Pursuing the pre-combustion route in oil refineries

-The impact on fired heaters

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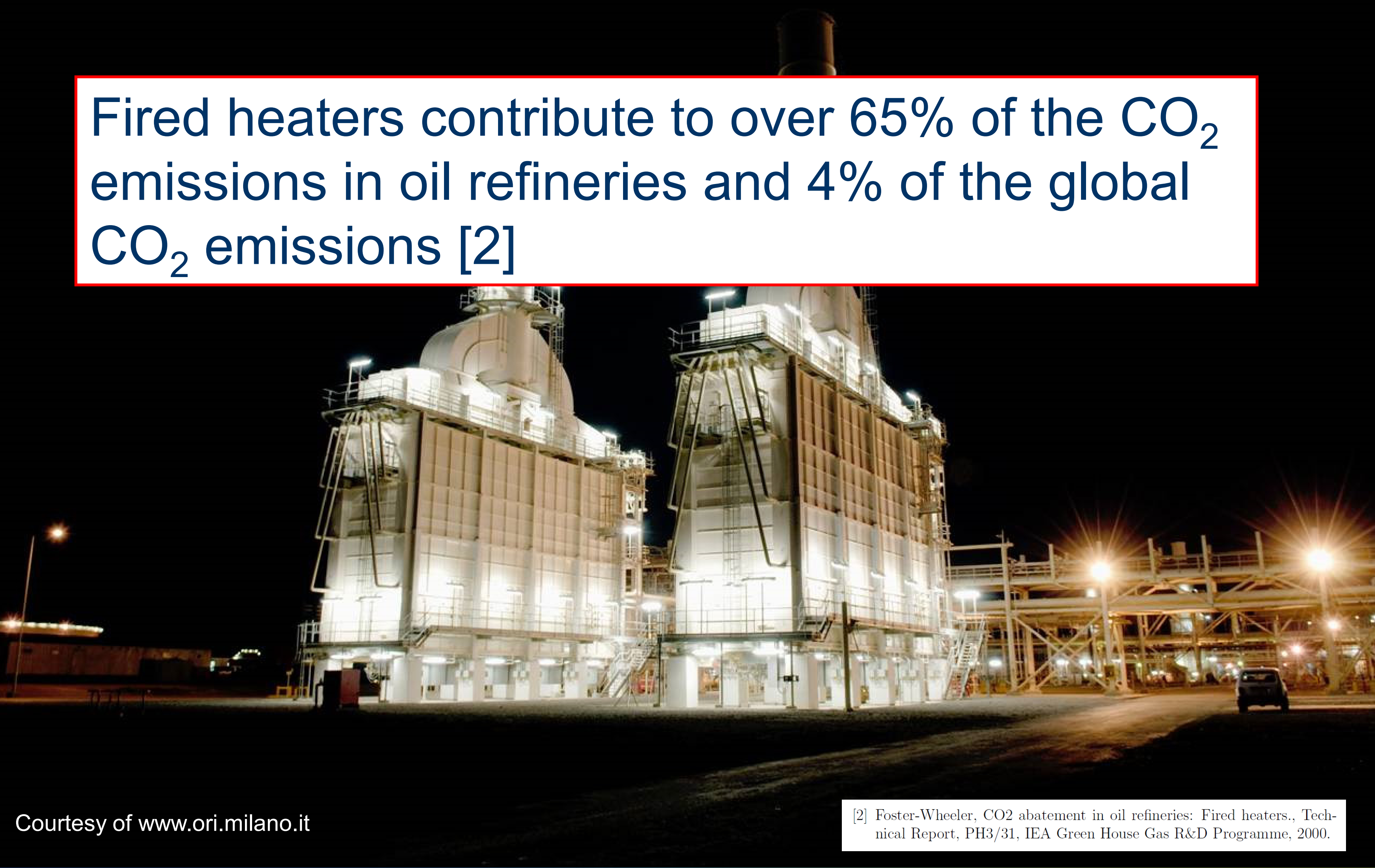
SINTEF

