How Can the Use of Advanced Oxidation Technologies Promote Energy Efficiency in a Ceramic Kiln?

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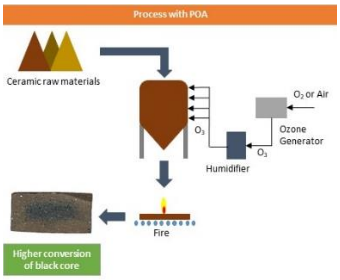

Natural gas is used as a source of thermal energy in the production of ceramic materials, which is one of the highest costs. As a consequence, it seeks to reduce the use of this input per square meter produced. However, some energy efficiency measures directly affect the quality of the product. This is the case of the reduction in the oxygen content (O_2) available in the oven, which can cause the defect called black core. This defect occurs due to the low O_2 content and the presence of organic matter (MO). Thus, the use of ozonation, one of the advanced oxidative processes, allows to reduce MO and total O_2 content in the oven. Based on experiments, a concentration of 24 g/m^3 of ozone (O_3) provides a black core conversion of 54% in 4 hours of exposure and in an atmosphere with 1% O_2, i.e. a scarce atmosphere. In real industrial situations, with the application of ozonation it would be possible to reduce the average O_2 content to 9%, achieving a 100% conversion of black core and an increase in energy efficiency of 25%.

Introduction

In the ceramic segment, natural gas (GN) is used as a source of thermal energy in various stages, representing 15 to 45% of the total cost of production [1]. The combustion of this fuel, mostly of fossil origin, results in the emission of CO_2 into the atmosphere. This requires an increase in the energy efficiency of this production process. Among the ways to increase energy efficiency, the optimization of the combustion system is highlighted. However, adjustments in the combustion system are limited to operating parameters [2].

Burners, responsible for the combustion of GN, may operate with excess air or gas and under stéchiometric conditions. In industries, burners are usually regulated to operate with excess oxygen (O_2). This is done so that all organic matter present in ceramic raw materials can be oxidized and there is no formation of the black core defect [3]. The black core is characterized by the formation of a dark core in the center of the ceramic piece, formed by the reduction of hematite (Fe_2O_3) by the presence of unoxidized organic matter [4]. Thus, the increase in energy efficiency by reducing the O_2 content in the kiln is limited by the formation of this defect.

In view of this, the present work aims to increase the conversion of black core through advanced oxidation of organic matter, using ozone (O_3) as an oxidizing agent. Thus, it is possible to estimate what would be the reduction in the amount of oxygen due to the conversion of black core obtained with the advanced oxidation technologies (AOTs) and how this would influence the consumption of GN.

Material and Methods

For the study, 100 grams of granulated ceramic mass was used, which was placed in a cylindrical stainless steel reactor. In the reactor the mass was subjected to a flow of 1 L/min and O_3 concentration of 24 g/m^3. O_3 was generated in an ozone generator from concentrated O_2 and then humidified in a bubble. The exposure times analyzed were 0.5 h, 1 h, 2 h, 4 h and 6 h. In order to verify the formation of the black core defect, test bodies of 1 cm thick and 2 cm in diameter were produced. For this, the dust moisture was corrected to 8.5%, the conformation to 750 kgf/cm^2, the drying at 110 °C for 18 hours and the burning in a tubular reactor with an atmosphere of 1% O_2, the heating rate of 10 °C/min and the maximum temperature of 1130 °C. Subsequently, the test bodies were cut and the conversion of the black core was analyzed by Equation 1 and by means of Equation 2 it can be verified the behavior of conversion in function of the concentration of oxygen [5]. Using these data, the percentage of reduction in the total O2 content in the kiln due to the conversion achieved with O3 treatment was estimated.

$$X = 1 - \frac{\lambda}{L} \tag{1}$$

$$X^2 = A + \frac{8 \cdot [O_2] \cdot D_{ef}}{\rho_c \cdot L^2} \tag{2}$$

Which is: λ the thickness of the black core at a given moment (m); L the width of the sample or piece (m); $[O_2]$ the concentration of oxygen in the kiln atmosphere (Kmol/m^3); Def the effective diffusiveness of O_2 through the porous solid in the presence of CO_2 (m^2/min); ρc the Kg of carbon present in the dark heart per m^3 of solid; A the constant whose value depends on the oxidation time (t) required for the phase of diffusion of the oxygen through the product crust to begin to control the process.

Results and Discussion

The argilominerals, the main raw material of ceramic compositions, present varying levels of organic matter, present in the form of natural contaminants [6]. This organic matter is made up of humic acids, complex substances with undefined structures. Ozone, a strong oxidizing agent, reacts with organic matter, forming as main products carboxylic acids, aldehydes and ketones [7]. During combustion in ceramic kilns, these compounds, which are smaller in weight and size, are oxidized more easily than humic acids. Because of this, a greater amount of CO_2 is generated, making less CO available to react with the hematite and form the black core defect. This mechanism is confirmed by experimental results, as can be seen in Figure 1.

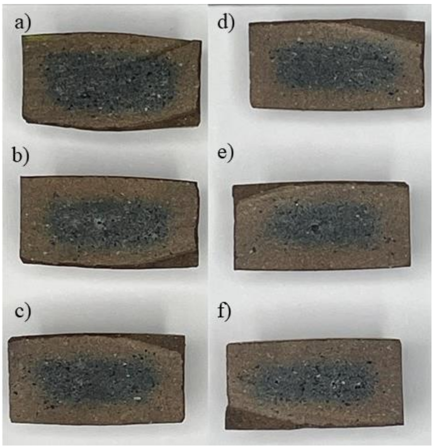

Figure 1. Reduction in the black core area at different ozone treatment times, a) 0 h; b) 0.5 h; c) 1 h; d) 2 h; e) 4 h and f) 6h.

As can be seen in Table 1, O_3 treatment provides an increase in the conversion of the black core even in conditions of O_2 shortage. This demonstrates that the treatment made it possible to regulate the burners to operate with a lesser excess of O_2 and thereby decrease the total concentration of O_2 inside the ceramic kiln. Furthermore, the increased conversion of the black core eliminates other problems, such as the production of waste by non-specified parts and makes it possible to use raw materials with a higher organic content. This allows industries to use raw materials that are closer to, and which would previously be discarded or underused, avoiding the need to travel long distances between deposits and factories.

Table 1. Black core conversion at different ozone treatment times

O_3 Time	Conversion	Partial Pressure O_2
0 h	41%	0,01 atm
0,5 h	47%	0,01 atm
1 h	50%	0,01 atm
2 h	47%	0,01 atm
4 h	54%	0,01 atm
6 h	52%	0,01 atm

Second [1] during combustion in a ceramic kiln, the O_2 content is on average 12%, indicating a consumption of 3,276 kW. Since the formation of black core depends on numerous factors, and not only on the concentration of O_2 inside the kiln, with AOTs it would be possible to reduce about 25% of the total content, i.e. to reduce the average content to 9%, which would reduce the consumption of GN to 2,457 kW. Moreover, this reduction represents a lower amount of CO_2 being emitted into the environment. According to Equation 2, the conversion of black core does not vary linearly with the partial pressure of O_2, having a parabolic behavior. Thus, a reduction to 9% O_2 content in a system without O_3 treatment would represent a conversion of approximately 65%. However, with O_3 treatment this conversion is 100%.

Conclusions

Thus, the results achieved in this work demonstrate that the use of AOTs as a form of removal of organic matter from ceramic raw materials not only promotes the increase in energy efficiency but also helps in the process of reducing greenhouse gas emissions in the ceramic sector.

Acknowledgments

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