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Submitted by
Linde
10 Riverview Drive
Danbury CT 06810

Submitted to
California Energy Commission
docket@energy.ca.gov

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Introduction

Linde is very pleased to respond to the California Energy Commission’s (CEC) “Request for Information” on developing and demonstrating advanced combustion systems. Linde is the world’s largest industrial gases and engineering company with 2019 sales over USD 28 billion (EUR 24 billion). The company employs approximately 80,000 people globally and serves customers in more than 100 countries worldwide. Linde delivers innovative and sustainable solutions to its customers and creates long-term value for all stakeholders. Linde is also a member of the Dow Jones Sustainability Index. In 2019, a subset of the company’s applications technologies enabled 2x more greenhouse gas (GHG) emissions to be avoided by our customers than were emitted from Linde’s entire operations. Linde is making our world more productive by providing products, technologies and services that help customers improve their economic and environmental performance in a connected world.

Linde and its legacy companies have a long history deploying oxy-fuel and oxygen-enriched combustion technologies in a wide variety of high temperature industries like chemicals, refining, glass, cement, steel, and non-ferrous metals processing. The company also has more than sixty years of experience in designing and building fired heaters and has supplied more than 3,000 fired heaters around the world. Linde’s customers use the advanced combustion systems to increase efficiency, drive productivity, reduce emissions, and improve the quality of their products.

Some of the Linde advanced combustion technologies, e.g. our 3rd generation OPTIFIRE™ Wide Flame Burner, have been successfully deployed and adopted in California. However, there are several other programs at various Technology Readiness Levels that face unique barriers for implementation in California due to challenges in demonstrating improved capital efficiency and economies of scale.

Grant funding from the CEC will help to reduce risks for both Linde and its industrial partners and increase the likelihood that a field project will not only proceed, but also successfully demonstrate a first-of-a-kind full scale deployment of new advanced combustion systems in California.



1. **The following will help us target our specific research:**
 - a. **What are major barriers (technical, economical, and other) for wide adoption of oxygen-enriched combustion?**

Oxygen enriched combustion (OEC) has been commercially adopted by a wide range of industrial furnaces and boilers for production rate increase, energy savings and product quality improvements and emissions reduction such as nitrogen oxides (NO_x). Many different burners and lancing techniques have been successfully developed to control combustion and heat transfer conditions. With over fifty years of R&D and a wide range of practical commercial experiences, there are basically no technical barriers in applying OEC in conventional industrial combustion processes using natural gas. OEC or oxygen enriched gasification applications with unconventional fuels such as municipal solid wastes (MSW), sludge, and agricultural residues have not been well developed and new OEC equipment and processes need to be developed/demonstrated to facilitate the use of carbon neutral biomass fuels.

The main barrier for wide adoption of OEC with conventional fuels is the economics. OEC applications for production rate increase or product quality improvements are generally economic as the value of extra products produced is typically much larger than the cost of the relatively small amounts of oxygen required to partially replace combustion air. For wide adoption of OEC to achieve the benefits of fuel savings, carbon dioxide (CO₂) and NO_x reduction, the economic conversion of the air-fired combustion process to a full oxy-fuel combustion process is required. The economics of full OEC conversions are largely determined by the value of fuel saved, the cost of oxygen and the initial capital expenditures (CAPEX) required. CO₂ and NO_x reduction also adds benefits, but they are not sufficient to change the overall economics of OEC at present. Two key technology advancements required for wide adoption of OEC are (1) efficient waste heat recovery technologies from high temperature OEC flue gas, and (2) improved air separation technologies to reduce the cost of oxygen production.

The current low cost of natural gas and little/no CO₂ tax are also major barriers for OEC. As the costs of natural gas and CO₂ tax increases, the relative economics of OEC will improve.

- b. **What are examples of research that could eliminate barriers to wide adoption of oxygen-enriched combustion?**

OEC, especially 100% oxy-fuel combustion, is typically used in high temperature processes such as glass melting, steel reheating, and aluminum re-melting. For example, 100% OEC has been used in container glass furnaces in California and reduced fuel consumption by 10-20% compared to air



fired furnaces with regenerators to preheat combustion air¹. About 30% of fuel input is still lost in the hot flue gas from the oxy-fuel fired glass melting furnace. If cost effective waste heat recovery technologies for OEC are developed and adopted, additional fuel reduction of 20-30% is projected. The overall OEC conversion economics improves substantially as the oxygen requirement is also reduced by 20-30%².

