen-enriched air or pure oxygen is used for combustion, the adiabatic flame temperature increases and the flue gas composition changes because the oxidant contains less or no nitrogen. Combustion efficiency is improved as the flue gas flow rate decreases. Combustion efficiency declines, as the flue gas temperature increases. If the oxygen concentration of the combustion air is increased, the reduced flue gas flow rate raises combustion efficiency.

The effect of oxygen concentration on NO formation is not straightforward. Increasing oxygen concentration from the 21 \% O\textsubscript{2} in ambient air to around 60 \% O\textsubscript{2} actually increases the equilibrium NO concentration. This is a result of the higher flame temperature and higher O\textsubscript{2} concentrations. Above 60 \% O\textsubscript{2}, the equilibrium NO concentration decreases, due to the lower N concentration, even though the adiabatic flame temperature continues to increase. Another way to look at NO formation for glass melting is to plot the weight of NO formed per unit weight of glass produced, e.g., kg NO/ton glass produced. Glass production is directly proportional to net energy transferred to the glass product, which is in turn directly proportional to the fuel firing rate.

According to literature, thermal NO formation tends to be zero for normal industrial gas burner residence times as long as the flame temperature does not exceed 1,600 °C. Therefore burners should be designed to avoid peak temperatures above 1,600 °C in high-oxygen zones of the flame. Staged combustion, off-gas recirculation and flame dilution are techniques which can reduce NO\textsubscript{x} emissions substantially.
In this publication two methods of NO\textsubscript{x} reduction for oxy-fuel burners are discussed:

- Oscillating combustion
- Flame dilution through off gas recirculation

Oscillating combustion is an alternative to replacing a conventional burner with a low-NO\textsubscript{x} burner. It consists of a high-speed fuel valve partnered with a controller. The valve rapidly varies the amount of fuel supplied to the combustion chamber so that the flame consists of alternating sections of oxygen-rich and oxygen-deficient zones. The flame is reported to be brighter and more turbulent than a flame from a conventional burner. Stoichiometric combustion can be avoided by using oscillating combustion, which creates alternating NO\textsubscript{x}-retarding fuel-rich and fuel-lean zones within a flame. Heat is removed from the zones before they mix, reducing overall peak flame temperature and reducing NO\textsubscript{x} formation. Heat transfer from the flame to the load increases due to the more luminous fuel-rich zones and the breakup of the thermal boundary layer. This technology can be applied with ambient air, preheated air, enriched air, and oxygen based combustion.

Flame dilution techniques have been investigated first to abate NO\textsubscript{x} emissions. Dilution means that fuel and oxidiser are mixed “locally” with a ballast of inert gases before they react so that the oxygen concentration in the reactants is substantially reduced with respect to the 21% of the standard oxidising air. Recirculation of flue gases or products of combustion from inside the combustion chamber carry out the most common dilution mechanism. With the reactants and inert flue gases mixture at auto ignition temperatures and no aerodynamic means of having a stable flame front a volumetric combustion regime occurs. No flame front exists and the combustion is almost transparent, this regime is known as flameless combustion. The heat distribution across the furnace is much more uniform when the combustion is flameless. Peak flame temperatures are lower and this results in reduced NO\textsubscript{x} emissions. This reduction in peak temperatures and the uniform temperature distribution leads to higher radiant heat flux and an increased thermal increases efficiency.

**Oxygen in the combustion process**

Combustion occurs as a result of high energy collision between molecules of fuel and oxygen. In the case of a conventional air fuel system this mechanism is retarded by the presence of nitrogen. Air consists of 21% oxygen and 78% nitrogen with small quantities of inert gases. The nitrogen reduces the flame temperatures in the conventional combustion process since this inert gas must be heated. The case of using pure oxygen increases the partial pressures, the flame temperatures, lengthens the residence time of the molecules in the firing zone due to a reduced gas velocity. Therefore the application of oxygen results in process advantages such as:
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- Higher process temperatures
- Higher reaction rate
- Decreased ignition temperatures
- Higher combustion efficiency
- Lower fuel consumption
- Higher output
- Lower exhaust gas volume

Conventional air – fuel combustion systems produce flame temperatures of up to ca. 2000°C. The flame temperatures are increased dramatically by increasing the proportion of oxygen in the combustion air in order to reach the maximum of ca. 2700°C for 100% oxy-combustion. The effect is illustrated in Figure 2.

