CO₂ Reduction by Oxy-Fuel Combustion: Economics and Opportunities

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Worldwide Oxygen Market and Applications

(Market Size $8.3B)

- Most of oxygen is used for high temperature metallurgical processes and combustion applications

Primary Metal
- Steel
  - BOF*
  - Blast Furnace*
  - EAF*
  - Corex*
  - Direct Reduction*
  - Reheating Furnace*
- Aluminum
  - Melting Furnace*
- Copper
  - Smelting Furnace*
  - Anode Furnace*

Healthcare

Glass/Clay/Concrete
- Melting Furnace*
- Cement Kiln*

Welding & Cutting*

Chemicals/Refinery
- Ethylene Oxide
- Syngas*
- TiO₂*
- Claus Sulfur*
- FCC Regenerator*
- Sulfuric acid recovery*

Others - Waste Water
- Aerospace*
- Coal Gasification*

Pulp & Paper
- Delignification
- Black Liq. Gasification*

Source: Salomon Smith Barney 2002
**Oxy-Fuel Combustion History of Applications Development**

1. **Welding**
   - Cutting
   - Flame polishing
   - High Temp Applications 1940-1950s

2. **Glass Melting**
   - (30% of US capacity)
   - Steel
   - Copper
   - Incineration
   - Coal Fired boilers
   - Glass Aluminum Cement 1960-1970s

3. **Fuel Savings**
   - Full Oxy-fuel Combustion 1980s
   - NOx Reduction 1990-2000s
   - Power generation
   - CO2 Reduction
   - -CO2 sequestration
   - IGCC
   - Oxy boilers

4. **Productivity Enhancement**
   - O2 Enrichment
   - 1960-1970s

5. **High Temp Applications**
   - 1940-1950s
Methods to Reduce CO2 Emissions by Oxy-Fuel Combustion

1. Oxy-fuel combustion to improve fuel efficiency to reduce CO2 emission
   1. Power required for oxygen production has to be considered.

2. Oxy-fuel combustion to produce flue gas with high CO2 concentration for sequestration
   1. Oxy-fuel with FGR for retrofitting existing air fired furnaces
   2. Direct oxy-fuel firing

3. Oxy-fuel combustion to increase productivity to reduce specific fuel consumption and CO2 emission
Fuel Savings With 100% Oxy-Fuel Conversion
Fuel: Methane, 2% O₂ In Flue Gas

Air Preheat Temperature (°F)

Flue Gas Temperature (°F)

Fuel Savings (%)

- Boiler
- Aluminum
- Steel
- Glass

Fuel Savings With 100% Oxy-Fuel Conversion
Fuel: Methane, 2% O₂ In Flue Gas
Current technologies to produce 95% O2 purity requires
~200 Kwh/ton O2
2 MMBtu of fuel /ton O2 at 10,000 Btu/kwh (e=34%hhv)
1.2 MMBtu of fuel /ton O2 at 6,000 Btu/kwh (e=57%hhv)

To reduce net energy consumption in furnaces by oxygen combustion fuel savings of about 9 to 14% are required to compensate for the energy for oxygen production.

For Oxygen-CH4 Fired Power Plant
17% Of power output is consumed at e=34% hhv
10% Of power output is consumed at e=57% hhv
Minimum fuel savings of 20% are required to pay the cost of oxygen. (without considering other oxy-fuel benefits)

Most current oxy-fuel applications save more than 20% fuel and result in net reduction in CO2 emissions
Oxygen-Recycled Flue Gas Fired Boiler for CO2 Sequestration (retrofit)

- Technically feasible
  - Oxy-coal firing tested in pilot scales
- Engineering issues
  - Air leakage
  - Burner design

- ASU issues
  - High O2 cost
  - High power consumption

Diagram:
- Boiler furnace
- Feed water
- Flue gas recycle
- Oxygen
- ASU
- N2 off gas
- Steam
- Exhaust compression
- Supercritical CO2

Flow:
- FUEL
- Oxygen
- Feed water
- Flue gas recycle
- ASU
- N2 off gas
- Steam
- Exhaust compression
- Supercritical CO2
**Direct Oxygen Fired Boiler for CO2 sequestration (new)**

- Technically feasible
  - Oxy-oil firing tested in a pilot-scale in Japan

- Engineering issues
  - Boiler design
  - Burner design

- ASU issues
  - High O2 cost
  - High power consumption

Diagram:
- FUEL
- boiler furnace
- Feed water
- Oxygen
- ASU
- Air
- N2 off gas
- Steam
- Exhaust compression
- Supercritical CO2
- Water
1. Technologies to control flame temperature and heat flux have been developed for most gas and oil-fired furnace applications
   -> Oxy-fuel flames can be used in any air-fired furnaces
   -> 30% of glass melting furnaces have been converted to oxy-fuel firing
2. Large NOx reduction has been demonstrated for both thermal and fuel NOx
3. Limited experiences with oxy-coal burners
   -> engineering issues remain on optimum burner configurations for O2 and RFG streams
4. Limited fundamental data on coal combustion under oxygen atmosphere
Praxair “A” Burner
In-furnace FGR to control flame temperature and heat flux

• High velocity O2 jets aspirate furnace gas and reduces the flame temperature
High velocity fuel jet reacts with hot diluted oxygen (2-10%) in the furnace to achieve uniform heating and ultra low NOx.
Oxygen Production Technologies