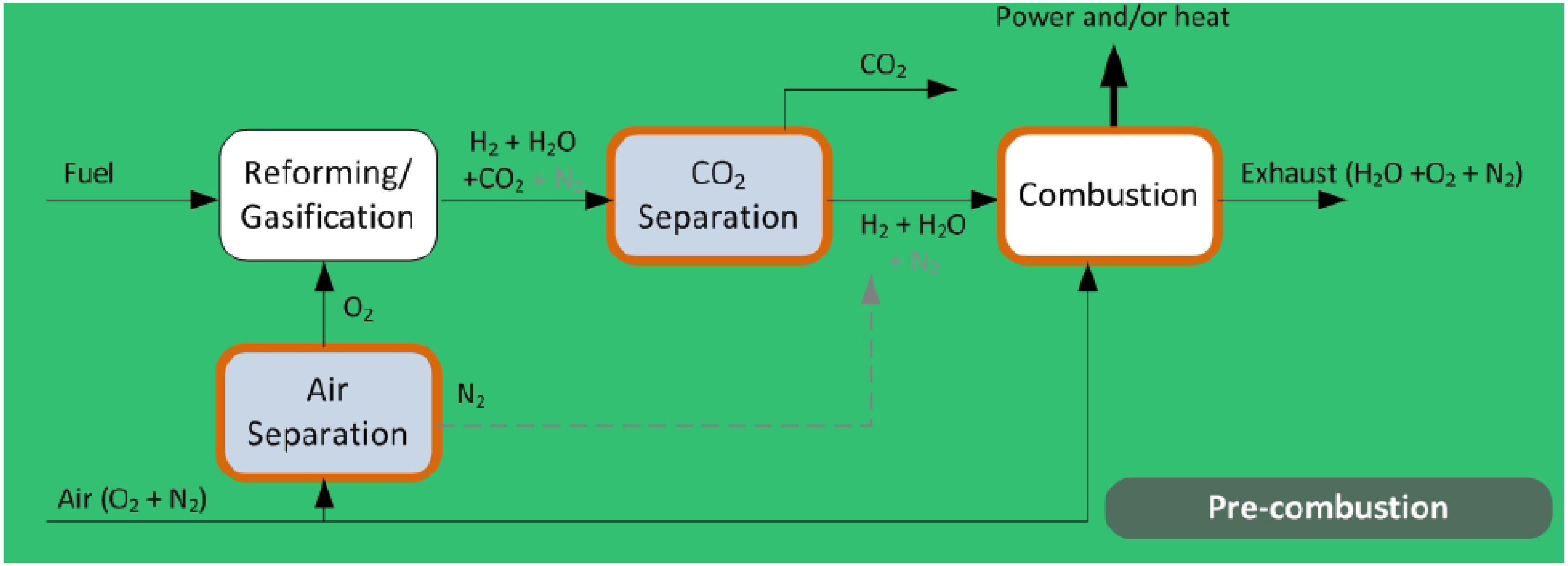
Fired heaters contribute to over 65% of the CO_2 emissions in oil refineries and 4% of the global CO_2 emissions [2]



Courtesy of www.ori.milano.it

[2] Foster-Wheeler, CO2 abatement in oil refineries: Fired heaters., Technical Report, PH3/31, IEA Green House Gas R&D Programme, 2000.

Pre-combustion CO_2 capture in oil refineries



- The pre-combustion alternative in previous reports:
  - is described as feasible, but with a somewhat higher cost than corresponding oxy-fuel or post-combustion options
  - The integration aspect has not been fully taken into account
  - The level of detail is also limited in order to map technical challenges

Objective

- The main objective:
  - H_2-fired heaters: Low-cost retrofit or high-cost complete rebuild?
- Present sub-objective:
  - Investigate the effect of burning H_2 instead of refinery gas in the radiant section burners:
    - Radiative heat load distribution on the tubes
    - Emissions
    - Heat transported to the convective section
- Method: Computational Fluid Dynamics (CFD)

