

**iets**

Industrial Energy-Related Technologies and Systems

An Implementing Agreement established under the auspices of the International Energy Agency

INTERNATIONAL WORKSHOP

Energy Optimization in Industry and the Reduction of CO<sub>2</sub> Emissions



# CO<sub>2</sub> and NO<sub>x</sub> Emissions Reduction in Combustion Systems

Isabel Cabrita, Pedro Azevedo & Ibrahim Gulyurtlu

**RE.NEW.ABLE.**  
A INSPIRAR PORTUGAL

**meid**  
Ministério da Economia,  
da Inovação e do Desenvolvimento

# Contents

---

Fuels and Combustion

Pollutants Production

Oxy-Fuel Combustion

Heat Transfer

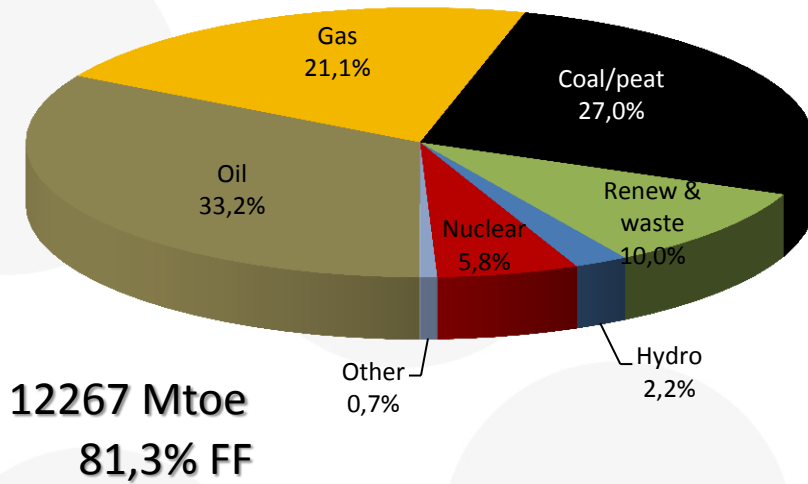
Computational Models

Conclusions & Future R&D

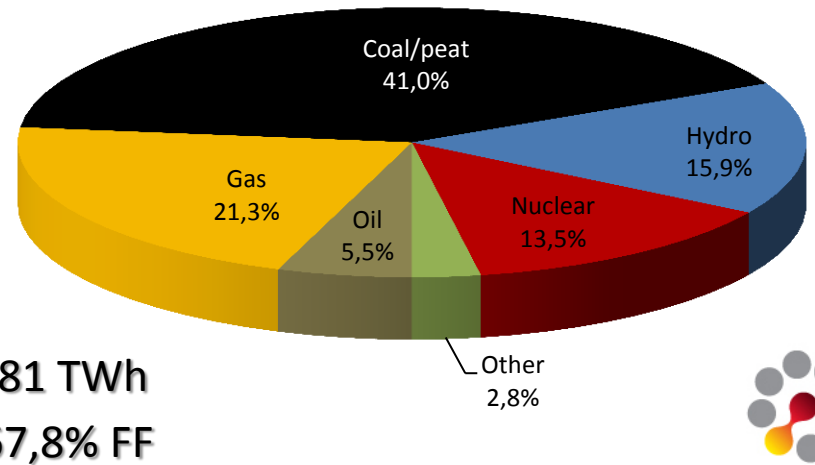
# Fuel Dependence

2008

### Total primary energy supply

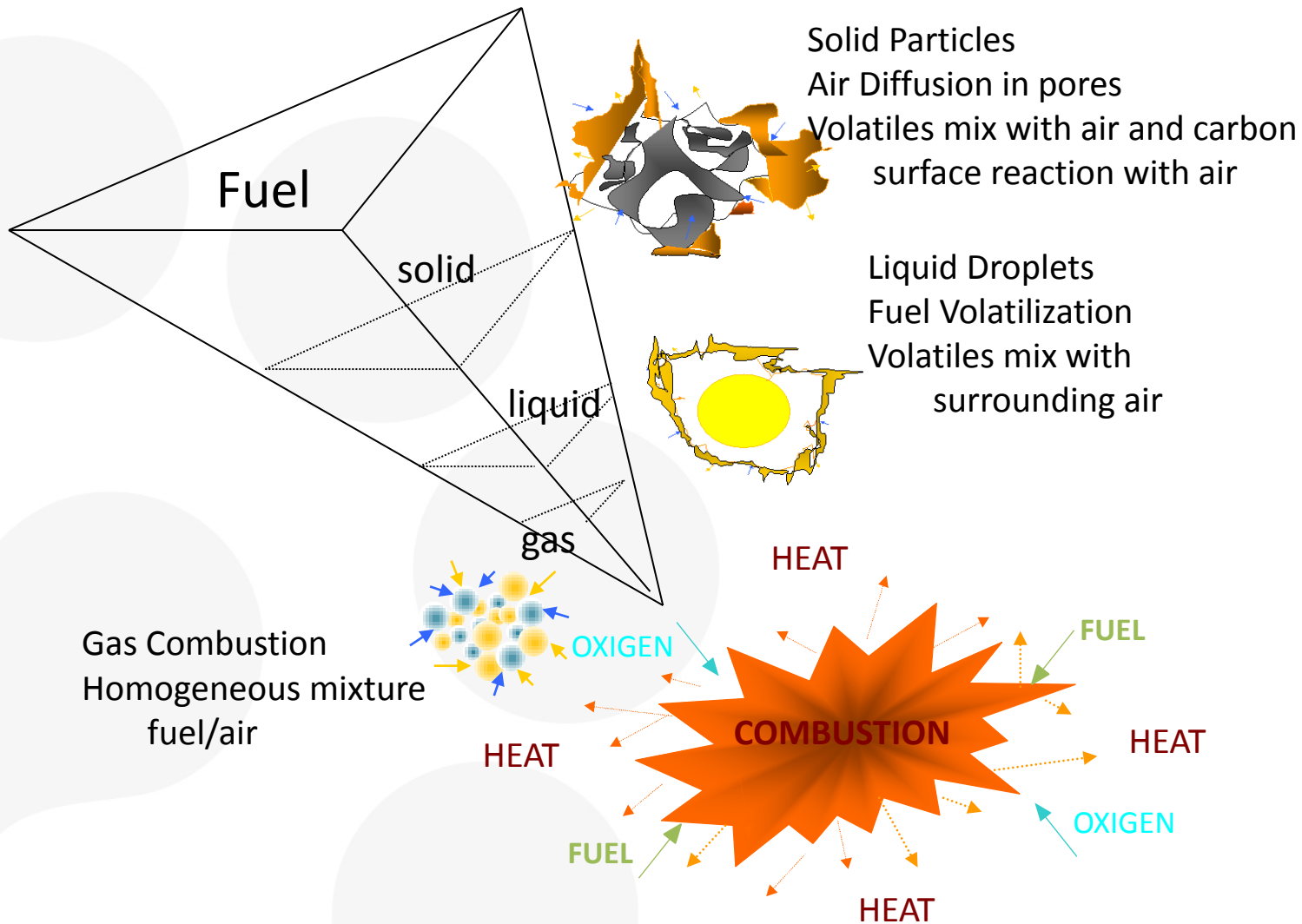


### Electricity Generation



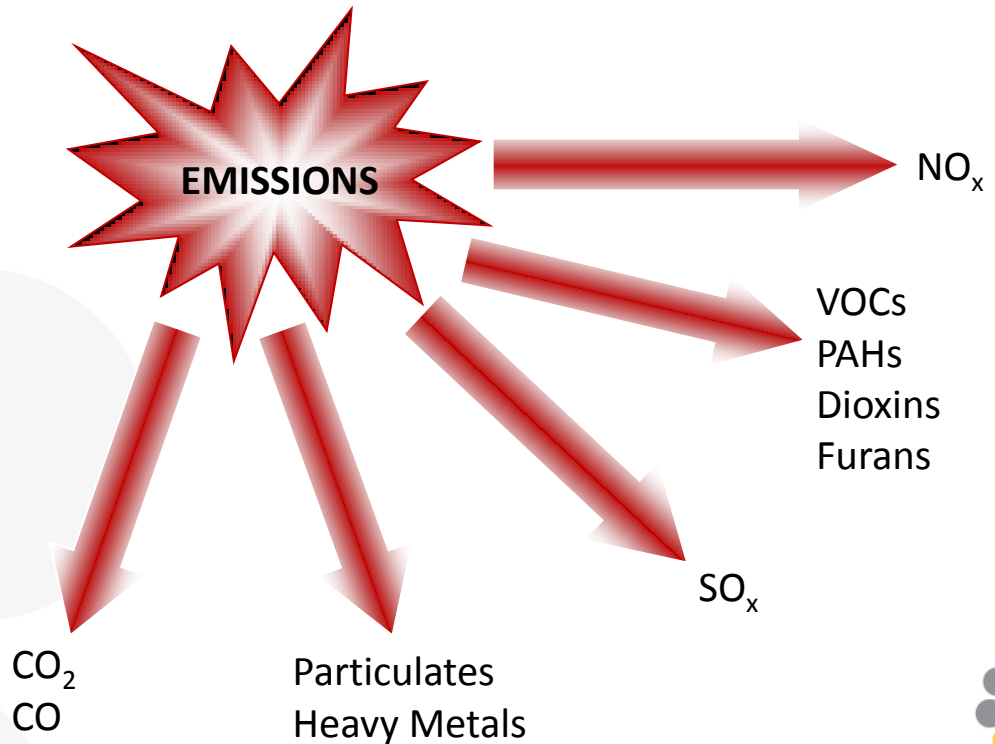
Source: IEA Key World Energy Statistics (2010)

