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Use Oxygen to Improve Combustion and Oxidation

Reed J. Hendershot
Timothy D. Lebrecht
Nancy C. Easterbrook
Air Products and Chemicals, Inc.

Substituting oxygen for air is often a low-cost, easy-to-implement option that can reduce capital costs, lower emissions, and improve process flexibility and reliability.

Manufacturers today face increasing pressure to cut fuel, capital, and operating costs, reduce emissions (especially of CO_2), and improve quality, consistency, process flexibility, and capacity. Incorporating oxygen in conjunction with or instead of combustion or reaction air is an excellent way to achieve all of these results. Processes such as oxidation, fermentation, combustion, and wastewater treatment (among others) can benefit from the use of oxygen in place of air. This article focuses on oxidation and combustion.

The most common reason for enriching process air with oxygen or substituting oxygen for air is to increase the capacity of the process, because oxygen enrichment or substitution can be implemented at a fraction of the cost of expanding the original process. Limiting the amount of nitrogen in the process permits the use of smaller, less-expensive equipment. The overall flow is lower than that of an air-based process, which minimizes pressure drops in air-handling equipment (*e.g.,* blowers, fans, compressors) and downstream equipment, thereby reducing operating (energy) costs.

Because removing some or all of the nitrogen allows more oxygen to be present, higher reaction rates are achieved with fewer molecules. Combustion and reaction temperatures are higher and residence times longer, which contribute to more-complete destruction and conversion, ultimately resulting in better product quality. Fluegas volumes and emissions are also reduced, which simplifies fluegas cleanup.

Oxygen-enhanced combustion

Oxygen-enhanced combustion is used in many different applications, including glass manufacturing, ferrous and nonferrous metal processing, waste incineration, sulfur recovery, fluid catalytic cracking, and other processes *(1)*. New applications are emerging in the production of biofuels *(2)*, petcoke *(3)*, and solid fuels *(4)*, as well as in oxy-coal combustion with CO_2 capture *(5)*.

Oxygen-enhanced combustion can be accomplished with low-level, medium-level, or high-level enrichment. Low-level enrichment is defined as a mole fraction of oxygen in the oxidant stream between 21% and 28%. This is the simplest and lowest-cost implementation, since oxygen can typically be added directly to the main air duct and the existing burners can be used. Higher levels of oxygen enrichment require specialized burners and equipment, but they also provide higher levels of benefits.

Oxygen-enhanced reactions

Oxygen is essential in manufacturing a variety of industrial chemicals and monomers *(6)*. Table 1 lists major petrochemical oxidation processes that can utilize

Table 1. Many petrochemical oxidation processes can utilize pure oxygen, air, or oxygen enrichment *(6)*.

Chemical	Manufacturing Process Options
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

Table 2. Certain types of processes are good candidates for oxygen enrichment *(6)*.

Process that involve …	Can benefit from using pure oxygen or oxygen enrichment because …
High pressure	Compression savings offset the higher cost of oxygen (relative to air)
Catalysts and a low per-pass conversion	Elimination of the inert nitrogen reduces the amount of unreacted feed that needs to be recycled
Toxic or hazardous materials	The vent gas streams are more manageable without nitrogen acting as a diluent
Oxygen incorporated into the product	Oxygen adds value to the product rather than being disposed of in a waste stream
Significant quantities of byproducts in the reactor effluent	The byproducts can be more readily recovered from a nitrogen-free stream
Oxidation reactions that are mass-transfer-limited	Reactants have a higher partial pressure without the diluent nitrogen

pure oxygen, oxygen enrichment of air, oxygen within air, or another means of manufacture.

In many cases, the use of oxygen in place of air improves reaction performance because it allows the process to be optimized around multiple sets of operating conditions. Therefore, the use of oxygen can often be justified by improved reaction rates, reaction selectivities, and reaction yields.

The production of ethylene oxide from ethylene is one such reaction *(7)*. Because nitrogen does not need to be purged from the reactor, which is typically carried out in a series of three steps, and because the use of pure oxygen allows the reaction to occur at optimum kinetic conditions, a three-stage process has been reduced to a single stage. The vastly improved reaction performance using oxygen justifies the economics and has led to almost universal acceptance of the oxygen-based route for the production of ethylene oxide *(8)*.

