Optical Emission Spectroscopy as a Tool For Process Control of Steelmaking Burners

H. Pauna\textsuperscript{1}, M. Aula\textsuperscript{2}, S. Kaukonen\textsuperscript{3}, M. Huttula\textsuperscript{4}, and T. Fabritius\textsuperscript{1}

\textsuperscript{1}Process Metallurgy Research Unit, University of Oulu
Pentti Kaiteran katu 1, P.O. Box 4300, FI-90014 Oulu, Finland
Email: henri.pauna@oulu.fi

\textsuperscript{2}Luxmet Ltd
Paavo Havaksen Tie 5 D, FI-90570 Oulu, Finland

\textsuperscript{3}Sapotech Ltd
Paavo Havaksen Tie 5 D, FI-90570 Oulu, Finland

\textsuperscript{4}Nano and Molecular Systems Research Unit, University of Oulu
Pentti Kaiteran katu 1, P.O. Box 3000, FI-90014 Oulu, Finland

ABSTRACT

In contemporary steelmaking, burners are widely used for heating slabs in walking beam and annealing furnaces, heat-up of empty ladles, flame cutting of steel, as well as providing additional energy in electric arc furnaces. To facilitate the future of carbon-neutral steelmaking, a transition from natural gas-based burners toward hydrogen-based burners is essential to reduce the CO\textsubscript{2} emissions associated with the burners. In addition to this transition, it is important also to optimize the burner practices that are used today, since the transition will take its time. To this end, CO\textsubscript{2} reductions could also be realized with process control aiming toward more efficient use of energy and gas resources. This study presents how optical emission spectroscopy could be used for on-line monitoring and process control of the burner flame. A case study of oxy-fuel cutting is presented, where optical emissions from H\textsubscript{2}O, C\textsubscript{2}, FeO, Na, and K together with thermal radiation were observed. The flame’s properties, such as temperature and radiative heat transfer, identification of the flame species and impurities, and detection of rapid changes in the flame are analyzed from the OES data.

Keywords: Burner, oxy-fuel cutting, process control, optical emission spectroscopy

INTRODUCTION

The steel industry is facing an unprecedented change toward fossil-free and environmentally friendly steelmaking, where electrification and transition toward hydrogen-based reduction and heating have an essential role\textsuperscript{1}. In this transition, a significant change can be realized by replacing carbon-based metallurgy with carbon-lean and carbon-free route\textsuperscript{2}. Currently, natural gas is used in the direct reduction and as a source for primary or additional energy\textsuperscript{3}. The European Steel Association states in their low carbon roadmap that the pathways toward CO\textsubscript{2}-neutral steel industry include replacing carbon-containing gases\textsuperscript{4}. In this roadmap, they state that, with the ongoing retrofitting, 15 \% CO\textsubscript{2} reduction could be achieved, and with alternative pathways with CO\textsubscript{2}-free energy up to 95 \% reduction could be realizable. Due to the fact that total transition to e.g. hydrogen as an alternative reducing agent and energy source will take several years, increasing the efficiency of the usage of carbon-containing resources is important until the transition is realized gradually over the years.

Gases have many purposes in a steel plant: providing additional energy to the melting process of electric arc furnaces, reheating of casted steel in reheating furnace, annealing, and oxy-fuel cutting, just to name a few. Due to the vast quantity of gases used in the steel industry, it is important to monitor the burning process to increase energy efficiency and decrease the formation of undesirable species, such as NO\textsubscript{x}. Improved efficiency benefits the steel plant also by lowering costs, and decreased CO\textsubscript{2} emissions could bring cost savings related to possible CO\textsubscript{2} taxation/fees in the future.
To achieve even better process control and resource efficiency for burners, this paper aims to provide basic information on how optical emission spectroscopy (OES) can be used for on-line in situ monitoring of the flames. Oxy-fuel cutting of a steel slab is presented as a case study with spectra and camera images. Due to the nature of flame as a source of radiation, its temperature and species that radiate in the flame can be analyzed from the OES spectra. OES is suitable for flame studies regardless of the burning gas species. Consequently, the OES-based methods that will be developed today will work, with some adjustment, in the future when the gases would have been replaced.

METHODS AND MATERIALS

The propane oxy-fuel cutting at SSAB Raahe has been used as a case study in this work. Images of the process were taken with Sapotech’s Basler acA2440-20gm GigE camera, and OES spectra were measured with Luxmet’s Avaspec-ULS2048 Czerny–Turner spectrometer covering 490 – 1000 nm, i.e., the visible and partly the near-infrared regions of the spectrum of light. Eight images and spectra were recorded per second, and they were analyzed with a Matlab algorithm after the experiment.