# Fuels & Combustion

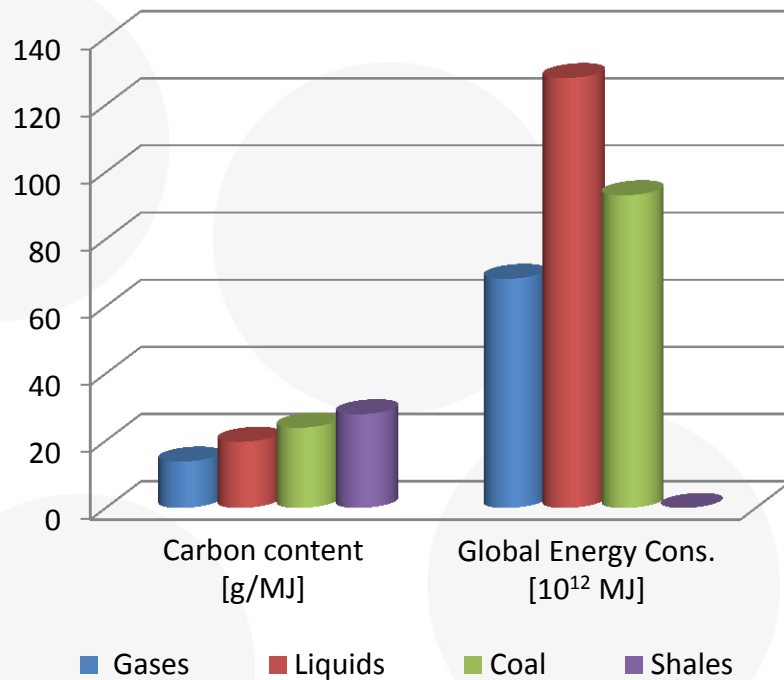


# Efficiency in Combustion and the Environment

$\text{NO}_x$  is produced, during combustion, either by the oxidation of nitrogen from the air or by the oxidation of nitrogen present in the fuel. Generally, to achieve high efficiency of fuel combustion the flame temperature is increased, and hence the amount of  $\text{NO}_x$  emission from the oxidation of nitrogen in the air.



# The CO<sub>2</sub> Emissions



Type of fuel	g CO <sub>2</sub> /MJ
Lignite	101.2
Sub-bethuminous Coal	96.1
Coke	94.6
Residual Fueloil	77.4
Diesel/Gasoil	74.1
Natural Gas	56.1

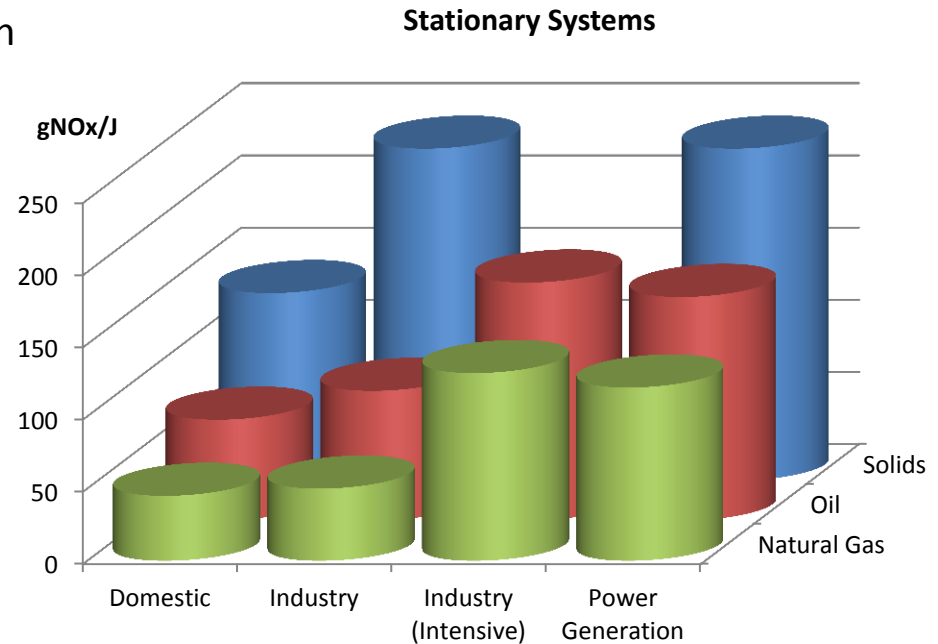
# The NO<sub>x</sub> Emissions

Parameters known to influence the production of NO<sub>x</sub>:

- Fuel Properties;
- Combustion System;
- Operating Conditions; and
- Size of the Combustion Installation.

Parameters known to influence NO<sub>x</sub> emissions :

- Optimised combustion conditions;
- Fuel staging (40 to 60%);
- Combustion air staging;
- Recirculation of combustion gases (55 to 65%);
- Above-stated conditions are achieved in low NO<sub>x</sub> burners (30 to 55%).



