Development of In-Situ Sensors for the Chemical Industry

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Process Analysis
The Dow Chemical Company

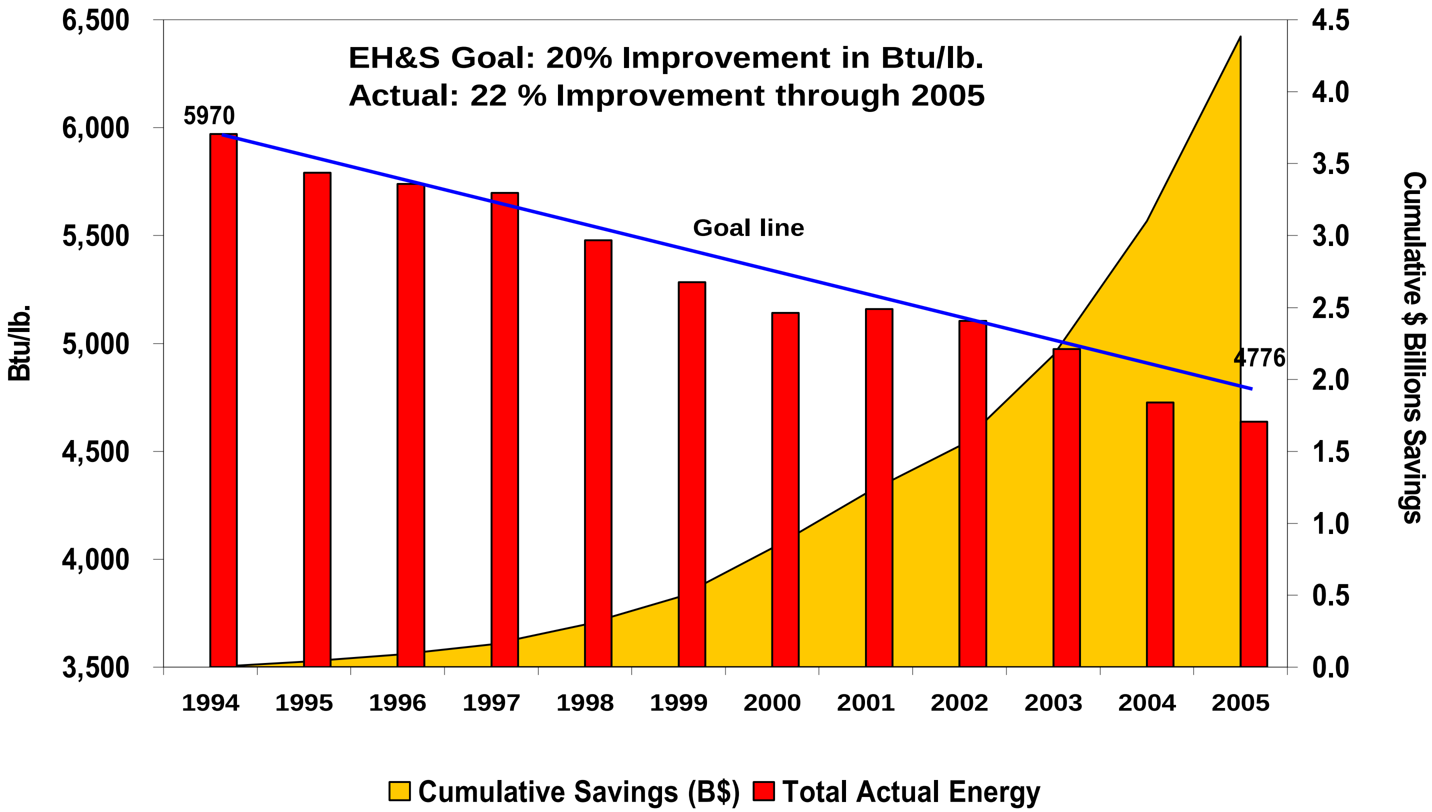
Need for Improvement

- Dow continually searching for technologies to allow better measurements and control
- The Process Analytical world is slow to develop or adapt new technologies
- In 2002, Dow received an award from DOE OIT to develop laser based analyzers for in-situ measurements
- Partnering with Analytical Specialties Inc. (commercialization entity), this program has resulted in 2 analytical tools with numerous applications

