Improving Combustion and Oxidation Reactions: When to use Oxygen

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Today's market demands are everywhere: reduce capital costs, reduce process costs, reduce emissions - especially CO2, provide more process flexibility, find a way to reduce fuel costs, increase quality and consistency, increase capacity while not increasing costs. The use of oxygen is an excellent way of achieving all of these results. Incorporating oxygen in conjunction with or in place of combustion or reaction air can be used to realize the following results:

- ***Operational savings and fuel savings***: Enriching air with oxygen decreases the overall flow when compared to air. Doing so increases residence time in a heater, reactor, or furnace and minimizes pressure drop in any downstream heat or cooling treatment of outlet gases.
- ***Capital savings***: Oxygen enrichment can be implemented at a fraction of the cost of expanding the original process. Equipment size is decreased by limiting the amount of nitrogen present in the process.
- ***Reduced emissions***: Reduced nitrogen means lower flue gas volumes and thus better flue gas clean up.
- ***Flexibility and reliability***: Operating rates can be changed frequently based upon plant loading. Oxygen enrichment provides the flexibility to constantly match process requirements.
- ***Better quality:*** Oxygen enrichment results in higher combustion temperatures and residence times which contribute to more complete destruction or more complete reactions.
- ***Increased capacity:*** The most common reason for implementing oxygen enrichment is to increase process capacity. Removing nitrogen allows more oxygen to be present enabling greater reaction rates with fewer molecules.

Chemical processes which are amenable to the above list of benefits from the use of oxygen in place of air include oxidations, fermentations, wastewater treatment, and combustion among others. This paper will focus on oxidation and combustion.

Oxygen Enhanced Combustion

Oxygen enhanced combustion (OEC) is used in many different industries including glass, ferrous and nonferrous metals, waste incineration, sulfur recovery units (SRU), fluid catalytic crackers (FCC), and other unit operations (1). New applications for oxygen enhanced combustion are also emerging in biofuels (2), petcoke (3), solid fuels (4), and oxycoal combustion for CO2 capture (see (5) and other articles in same issue).

Oxygen enhanced combustion can be divided into three operating regimes: low level enrichment, medium level enrichment, and high level enrichment. Low level enrichment is used to define systems where the mole fraction of oxygen in the oxidant stream is between 21 and 28%. This is the simplest and lowest cost implementation since typically oxygen can be added directly to the air main and current air/fuel burners can be used. For higher levels of oxygen enrichment, specialized burners and equipment are needed, but higher levels of benefits are also derived.

Oxygen Enhanced Reactions

Oxygen can also be a key step in the manufacture of a wide variety of industrial chemicals and monomers (6). Table 1 shows a list of major petrochemical oxidation processes that can utilize pure oxygen, oxygen enrichment of air, or simply the oxygen that is present in air.

Table 1. Major Petrochemical Oxidation Products (6).

Chemical	**Manufacturing Process**
Ethylene Oxide	Oxygen/Air
Propylene Oxide	Oxygen/Air/Chlorine
Acetaldehyde	Oxygen/Air
Vinyl Chloride	Oxygen/Air/Chlorine
Vinyl Acetate	Oxygen
Caprolactam	Oxygen/Air
Terephthalic Acid	Air/Enrichment
Maleic anhydride	Air/Enrichment
Acrylonitrile	Air/Enrichment
Phenol	Air/Enrichment
Acrylic Acid	Air
Acetone	Air
Phthalic anhydride	Air
Isophthalic acid	Air/Enrichment
Acetic anhydride	Air
Formaldehyde	Air
Methyl Methacrylate	Air/cyanohydrins
Adipic acid	Air/nitric acid
1,4 Butanediol	Acetylene/air

Oxygen rather than air leads to improved reaction performance in many cases. It leads to added degrees of freedom and also potential reaction condition versatility. In other words, the use of oxygen can often be justified by improved reaction rates, reaction selectivities, and reaction yields. The reaction of ethylene to ethylene oxide is one such reaction. An article from M. Gans highlights this application (7). Two stages of a three stage process were no longer needed. Nitrogen did not need to be purged after each stage and the use of pure oxygen allowed the reaction to occur at optimum reaction kinetic conditions. The use of oxygen justified itself economically through vastly improved reaction performance and has led to almost universal acceptance of oxygen instead of air (8).