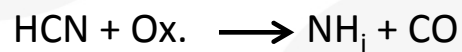
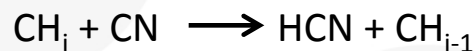
# NOx Production from Combustion

- Thermal NO

- Prompt NO

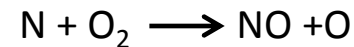
- Fuel NO

- It is formed through combustion of fuels containing nitrogenous organic species (in coal range from 0,5 to 2%).
- This becomes important when combustion occurs at relatively low temperatures, lower than 700 °C.
- Fuel-N Mechanism:

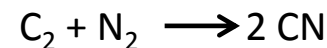


Nitrogen free Combustion  
OXY-COMBUSTION

- It is formed in the oxidation zone of the flame at temperatures above 1300 °C; and
- It is produced by the combination of N<sub>2</sub> and O<sub>2</sub> in the air and it is known as mechanism of Zeldovich:

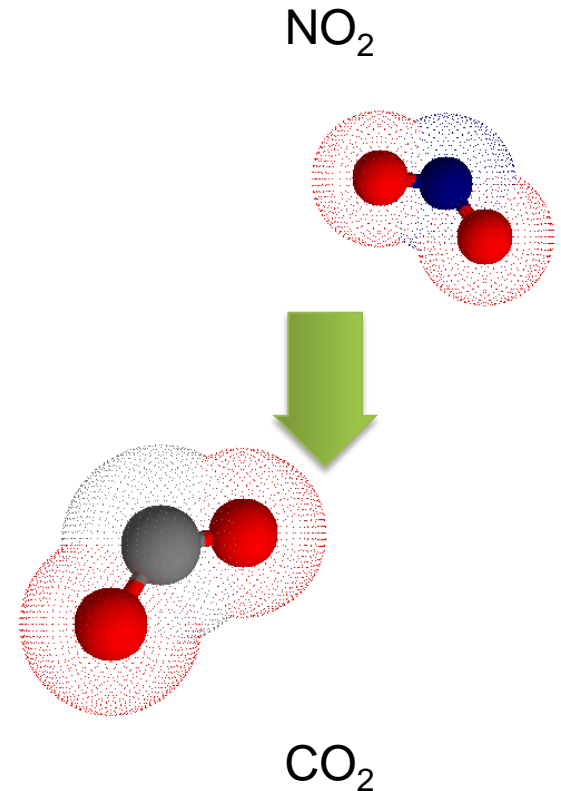


- It is formed in the oxidation zone of the flame, initiated by combination of the nitrogen in the air and HC radicals, giving rise to HCN or CN.
- Mechanism of Fenimore:



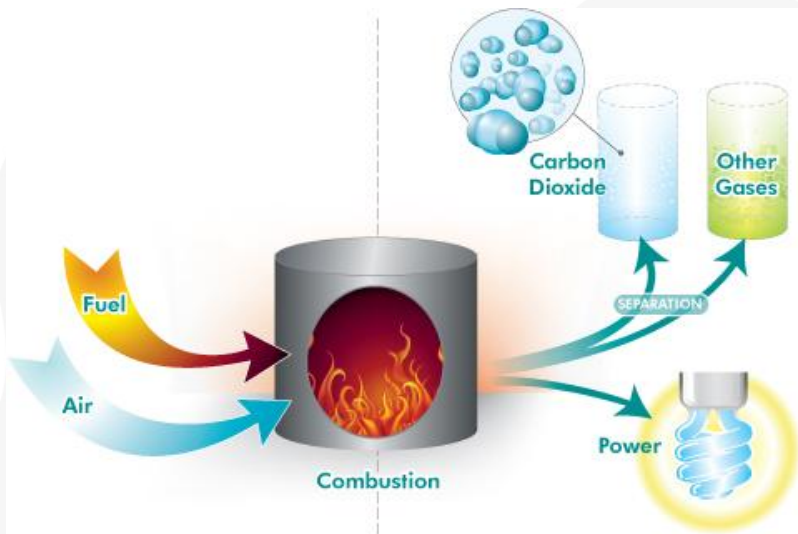
# The emerging problem

- Part of the work developed in the past by the team of LNEG focused on  $\text{NO}_x$  removal from combustion systems;
- $\text{CO}_2$  that was considered a natural product of combustion, now is believed to be major contributor to global warming;
- Responding to this, the main efforts of the Unit of Emissions “Zero” (UEZ) mostly consider  $\text{CO}_2$  reduction and removal;
- With the current push for  $\text{CO}_2$  sequestration, it is imperative to develop cost-effective processes that enable  $\text{CO}_2$  capture;
- Technically oxy-fuel combustion appears to be one of feasible solutions to facilitate  $\text{CO}_2$  capture leading to the reduction of  $\text{NO}_x$  emissions;
- It is the object of UEZ work in coupling the achieved results regarding  $\text{NO}_x$  emissions with  $\text{CO}_2$  removal.