In Europe, different types of waste heat recovery systems have been adopted by several oxy-fuel fired glass melting furnaces in recent years. Recuperators, preheating both oxygen and natural gas, have been installed in a few furnaces and achieved fuel reduction of 8 to 10%. Only one third of the available waste heat is recoverable as the preheat temperatures for oxygen and natural gas are limited to 600 °C and 400 °C respectively, due to material compatibility and cracking of natural gas. Several cullet preheating (CPH) systems have been installed and achieved fuel reduction of about 10% in Europe. A thermochemical regenerator (TCR) system was installed in a small glass furnace and achieved 13% fuel reduction. These heat recovery systems recovered about 30 to 50% of the waste sensible heat available in the flue gases.

Research, development and demonstration of advanced waste heat recovery systems that can recover 50 to 90% of the available sensible heat in the waste flue gas stream would significantly improve the economics of OEC and facilitate wide adoption in high temperature process furnaces. A pilot scale rapid cycle compact TCR was demonstrated to recover more than 90% of the flue gas sensible heat from oxy-fuel combustion.³ Rapid cycle TCRs can be deployed for efficient heat recovery in OEC fired steel reheat furnaces and process heaters. Examples of heat recovery systems for glass melting furnaces to recover 60 to 80% of the available waste heat include a combined batch and cullet preheating (BCP) system and a TCR system combined with oxygen and/or natural gas preheating. Another research example is a new rapid melting or heating furnace design. OEC increases heat transfer rate and the size of the furnace can be reduced. Reduction of furnace size reduces wall heat losses and reduces the fuel and oxygen requirements.

Further research to advance air separation technologies to reduce the cost of oxygen is also important. The electric power required to separate oxygen from air typically constitutes ½ to 2/3

¹ Tuson, G.B., Kobayashi, H. and Campbell, M.J., "Oxygen Enriched Combustion System Performance Study," Phase II Final Report – 100 per cent Oxygen Enriched Combustion in Regenerative Glass Melters, U. S. Dept. of Energy Report No. DOE/ID/12833-1, August 1994

² H. Kobayashi, "Future of Oxy-Fuel Glass melting: Oxygen production, Energy efficiency, Emissions and CO₂ Neutral Glass Melting", Glass Problems Conference, Columbus, OH, October 2019

³ Wang, Y, and Kobayashi, H., "Dilute Oxygen Combustion" Phase II Report for U.S. Dept. of Energy DE-FC36-95ID13331, September 2005



of the total cost of an on-site oxygen generation system. The electric power consumption for oxygen generation has been reduced substantially over the past decades and further power reduction of 10 to 20% is expected in the next decade.

A new technology to fully integrate high temperature oxygen transport membranes and oxy-fuel combustion has been developed recently. For over twenty years, Linde Inc. (formerly known as Praxair Inc.) has been developing ceramic membrane technology, which can be integrated into a process as ‘flameless-oxidizer’ (FOx) burner arrays that replace air-fired burners. Pure oxygen transported across the dense membrane of the FOx burners enables the release of heat through oxy-combustion of the fuel gas, with the combustion products, CO₂ and H₂O, remaining inside the tubular membrane. This unique arrangement allows for the firing of a furnace for process stream heating with concentration of CO₂ within the membrane, yielding high rates of carbon capture from the process. A substantial reduction in both the carbon intensity and cost of CO₂ capture can be achieved with the FOx technology compared to the other established carbon capture processes. Linde is widely accepted as being the global technology leader in ceramic membranes and is manufacturing the technology in the United States.

The FOx burner elements combine air separation, oxy-combustion, and CO₂ capture in a single component. The combustion process provides high rates of carbon capture (90-100%) but does not require a separate amine-based CO₂ capture plant, which drives the cost of capture for traditional furnace technologies. The ceramic elements allow for very efficient radiant coupling resulting in furnace efficiencies of 88% which led to fuel savings of 10-15% over conventional process heaters. In addition, the FOx burners, operating at temperatures considerably below flame temperatures typical of conventional SMR burners, enable very low NO_x emissions from the furnace. Ideal industrial applications for Linde FOx technology are steam-methane reformers, steam superheaters, process gas heating, and glass annealing.

c. What are examples of current or past projects involving oxygen-enriched combustion? What are important lessons learned from these projects?