DOW TAKING ACTION

Focusing on Energy Efficiency

Energy Intensity Performance



Cumulative Energy Savings = ~900 Trillion Btu's

Cumulative Cost Savings = >$4 Billion

ETHYLENE PRODUCERS

- **Ethylene Producers consume significant energy and continue to improve efficiency**

Company	No. of Sites	Capacity (tpy)
1. Dow Chemical	14	12,900,000
2. ExxonMobil	15	11,467,000
3. Shell Chemicals Ltd.	10	8,432,000
4. Saudi Basic Industries	5	6,890,000
5. Equistar Chemicals LP	6	4,880,000
6. BP PLC	7	6,009,000
7. Chevron Phillips Chemical	4	3,993,000
8. Sinopec	8	3,505,000
9. Atofina	9	5,653,000
10. Nova Chemicals	2	3,537,000

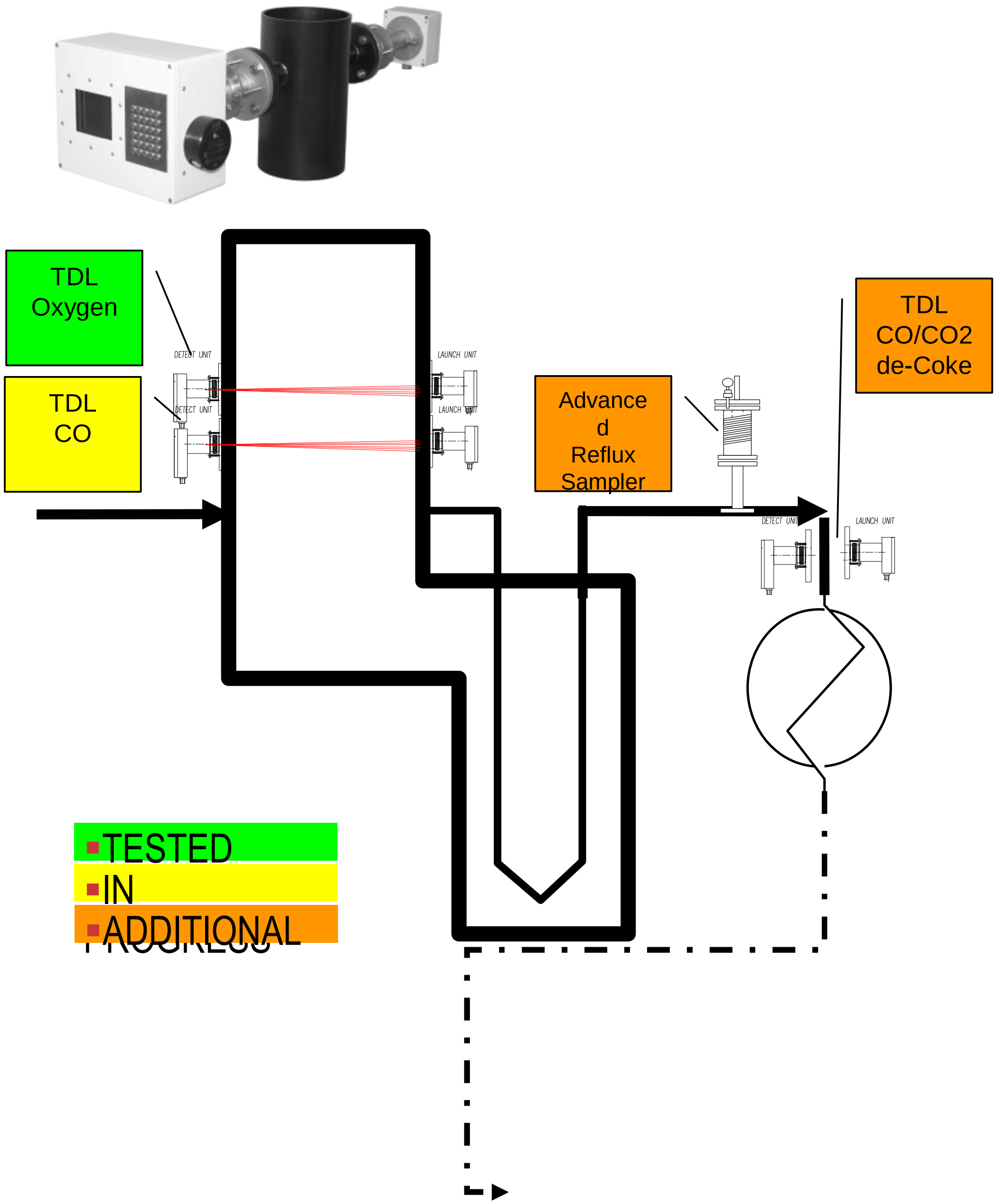
APPLICATIONS

PLATFORM / APPLICATION	STATUS
TDL Platform	Commercially available
Ethylene combustion (O2)	Field trial underway
Ethylene combustion (CO)	Field trial planned
Chlorine cell monitoring (O2)	Commercially available
THROX/Kiln combustion (O2)	Commercially available
Chlorine (H2O ppm levels)	Commercially available
ICOS Platform	Transfer to production design
C2H2 in ethylene	Field trial complete
Ppb-ppm impurities	Commercially available

TECHNOLOGY ADVANTAGES

- In situ measurement, measure at process conditions (simultaneous background / pressure / temperature changes)
- High temperature operation (1500C)
- High pressure operation (20 bar)
- Non-contacting measurement suitable for aggressive applications
- Near real time analysis (1-20s)
- No cross interference
- Low LTCO, No moving parts , High MTTF on components
- Typically no sample conditioning or analyzer shelter required
- Priced comparable to current process oxygen technologies
- On board diagnostics
- Field repairable

