Fire Seat

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Prediction of toxic species in fires

Stephen Welch & Sreebash C Paul
School of Engineering
The University of Edinburgh

Why bother?

- **Fire – human interface**
  - Toxic gases lead to incapacitation, and death
    - Asphyxiant gases: CO, HCN, Low O_2, CO_2
- **Extending scope of fire safety engineering**
  - Forensics
  - Supplementing testing
  - Design
- **Existing "models" inadequate**
  - Challenged by complexity of phenomena
  - Lack of knowledge of required inputs

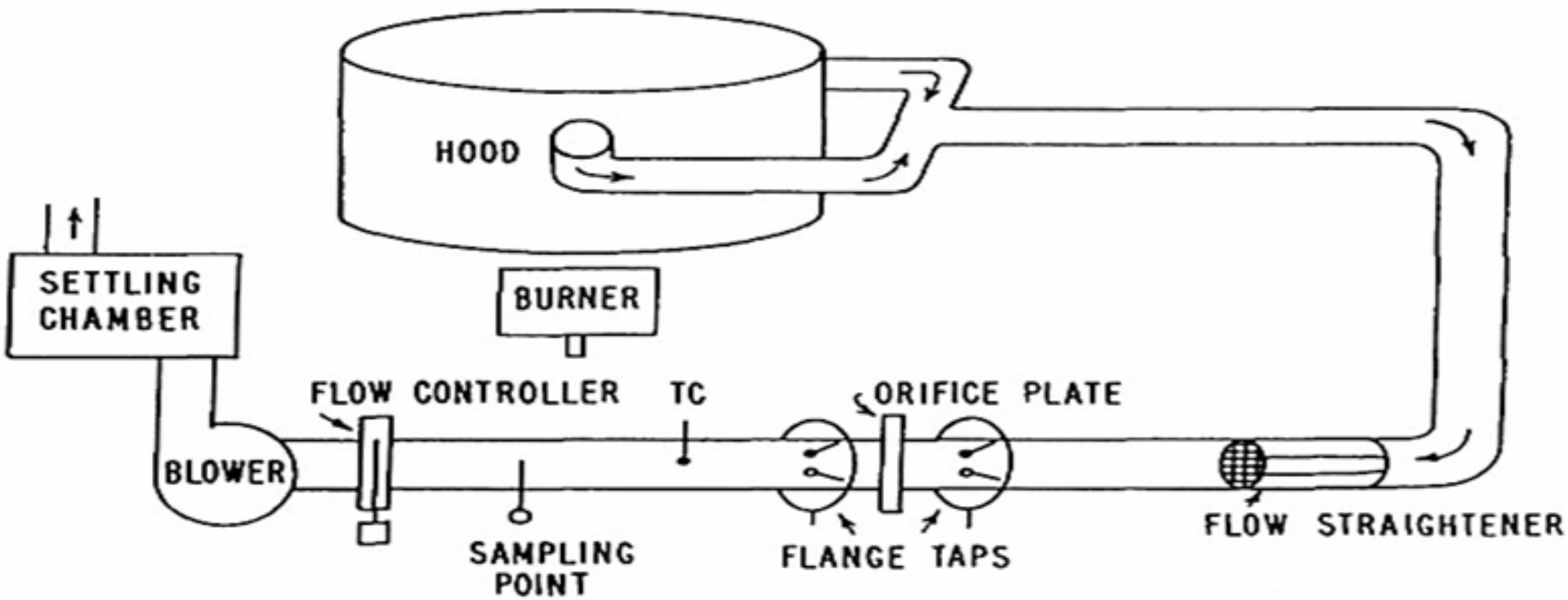
CO fundamentals

- **Experimental characterisation**
  - Correlation to "equivalence ratio", ϕ
    - Measure of fuel-air balance