The higher temperatures resulting from oxygen addition create higher heat transfer rates by radiation, conduction and convection; with the heat transfer rate proportional to the fourth power of the temperature difference radiation is being the most affected one. Reducing the amount of heat absorbing inert nitrogen dramatically increases the thermal efficiency of any process.

The combustion efficiency is among other parameters also dependent on the oxygen content of the combustion air, as illustrated in figure 1. Estimates show that the overall efficiency is approximately proportional to the combustion efficiency.

![Figure 1: Dependence of combustion efficiency on oxygen content (1)](image1)

![Figure 2: Theoretical combustion temperature for stochiometric combustion of natural gas](image2)
Process technology of oxygen addition
There exist a variety of techniques for implementing oxygen enrichment to the combustion process. The choice of the chosen technique will have influence on the furnace operation, on productivity changes and on possible cost savings.

Total Enrichment
The oxygen is added and premixed to either the primary or secondary combustion air of the existing air burners. This result is an uniform raise of the oxygen content in the whole flame. No additional preparations of furnaces are needed. The addition of oxygen whilst maintaining a constant air supply permits combustion of additional fuel. It is the simplest solution with the lowest investments needed, is though limited <30%O₂ because of the oxygen compatibility reasons and the temperature limits of existing burner components.

Lancing
The oxygen is injected through a separate lance beside, beneath or through the air burner and causes glass melting furnaces to reach a higher pull rate, fuel efficiency and glass quality. This leads to a local affection of the flame and therefore this technique is directional and specific. If applied correctly it can protect refractory from overheating and prolong furnace life. Through this application there is a change of the flame shape according to the positioning of the lance.

Pure Oxygen Burners
Of all the methods presented this is the most directional and is used in melting applications where the large temperature difference between the charge and flame results in higher transfer rates. Oxy-fuel boosting is used to increase the pull rate on a glass furnace which is equipped with conventional combustion.

NOx reduction technology
NOx emissions are generated in the melting furnace in glass plants by the homogeneous gas-phase reaction of oxygen and nitrogen present in the combustion gas, at the high temperatures inherent to this process. Such "thermal NO" is essentially all in the form of NO x with very little NO . Because natural gas is used as the fuel in almost all glass furnaces, there is 2 little contribution of fuel bound nitrogen to NO emissions. However, some glass raw materials contain nitrates ("niter") which may emit NO when heated. Uncontrolled NO emissions depend primarily on various process parameters including fuel firing rate, furnace geometry, fuels used, and raw materials. NO emissions can vary significantly from site-to site and from furnace to furnace. The vast majority however is thermal NOx, generated by the oxidation of nitrogen in the high temperature combustion atmosphere present in the glass furnaces (typically 1650 - 2000°C).
The formation of thermal NOx can be evaluated by the following formula:

\[ \text{NO}_x = A \times \exp\left[-\frac{B}{T}\right] \times N_2 \times (O_2)^{0.5} \times t \]

A, B ..... constants
T ..... flame temperature
t ..... residence time at T

Reduction of NOx can be achieved to a large extent at source by special furnace designs or by primary means of combustion control applied on conventional furnaces. In general however a combination of these with secondary techniques is required to achieve the emission limit.

A combination of the following techniques, in agreement with the regulator, should be used for the control of NOx emissions:

**Primary techniques**
- IoNOx melter - capable of achieving emissions of < 1kg of NOx per tonne of glass melted
- oxy-fuel melter - to be considered at major rebuild or for a new installation
- FENIX process - developing technology
- prevent ingress of air into the furnace - 10% reduction of NOx possible
- reduced air/fuel ratio - 40% reduction of NOx possible
- staged combustion - 35% reduction of NOx possible
- IoNOx burners - 30% reduction of NOx possible

**Secondary techniques**
- 3R process - developing technology, 85% reduction of NOx possible
- reburning - 60% reduction of NOx possible
- SNCR - to be considered for a new installation, up to 70% reduction of NOx possible

In the figures 3 and 4 are shown the technologies available for NOx reduction and the specific costs for the abatement techniques in Euros/tonne glass indicating that just 3 possibilities can reduce NOx over 75% - SCR, 3R and oxy-fuel.
Table 3: Specific costs for the abatement techniques in Euros/tonne glass (2)