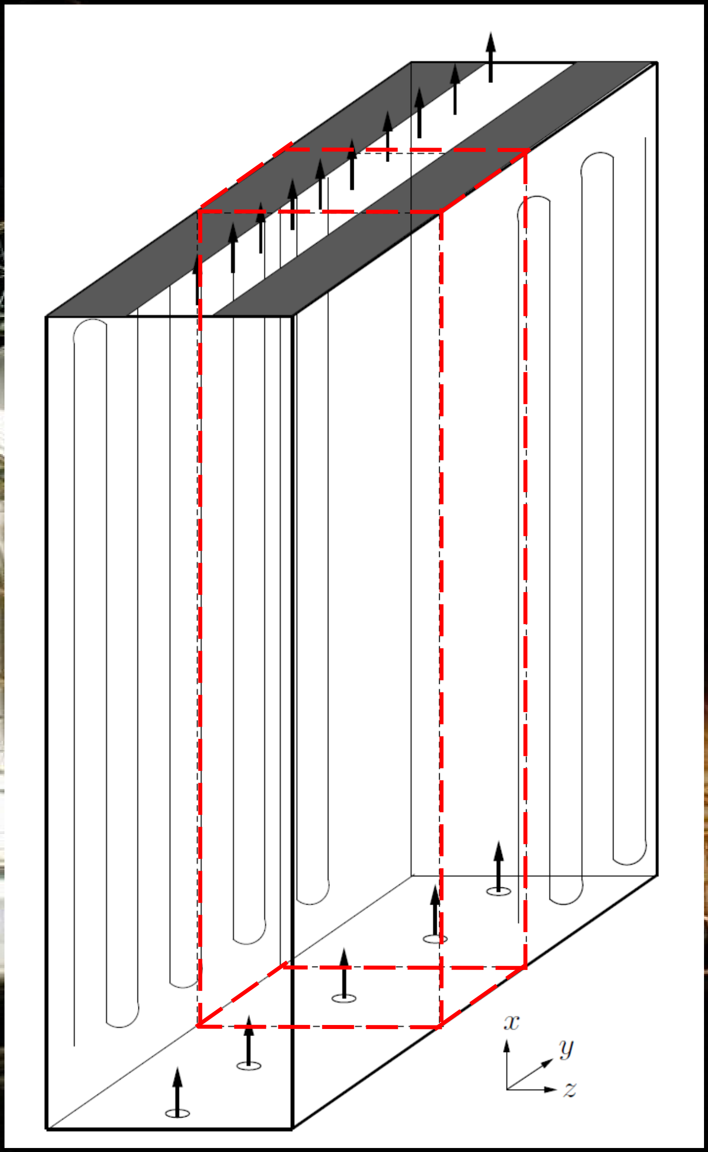
3 cases with the same thermal power load:

1. Base case: Refinery gas as fuel:
    - H_2: 20 mole%
    - CH_4: 45 mole%
    - C_2H_6: 10 mole%
    - C_3H_8*: 25 mole%
2. H_2-case: 100% H_2 as fuel
3. H_2/H_2O-case: H_2-case with steam dilution such that the air/fuel momentum ratio is matching the base case (~11mole% H_2O)

Fired heaters are complex process units

We apply a generic model of the radiant section of the fired heater

Courtesy of www.ori.milano.it



Input data

- Furnace

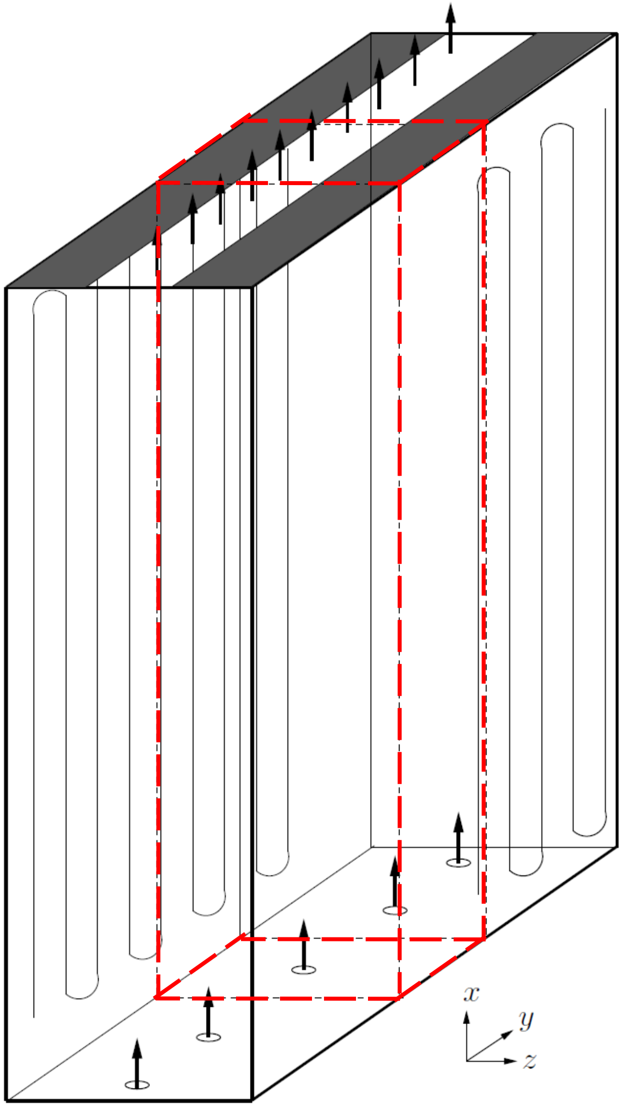
Height x Width:	8.5 m x 2 m
Outlet duct width:	0.6 m