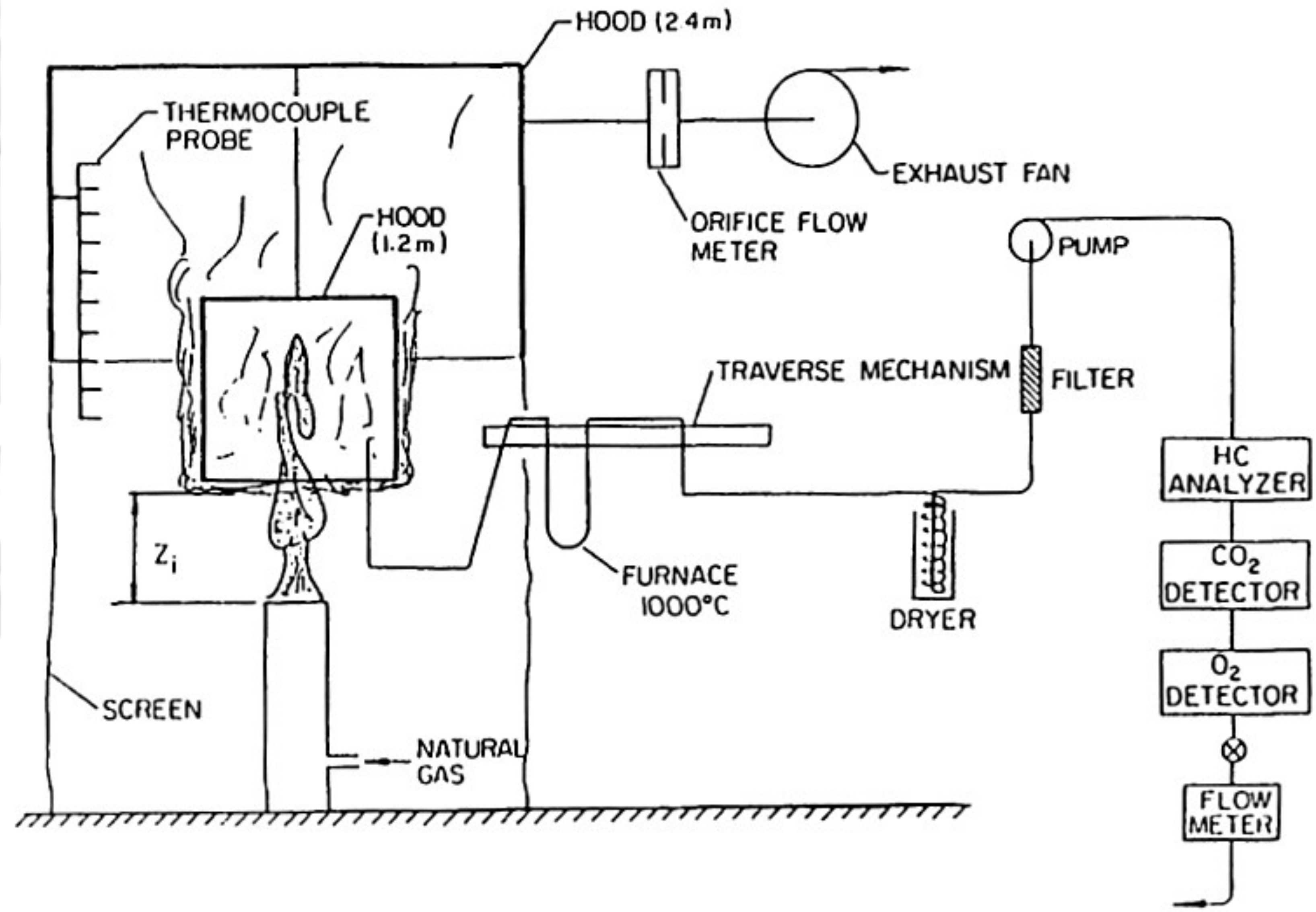
$\phi<1$ lean

$\phi=1$ stoichiometric

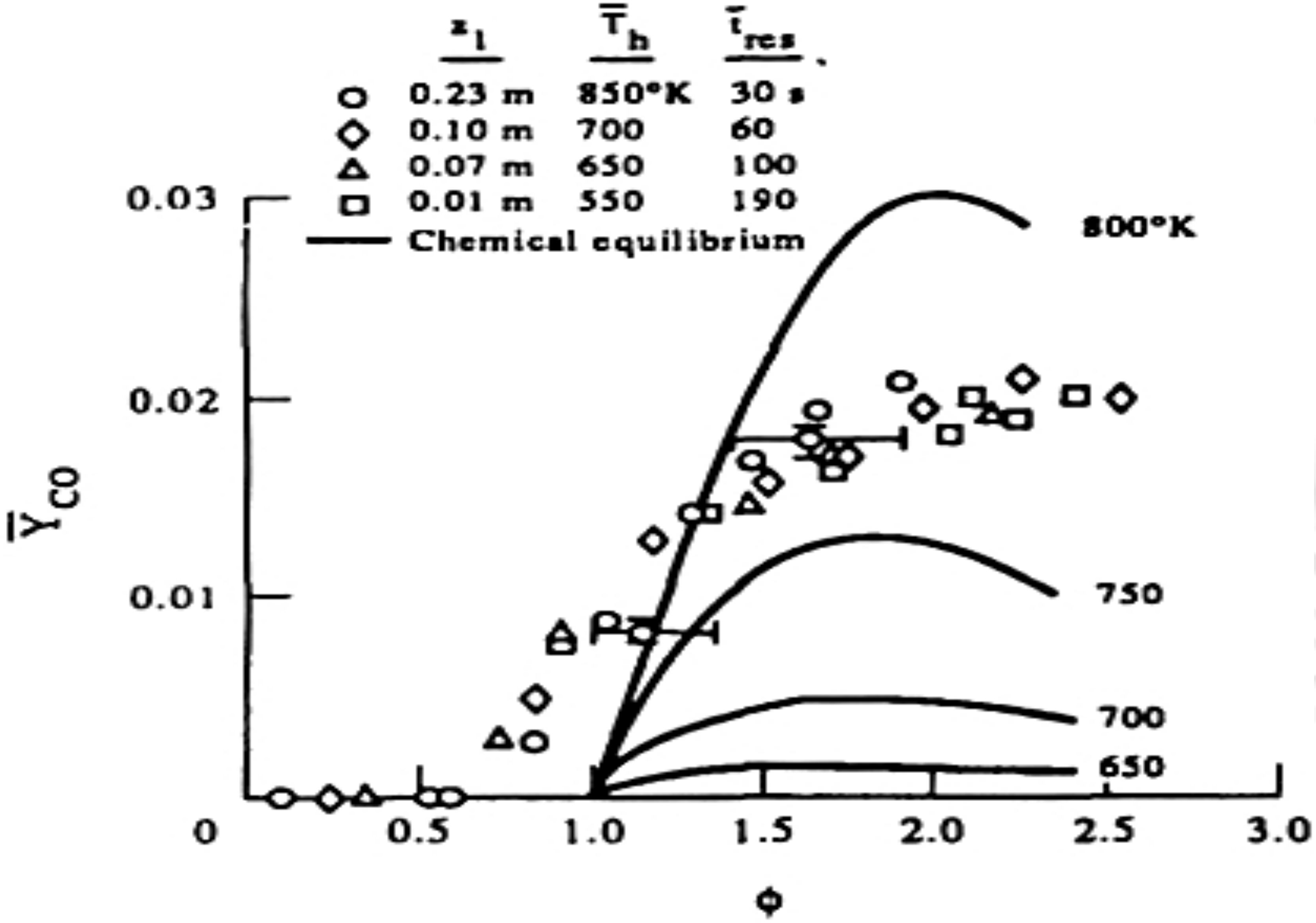