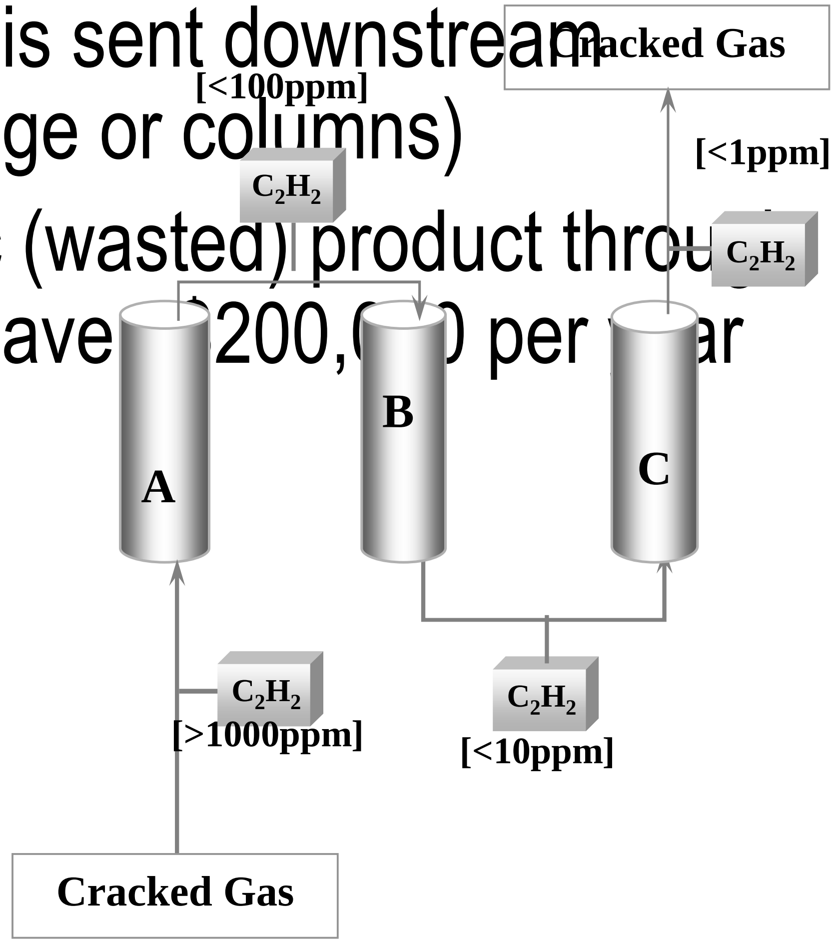
ETHYLENE PROCESS OPTIMIZATION



- Current focus on primary measurement needs
  - O2/CO/NO in combustion zone
  - C2H2 as impurity for Acetylene Reactor Unit control
- Pending targets result in fully instrumented furnace for advanced control
  - CO in combustion zone to further reduce excess oxygen
  - CO/CO2 Analysis for improving de-coke efficiency (reduction in steam + higher run time %)