Another reaction that benefits from the use of oxygen is the oxychlorination of ethylene using a fluidized bed catalyst to make vinyl chloride monomer. Optimum reaction conditions include an excess of ethylene and an oxygen concentration below the lower flammability limit of the system. If air is used, maintaining an excess of ethylene would incur large ethylene losses. Pure oxygen allows the desired proportion of reactor gases to be recycled to achieve optimum reaction conditions.

The use of pure oxygen instead of air in chemical reactions must be thoroughly evaluated. Table 2 summarizes several general guidelines that indicate where the use of oxygen can usually be economically justified *(6)*.

Energy efficiency

From an energy efficiency perspective, the nitrogen and argon in combustion air are detrimental, because they amount to about 79% of dry air (on a molar basis). These gases do not aid in the combustion process, but must still be heated to the same temperature as the combustion products. Since not all of the fluegas enthalpy can be recovered, exhausting these gases involves an inherent loss of energy, as illustrated in Figures 1 and 2. Figure 1 is a Sankey diagram for energy use in a furnace where methane is combusted in air (21% O_2, 79% N_2) at ambient temperature and a fluegas temperature of 815°C. Figure 2 depicts the same analysis for methane combustion in pure oxygen at the same ambient and fluegas temperatures.

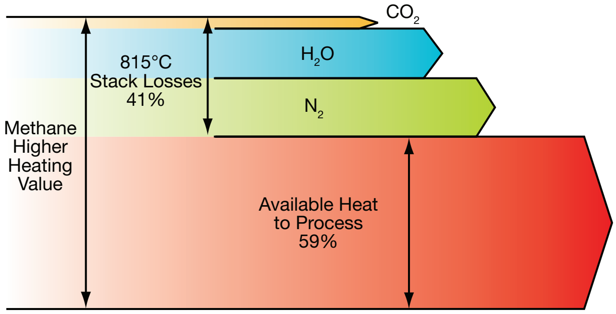
As these figures demonstrate, removing the inert gases from the combustion air increases the useful heat available to the process from 59% to 79% of the higher heating value with an expected fuel savings of 26%. The actual increase in available heat is system-dependent, but fuel savings on the order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

The use of pure oxygen in the oxychlorination process also has energy benefits. When using oxygen, the reactor in both the fluid-bed and fixed-bed configurations is operated at a lower temperature, which improves 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 lower catalyst activity and selectivity, the formation of undesirable chlorinated hydrocarbon byproducts, and reduced catalyst life *(6)*. Just as combustion efficiency can be improved, reaction efficiency can also be increased by removing the inert nitrogen.

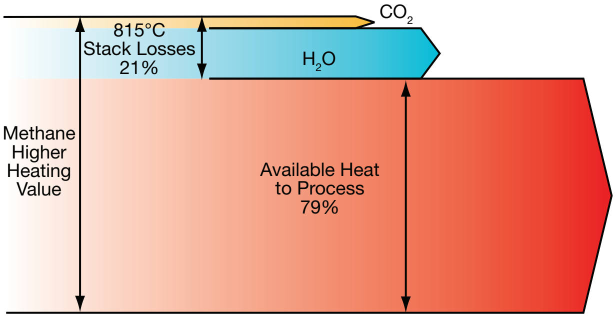
Lower emissions

Along with fuel savings, oxy-fuel combustion can also reduce emissions. Reducing fuel consumption directly reduces carbon emissions. Since fuel savings on the order of 25–60% can be achieved by using oxygen, the same 25–60% reduction in CO_2 emissions can be realized. Even when taking into account the energy used to separate the oxygen from air, in many cases, oxy-fuel and oxygen-enhanced combustion will have lower overall CO_2 emissions. The actual net CO_2 reductions will be case-specific because of variabilities in the process fuel, heat recovery, distance to the air separation unit, and carbon intensity of the local power grid.