# Standard Combustion Process

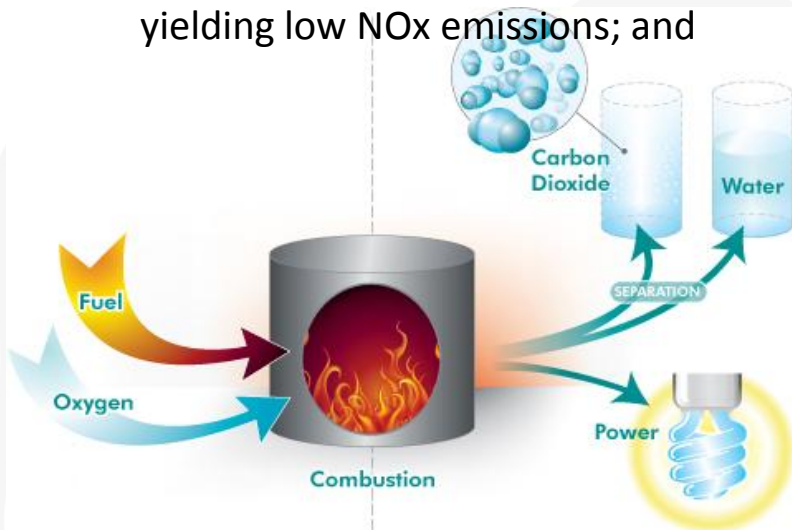
- In most conventional combustion processes, air is used as the source of oxygen;
- The use of pure oxygen in the combustion process instead of air eliminates the presence of nitrogen in the flue gases, thus yielding much higher temperatures and lower volumes of gases to be handled;
- Nitrogen is not necessary for combustion and causes problems by reacting with oxygen and HC radicals at combustion temperature (Zeldovich and Fenimore mechanisms); and



- A high concentration of nitrogen in the flue gas can make CO<sub>2</sub> capture both technically and economically unattractive.

# The Oxy-Fuel Approach

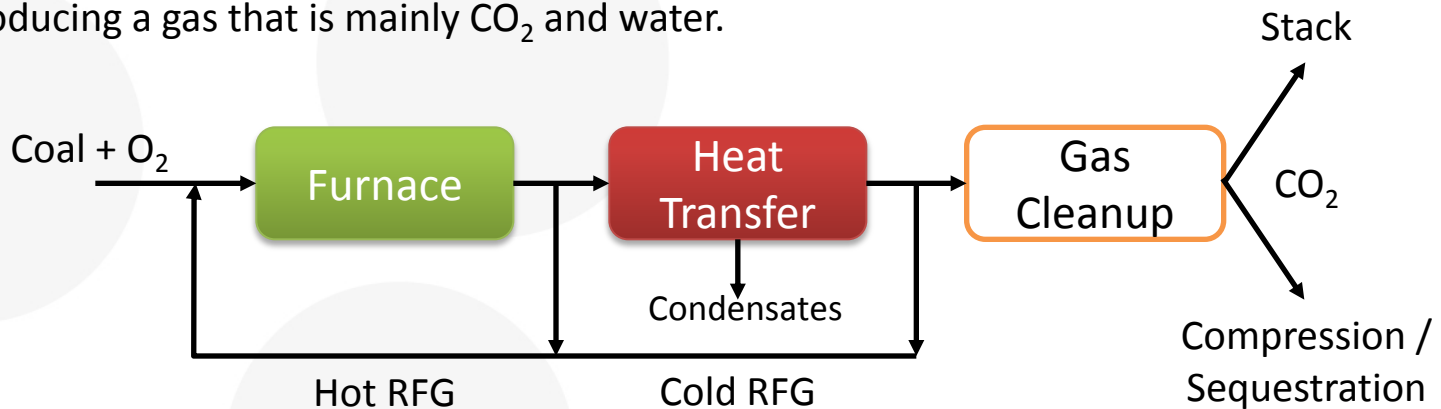
- The energy released by the combustion process being the same and in the absence of nitrogen mass, the flue gases temperature tends to be higher;
- In order to solve the temperature control problem, it is necessary to increase the volume flow of flue gases which is possible by recycling part of flue gases;
- As temperature decreases to more accustomed levels and introducing recycled flue gases in correct locations, the absence of air nitrogen inhibits the Zeldovich and Fenimore mechanisms as well as reducing the oxygen availability for fuel-N, thus yielding low NO<sub>x</sub> emissions; and