Another reaction where oxygen has an advantage is the production of vinyl chloride monomer – oxychlorination of ethylene. The typical process is based on a fluidized bed catalyst and a reaction system originally developed by Monsanto. Optimum reaction conditions call for an excess of ethylene, and an oxygen concentration which is limited by the lower flammability limit of the system. If air is used, an excess of ethylene cannot be achieved without large ethylene losses. The use of pure oxygen becomes necessary to allow recycle of the desired proportion of reactor gases to achieve optimum reaction conditions.

The use of pure oxygen versus air in chemical reactions must be thoughtfully evaluated. Gunardson highlights several general rules where the use of O2 can be economically justified (6):

- High pressure processes tend to favor the use of oxygen because compression savings offset the cost of oxygen over air.
- Processes with catalysts that have a low conversion per pass favor oxygen because they require recycling unreacted feed and therefore elimination of the inert nitrogen is beneficial.
- Processes that involve toxic or hazardous materials favor oxygen because the vent gas streams are more manageable without the nitrogen acting as a diluent.
- Processes where oxygen is incorporated in the product favor oxygen because oxygen adds value to the product rather than being disposed of in a waste stream.
- Processes that have significant quantities of by-products in the reactor effluent favor oxygen because the by-products can be more readily recovered from a nitrogen free stream.
- Oxidation reactions that are mass transfer limited benefit from high purity oxygen due to the higher partial pressure of reactants without the diluent nitrogen.

Energy Efficiency and Environmental Emissions

From an energy efficiency viewpoint, the nitrogen in combustion air is detrimental. The nitrogen and the small amount of argon make up ~79% on a molar basis of dry air. These gases do not aid in the combustion process but must still be heated up to the same temperature as the combustion products. Since not all of the flue gas enthalpy can be recovered into the process, the exhaust of these gases inherently leads to a net loss on the system. This is displayed graphically using a Sankey diagram for energy use in a furnace in Figure 1. The numbers in the figure correspond to methane combustion in ambient temperature 21% oxygen / 79% nitrogen mixture with a flue temperature of 815 ^{o}C. In Figure 2, the same analysis is displayed graphically for methane combustion in ambient temperature oxygen both with the same flue temperature.

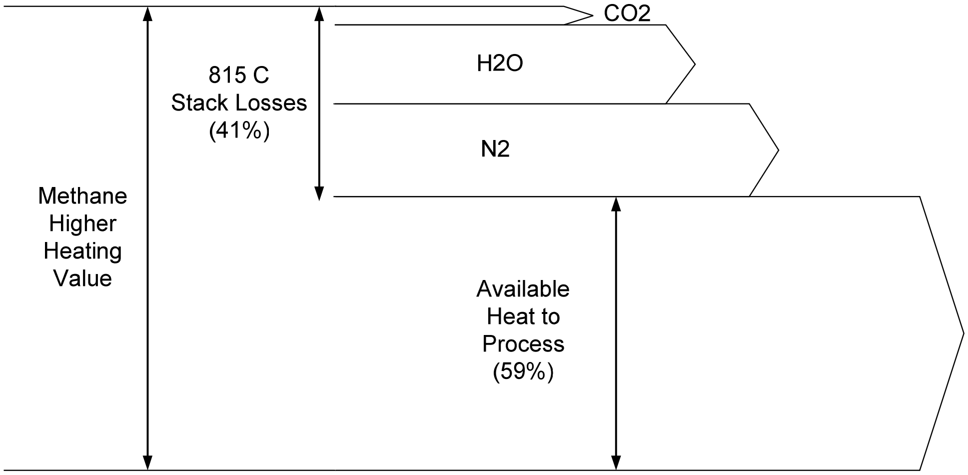

Figure 1: Sankey diagram showing energy distribution for stoichiometric methane and air (21% O2 / 79% N2) combustion in a simplified manner considering only stack losses at 815 C.