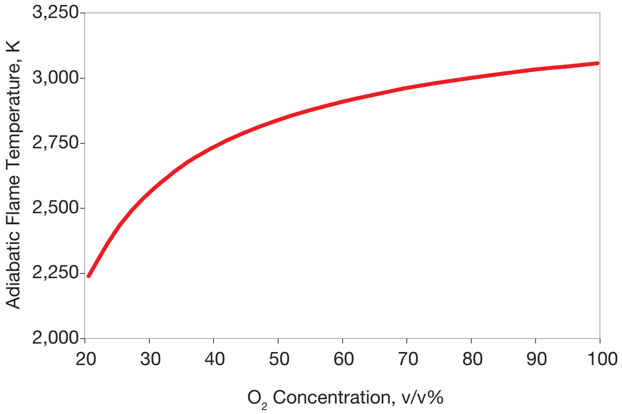
Nitrogen oxide (NOx) emissions from combustion sources are also strongly influenced by oxygen enrichment. In gaseous fuel systems, thermal NOx (which is produced by the Zeldovich mechanism *(9)*) is typically the primary source of nitrogen oxide emissions. This reaction depends on both the availability of nitrogen and, more importantly, the reaction temperature. For combustion in air, the limiting factor in NOx production is the reaction or flame temperature; for combustion in pure oxygen, the limiting factor is nitrogen availability. The competing effects of flame temperature and nitrogen availability cause NOx production to increase at lower levels of oxygen enrichment before decreasing at oxygen concentrations of 80–90% in the oxidant. (See Ref. 1 for further explanation.)



▲ **Figure 1.** When methane combustion takes place in air (21% O_2, 79% N_2), a significant portion of the methane's heat content is lost through the stack.



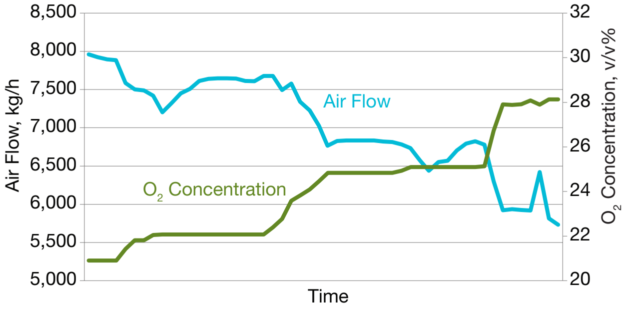
▲ **Figure 2.** Combustion in pure oxygen converts 79% of the methane's energy content into useable heat.



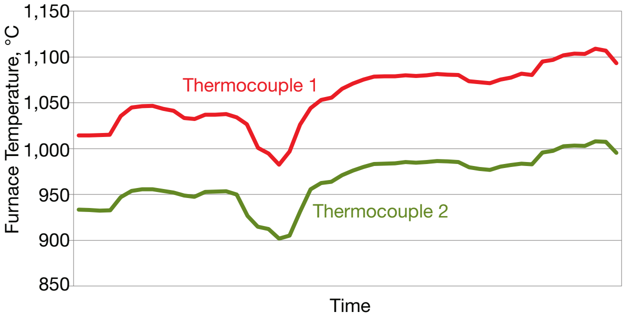
▲ **Figure 3.** Increasing the oxygen concentration via enrichment or switching to pure oxygen increases the temperature of the flame and thus the heat-transfer rate.

Process and capital cost benefits

Using oxygen can increase the capacity of many processes with minimal capital investment, such as in systems that are hydraulically limited or heat-transfer-rate limited. In the first case, the existing equipment does not support increasing the flowrate due to pressure requirements. By replacing some or all of the nitrogen with oxygen, some of the hydraulic limitations can be relieved and process flows can be increased. In the second case, the presence of nitrogen lowers the flame temperature and thus decreases the radiant intensity of the combustion. Increasing the flame temperature with oxygen will increase the heat-transfer rate. Figure 3 illustrates the effect of nitrogen on the adia-



▲ **Figure 4.** To study oxygen enrichment in a sulfur recovery unit, the oxygen concentration was gradually ramped up from 21% to 28% and the air flowrate decreased accordingly.



▲ **Figure 5.** Oxygen enrichment in the SRU increased the flame temperature and the furnace temperature at the two locations where thermocouples were installed.

batic flame temperature during methane combustion.

The effect of higher oxygen concentration in the oxidant cannot be fully described by a thermodynamic analysis of available heat. Since radiant heat transfer is proportional to temperature to the fourth power, an increase in flame temperature with increased oxygen concentration and changes in flame properties can increase the heat-transfer rate over that of combustion in air. Specially designed oxy-fuel burners maximize efficiency by adjusting the flame to optimize its radiation properties and wavelength. One such burner for glass melting has been shown to increase melting efficiency (firing rate per mass of glass produced) by 9.2% *(10–12)*.

Another benefit of oxygen enrichment is that it provides operational flexibility not available in air-only operations. For instance, oxygen can be employed only when needed. The throughput of certain units could be increased with oxygen enrichment while other units are undergoing modifications or maintenance. In this manner, production rates are maintained during partial shutdowns without significant capital investments in spare capacity.