Using biomass or municipal solid wastes to fire electric power boilers or incinerators is an attractive strategy for generating low-carbon power. In some cases, previously coal-fired boilers are converted to biomass firing. This retrofit can lead to a significant derating of the boiler. Emissions of some pollutants, such as carbon monoxide (CO), may also increase with conversion to biomass firing. Even purpose-built biomass combustors can experience operational issues with a change in feed characteristics, such as moisture content. Oxygen enhanced combustion can be used to offset many of the problems associated with biomass firing. For example, one of the easiest ways to reduce specific flue gas volume is to remove some or all of the nitrogen from the combustion air. In this strategy, which has been used for several furnace types, the flue gas reduction is essentially proportional to the amount of nitrogen removed from the oxidant. The



degree of nitrogen removal is often represented by the oxygen concentration in the overall oxidant (also called oxygen enrichment). Although effective, this direct replacement strategy means the recovered capacity, or increased firing rate, is directly proportional to the amount of oxygen use. In waste-to-energy applications, such as incineration of MSW, OEC can substantially increase the feed rate of low Btu wastes such as waste-water treatment sludge and wet biomass without increasing furnace temperature or the flue gas flow rate.

Another way to implement OEC is to use a small amount of oxygen to enhance and control combustion as a means to reduce pollution emissions and to recover lost generating capacity. This strategy has been used successfully on several coal fired boilers, and one boiler that co-fired coal and wood [Reference 7]. These demonstrations, and others [References 1,3-4,8-9] show that increasing the local oxygen concentration enhances combustion. The enhanced combustion, in turn, improves flame stability and ensures more complete combustion of the fuel. In general, by using oxygen to enhance the combustion process it is possible to reduce the excess air flow, and thereby reduce the specific flue gas volume, without increasing carbon monoxide (CO) emissions. In fact, through careful use of OEC it can be possible to reduce the CO emissions. The lower specific flue gas volume allows the boiler operator to increase the firing rate to regain some of the generating capacity lost when the boiler was converted to biomass firing. Figure 2, based on the same unit as Figure 1, illustrates this effect. Even small reductions in excess air can allow boiler capacity lost during the conversion to biomass to be recovered (reducing the required boiler derate).