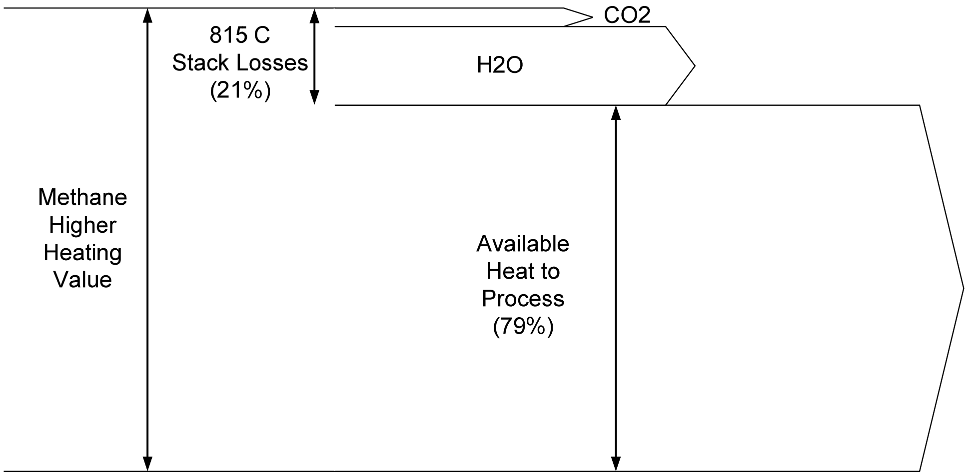

Figure 2: Sankey diagram showing energy distribution for stoichiometric methane and oxygen combustion in a simplified manner considering only stack losses at 815 C.

As the figures show, removing the inert N2 from the combustion air increases the useful heat available to the process from 59% to 79% of the higher heating value leading to an expected fuel savings of 26%. The actual increase in available heat is system dependent but fuel savings on the order of 25-60% are possible using oxygen (1).

As previously mentioned, oxygen also benefits the chemical process of oxychlorination. When using oxygen, the reactor in both the fluid bed and fixed bed configurations is operated at a lower temperature which results in an improved operating efficiency and product yield. The higher heat capacity of the ethylene-rich reaction mixture without nitrogen in the stream has a modulating effect on the operating temperature. Higher operating temperatures are detrimental because they lead to decreased catalyst selectivity and the formation of undesirable chlorinated hydrocarbon by-products. At higher temperatures catalyst activity is decreased and catalyst life is shortened (6). Just as fuel efficiency can be gained in combustion, reaction efficiency can be gained by removing the inert gas nitrogen.

Along with fuel savings, oxy-fuel combustion can also reduce environmental emissions. Decreases in fuel consumption lead directly to reductions in carbon emissions. Since fuel savings on the order of 25-60% can be achieved through the use of oxygen, this leads to the same 25-60% reduction in CO2 emissions at the site. Even when taking into account the energy used in separating the oxygen from air, oxy-fuel and oxygen enhanced combustion can still reduce overall CO2 emissions in many cases. The actual net CO2 reductions will be case dependent because of variability in process fuel, heat recovery, distance to air separation unit, and the carbon intensity of the local power grid.

In addition to carbon emissions, nitrogen oxides (NOx) emissions are strongly influenced by oxygen enhanced combustion. In gaseous fuel systems, thermal NOx by the Zeldovich mechanism (9) is typically the primary source of nitrogen oxides. This reaction depends on both the availability of nitrogen and more importantly the reaction temperature. For air fuel combustion, the limiting factor in NOx production is reaction or flame temperature. For full oxy-fuel combustion, the limiting factor in NOx production is nitrogen availability. There is a range between air and full oxygen combustion in which NOx production increases prior to reductions in NOx when oxygen concentrations of 80-90% are reached (see (1) for more information).

Process and Capital Benefits

The use of oxygen can increase the capacity of many processes with minimal investment in capital. Two example systems where capacity can be increased through the use of oxygen are hydraulically limited systems and heat transfer rate limited systems. In the first case the current equipment does not support increasing the flow rate due to pressure requirements. By replacing some or all of the N2 with O2, some of the hydraulic limitations can be relieved and process flows can be increased. In the second case the heat transfer rate can be increased by increasing the flame temperature through oxygen use. The presence of nitrogen in the combustion process lowers the flame temperature and thereby decreases the radiant intensity of the combustion. The effect of nitrogen on the adiabatic flame temperature is shown in Figure 3.