Similarly, air combustion and oxygen-enhanced combustion can be alternated during a single day. For example, in batch furnaces, air combustion can be used during holding or charging and oxygen-enhanced combustion when a high heat load is required.

The production of propylene oxide via isobutene peroxidation takes place at 500–600 psig. Eliminating nitrogen from the process reduces the gas volume that needs to be compressed. The oxidation reaction has a low per-pass conversion, and eliminating nitrogen from the recycle gas allows the use of smaller, lower-horsepower compressors. Oxygen is also incorporated into the main product, propylene oxide, and the major byproduct, tert-butyl alcohol (TBA). Therefore, oxygen has a higher intrinsic value in this process because it increases the yield of the desired material rather than leaving the process as part of the waste stream. Combined, these factors make oxygen an economically attractive oxidant *(6)*.

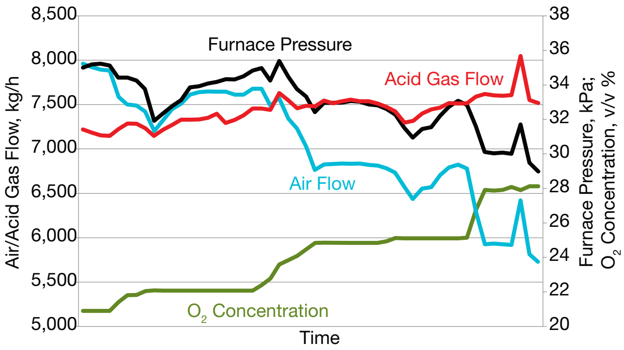
In addition to the overall process benefits, oxygen enhancement can typically be implemented quickly with a low capital investment. Expanding the capacity of an air-based process typically requires construction of an additional process line or reaction furnace. In contrast, low-level air enrichment can increase the capacity of the exiting process at minimal cost. Many times the changes can even be implemented while the current process continues to run. Higher levels of oxygen can achieve even larger increases in throughput.

Field demonstration

Recently, the Ćeská Rafinérská Litvinov facility tested low-level enrichment (up to 28% O_2) in a sulfur recovery unit (SRU) that used the Claus process. The primary purpose of the test was to increase the reaction furnace temperature to allow for more-complete destruction of ammonia; a secondary purpose was to evaluate low-level enrichment as a means of increasing capacity.

During the trial, the concentration of oxygen in the combustion air was increased in increments of 1–2% to allow the furnace conditions to stabilize after each change. Figure 4 shows the air flowrate and oxygen concentration throughout the trial, and Figure 5 shows the temperature at two different positions within the furnace during the same time period. (Note that the decrease in furnace temperature near the end of the run, at 22% O_2, was caused by a change in the feed composition.) The temperature of the furnace increased by 115ºC as the oxygen concentration was ramped up from 21% to 28%. This compares very well with a simulation of the process that predicted a temperature increase of 110ºC.

The next phase of the trial used low-level enrichment to test the potential of oxygen enrichment to increase capacity. Due to the addition of oxygen, a lower airflow



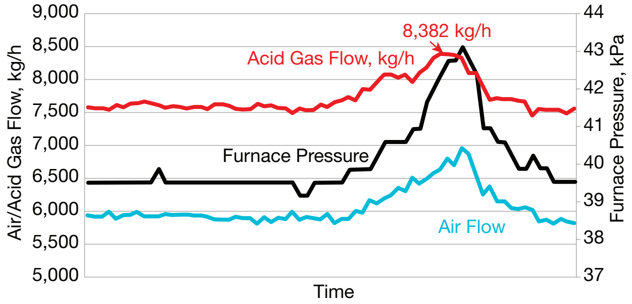
▲ **Figure 6.** During the SRU enrichment trial, increasing the oxygen concentration allowed a higher acid gas throughput at a lower pressure.

to the furnace was needed. Consequently, the pressure in the furnace decreased during the test even though the feed acid gas flowrate was increased, as indicated in Figure 6. This result demonstrated that the capacity could be increased through the use of oxygen.

Figure 7 presents additional data collected after the last increase in acid gas flowrate near the end of the trial. The peak flowrate of acid gas (~8,400 kg/h) 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. However, the capacity test was stopped due to limited availability of acid gas, and although the potential capacity increase was not demonstrated, it was predicted by simulation to be 18%.