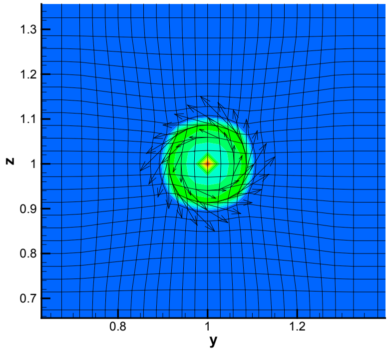
- Refinery Tubes

Tube wall thickness:	5 mm
Inner temperature:	873 K
Thermal conductivity:	31 W/(m K)
Heat transfer (inner):	200 W/(m2 K)
Emissivity:	0.95

- Swirl burner (same for all cases)

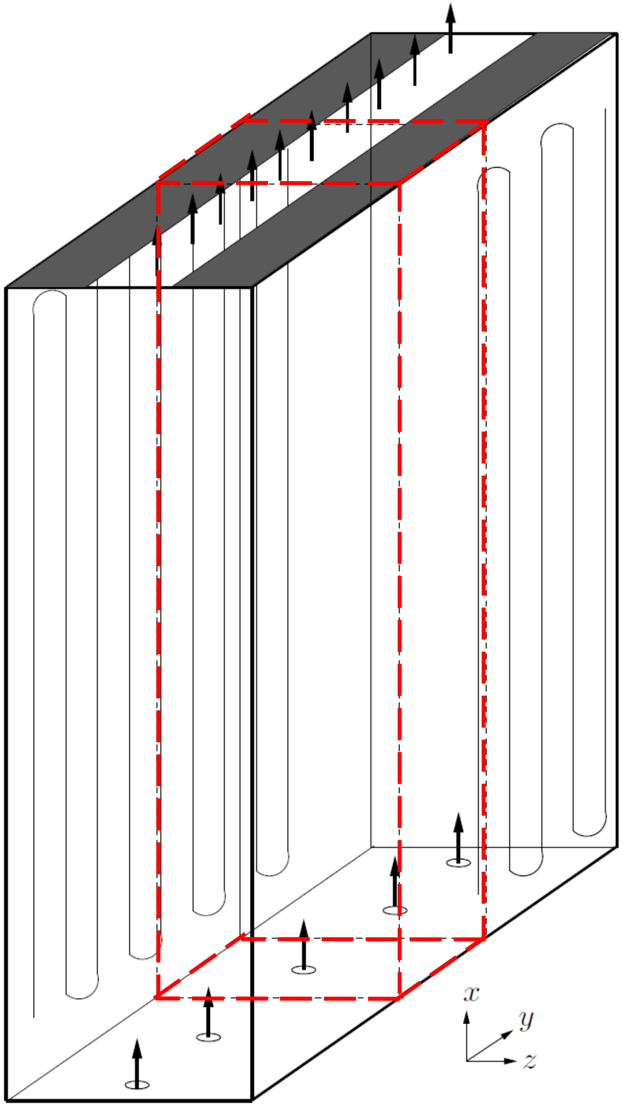
Heat input:	1.8 MW
Excess air number:	1.1
Burner/fuel pipe diam.:	20 cm/3.3 cm