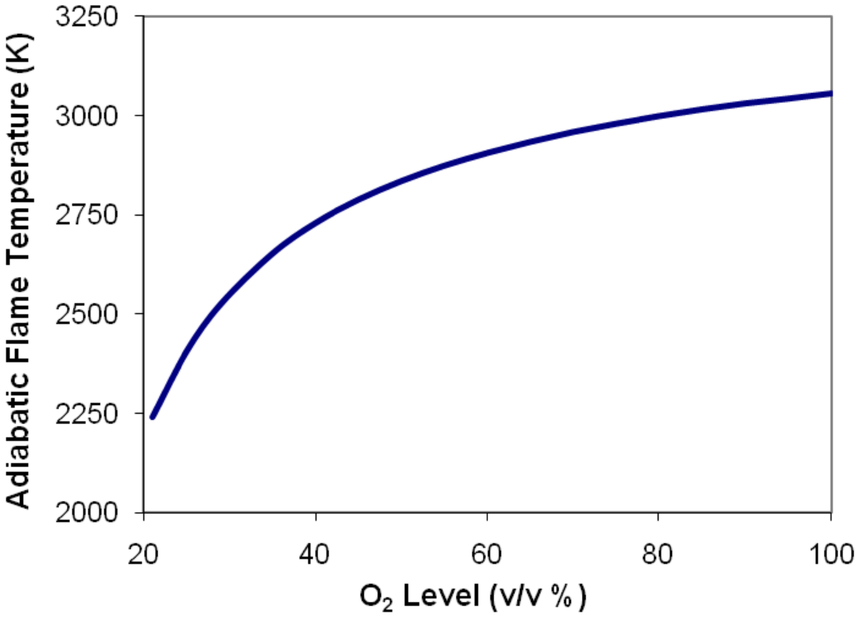

Figure 3: Adiabatic flame temperature for methane combustion in oxygen/nitrogen mixtures.

The effect of higher oxygen concentration in the oxidant cannot be fully described using a thermodynamic analysis of available heat. Since radiation heat transfer is proportional to temperature to the fourth power, an increase in flame temperature with oxygen and changes in flame properties can increase the heat transfer rate over air combustion. Specially designed oxy-fuel burners can take advantage of this by adjusting the flame properties to optimize the radiation wavelength and the radiation properties to maximize efficiency. This has been done with the Air Products Cleanfire ® HR burner (10) (11) for glass melting which has shown increased melting efficiency of 9.2% while using 5% less (12).

Another benefit of oxygen is that it provides flexibility in operations not available with air only operations. For instance, oxygen use can be temporary and employed only when needed. It is possible to increase furnace throughput on a subset of units using oxygen enrichment while another set of units is undergoing modifications or maintenance. In this manner production rates are maintained during partial shutdowns without significant capital investments into spare capacity. Similarly air combustion and oxygen enhanced combustion can be alternately used during a single day. For example in batch furnaces air fuel combustion can be used during furnace hold or charge times while oxygen enhanced combustion can be used during times of high heat load.

Another reaction example of oxygen use is the propylene oxide, isobutene peroxidation process. The process is at 500 to 600 psig, and elimination of nitrogen from the process reduces the gas volume that needs to be compressed. The oxidation reaction has a low conversion of isobutene per pass and elimination of nitrogen from the recycle gas yields savings in compressor size and horsepower. Oxygen is also incorporated in the main product, propylene oxide, and the major by-product, tert-butyl alcohol (TBA) and therefore it has a higher intrinsic value than if it were disposed of as a waste product. These factors combine to make oxygen economically desirable (6).

In addition to the overall process benefits, oxygen use can typically be implemented quickly with a low capital investment. Expanding capacity using air typically requires construction of an additional process line or reaction furnace. In contrast, low level enrichment of air can expand capacity of the exiting process with very minimal cost. Many times the changes can even be implemented while the current process continues to run. Even higher increases in throughput can be achieved by use of higher levels of oxygen.

Case Study

Recently the Ćeská Rafinérská Litvinov facility performed a trial with low level enrichment up to 28% oxygen in a sulphur recovery unit (SRU) using the Claus process. The primary purpose of the trial was to increase the reaction furnace temperature to allow for more complete destruction of ammonia. A secondary purpose of the trial was to test for capacity increase using low level enrichment.

The trial was run by increasing the oxygen concentration in the combustion air by 1-2% at a time and then allowing the furnace conditions to stabilize. Figure 4 shows the air flow and oxygen concentration during the course of the trial while Figure 5 shows the temperature of two different furnace thermocouples during the same time period located at different positions within the furnace. It should be noted that the decrease in furnace temperature toward the end of the run at 22% oxygen is due to a change in the feed composition. Overall, the temperature of the furnace increased by 115 ^{o}C due to an increase in the oxygen concentration of the oxidant from 21% to 28%. This compares remarkably well with a simulation of the process that predicted a temperature increase of 110 ^{o}C.