<table>
<thead>
<tr>
<th>Group</th>
<th>NOx Reduction</th>
<th>NOx Technology</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30% max.</td>
<td>controlled combustion</td>
<td>used</td>
</tr>
<tr>
<td>1</td>
<td>30% max.</td>
<td>regulated burners</td>
<td>used</td>
</tr>
<tr>
<td>2</td>
<td>50% max.</td>
<td>air staged combustion</td>
<td>not mounted any more</td>
</tr>
<tr>
<td>2</td>
<td>50% max.</td>
<td>OEAS</td>
<td>Pilot</td>
</tr>
<tr>
<td>2</td>
<td>50% max.</td>
<td>SNCR</td>
<td>used</td>
</tr>
<tr>
<td>3</td>
<td>75% max.</td>
<td>LoNOx Melter</td>
<td>used</td>
</tr>
<tr>
<td>3</td>
<td>75% max.</td>
<td>gas staged combustion</td>
<td>used</td>
</tr>
<tr>
<td>3</td>
<td>75% max.</td>
<td>Electrical melter</td>
<td>used</td>
</tr>
<tr>
<td>4</td>
<td>over 75%</td>
<td>Pilkington 3R</td>
<td>used</td>
</tr>
<tr>
<td>4</td>
<td>over 75%</td>
<td>Oxy - Fuel</td>
<td>used</td>
</tr>
<tr>
<td>4</td>
<td>over 75%</td>
<td>SCR</td>
<td>used</td>
</tr>
<tr>
<td>4</td>
<td>over 75%</td>
<td>total electrical melter</td>
<td>used</td>
</tr>
</tbody>
</table>

Figure 3: Specific costs for the abatement techniques in Euros/tonne glass (2)

Figure 4: Technologies for NOx reduction
Furthermore in figure 5 we can see a development on container furnaces since 1990 with projected performance of 625 Kcal/kg (at 60% cullet) for a furnace with a fully integrated batch and cullet preheater with NOx values < 0.2 g/kg.

**Oscillating Combustion**

Oscillating combustion is a retrofit technology that involves the forced oscillation of the fuel flow rate to a furnace. These oscillations create successive, fuel-rich and fuel-lean zones within the furnace. According to literature, heat transfer from the flame to the load increases due to the more luminous fuel-rich zones, a longer overall flame length, and the breakup of the thermal boundary layer. The fuel-rich and fuel-lean zones also produce substantially less NOx than firing at a constant excess air level (Figure 6). The longer flames and higher heat transfer rate reduces overall peak flame temperature and thus reduces additional NOx formation from the eventual mixing of the zones and burnout of combustibles from the rich zones.

According to the literature (4) was the large amount of NOx emissions reduction achieved when the combustion air was enriched with oxygen which suggest that a combined retrofit of oscillating combustion and oxygen enrichment would offer the increased furnace efficiency inherent with oxygen enrichment without the increase in NOx emissions associated with oxygen enrichment alone. Furthermore was oscillating combustion not found suitable for burners with staged combustion or high momentum.
Diluted Combustion
Flame dilution techniques have been investigated first to abate NOx emissions. Dilution means that fuel and oxidiser are mixed “locally” with a ballast of inert gases before they react so that the oxygen concentration in the reactants is substantially reduced with respect to the 21% of the standard oxidising air. Recirculation of flue gases or products of combustion from inside the combustion chamber carry out the most common dilution mechanism.

Messer trials
Aim of the trials
The influence of three types of combustion (immediate, staged and diluted combustion) on the formation of NOx were compared during the trials. Furthermore, in order to verify the literature data concerning the influence of oscillation on the NOx values at high temperatures, trials were made on those different oxy-gas burner types. During the trials a comparison was done between 3 different oxy-gas burner models, a dilution burner and 2 burners already operating in the glass industry, P-LOX and Quadroflo (Figure 7).
**Explanation of the trials**

The experimental work was done on the trial furnace number 2 at the institute GWI (Figure 8). The length of the furnace was 5000mm, the width 1000mm and the height 1200mm. This furnace is equipped with a cooling system consisting of up to 12 water cooled stainless steel pipes, which allows to obtain results at defined furnace temperatures up to 1650°C. The off gas channel is equipped with a damper giving the possibility to operate at similar furnace pressures at different burner ratings.