Final thoughts

Consider the use of oxygen in your processes to meet the operational and environmental demands and challenges that your facility faces. Oxygen enrichment can help the plant achieve operational excellence by reducing costs, increasing capacity, reducing emissions, providing operational flexibility to handle peaks and valleys in product demand or environmental load, and improving quality and consistency, all with minimal capital expenditures. However, the use of oxygen requires expert analysis to maximize its benefits in each unique application.



▲ **Figure 7.** A peak acid gas flowrate of nearly 8,400 kg/h was achieved during the SRU enrichment trial.

REED J. HENDERSHOT is a senior principal research engineer at Air Products and Chemicals, Inc. (Phone: (610) 481-8357; E-mail: henderr2@airproducts.com). He has been with Air Products for six years and is currently working on combustion research and development, specifically in the areas of reforming combustion and oxy-fuel combustion. Hendershot holds one patent and has published 11 technical articles and six patent applications. He holds a BS from Brigham Young Univ. and a PhD from the Univ. of Delaware, both in chemical engineering.

TIMOTHY D. LEBRECHT is a lead industry engineer for refinery, biofuels and chemicals applications at Air Products (Phone: (610) 481-8388; E-mail: lebrectd@airproducts.com). In his 19 years with Air Products, he has had roles in process engineering, scope and project development, product management, and commercial technology. His process expertise ranges from specialty gases to industrial gases, specifically in support of refining, and chemical and process industry applications. Lebrecht earned a BS in chemical engineering from Purdue Univ. and an MBA from Lehigh Univ.

NANCY C. EASTERBROOK is a market manager for chemical process industries at Air Products (Phone: (610) 481-3261; E-mail: easternc@airproducts.com). She has 22 years of Air Products experience and has been a member of AIChE since 1988. Easterbrook earned a BS in chemical engineering from Rensselaer Polytechnic Institute.

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For More Information

If you would like additional information on our oxygen-enhanced combustion technologies, please contact Air Products at a location near you.

Americas
Air Products and Chemicals, Inc.
7201 Hamilton Boulevard
Allentown, PA 18195-1501
Tel 800-654-4567
Fax 800-272-4449
Email gigmrktg@airproducts.com

Europe
Air Products PLC
Hersham Place
Molesey Road
Walton-on-Thames
Surrey K12 4RZ - UK
Tel +44 (0)1270 614314
Email apbulkuk@airproducts.com

China
Air Products and Chemicals (China)
Investment Co., Ltd
Floor 4&5, Building 72
Lane 887, Zu Chong Zhi Road
Zhangjiang Hi-tech Park
Shanghai, China
Tel 400-888-7662
Fax 021-50805555

India
INOX Air Products Ltd.
7th Floor, Ceejay House
Dr. Annie Besant Road
Worli, Mumbai - 400 018

Tel +91 (0)22 40323960/ 40323195
Fax 40323191/ 40323991

Indonesia
PT AIR PRODUCTS INDONESIA
Cikarang Industrial Estate
Blok F 1 - 3
Cikarang - Bekasi 17530
West Java, Indonesia
Tel (62-21) 286-38600
Fax (62-21) 898-40059

Korea
Air Products Korea Inc.
7th Floor, Gatewat Tower
12, Dongja-Dong, Yongsan-Gu
Seoul, 140-709, Korea
Tel (82) 2 2170 8000
Fax (82) 2 733 0287

Malaysia
Air Products Malaysia Sdn Bhd
Petaling Jaya
Level 2, Bangunan TH Uptown 3
No. 3, Jalan SS21/39, 47400 Petaling Jaya
Selangor, Malaysia
Tel +603 7727 1836
Fax +603 7726 1832

Singapore
Air Products Singapore Pte Ltd
2 International Business Park
The Strategy, #03-32
Singapore 609930
Tel +65 6494 2240
Fax +65 6515 5946

Taiwan
Air Products San Fu Co., Ltd.
5th Floor
21 Chung Shan North Road, Section 2
Taipei 104, Taiwan, R.O.C.
Tel 02-2521 4161
Fax 02-2581 8359

Thailand
Bangkok Industrial Gas Co. Ltd
11th Floor, Rajanakarn Bldg
183 South Sathorn Road
Yannawa, Sathorn
Bangkok 10120, Thailand
Tel (662) 676-6262
Fax (662) 676-6288-9
E-mail mkt@bigth.com

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