- Measurement Suite would allow control of competing constraints:
  - Energy efficiency
  - Throughput optimization
  - Run-time %

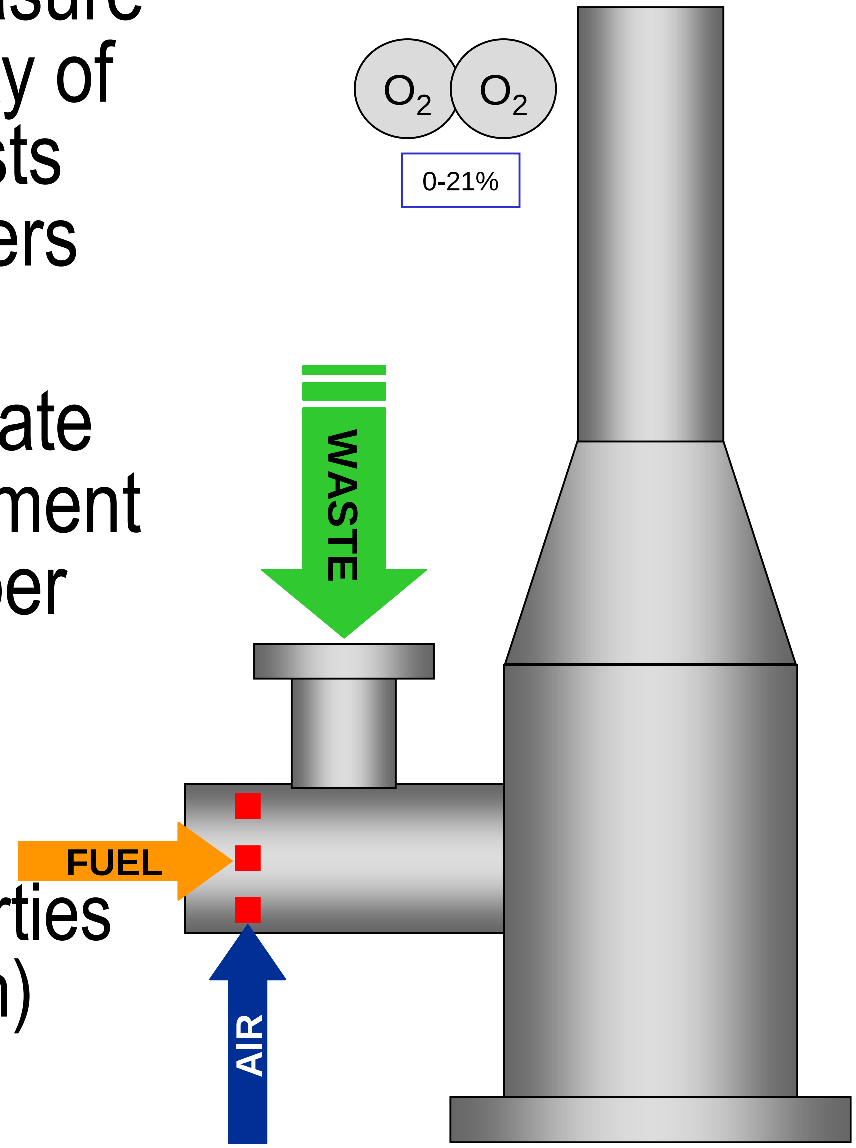
ICOS Acetylene Reactor Measurement

- C2H2 is a product contaminant, ppm levels are not acceptable
- Rapid analysis is needed to reduce the amount of offspec product that is sent downstream (contaminating storage or columns)
- Reduction in offspec (wasted) product through faster analysis can save $200,000 per year