The spectrometer and camera were placed a few meters away from the oxy-fuel cutting in order to avoid damage to the devices. Figure 1 displays an example image of the cutting, where the cuts, slab, burners, and flames have been highlighted with different colors. The flame that is enclosed by a red circle is the flame that is used to cut, and the one with a yellow circle is used for the preparation of sample cutting if needed.

Figure 1. Image of the flame cutting with highlighted cuts (cyan), burners (green), slab’s edges (orange), and cutting flame (red). The flame/torch highlighted with yellow is used for preparation of sample cutting if needed.

THEORETICAL

The flame’s spectra have two distinctive forms of radiation, i.e., thermal radiation and characteristic optical emissions from various species within the flame. Altogether, these two types of radiation describe the radiative energy transfer of a radiative source. Thermal radiation is generated by the thermal motion of particles in the flame and hot surface when the heat energy is released as electromagnetic radiation. The intensity distribution of the thermal radiation follows Planck’s law and forms a wide background to the spectrum. By simplifying Planck’s law, the temperature of the observed object can be estimated with
\[ T = \left( \frac{1}{\lambda_2} - \frac{1}{\lambda_1} \right) \frac{hc/k}{\ln\left[ \frac{I_1}{I_2} \right]} \]  

(1)

where \( \lambda_1 \) and \( \lambda_2 \) are the wavelengths at chosen points in the spectrum, \( h \) is the Planck’s constant, \( c \) is the speed of light, \( k \) is the Boltzmann constant, and \( I_1 \) and \( I_2 \) are the spectrum intensities at \( \lambda_1 \) and \( \lambda_2 \), respectively. The wavelengths have been selected to be \( \lambda_1 = 600 \) nm and \( \lambda_2 = 800 \) nm because there are no interferences from atomic or molecular optical emission lines near these wavelengths.

The atomic and molecular optical emissions occur when a particle absorbs energy, and its electron is excited to a higher energy state. This excess energy can then be consequently released as a photon, which has an energy equal to the energy difference between the upper and lower energy states. Due to the unique structure of each atom and molecule, the photons have characteristic energy, or wavelength, specified by the atom or molecule. The basis of OES is to measure these photons and identify the atoms and molecules from which they have originated.

**DISCUSSION**

1. Oxy-fuel cutting case study

Figure 2 shows four images and spectra of the cutting at different process steps, the time evolution of the temperature calculated with Equation (1) together with \( \text{H}_2\text{O} \) and \( \text{C}_2 \) molecular optical emission intensities. The rising background in the spectra represents the heat radiation. However, the transmission of the spectrometer starts to decrease above 950 nm, and thus the spectral features are noisy above this wavelength. In Figure 2 a), the cutting is initiated and the flame goes across the edge of the slab. In this instance, FeO optical emissions are observed on both sides of the intense and sharp Na I doublet at 588 nm. Molecular optical emissions usually consist of a multitude of spectral lines, which merge into a single wide intensity distribution with low spectral resolution. Also, K I doublet at 766 nm, and some activity above 900 nm can be seen. When the cutting progresses further in b) and c), the \( \text{H}_2\text{O} \) molecular optical emissions are more clearly seen near 920 nm, and \( \text{C}_2 \) emissions at and below 517 nm. Near the end of the cutting in d), the torch is brought next to the cutting flame, and a clear increase in \( \text{H}_2\text{O} \) and \( \text{C}_2 \) intensities are observed. Furthermore, the FeO emissions are present again at d).