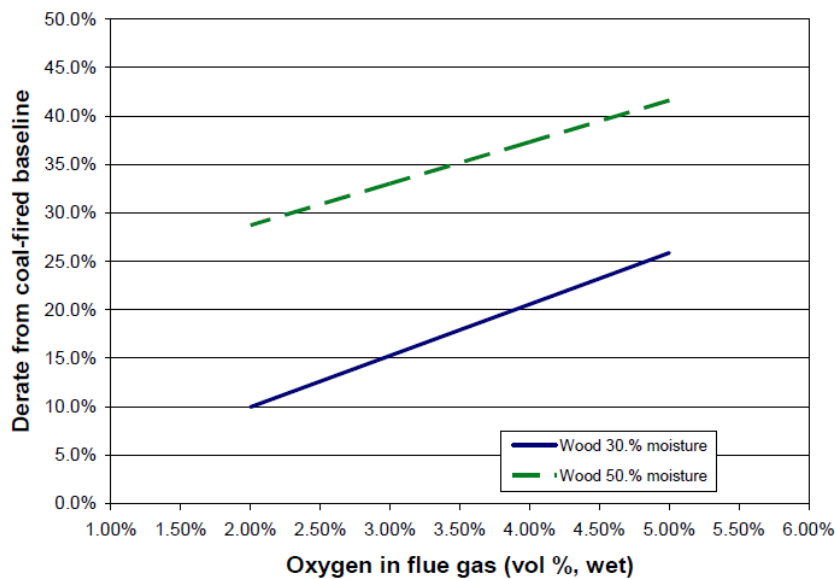


Figure 1. Estimated effect of excess oxygen and moisture on boiler derating

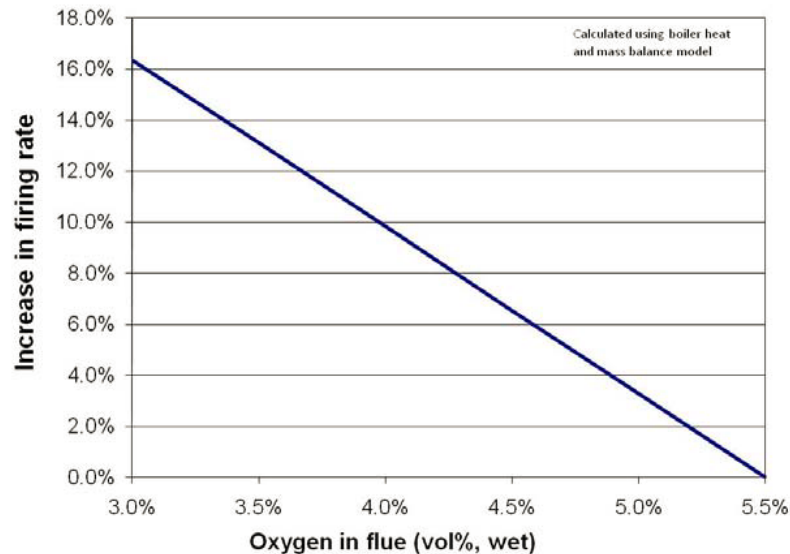


Figure 2. Estimated effect of oxygen in flue on available firing rate

Another operational benefit of oxygen injection is that less heat will be ‘pushed’ into the convective section due to both the reduced specific flue gas and the increased temperature near the bed. Both of these effects lead to increased heat absorption in the radiative part of the boiler – reducing the need to ‘spray’ to control superheat and reheat temperatures in the convective section.

The combustion efficiency of the boiler can also be improved through the use of oxygen. Improved combustion on the grate and in the furnace can reduce the LOI; this lowers fuel and ash disposal costs. Further, while the effect is relatively small, reducing the amount of excess oxygen in the flue can reduce the sensible heat losses per mega-watt (MW) of power produced. Both of these effects can offset some of the oxygen cost.

Project Examples

Capacity recovery and pollutant control from biomass-fired boiler (L’Anse Warden)

A demonstration of OEC for biomass fired boilers was done at the L’Anse Warden Electric Co. (LWEC)⁴. The trial at LWEC demonstrated that selective oxygen use can stabilize combustion on a grate and enable recovery of some of the generating capacity lost in the retrofit to biomass firing.

⁴ L. Bool, B. Damstedt, H. Kobayashi, and D. Thompson; “Oxygen Enhanced Combustion in Biomass Fired Boilers” 36th International Technical Conference on Clean Coal and Fuel Systems 2011.



CO emissions were significantly reduced and stabilized with OEC. These results also suggest that the optimal OEC strategy will be plant specific.

Oxygen fuel combustion for steel reheating and processing

Using oxygen-fuel combustion in steel reheating provides higher throughput and substantial fuel savings. Over the past three decades, Linde has made more than 160 oxygen-fuel installations in all types of reheating furnaces, both batch and continuous, and for production of all different steel grades. Since 2003, focus has been on using Flameless Oxyfuel, hitherto resulting in 112 successful installations, 90 of these operating fully with 100% Flameless Oxyfuel. Results from these installations, which include fuel savings of up to 60%; increased throughput by up to 50%; substantial reductions of CO₂ and NO_x emissions; much improved temperature uniformity of the heated steel; reduction of scale losses by up to 50%.

The below reference papers describe examples of OEC, and lessons learned.