THROX / INCINERATION APPLICATIONS

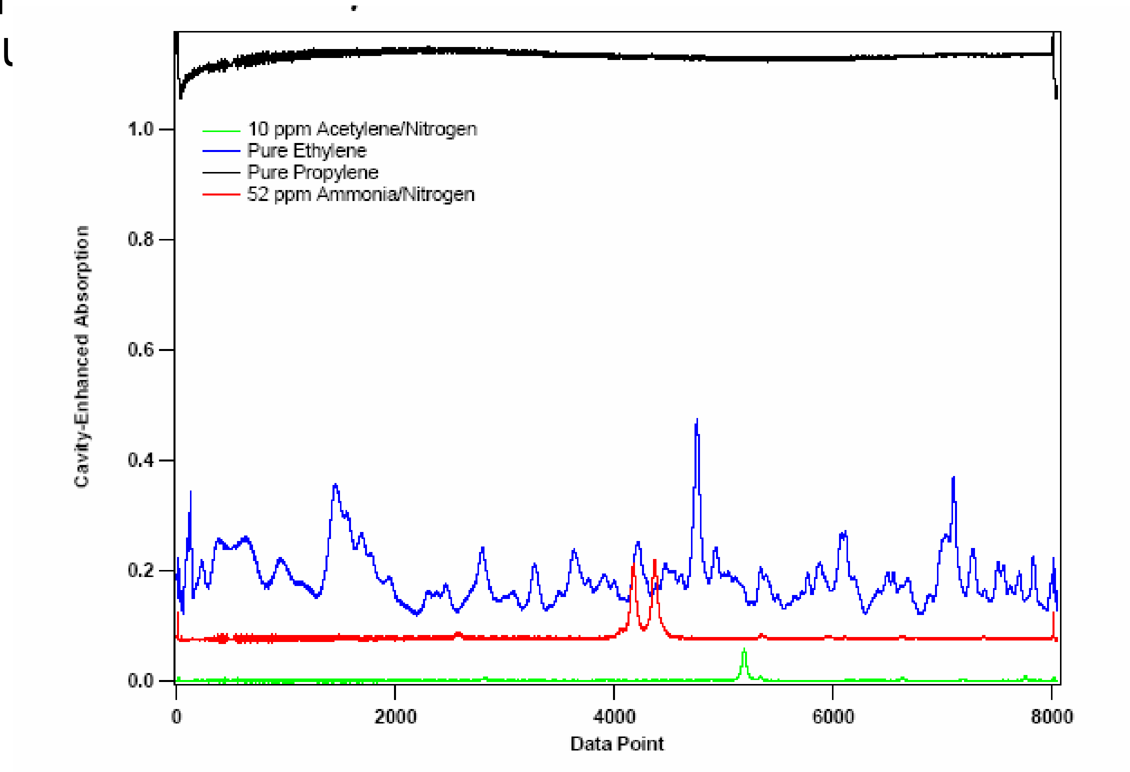
- Many incinerators do not measure excess oxygen due to difficulty of application. Maintenance costs using zirconia oxygen analyzers can be too high to justify.
- Energy savings with an accurate and reliable oxygen measurement can be $3-500,000 per year per incinerator



- Application Difficulties:
  - Changing combustion properties during burns (waste variation)
  - Temperature
  - Particulate