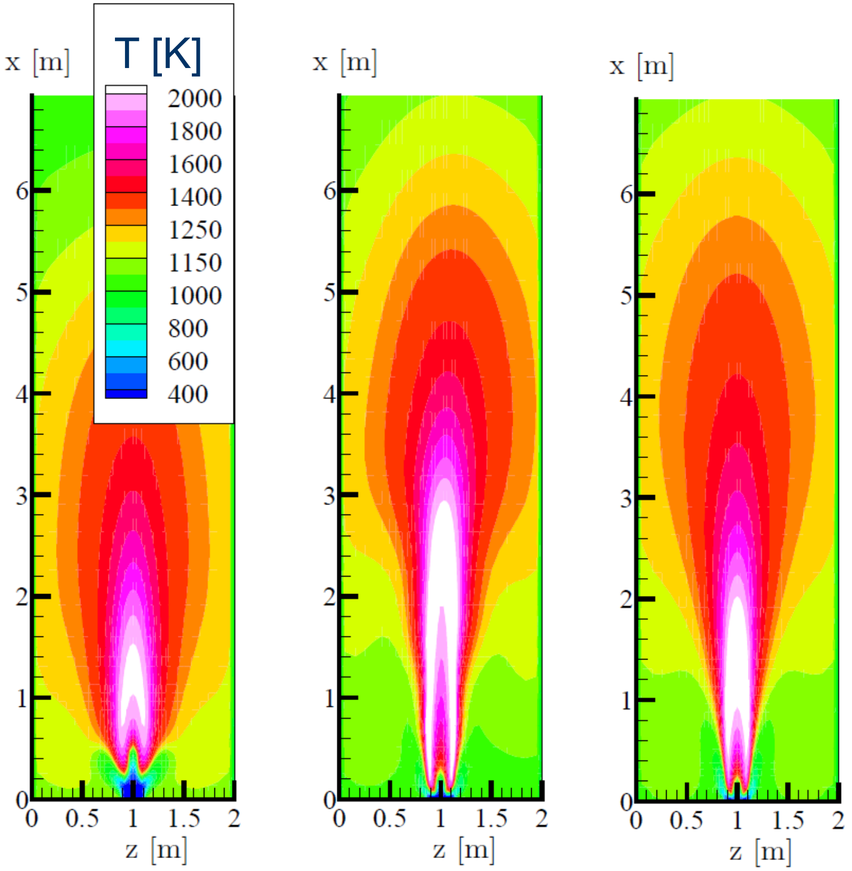


The model

- Flow and combustion modeling with in-house code SPIDER:
  - Mass, momentum, energy and species transport
  - k-epsilon model for turbulence
  - Eddy Dissipation Concept with **finite rate** chemistry (53 species, 325 reactions)
  - Discrete ordinates method (in 24 directions) with WSGG for radiation
- The following effects are neglected in the modeling:
  - Soot and particles
  - Buoyancy
  - Differential diffusion effects