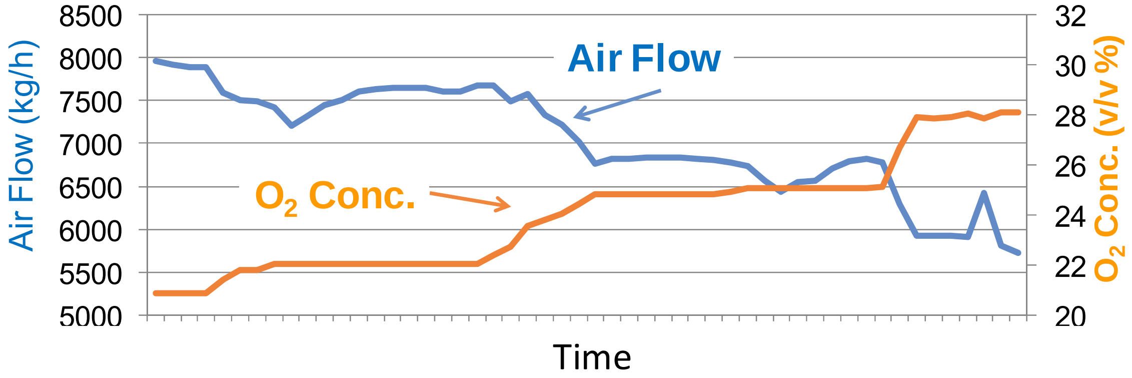

Figure 4: Air flow and oxygen concentration in the oxidant stream during the low level enrichment trial.

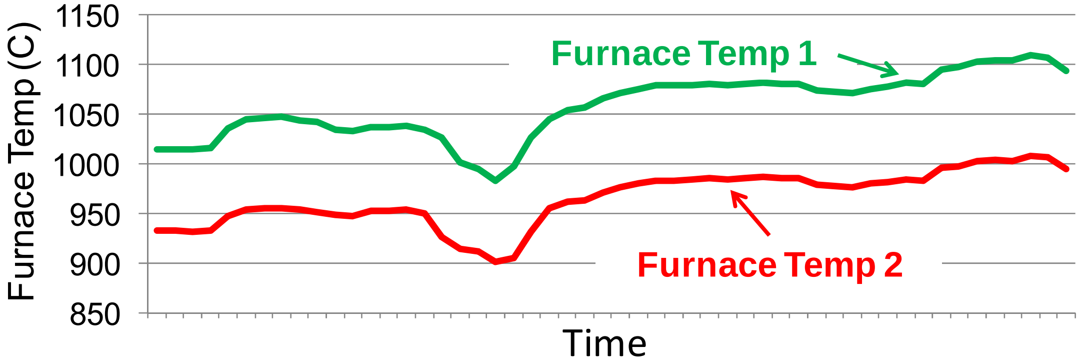

Figure 5: Temperature measurements from two different thermocouples located at different locations within the test furnace.

After increasing the oxygen concentration to 28% and monitoring the furnace temperature, the trial then consisted of testing the capacity increase possible with low level enrichment. Due to a decrease in the air flow to the furnace, the furnace pressure dropped during the test even though the feed acid gas flow increased as shown in Figure 6.