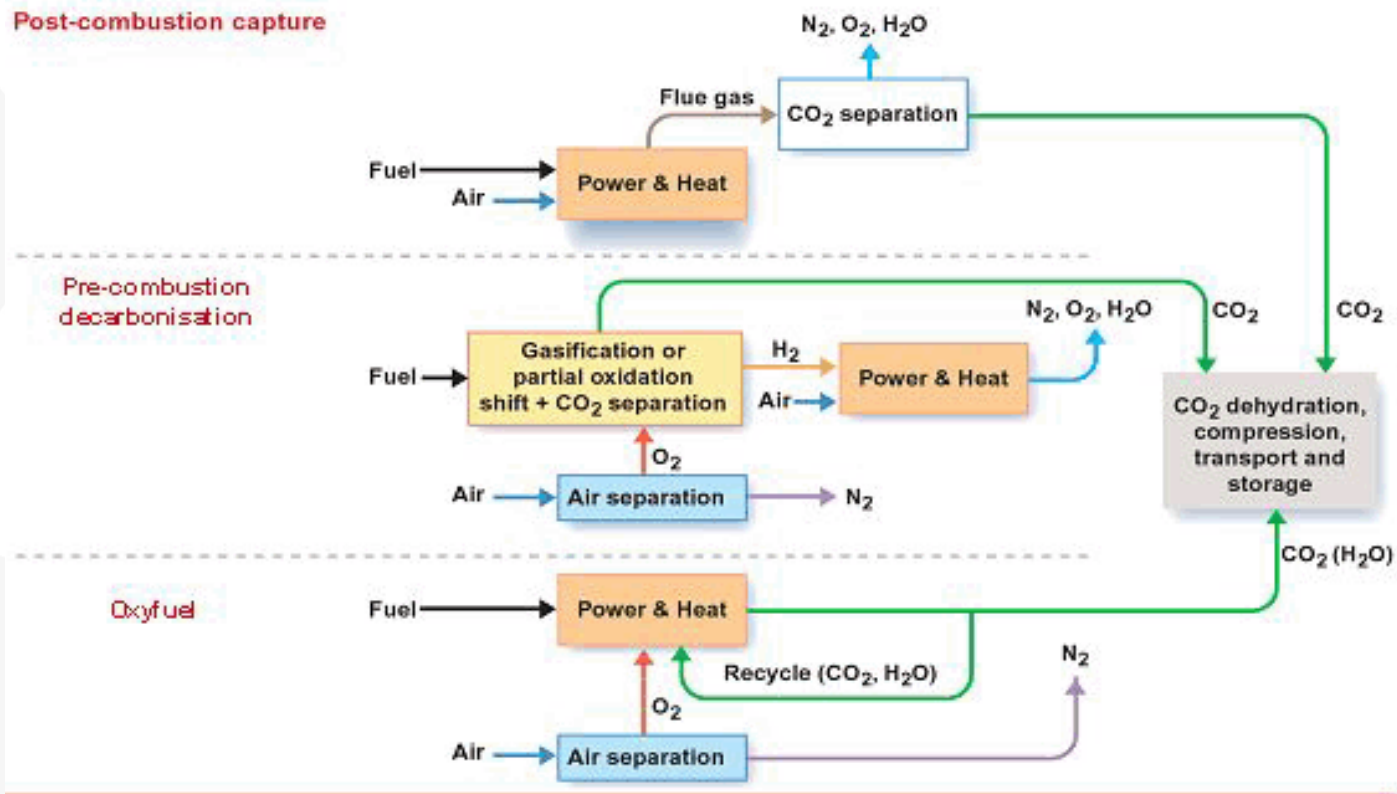
- Recycled flue gas is also used to control the flame temperature and replace the volume of the missing nitrogen needed to carry heat through the combustion system.

# Oxy-Fuel Background

- In 1982 oxy-fuel combustion was proposed to produce CO<sub>2</sub> for Enhanced Oil Recovery;
- Recycling of hot flue gas has also been suggested to reduce furnace size and NO<sub>x</sub> emissions for metal heating furnaces;
- Lately, interest on oxy-fuel combustion is more considered as a means to reduce pollutant emissions control cost and create a CO<sub>2</sub> rich gas stream that can easily be captured through many ways for sequestration; and
- Oxygen at greater than 95% purity and recycled flue gas are used for fuel combustion, producing a gas that is mainly CO<sub>2</sub> and water.



# Gas side process flow diagram for CO<sub>2</sub> separation



CO<sub>2</sub> capture processes (Linde AG Linde Engineering Division)

# Operational Issues

---

- To have similar adiabatic flame temperatures, oxygen must have a concentration of about 30%;
- For an oxygen concentration of 30%, about 60% of the flue gases are recycled;

Chem. Species	Air	O <sub>2</sub>
CO <sub>2</sub>	13,7%	60,9%
O <sub>2</sub>	3,5%	3,5%
N <sub>2</sub>	73,5%	2,1%
H <sub>2</sub> O	8,3%	32,7%
SO <sub>2</sub>	0,2%	0,9%
Ar	0,9%	0,0%

- Flue gas volume after recycling is 80% smaller than in conventional combustion, and its density is increased;
- Instead of 20% excess oxygen for air-firing, only 3-5% is required; and
- The remaining species present in flue gases are in higher concentrations after oxy-fuel combustion.