Lessons Learned References

- 1) Denig, F., “*Method and Apparatus for Incinerating Combustible Refuse, Rubbish, and Miscellaneous Waste Organic Material*”, **U.S. Patent No. 3,403,643** issued October 1, 1968
- 2) Kobayashi, H., Bool (III), L.E., Wu, K.T., “*Oxygen Enhanced Switching to Combustion of Lower Rank Fuels*”, **U.S. Patent No. 6,699,029**, issued March 2, 2004
- 3) Martin, J.J.E., Horn, J., Busch, M., “*Buring Fuels, Particularly for Incinerating Garbage*”, **U.S. Patent No. 5,762,008** issued June 9, 1998
- 4) Kira, M., Doi, T., Tsuneizumi, S., Takuma, M, Kitta, T., “*Development of New Stoker Incinerator for Municipal Solid Wastes Using Oxygen Enrichment*”, **Technical Review**, Mitsubishi Heavy Industries Ltd, Vol. 38, No.2, June 2001
- 5) Bool, L.E., and Kobayashi, H., “*NO_x Reduction from a 44 MW Wall-fired Boiler Using Oxygen-Enhanced Combustion*”, **Proceedings of the 28th International Technical Conference on Coal Utilization and Fuel Systems**, March 9-13, 2003, Clearwater, FL
- 6) Bradley, J.L., Bool, L.E., and Kobayashi, H., “*NO_x Reduction from a 125 MW Wall-fired Boiler Using Oxygen-Enhanced Combustion*”, **Proceedings of the 29th International Technical Conference on Coal Utilization and Fuel Systems**, April 2004, Clearwater, FL
- 7) Bool, L.E., “*Implementation of Praxair’s OEC for NO_x Control on Two Industrial Boilers*”, **Proceedings of 2006 Energy Utility and Environment Conference**, January 2006, Tucson, AZ
- 8) Mullen, W.T., “*Combustion of Low B.T.U./High Moisture Content Fuels*”, **U.S. Patent No. 4,928,606** issued May 29, 1990
- 9) Mullen, W.T., “*Combustion of Low B.T.U./High Moisture Content Fuels*”, **U.S. Patent No. 5,107,777** issued April 28, 1992



d. What California industries could benefit most from oxygen-enriched combustion?

Any industry that has the goal of transitioning to a low carbon fuel, such as hydrogen, can benefit from oxygen enriched combustion. Many of these low carbon fuels are significantly more expensive than conventional fuels they replace. This creates a significant economic hurdle for the adoption of low carbon fuels. Oxygen enriched combustion has been shown to significantly increase the efficiency of high temperature process, especially with the heat recovery approaches described above. Using oxygen enriched combustion can, therefore, reduce the net cost of energy even when the cost of oxygen is included.

The drive to adopt low carbon fuels can also be hampered by lack of regional infrastructure for distribution of fuels such as hydrogen, or the technical uncertainty of using these fuels in industrial processes. In this case the use of oxygen enriched combustion allows companies to reduce their carbon impact through the adoption of biofuels, such as pyrolysis oil. The increased fuel efficiency obtained from oxygen enriched combustion helps offset increased costs associated with these fuels. Challenges, such as atomization or flame stability, can also be addressed using oxygen-based technologies.

Industrial heating processes with high flue gas exit temperatures are primary candidates for OEC applications at present. They include glass, steel, aluminum, cement and paper industries. When CO₂ reduction or CO₂ capture and sequestration becomes a stricter requirement, then OEC may become the economic choice for petroleum/chemical, oil/gas, power generation and other broader industries. Also, OEC or oxygen-based gasification of biomass and waste materials may gain wider acceptance.

e. What are technical challenges that could result from higher oxygen content and higher combustion temperature (e.g., increased NO_x emissions; accelerated degradation of materials in burners, furnaces, kilns)?

Variations in the furnace atmosphere using OEC, such as changes to the water vapor concentration, can adversely affect the product quality or melting process (e.g., scale formation in steel heating, dross formation in aluminum melting, foaming in glass melting, etc.). The flame temperature does not necessarily increase with OEC since it is controlled by the burner design. NO_x emissions are substantially reduced by OEC by reduced nitrogen concentration and by burner design. OEC has been successfully applied to reduce NO_x emissions from coal fired utility boilers.