Results: Flame structure



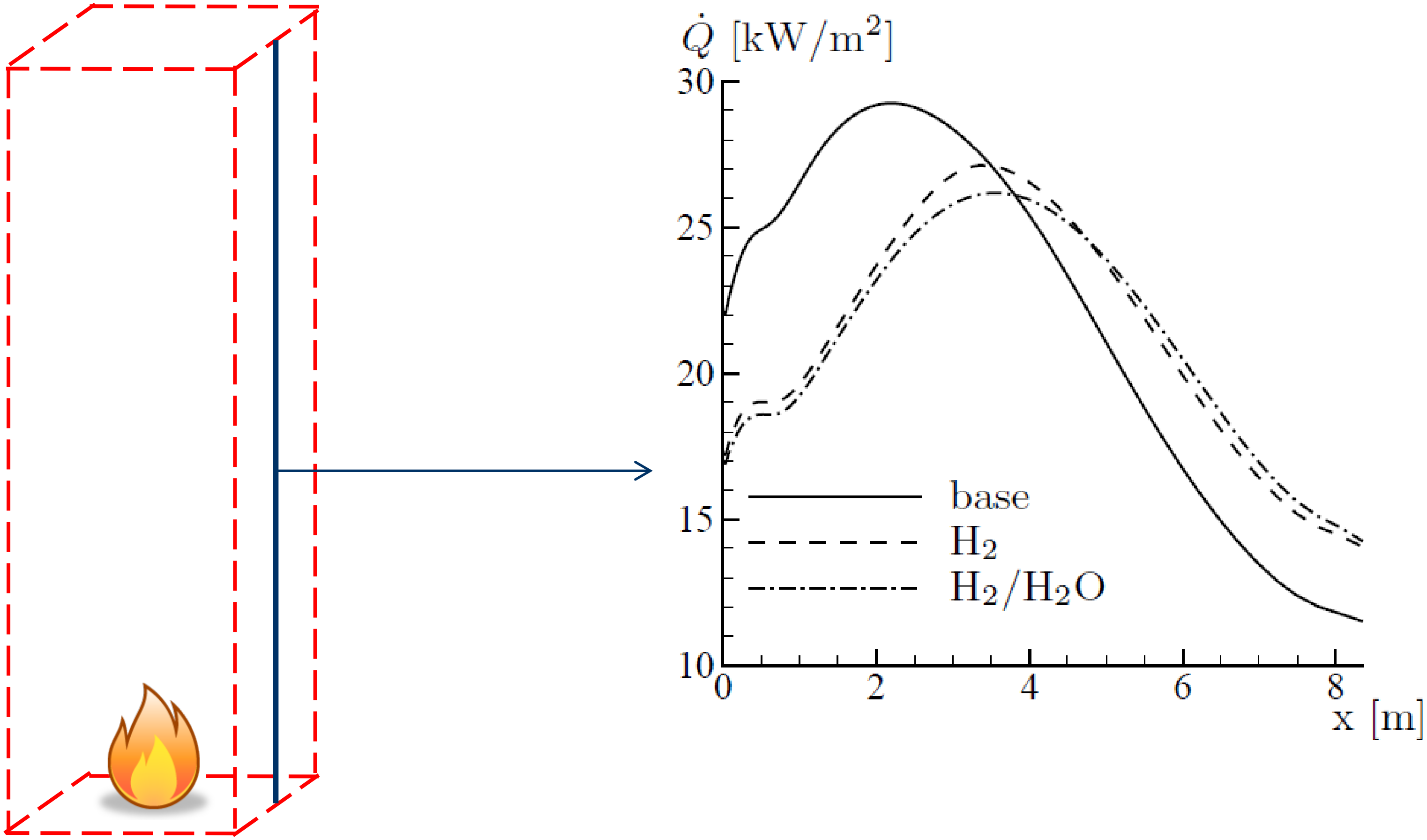
1. Base case

2. H_2-case

3. H_2/H_2O-case

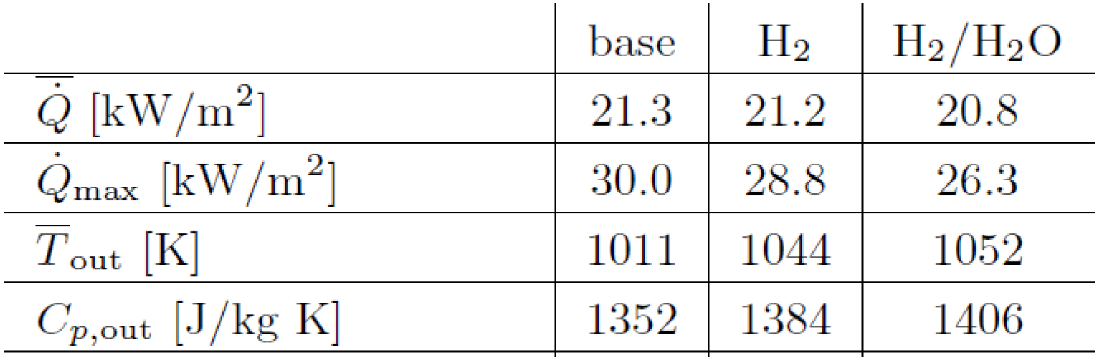
- H_2-cases:
  - Longer flame due to higher fuel outlet velocity
  - The flames are more attached to the burner
- H_2/H_2O-case:
  - Shorter flame than H_2-case due to cooling
- Recirculation zones