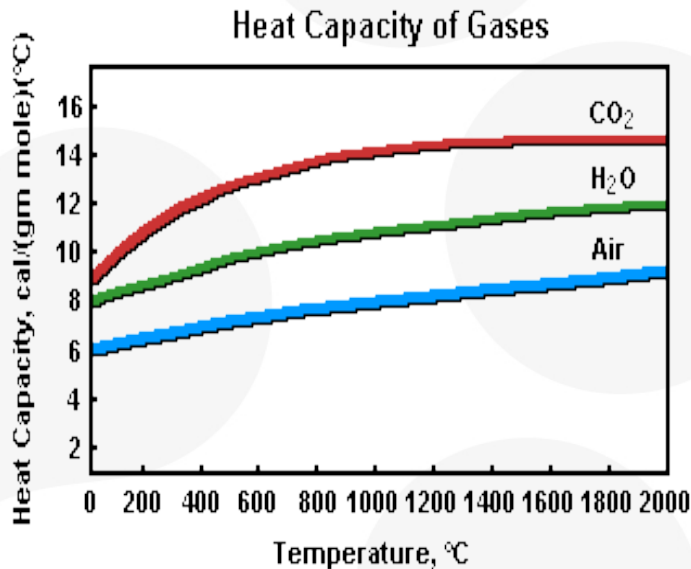
# Pollutants

- A maximum  $\text{CO}_2$  concentration of about 92% is achieved on dry basis and  $\text{CO}_2$  can be cooled down to low temperatures and compressed for transportation and storage;
- $\text{NO}_x$  and  $\text{SO}_x$  emissions are lower.  $\text{NO}_x$  reduction (in some cases by 50%) occurs due to the rapid reduction of recycled  $\text{NO}_x$  into cyanide ( $\text{HCN}$ ) and ammonia ( $\text{NH}_3$ );
- A large reduction of unburnt carbon in fly ash is obtained; and
- Increasing  $\text{O}_2$  concentration decreases  $\text{CO}$  emission. However, the decrease in  $\text{CO}$  concentration along the flame is slower than conventional conditions because of a higher  $\text{CO}_2$  concentration.



# Heat Transfer

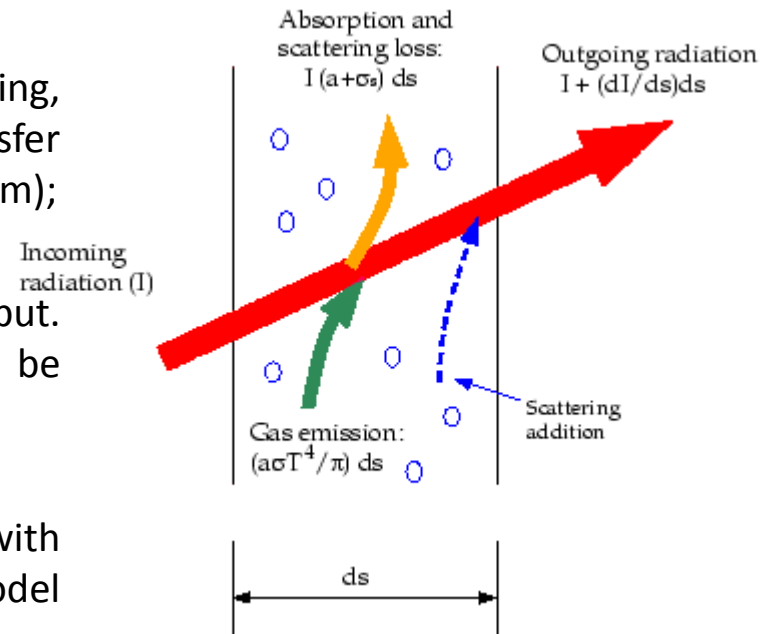
- Concentration of tri-atomic flue gas molecules is much higher in oxy-fuel combustion and leads to changes in emissivity. **It is not clear how this change will influence the radiative heat transfer;**
- CO<sub>2</sub> and H<sub>2</sub>O also have higher heat capacities compared to nitrogen, so more energy will be needed to raise flue gases temperature. **Heat transfer in the convective section of the equipment may be enhanced ;** and



- The less amount of gas passing through the system will transport more energy and the heat transfer both in convective and radiative sections **should be enhanced.**