Product Impurities

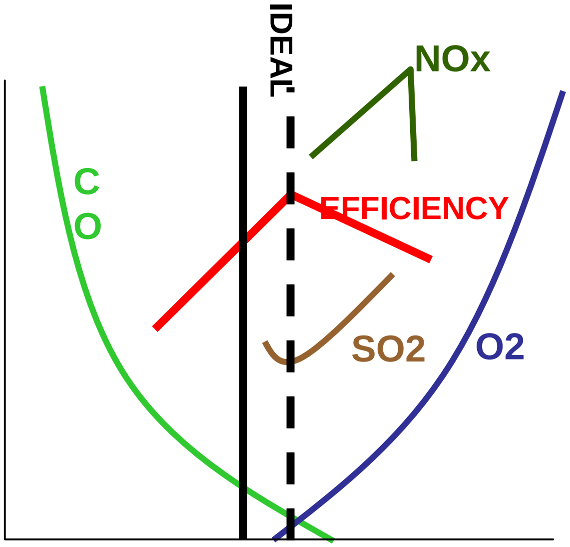
- As with TDL, ICOS can be applied to the measurement of a number of gases. Limitation is only the available wavelengths from laser suppliers:
- Measurable gases (ppb-ppm detection limits possible) inclu
  - NH_3
  - CO
  - CO_2
  - C_2H_2
  - H_2O
  - H_2S
  - O_2
  - Others available

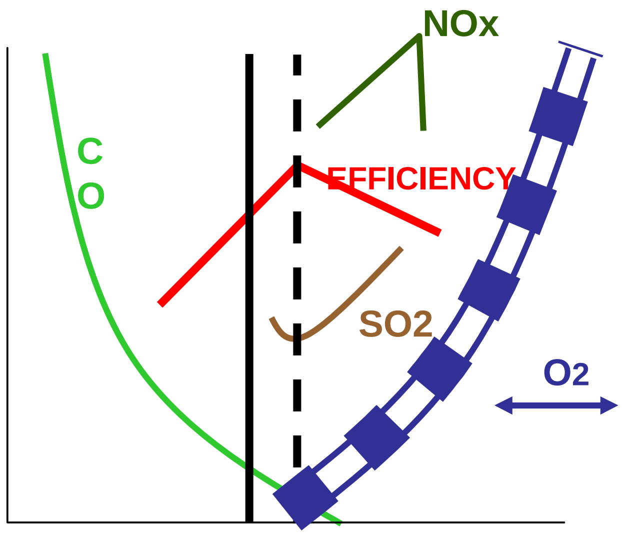


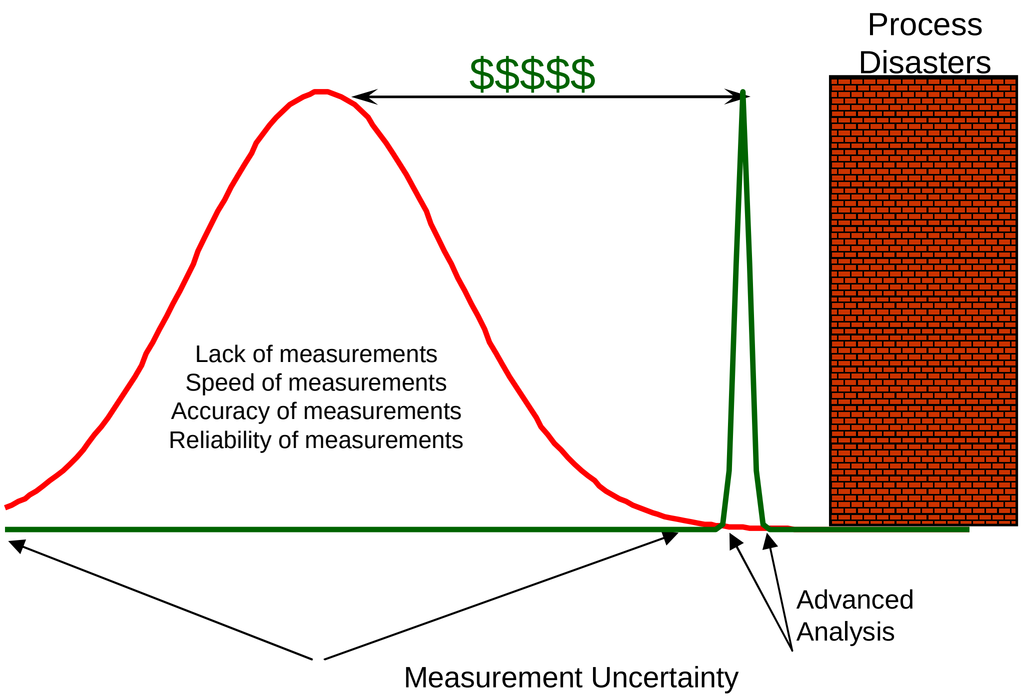
Combustion Analysis Background

The "IDEAL" oxygen level can vary due to:

- Boiler load
- Burner characteristics
- Tramp air (erroneous reading)



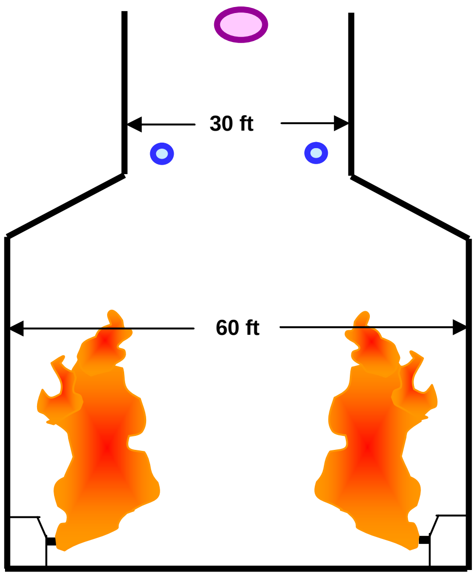




Current Approaches

- Majority of systems use oxygen measurement only with ZrO2 analyzers
- Oxygen measurements can be installed
  - Close to the firebox with close coupled extractive
  - Further downstream with in-situ
- When close to the firebox oxygen distribution errors will be greatest
- When further downstream the readings can be affected by tramp air ingress

Both errors (distribution and tramp air) can be large



Analytical Requirements for Improving Control

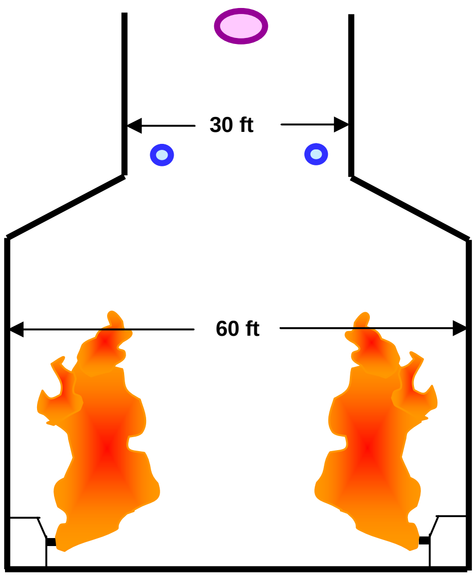
In order to improve control, current limitations have to be overcome

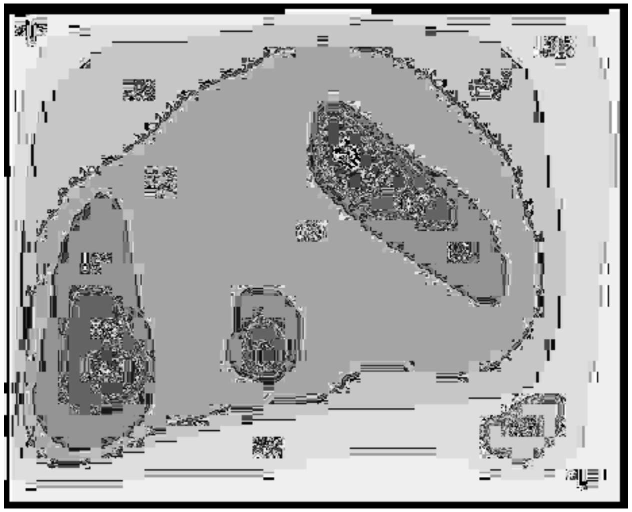
- Oxygen analysis must be fast (response time + location near the firebox)
- Oxygen analysis must not suffer from large distribution errors (path average), or tramp air (near the firebox)
- Oxygen analysis must not be affected by CO and combustibles

Measurement Location Issues

- Typically there are two types of “location” issues for measuring O2
  - Distribution of oxygen near the burners is inconsistent. To overcome this either a “path average” or multiple single point measurements must be provided.
  - Further downstream mixing can be improved (less distribution), however air leaks into the system (tramp air) will offset the oxygen reading.
  - Both of these “location errors” can be severe