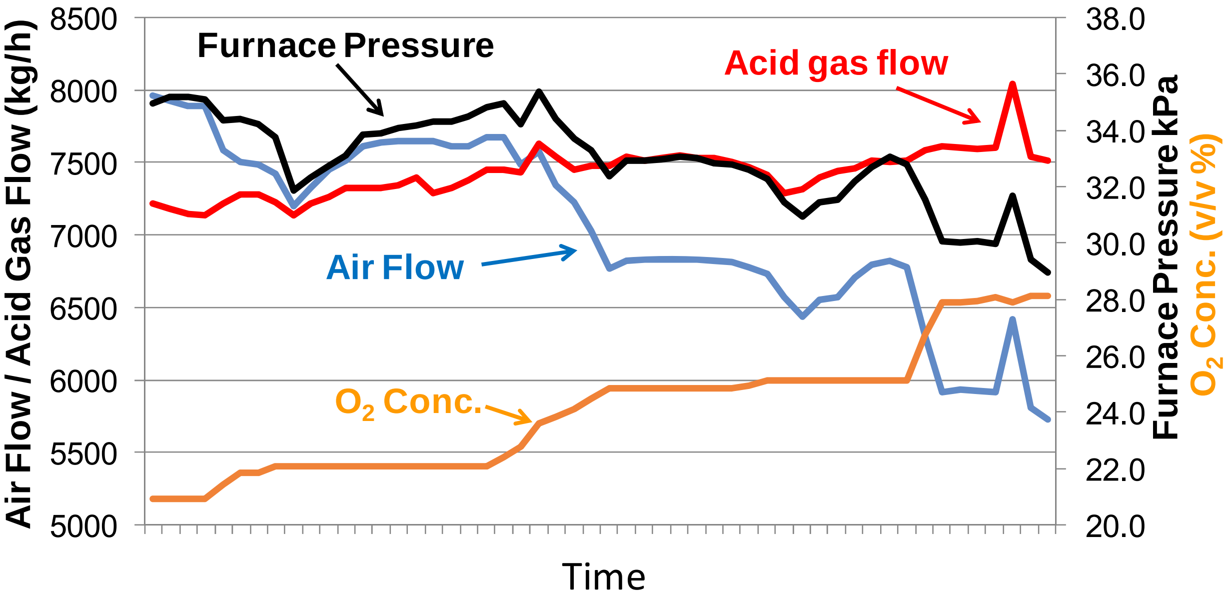

Figure 6: Furnace process conditions during low level enrichment trial.

In Figure 7 additional data are shown from the last increase in acid gas flow near the end of the trial. The final feed gas flow of acid gas of ~8400 kg/hr was 17.6% higher than the baseline conditions at the beginning of the test. Even at this level of feed, the limits of the SRU furnace were not reached but the capacity test was stopped due to a limitation in the availability of acid gas. Therefore the actual capacity increase possible was not demonstrated, but the capacity increase predicted by simulation is 18%.

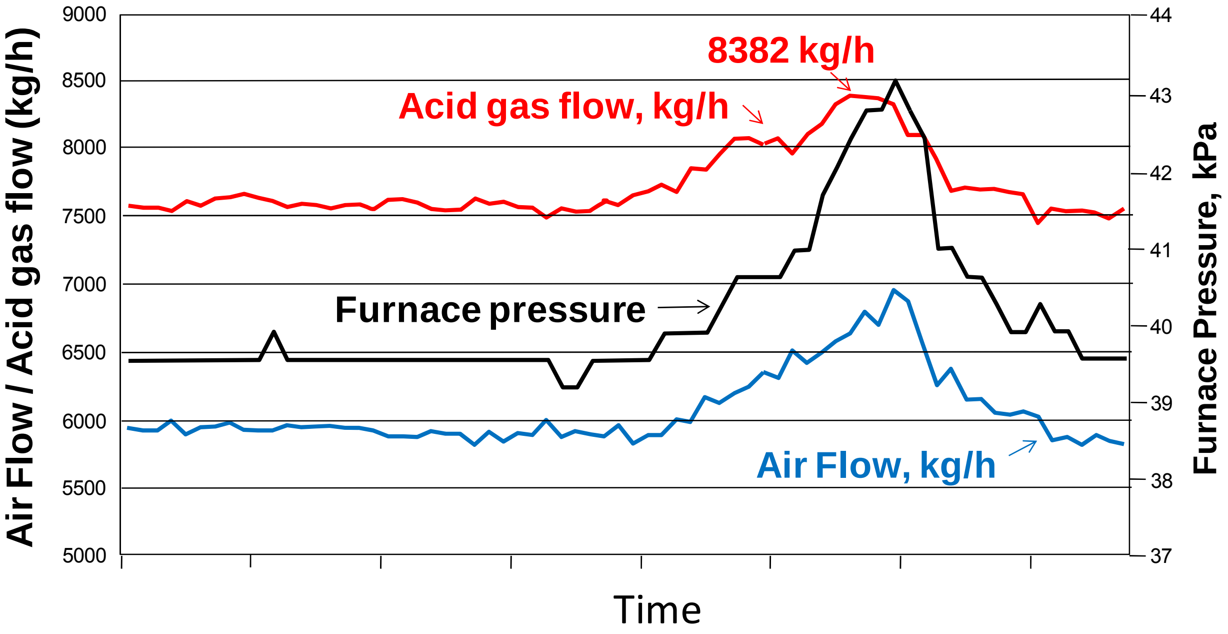

Figure 7: Furnace process conditions during low level enrichment trial at higher time resolution than Figure 6.

Conclusion

Oxygen is a tool which is both powerful and flexible. Engineers and plant managers should evaluate the possibilities of oxygen use within their own processes in order to meet the operational and environmental demands and challenges placed on a chemical facility in these times. However oxygen use requires expert analysis to maximize its benefits for each unique application. Oxygen will help plants achieve operational excellence, reduce costs, achieve environmental compliance through reduced emissions, provide operational flexibility to handle peaks and valleys in product demand or environmental load, increase quality and consistency, and increase capacity, all with minimal capital costs. The use of oxygen is a great way to solve many of today's market and operational challenges.

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