Cryogenic
- Uses low temperature distillation
- $\text{O}_2$ purities up to 99.9%

Vacuum Pressure Swing Adsorption (VPSA)
- Uses the adsorbent properties of zeolites
- Typical $\text{O}_2$ purities: 90-94 %

Ceramic Membranes (Oxygen Transport Membranes)
- Uses ceramic materials that are selective for oxygen ions at elevated temperature: $\text{O}_2$ purities 99+ %
Oxygen Production Costs vs. Plant Capacity

![Graph showing oxygen production costs vs. plant capacity. The graph compares different processes such as VPSA (variable pressure swing adsorption) and Cryo (cryogenic distillation) with varying production capacities.](image-url)
Theoretical Energy Requirement to compress O2 from 0.21 to 1 atm
About 30 Kwh/ton O2

Current Cryo and VPSA For 90-95% O2 Purity
About 200 Kwh/ton O2

The current oxygen production technologies consume more than six times the theoretical energy requirement. Although the unit energy consumption to produce O2 by cryogenic and VPSA processes continues to decrease, a step change technology is needed for CO2 sequestration applications.
Oxygen Transport Membrane (OTM) Technology

ELECTRICALLY DRIVEN

Air
$O_2 + 4e^- \rightarrow 2O^{--}$

Porous Electrodes

 Ion Conductor

$2O^{--} \rightarrow O_2 + 4e^-$

Oxygen

PRESSURE DRIVEN

High Pressure Air
$O_2 + 4e^- \rightarrow 2O^{--}$

Mixed Conductor

$2O^{--} \rightarrow O_2 + 4e^-$

Low Pressure Oxygen

OXIDES OF METALS
OXGEN ION TRANSPORT
INFINITE O$_2$ SELECTIVITY
HIGH TEMP OPERATION (400-1000°C)
Mixed Conductor O2 Transport mechanism

- Charge Transfer
- Dissociation
- Ion Migration
- Electron Migration
- Charge Transfer
- Recombination
- Desorption
- Bulk Diffusion
- Adsorption
- O2 Bulk Diffusion
O2 Flux and Compression Requirements

\[ \text{O2 Flux Across OTM} = C \ln\left(\frac{P_1}{P_2}\right) \]

\[ \left(\frac{P_1}{P_2}\right) = 3 \text{ Required for High O2 Flux} \]

(Ideal compression power of 53 kwh/ton O2 at 80 F)

Air compressed to 14.3 atm to produce pure O2 at 1 atm

(Ideal compression power of 250 kwh/ton O2 at 80 F), or

Air at 1 atm and Dilute Oxygen Combustion at 7% O2
OTM-Dilute Oxygen Combustion Concept

Air, 21% O2

Fuel

OTM Air Separation Chamber

O2

1,000 C

5% O2

1% O2

Flue gas
CO2+H2O+1% O2

Combustion Chamber

Fuel

Flue gas
CO2+H2O+1% O2
• Integrates air separation using oxygen transport membranes and combustion

• Uses chemical potential to minimize air separation power required

• Produces flue gas containing only CO₂, H₂O and inerts from fuel that can be readily cleaned up for sequestration.
Conceptual NG Fired OTM Boiler Process

- OTM boiler reduces air separation power by 90%
- High purity CO₂ exhaust reduces the cost of capture
- Cost of CO2 capture and compression $3-$5/ton
Conceptual Coal-Fired OTM Boiler Process

- Indirect compressed air heating and external OTM
- Hot compressed air topping cycle to boost power
Oxy-Fuel Combustion Without Producing Pure O2 Appears Promising for CO2 Sequestration

1. OTM-Dilute Oxygen Combustion Integration

2. Chemical Looping Combustion
   Oxygen carried from air to fuel by metal oxides, sulfates, etc.
Example 1 – Steel Reheat Furnace

Baseline fuel consumption 1.5 MMBtu/ton
CO2 emissions 174 lb/ton
Throughput increase 20%
Incremental fuel consumption 0.75 MMBtu/ton
CO2 emissions 87 lb/ton

Example 2 – Gas Turbine Topping Cycle

-Generate power at an incremental heat rate of 4000 to 6000 Btu/kwh (57 to 85% HHV efficiency)
-No incremental CO2 emissions
-Net Reduction of NOx Emissions
GAS TURBINE TOPPING CYCLE RETROFIT WITH O2 INJECTION

O2 Enhanced Hot Windbox

Incremental power at 4,000-6,000 Btu/kwh
No increase in total CO2
NOx reduction to 0.15 lb/MMBtu
100% oxy-fuel firing of coal fired boilers is feasible for CO2 sequestration.

- Stand alone oxygen generation plant consumes 10 to 20% of the power plant output and is not economically attractive

“Oxy-fuel combustion” without producing pure O2 appears promising for CO2 sequestration.

- OTM-Dilute Oxygen Combustion Process
- Chemical Looping “Combustion” Process

Oxy-fuel combustion for retrofit applications offers viable near-term opportunities for CO2 reduction

- Oxy-fuel fired industrial furnaces
- O2 enhanced gas turbine topping cycle of PC fired boilers

There are needs for experimental data on coal combustion under oxygen fired conditions