<u>Ideally the measurement should be path average near the burners</u>





Tunable Diode Laser for Combustion Analysis

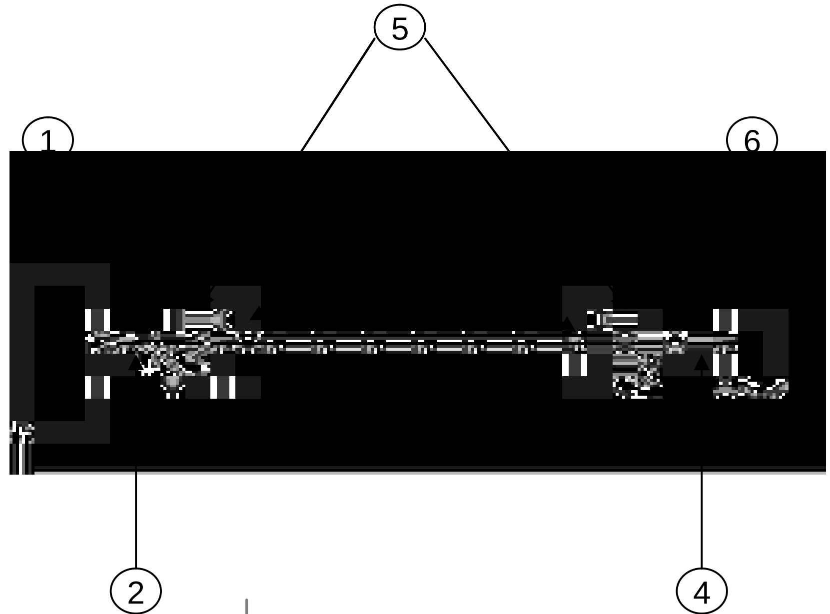
Using the following requirements as a minimum target, TDL can offer significant benefits for combustion optimization:

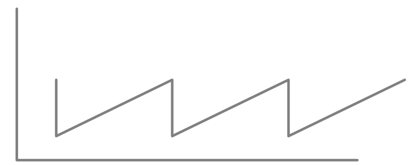
- Oxygen analysis must be fast (response time + location near the firebox). TDL response time is typically <5 seconds, measurements can be made at 1500C
- Oxygen analysis must not suffer from large distribution errors (path average), or tramp air (near the firebox). TDL is a path average measurement "counting" the total oxygen in the laser path.
- Oxygen analysis must not be affected by CO and combustibles. TDL has no spectral interference from other combustion by-products.

TDL Theory

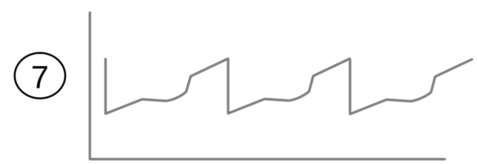
- TDL is an optical measurement. The measured gas absorbs the laser light at a specific wavelength. The amount of light absorbed is a function of gas concentration, pressure, temperature and optical path length.

- Method of operation
  - The system electronics control the current fed to the laser (1)
  - The laser (2) wavelength changes with current
  - The modulated laser light is collimated to a circular beam (2), and sent through process windows (3) and the process gas
  - The light transmitted through the process gas strikes a detector (4)
  - This signal will show an absorption (loss of light) at the wavelengths the gas absorbs

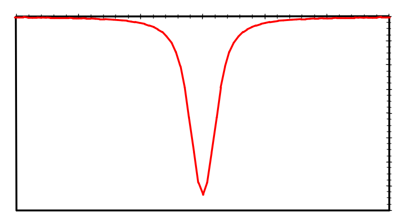




Current ramp to laser



Signal at Detector



Flattened Detector Signal

Summary

With rising energy prices, optimizing combustion systems can provide significant savings

New analytical tools are needed to reduce excess oxygen set-points and control points

TDL technology shows promise, but as with any "new" type of measurement, careful attention must be given to installation and operation issues

With new "types" of measurements, control strategies must be adapted

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