The sample cutting torch (marked with yellow in Figure 1) is brought to the vicinity of the cutting flame at 80 s, but \( \text{H}_2\text{O} \) and \( \text{C}_2 \) intensities increase already 10 s earlier at 70 s. When looking at the images between instances 3 and 4 in Figure 2, no apparent change happens in the cutting flame except at 80 s when the sample cutting torch is moved. The reason why \( \text{H}_2\text{O} \) and \( \text{C}_2 \) intensities increase at 70 s remains unknown. This change at 70 s does not affect the estimated temperature, whereas at 80 s the temperature rises significantly and starts to fluctuate. The temperatures above 3500 K are most probably caused by changing optical conditions in the flame that affect the spectra, rather than such a high increase in the actual temperature. To assess the reason behind the increase in \( \text{H}_2\text{O} \) and \( \text{C}_2 \) intensities, including also process data, such as gas flow rate, electrical parameters, etc., would be very important when planning the future studies.
During the case study, only a few species were observed: Na I, K I, FeO, C_2, and H_2O. This is the result of two factors; i) the wavelength range was from 490 to 1000 nm, thus covering only part of the visible and very near-infrared, and ii) oxy-fuel cutting and the gas mixture related to industrial practice as the phenomenon that was measured. First, 490 to 1000 nm is only a narrow part of the spectrum of light and several optical emissions occur below and above 490 and 1000 nm, respectively. Optical emissions in the ultra-violet occur below about 400 nm, violet – blue emissions between 400 and 500 nm, and both optical emissions and absorptions above the 1000 nm in the infrared. Second, the source of the flame significantly affects the spectral characteristics of the flame, and various flames will have different optical spectra. To emphasize the importance of wider spectral coverage and the effect of the burning species, various optical emissions that can be identified from several different flames have been listed in Table I. The table is not, by any means, all-encompassing, and only includes optical emissions between 300 and 1000 nm.

Above 1000 nm, optical absorption, i.e. the absorption of light by e.g. gases in the atmosphere, are more likely to be observed than optical emissions. In this case, a decline in spectral intensity will be observed instead of increased intensity. The absorption can be so intense that a clear notch is formed in the spectra, which might even bring the intensity to zero if the absorption is strong enough. Similar to emissions, also absorptions occur at characteristic wavelengths for each species, and the absorbing species can be identified. For more information on the absorption behavior of various species, see the work of Zeller et al.⁵
Table I: Different species that can be identified in the UV – NIR spectra of various flames.

<table>
<thead>
<tr>
<th>Species</th>
<th>Wavelength (nm)</th>
<th>Flame source</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>890 – 910</td>
<td>Nitromethane-air</td>
<td>[6]</td>
</tr>
<tr>
<td></td>
<td>917 – 950</td>
<td>Nitromethane-air, ammonia/air</td>
<td>This study, [6], [7]</td>
</tr>
<tr>
<td>H₂</td>
<td>612 – 650</td>
<td>Propane</td>
<td>[8]</td>
</tr>
<tr>
<td>FeO</td>
<td>554 – 640</td>
<td>Methane–iron–air</td>
<td>This study, [9]</td>
</tr>
<tr>
<td>C₂</td>
<td>450 – 475</td>
<td>Bio-oil, oil, natural gas, CH₄, propane</td>
<td>[8], [10 – 12]</td>
</tr>
<tr>
<td></td>
<td>498 – 517</td>
<td>Bio-oil, oil, natural gas, CH₄, propane</td>
<td>This study, [8], [10 – 12]</td>
</tr>
<tr>
<td></td>
<td>550 – 570</td>
<td>Bio-oil, oil, natural gas, CH₄, propane</td>
<td>This study, [8], [10 – 12]</td>
</tr>
<tr>
<td>Na I</td>
<td>588 (doublet)</td>
<td>Bio-oil, oil, natural gas, nitromethane-air</td>
<td>This study, [6], [10], [11], [13]</td>
</tr>
<tr>
<td>K I</td>
<td>766 (doublet)</td>
<td>Bio-oil, oil, natural gas, nitromethane-air</td>
<td>This study, [6], [10], [11]</td>
</tr>
<tr>
<td>OH</td>
<td>306 – 310</td>
<td>H₂–O₂ flame</td>
<td>[8], [14]</td>
</tr>
<tr>
<td>O₂</td>
<td>758 – 766</td>
<td>H₂–O₂ flame</td>
<td>[14]</td>
</tr>
<tr>
<td>CH</td>
<td>~ 390</td>
<td>Propane</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>~ 432</td>
<td>Bio-oil, oil, natural gas, nitromethane-air, CH₄, propane</td>
<td>[6], [8], [10 – 12]</td>
</tr>
<tr>
<td></td>
<td>812 – 848</td>
<td>Nitromethane-air</td>
<td>[6]</td>
</tr>
<tr>
<td>CN</td>
<td>380 – 390</td>
<td>Propane</td>
<td>[8]</td>
</tr>
<tr>
<td></td>
<td>915 – 940</td>
<td>Nitromethane-air</td>
<td>[6]</td>
</tr>
<tr>
<td>NO</td>
<td>800 – 900</td>
<td>Nitromethane-air</td>
<td>[6]</td>
</tr>
<tr>
<td>HNO</td>
<td>610 – 800</td>
<td>Nitromethane-air</td>
<td>[6]</td>
</tr>
<tr>
<td>NH</td>
<td>828 – 844</td>
<td>Nitromethane-air</td>
<td>[6]</td>
</tr>
<tr>
<td>NH₃</td>
<td>632, 734 (550 – 840)</td>
<td>Ammonia/air</td>
<td>[7]</td>
</tr>
<tr>
<td>AlO</td>
<td>440 – 560</td>
<td>Air and oxygen–argon/helium mixtures (continuous Al flow)</td>
<td>[13]</td>
</tr>
<tr>
<td>CaF</td>
<td>~ 554, ~ 606</td>
<td>Gasoline</td>
<td>[15]</td>
</tr>
<tr>
<td>SiO</td>
<td>200 – 250</td>
<td>Propane + HMDSO*</td>
<td>[8]</td>
</tr>
</tbody>
</table>