Results: Average net heat transfer



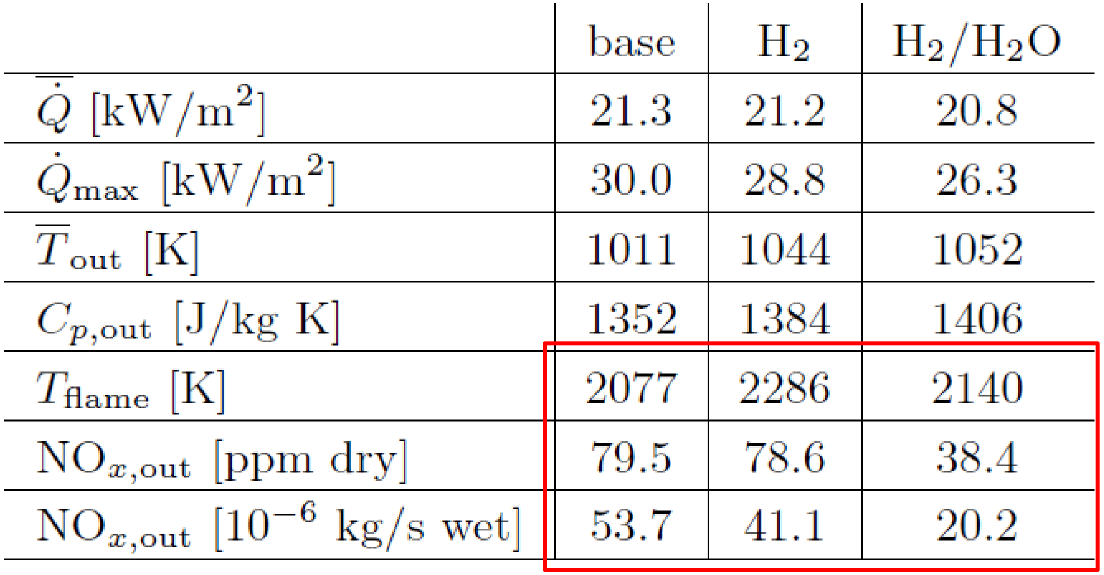
Overall heat distribution

- The same average heat transfer to the wall
- Differences in heat output to the convective section not significant



	base	H_2	H_2/H_2O
$\overline{\dot{Q}}$ [kW/m^2]	21.3	21.2	20.8
$\dot{Q}_{\mathrm{max}}$ [kW/m^2]	30.0	28.8	26.3
$\overline{T}_{\mathrm{out}}$ [K]	1011	1044	1052
$C_{p,\mathrm{out}}$ [J/kg K]	1352	1384	1406

What about the emissions?



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$C_{p,\mathrm{out}}$ [J/kg K]	1352	1384	1406
T_{flame} [K]	2077	2286	2140
$NO_{x,\mathrm{out}}$ [ppm dry]	79.5	78.6	38.4
$NO_{x,\mathrm{out}}$ [10^{-6} kg/s wet]	53.7	41.1	20.2

- Despite higher flame temperature, the NO_x emissions are similar/lower in the H_2-cases than in the base case!

A brief introduction NO_x

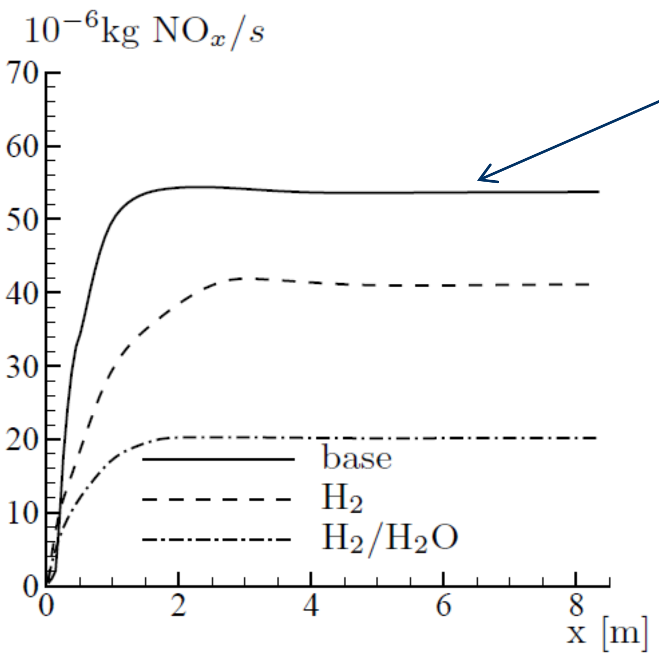
- Thermal NO_x
  - Highly temperature dependent
  - Relatively slow
  - The important “Zeldovich” reactions are:

$$\begin{aligned} \mathrm{O} + \mathrm{N_2} &\rightarrow \mathrm{NO} + \mathrm{N}, \\ \mathrm{N} + \mathrm{O_2} &\rightarrow \mathrm{NO} + \mathrm{O}, \\ \mathrm{N} + \mathrm{OH} &\rightarrow \mathrm{NO} + \mathrm{H}, \end{aligned}$$

- Prompt NO_x
  - Less temperature dependent
  - Fast
  - The important formation step is:

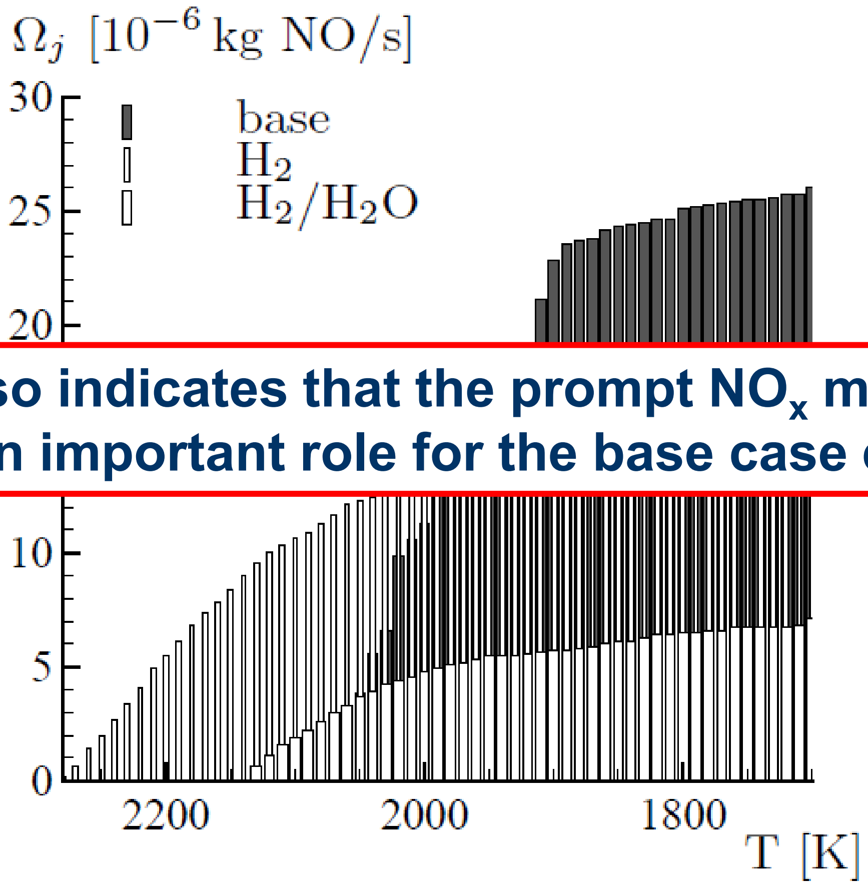
$$\mathrm{CH} + \mathrm{N_2} \rightarrow \mathrm{HCN} + \mathrm{N},$$

And back to the emissions…



- Are the higher base case NO_x emissions caused by the prompt NO_x mechanism?
- The rapid increase in NO_x-flow → Prompt NO_x

The cumulative distribution of NO production with temperature



This also indicates that the prompt NO_x mechanism plays an important role for the base case emissions

Two examples from experiments with swirl-burners in the literature

- Schefer et al. (2002): CH_4 with H_2 addition up to 45%:
  - No significant increase in NO with H_2 addition
- Rørtveit et al. (2002): CH_4 with H_2 addition up to 20%:
  - Slight increase in NO_x with H_2 addition

- To our knowledge: No experimental studies exist that compare NO_x emissions from 100% H_2 with 100% natural gas in swirl-stabilized burners at equal excess air ratio and thermal input. [Comment added after the presentation: See Lowe et al. "Technology Assessment of Hydrogen Firing of Process Heaters", Energy Procedia 4 (2011) 1058-1065: They compared NO_x emissions from a flat flame burner up to 100% H_2 and an ultra low NO_x burner up to 95% H_2 with corresponding 100% natural gas at equal thermal input. On mass basis, they found lower NO_x emissions with the ultra low NO_x burner at 95% H_2 than with 100% natural gas.]

Summary and further work

- The results **indicate** that hydrogen can replace refinery fuel with
  - the same average radiative heat load on tubes, but with slight changes in the radiative profile
  - comparable NO_x-levels (on ppm basis)
- This supports a low-cost retrofit rather than an expensive rebuild
- **BUT**, the results, and particularly the NO_x emissions, are very sensitive to the burner and furnace configuration!
- Further work:
  - Include more geometric details in the computational modeling
  - Measurement campaign to confirm some of the trends in radiation and NO_x

Thank you!