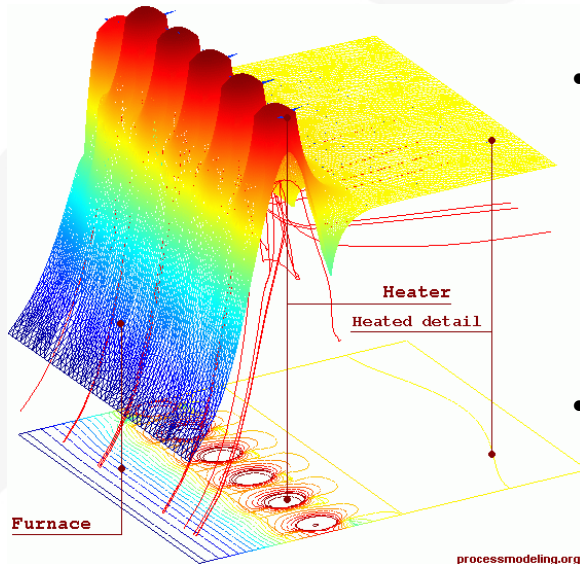
# CFD Modelling

- A better knowledge of the flue gases radiative properties and the possible increase of radiative heat transfer may lead to new and improved furnace designs and possibly to smaller furnace size;
- The radiative transfer equation (RTE) for an absorbing, emitting, and scattering medium computes heat transfer through an optical thickness (or opacity of the medium);
- Most models require the absorption coefficient as input. The absorption and scattering coefficients can be constants or computed variables; and
- The radiative heat transfer should be addressed with the inclusion of the Weighted-Sum-of-Gray-Gases model (WSGGM).



# Weighted-Sum-of-Gray-Gases Model (WSGGM)

- It is a **reasonable compromise** between the oversimplified gray gas model and a complete model, which takes into account particular spectrum absorption bands, and can be used for the computation of the absorption coefficient;
- It computes a **composition-dependent** absorption coefficient, with the local value of the absorption coefficient as a function of the local mass fractions of **water vapour** and **carbon dioxide** (other species can be added);



- However, its complete modelling is far from being complete due to various complexities in dealing with radiative properties of non-gray gases, multi-dimensional complex geometry, and computational efficiency as well as accuracy; and
- In addition, the computational effort may be increased as much as 95%.

# Conclusions

---

- Technically oxy-fuel combustion appears to be one of feasible solutions to facilitate CO<sub>2</sub> capture and it is the object of UEZ work in coupling the achieved results regarding NO<sub>x</sub> emissions with CO<sub>2</sub> removal (ongoing project **PRAXAIR/LNEG** comprising low LHT fuels combustion studies in enriched oxygen atmospheres);
- Considering that flue gases have different properties, which leads to alterations in the heat transfer process, more work on computational fluid dynamics models is justified, namely in identifying the influence of:
  - properties of flue gases (CO<sub>2</sub> and H<sub>2</sub>O specific weights and heat capacities) on both radiative and convective heat transfer performance;
  - volume flow of flue gases on the enhancement of heat transfer;
- Although absorption coefficient modelling is far from being complete and the computational effort may increase twofold, a composition-dependent absorption coefficient may be computed using local mass fractions of water vapour and carbon dioxide.

# Future R&D

- The Future is associated to... not one technological solution or energy resource, but a multiple contribution of resources and technologies.
- Areas of Research related to Oxy-Combustion:
  - Increase knowledge on heat transfer performance of new and retrofitted plants;
  - Study the impact of O<sub>2</sub> concentration and CO<sub>2</sub> recycle ratio;
  - Assess retrofits for electricity production cost vs. cost of CO<sub>2</sub> avoided;
  - Further studies on combustion behaviour of coal under O<sub>2</sub>/CO<sub>2</sub> conditions – ignition, burn-out, emissions;
  - As power must be provided for air separation, develop less costly O<sub>2</sub> generation processes; and
  - As some studies have shown problems with flame stability and ignition, research must be done in this domain.

# References

---

- IEA (2010), “Key World Energy Statistics”
- IPCC (2006), “Guidelines for National Greenhouse Gas Inventories”, Volume 2: Energy
- Ochs, T. (2003), “Capture of CO<sub>2</sub> From Recirculating Flue Gas Boilers”, in Proceedings of the 28th International Technical Conference on Coal Utilization and Fuel Systems, Coal Technology Association, pp. 456-464
- Ochs, T. (2004), “Oxy-fuel combustion systems for pollution free coal fired power generation”, Coal Technology Association, 601 Suffield Drive, Gaithersburg, US
- <http://www.processmodeling.org>, viewed at 10.28.2010
- Pinto F., André N., Abelha P., Crujeira T., Gulyurtlu I., (2009) *Chapter: “Chapter 1 – Control of flue gases produced by new coal utilization technologies: combustion and gasification”, in Flue Gases: Research, Technology and Economics*, ISBN: 978-1-60692-449-5, Editor: Theodore B. Naylor © 2009, Nova Science Publishers, Inc.
- Fluent UG (2005), “Fluent 6.2 User’s Guide”, Fluent Inc., Lebanon (NH), US
- Cabrita I. (1981), “Formation of nitric oxide in flames”, Ph.D Thesis, University of Sheffield, United Kingdom
- Azevedo P. (2007), “Study of Nitric Oxide Formation and Destruction in Hydrogen and/or Hydrocarbon Flames with or without Nitric Compounds Seeding”, Ph.D Thesis, Faculty of Engineering, University of Oporto, Portugal

# Thank you!

isabel.cabrita  
pedro.azevedo  
ibrahim.gulyurtlu



**LNEG**.pt

Laboratório Nacional de Energia e Geologia, I. P.

[www.lneg.pt](http://www.lneg.pt)