*HMDSO = hexamethyldisiloxane

2. OES as a process control tool

One of the most prominent applications of OES is to detect the species that radiate within the flame and hence evaluate the flame’s composition. In this way, also impurities and non-desirable species, such as NOₓ, could be identified on-line from the spectra. Na I and K I optical emissions increase significantly in Figure 2 a), which can be seen also in Figure 3 a). This means that some of the alkali emissions originate from the slab. Also, FeO optical emissions are clearly seen when the flame goes across the slab’s edge, as depicted in Figure 2 a) and Figure 3 b). Na I and K I are present at all instances, also in the free-burning flame, and increase after 70 s, whereas FeO is not observed between 10 and 80 s but becomes visible again after 80 s. Between 70 and 80 s, there are increases in FeO intensity according to Figure 3 b), but these are actually caused by changes in the background rather than in FeO optical emissions. After 80 s, the intensity increases for many consecutive spectra rather than individual spectra between 70 and 80 s, which is an indicator of increased FeO and not fluctuations in the background.
All in all, this information sheds light on the cutting process itself, what is occurring at which instance, and what species are within the flame. With the help of Table 1, also other species can be monitored to see what should be done to optimize the flame’s properties. Future studies should be aimed at a larger dataset with a wider wavelength range to capture more species that radiate in the flame. Several different scenarios could be tested e.g. at a burner laboratory, including intentional malfunctions, introduction of impurities, or changing the gas flow and mixture to see how they affect the spectra.

As can be seen from Figure 2 e), the estimated temperature varies drastically depending on the process step. The flame is brought to the slab’s edge and back from 4 to 8 s, and the cutting starts at 10 s. During these times, there’s a decrease in the temperature, indicating that the energy is transferred into the slab. The mean value of the temperature from the spectra is 3079 ± 40 K between 0 and 10 s, excluding the spectra between 4 to 8 s. This temperature is for the free-burning flame, and the calculated stoichiometric flame temperature for propane in oxygen at 1 atm pressure is around 3080 K16. However, it should be noted that the thermal radiation originates from both the flame and the heated slab, which can bring uncertainty to the temperature analysis.

In the steel industry, burners are a significant source of energy, especially for example for slab reheating, where also radiative energy transfer has an important role. OES collects all the radiation from the observed object, and the spectra hold information not only on the composition and temperature of the flame but also about the radiative heat transfer and how it evolves in different process steps. The spectra in Figure 3 c) showcase two spectra at around 70 s where the overall intensity of the spectra increases significantly. Even though there is no apparent change in the flame based on the flame images, the spectral characteristics change abruptly in this instance.

CONCLUSIONS

Burners have an important role in the steel industry and optimizing the burner practices has prospects for increasing resource efficiency and decreasing the formation of harmful compounds, such as CO2 and NOx. In this study, OES has been presented as a method to study an industrial burner’s flame with oxy-fuel cutting as a case study. The species that radiate within the flame were identified in the 490 – 1000 nm wavelength range and the temperature of the flame was estimated with the thermal background. The time evolution of optical emissions from H2O, C2, FeO, Na I, and K I was analyzed and discussed.

One of the benefits of using OES is the simple equipment and it can be placed at a safe distance from the flame. The procedures of OES measurements stay the same regardless of the burner and the gas that is used, making it a flexible analysis method for a wide variety of applications both in the steel industry and other energy-intensive industries. Future work aiming for process control should include a series of oxy-fuel cuts, where also the process data from the steel plant would be brought into the equation.
ACKNOWLEDGMENTS

This work was supported by the Academy of Finland under the Genome of Steel grant No. 311934 and Business Finland’s Towards Fossil-free Steel (FFS) research program, grant number 45774/31/2020. The authors would like to thank Joakim Leskelä for assistance at the SSAB.

REFERENCES