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**Figure 7: 2 Messer burner types used for the research tests**
Following data were measured during the trials:

- Temperatures (10 x furnace temperature, 12 x wall temperature, off gas temperature, temperature of the surrounding)
- Pressures (furnace pressure, pressure off gas channel, pressures of the media used in front of flow meters, reference pressure)
- Analytical analysis (NO, NO\textsubscript{2}, CO, CO\textsubscript{2}, O\textsubscript{2} in the off gas)
- Volumetric analysis (flows of natural gas and oxygen)

**Results of the experimental work**

**Results P-LON**

In the case of P-LON burner was the static basis of NOx 400ppm. Through the oscillation at all frequencies, big under pressure areas were produced in the furnace, with the result that false air was sucked in. Values could be measured just in one operation modus – with 30 Nm\textsuperscript{3}/h natural gas as basic gas load. In this case a decrease of NOx from 400ppm to 350ppm and an increase of CO concentrations from 100ppm to >400ppm at 1Hz were observed (Figure 9).

In order to have reliable data, the tests were repeated with 2 burners instead of a single one (2 x 200kW). The whole volume of natural gas was lead through one or the other burner. Since one burner was continuously operating there was no need for a basic volume of gas during the non operating times. The results show a decrease of 40% in case of no basic gas loads on the burners, from 430ppm to 250ppm at 0,5Hz. There is also a slight dependence of frequency...
on the NOX levels, the lower the frequency the lower the NOX level. The CO concentration decreased to the level without oscillation of 150ppm above 0,5Hz (Figure 10).

Figure 9: NOX and CO concentration for the P-LON burner (700kW), average furnace temperature 1550°C, 30Nm³/h basic gas flow

Figure 10: NOX and CO concentrations for double P-LON (2x200kW) operation, average furnace temperature 1550°C, (a) with 10 Nm³/h or (b) without basic gas load
Figures 11: NOx and CO concentrations for Quadroflo burner (400kW), average furnace temperature 1550°C, 10 Nm³/h basic gas flow

**Quadroflo**

The burner of 400 kW was successfully tested over the oscillation frequency range of 0 to 1,5 Hz. This burner had the highest starting NOx level of 600 ppm. It was shown that the NOx can be reduced for more than 50% down to ca. 230 ppm, and that the CO concentrations for frequencies of 0,8 to 1,5 Hz additionally decreases (Figure 11). In the case of Quadroflo there exists a frequency dependence of NOx. In order to obtain reproducible results the burner was operated with a basic gas flow of 10 Nm³/h. All tests of this burner were performed at the same ratio of primary to secondary oxygen.

**Dilution Burner**

The dilution burner which was tested has in comparison by far the lowest values of NOx in stationary state <80 ppm at the furnace temperature of 1550°C. In the stationary state are the CO levels <300 ppm. In the case of oscillation, it is visible that at all frequencies there is a decrease of NOx up to 30% but at low frequency levels CO increases. At frequencies above 0,5 Hz CO concentration stabilizes and stays at ca. 350 ppm.
Application of the dilution burner / flameless burner in glass industry. After the successful results the dilution burners were implemented both in glass and frit industry with positive results. In the Figure 13 the installation of such a burner is shown with the reached NO\textsubscript{x} values in operation (Figure 14).

*Figure 12: NO\textsubscript{x}, CO and O\textsubscript{2} concentrations for a dilution burner (700kW), average furnace temperature 1550\degree C*

*Figure 13: Flameless burners at our testing facility (a), in our testing chamber not at temperature (b), at customer site at temperature (c)*
Figure 14: Measured undiluted NO\textsubscript{x} values in operation at 1575°C

**Conclusion**

Oxygen combustion offers many advantages for the glass industry, among these a possibility of NO\textsubscript{x} reduction of up to 90%. In order to improve the possibilities of oxy-fuel application in the glass industry research concerning the influence of oscillation and of dilution combustion has been performed.

Three types of oxy-fuel burners were tested in static and oscillating modi. It was clearly shown that dilution combustion obtained the lowest values followed by staged combustion. The oscillation of natural gas in the case of different types of oxygen burners has shown a decrease of NO\textsubscript{x} values up to 50%. This method can be especially used for burners like P-LON but they have to be operated at least with two pieces in order to stop pulsation in the furnace. The dilution burner obtained by far the lowest NO\textsubscript{x} values both in static and oscillating tests - below 100ppm at a furnace temperature of 1550°C. Such dilution oxy-fuel burners might offer a future for developments of the oxygen combustion in the glass industry.
References:


