Syngas explosion reactivity in steam methane reforming process

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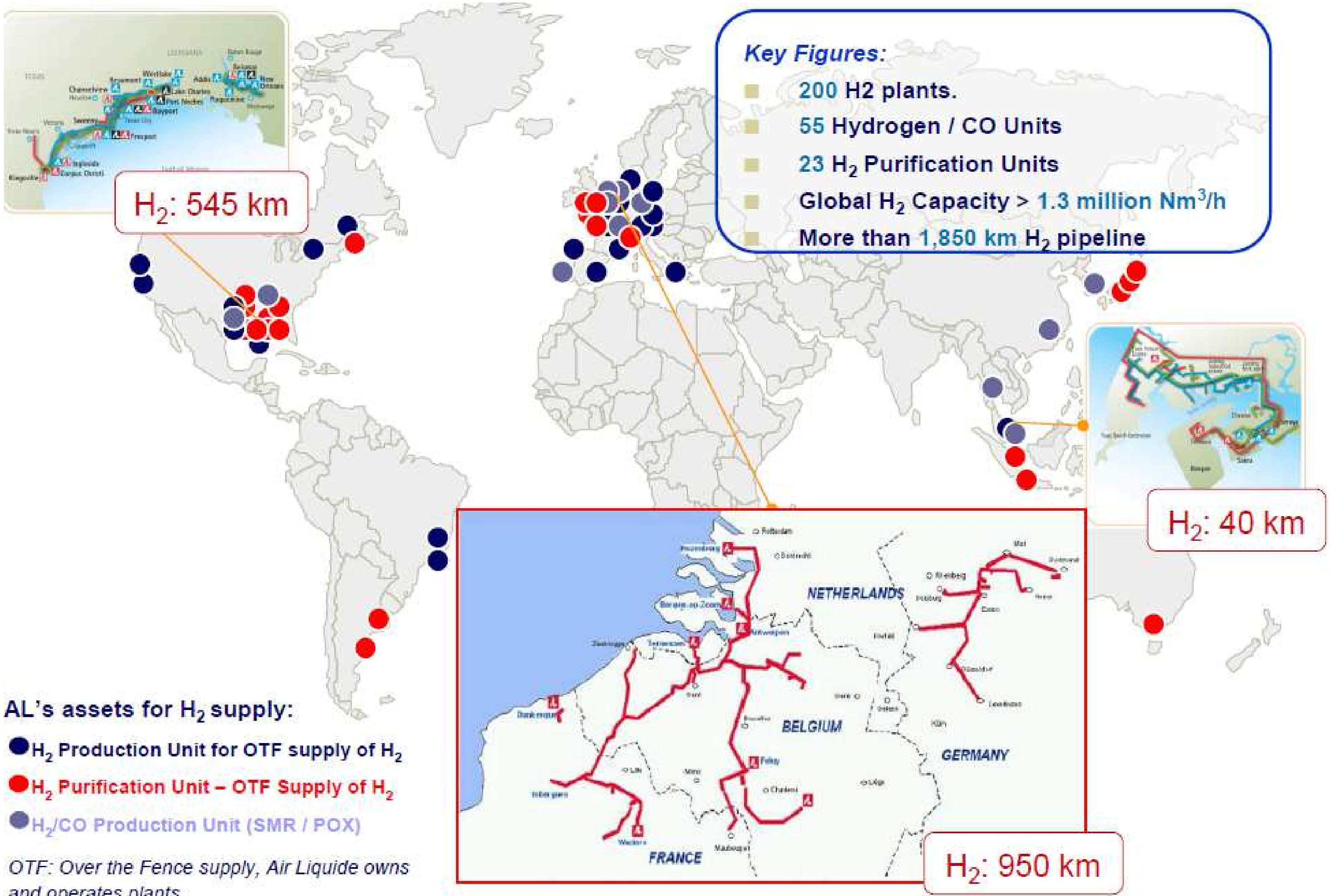
Content

I. Context

Actual H_2 infrastructure



Key Figures:

- **200 H2 plants.**
- **55 Hydrogen / CO Units**
- **23 H_2 Purification Units**
- **Global H_2 Capacity > 1.3 million Nm^3/h**
- **More than 1,850 km H_2 pipeline**

AL's assets for H_2 supply:

- **H_2 Production Unit for OTF supply of H_2**
- **H_2 Purification Unit – OTF Supply of H_2**
- **H_2/CO Production Unit (SMR / POX)**

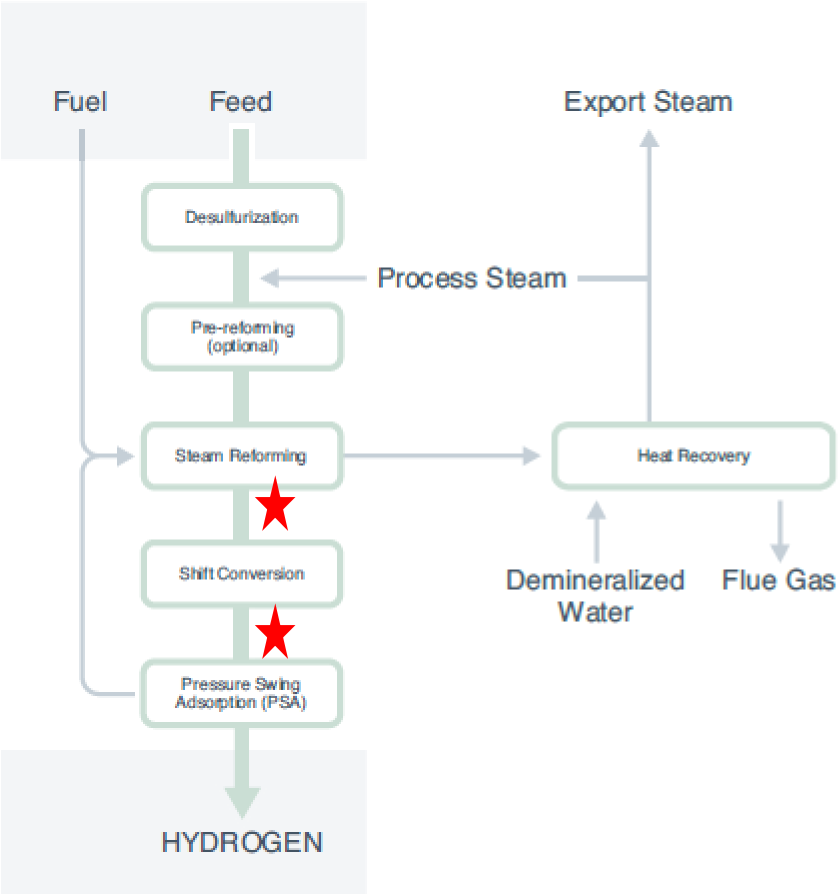
OTF: Over the Fence supply, Air Liquide owns and operates plants

Hydrogen production

- Virtually, H_2 could be produced by various ways :
  - Electrolysis using electricity generated from sunlight, wind and nuclear sources
  - Photoelectrochemical and photobiological processes using sunligt
  - Biomass fermentation
  - Water thermolysis
  - Biomass gasification
  - ....

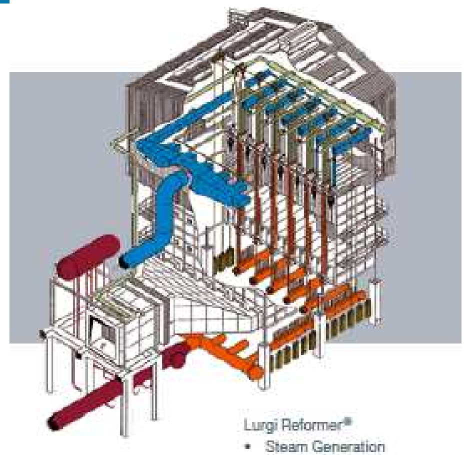
- Industrially, H_2 is mainly produced by STEAM METHANE REFORMING
  - $CH_4 + 2H_2O = CO_2 + 4\ H_2$
  - For the near term, this production method will continue to dominate.
  - Large scale units (up to 150.000 Nm^3/h or 320 t/d H_2)
  - Units included co-generation of high quality stream

Steam Methane Reforming (1/2)



- Steam Reforming
  - $CH_4 + H_2O = CO + 3\,H_2$

Shift Conversion
  - $CO + H_2O = CO_2 + H_2$



Lurgi Reformer®
- Steam Generation
- Reformed Gas Collector
- Combustion Air
- Reformer Feed

% (dry basis)	Reformer outlet	Shift outlet
CH_4	7.5	6.5
H_2	70	74
CO	16,5	3
CO_2	6	16,5

★ Possible leak point

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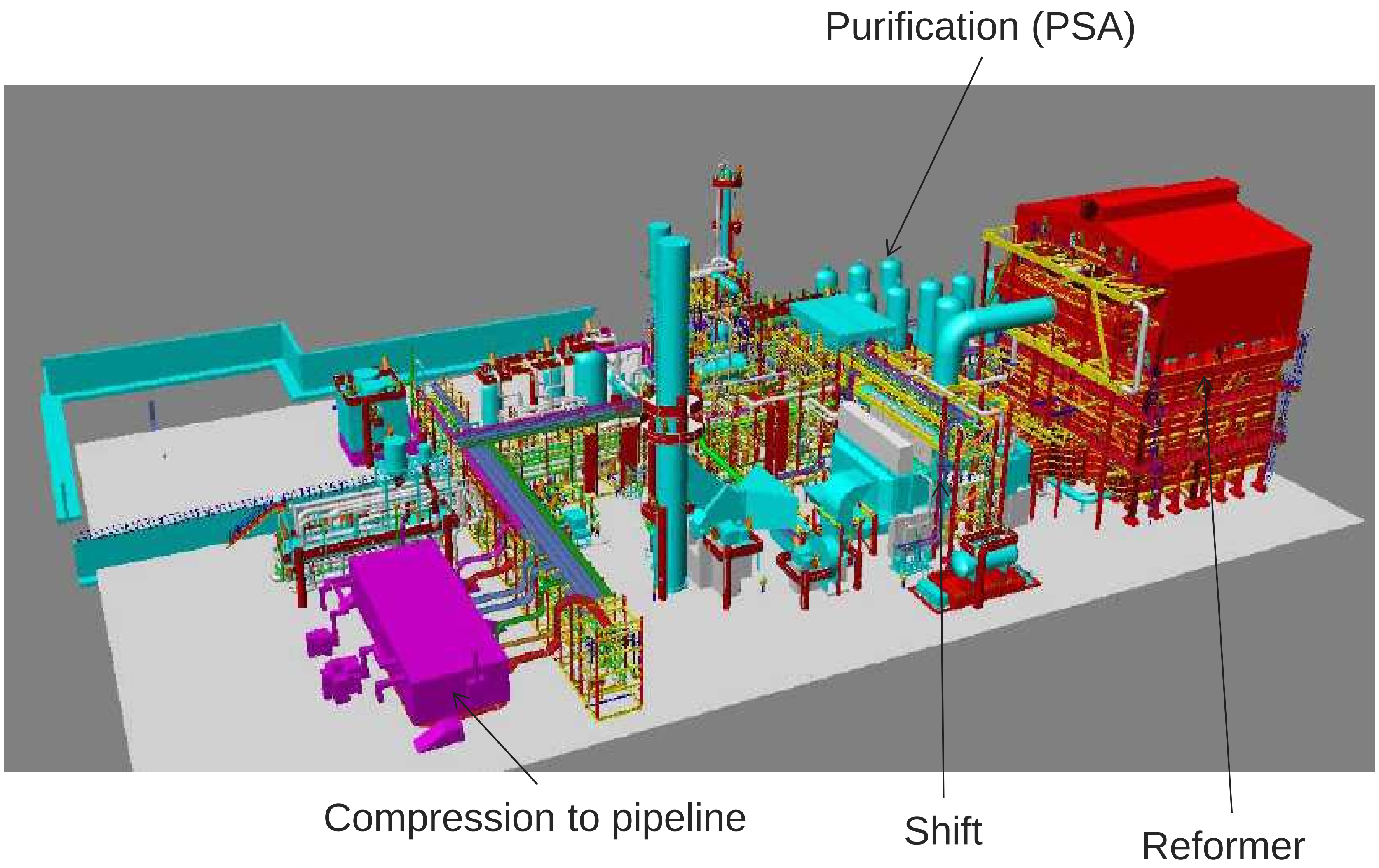
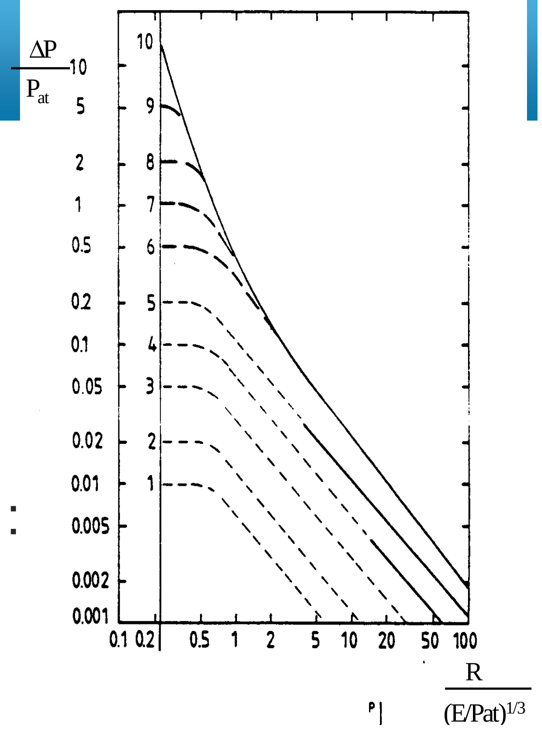
Steam Methane Reforming



II. Objectives

Objectives



- Accident consequences assessment studies for :
  - Definition of the limits of property (permitting)
  - Location of the control room
  - Domino effects
- Consequences evaluation for vapour cloud explosions :
  - Multi Energy Method (MEM)
  - Baker Strehlow Tang method (BSTM)
- In these methods, the reactivity of the fuel in part determines the severity of a Vapour Cloud Explosion (VCE).
  - If S_L > 75 cm/sec <u>or</u> λ < 50 mm ➔ High Reactivity Fuel ➔ High ME index (6 or more)
  - If S_L < 75 cm/sec <u>and</u> λ > 50 mm ➔ Medium Reactivity Fuel ➔ High ME index (between 4 to 6)
- <u>Could we considered the two syngas compositions (reformer and shift outlet) as medium reactivity fuel ???</u>

III. Binary mixture approach

Binary mixture approach : Composition (1/3)

- SMR gases are composed of mainly 4 gases (H_2, CH_4, CO, CO_2),
  - No exp. data for quaternary mixtures
  - ➔ Need simplification assumptions to compare with binary mixtures for which S_L and λ are known

- Different simplification approaches are evaluated:
  - 1. All non-H_2 gases act as CO (conservative approach)
  - 2. CO acts as H_2 and CO_2 acts as CH_4 (also conservative)
  - 3. CO acts as H_2 and CH_4 acts as CO_2 (could minor the reactivity)

% (dry basis)	Reformer outlet	Shift outlet
CH_4	7.5	6.5
H_2	70	74
CO	16,5	3
CO_2	6	16,5

1 →

% (dry basis)	Reformer outlet	Shift outlet
H_2	70	74
CO	30	26

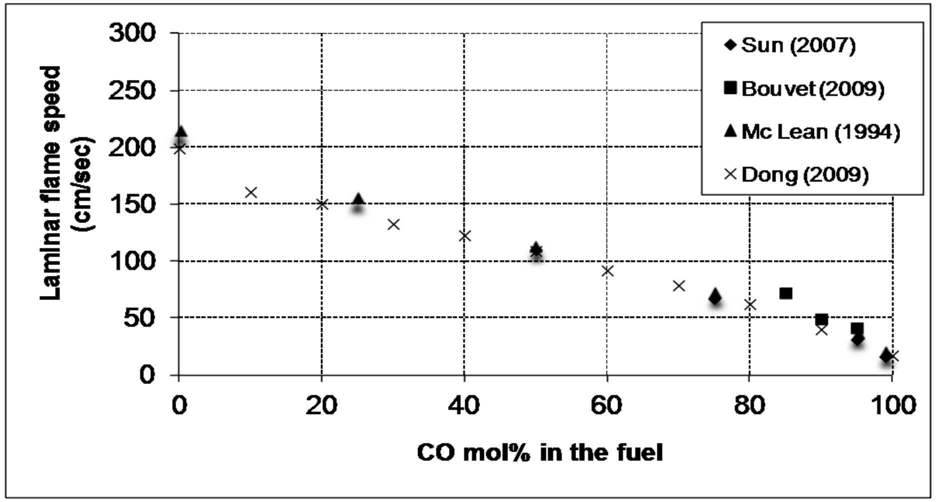
2 →

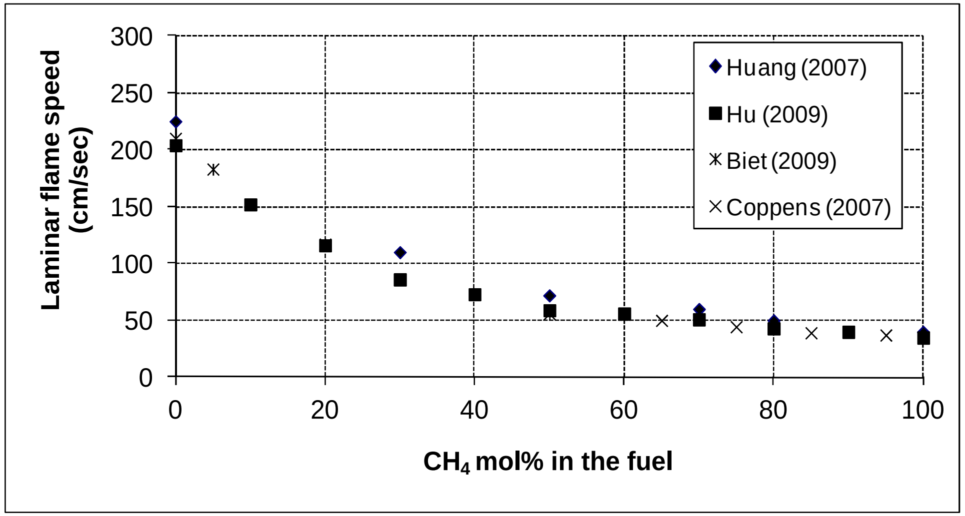
% (dry basis)	Reformer outlet	Shift outlet
H_2	86.5	77
CH_4	16.5	23

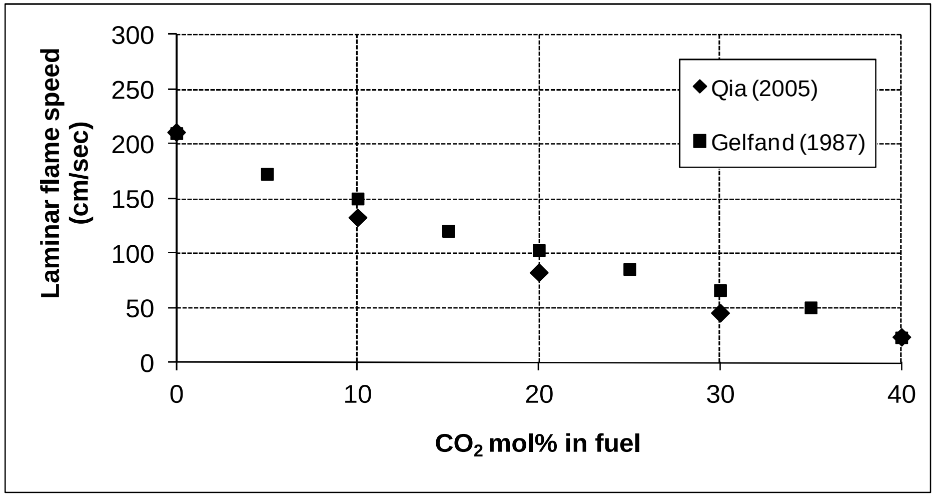
3 →

% (dry basis)	Reformer outlet	Shift outlet
H_2	86.5	77
CO2	16.5	23

Binary mixture approach : flame speeds (2/3)

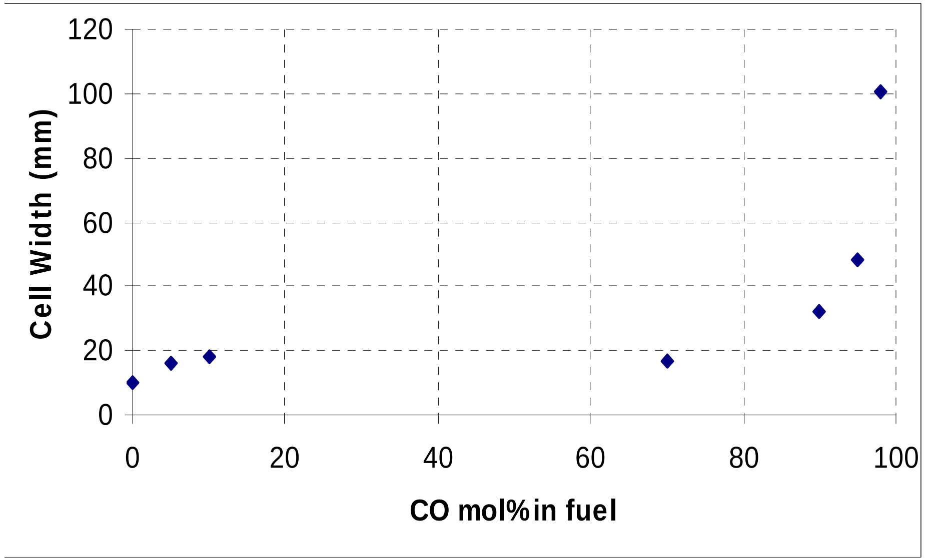


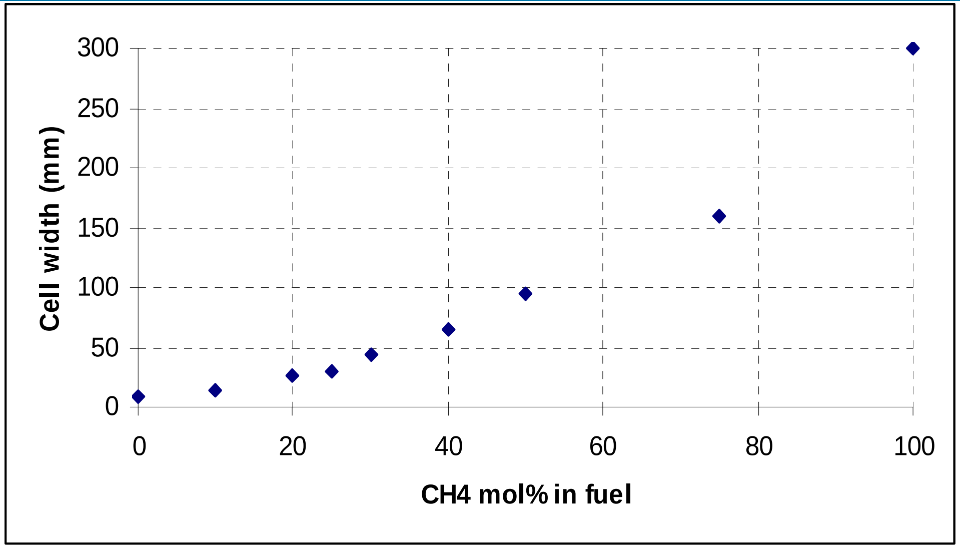


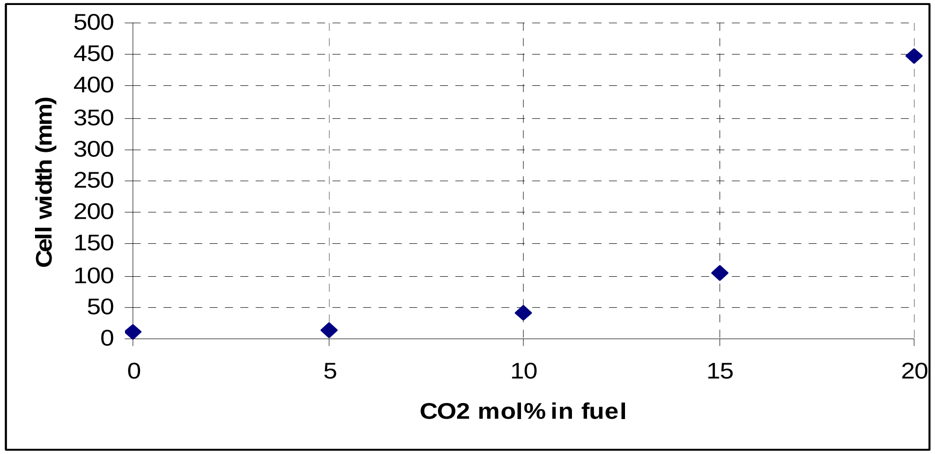


- Reformer Outlet
  - S_L(CO approach) = 134 cm/s
  - S_L(CH_4 approach) = 141 cm/s
  - S_L(CO_2 approach) = 86.5 cm/s
- Shift Outlet
  - S_L(CO approach) = 141 cm/s
  - S_L(CH_4 approach) = 109 cm/s
  - S_L(CO_2 approach) = 83 cm/s

Binary mixture approach : detonation cell size (3/3)





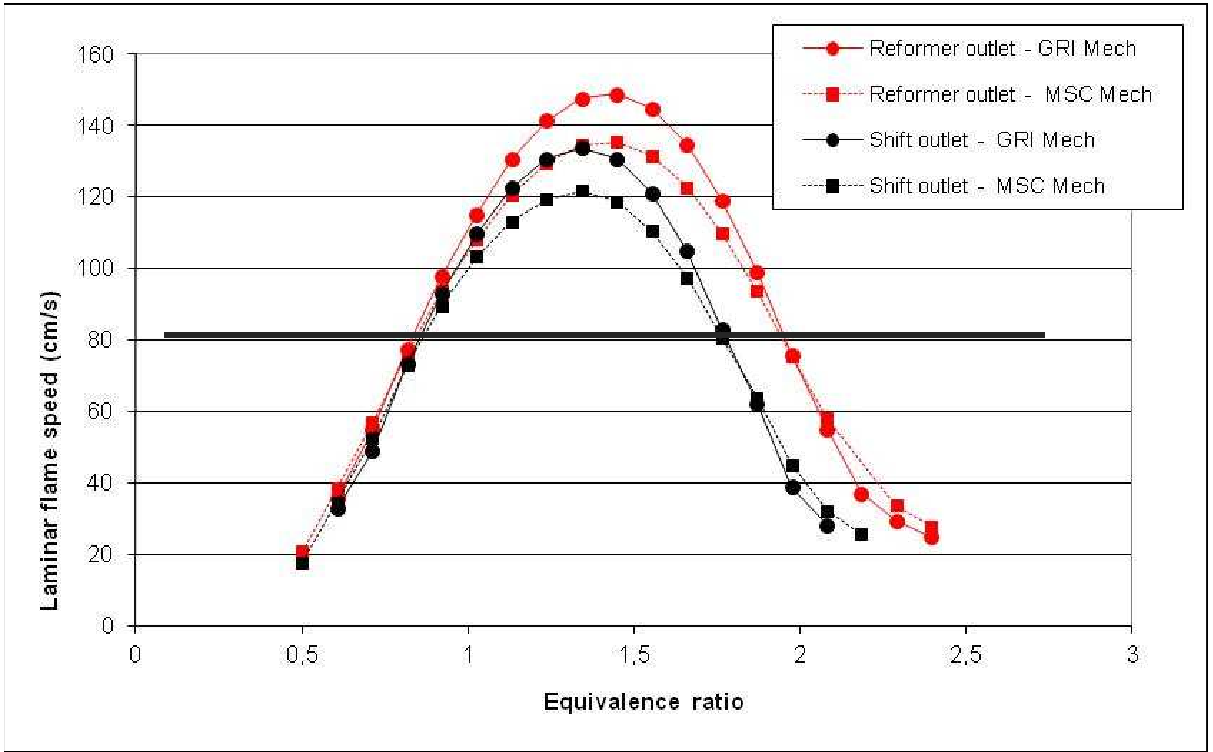


- Reformer Outlet
  - λ (CO approach) = 13 mm
  - λ (CH_4 approach) = 22 mm
  - λ (CO_2 approach) = 86 mm
- Shift Outlet
  - λ (CO approach) = 12 mm
  - λ (CH_4 approach) = 33 mm
  - λ (CO_2 approach) = No detonation

IV. Kinetic approach

Kinetic approach : Laminar Flame Speed

- Chemkin Premix v10
  - GRI-Mech 3.0 (34 species and 225 reactions)
  - USC Mech 2.0 (111 species and 784 reactions) with removal of C_3 and C_4 species and reactions (39 species and 250 reactions)

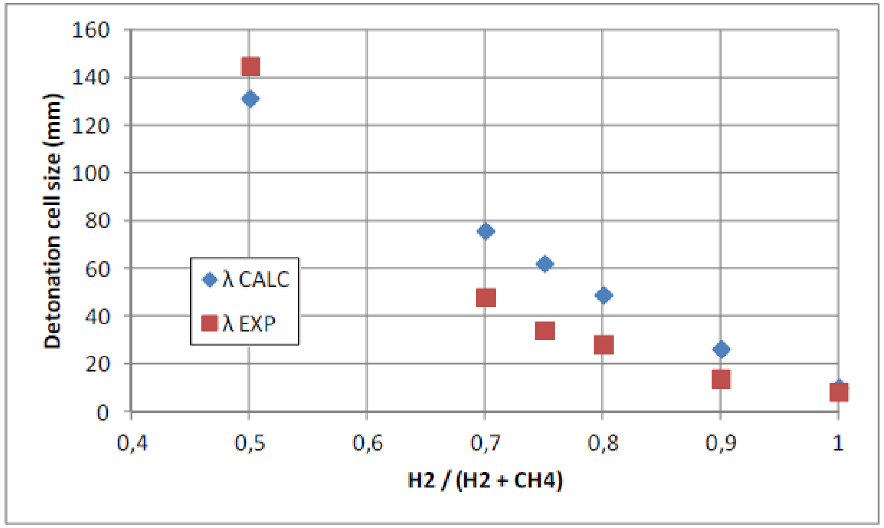


S_L (m/sec)	Reformer outlet	Shift outlet
GRI	1.15	1.10
USC	0.94	0.90

Kinetic approach : Detonation Cell Size (2/2)

- Cell_CH : kinetic based λ calculations
  - Validated using H_2/air mixtures (from 300 to 650 K, with and without steam or CO_2), $H_2/O_2/Ar$ mixtures and hydrocarbons – air mixtures (CH_4, C_2H_6, C_2H_4 and C_2H_2).

- Extended validation for H_2/CH_4 mixtures (Bozier et al. 2010)



- Applications to SMR streams

	Reformer outlet	Shift outlet
Cell size (mm)	30	42

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V. Conclusions and Perspectives

Conclusions & Perspectives

- Objective : assess the reactivity of SMR streams (H_2, CO, CH_4 and CO_2) on the basis of detonation cell size and laminar flame speed regarding vapour cloud explosions severity
  - Reactivity High : S_L > 75 cm/sec <u>or</u> λ < 50 mm
  - Reactivity Medium : S_L < 75 cm/sec <u>and</u> λ > 50 mm
- Two approaches have been compared :
  - Binary mixture approach : assimilation simplification rules have been assumed on the reactant chemical composition.
    - Laminar flame speeds (S_L) and detonation cell sizes (λ) extracted from literature
  - Kinetic approach : calculation of SL and λ using detailed kinetic tools
- <u>Using the two approaches → SMR streams could not be considered having a medium reactivity.</u>
- Applications to others syngas processes (POX, ATR and coal gasifier)
  - More CO after the first oxidation step and more CO_2 after shift.

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Thanks for your attention

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