2. **The following will help us establish performance metrics and technology status in California:**
- a. **Besides cryogenic separation, pressure/temperature swing absorption, ion transport membranes, are there any other promising technologies that should be considered?**

As discussed in Question 1b, waste heat recovery technologies are critical to oxygen-enriched combustion / oxy-fuel combustion. In the context of glass melting, multiple waste heat recovery technologies, e.g. CPH, TCR, have been deployed. However, these have recovered only 30 – 50% of the available waste heat. Improvements to these technologies as well as optimal combinations of batch and cullet preheating (BCP), TCR and/or natural gas (NG) and oxygen preheat systems can enable recovery of up to 80% of the available waste heat in the flue gases. Relative to air-fired regenerative furnaces, oxy-fuel furnaces with higher levels of waste heat recovery can achieve a 30% reduction in NG consumption, which translates to a 30% reduction in CO₂ emissions. Furthermore, depending on the operating conditions of the oxy-fuel furnace, the flue gas could contain >80% CO₂, potentially simplifying the complexity of an associated CO₂ capture system.

Ion transport membranes for the production of pure oxygen has been an active research area for multiple decades. While there have been instances of technical success, commercial viability remains a challenge since cryogenic and pressure swing adsorption technologies continue to be optimized for capital and operating cost. Rather than focusing on oxygen production, ion transport membranes should be adapted for producing more valuable products like syngas and/or H₂.

To summarize two types of technologies should be considered:

- 1) Advanced waste heat recovery solutions
- 2) Ion transport membranes for production of syngas and/or H₂.

b. For the technologies listed in item 2a:

- i. **What is the estimated energy requirement to produce oxygen at the following capacities: 1 metric ton of oxygen per day, 25 metric tons per day, 100 metric tons per day?**

The energy consumption will depend on the type of production technology – cryogenic or vacuum pressure swing adsorption (VPSA). Specific numbers are business confidential information. However, industrial gas companies continue to support R&D programs to continuously reduce capital and power consumption of oxygen production systems. The chart below provides a representation of reduction in electricity consumption for VPSA systems producing low purity O₂ (90 – 94 vol.%). A reduction of 20 – 30% in power consumption is expected over the next 10 years.

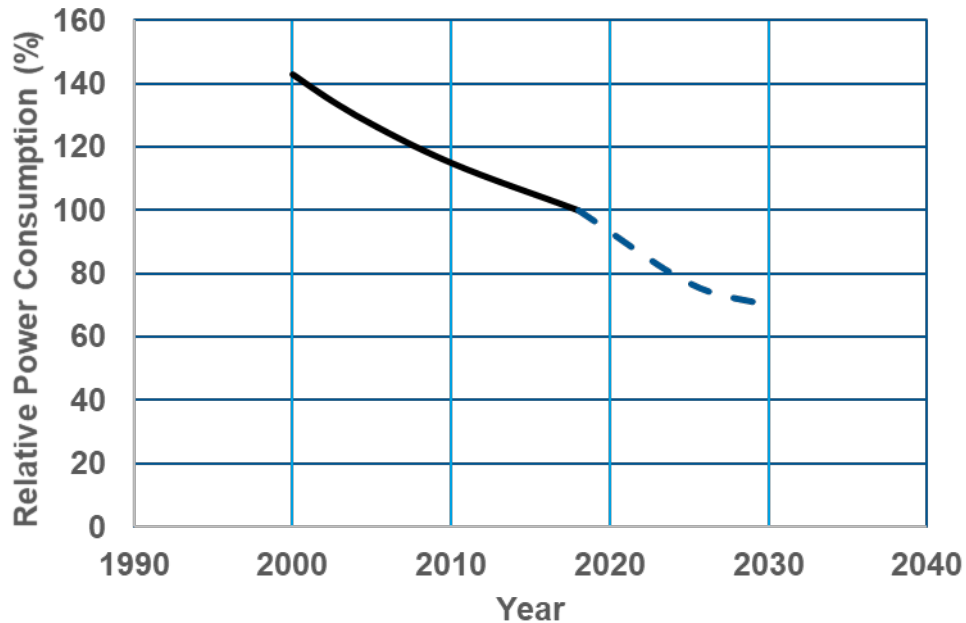


Figure 3. Expected future reductions in electricity consumption for VPSA systems

- ii. **What is the estimated capital and operational costs for 1 metric ton per day of oxygen production capacity? This is typically business confidential information. Actual cost will depend on the type of production technology, required O2 purity, price of electricity and other factors including backup requirements.**

This is typically business confidential information. The actual cost will depend on the type of production technology, the required O2 purity, the price of electricity and other factors, including backup requirements.