$\phi>1$ rich



Hood experiments - continued



Hood experiments

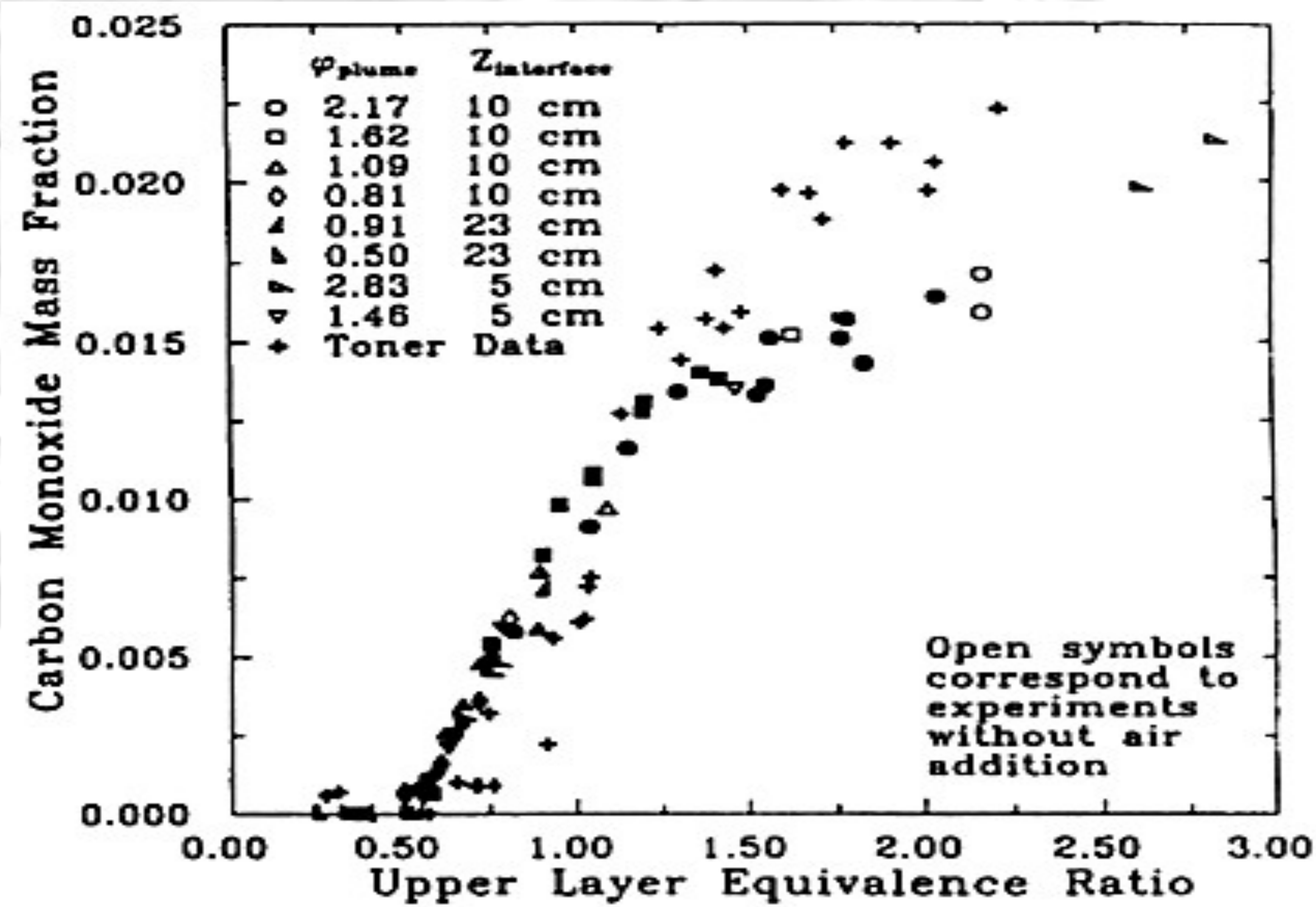


Hood experiments - continued

Fuel	Formula	CO volume[%]	CO yield [g/g]
Acetone	C_3H_6O	4.4	0.30
Methanol	CH_3OH	4.8	0.24
Ethanol	C_2H_5OH	3.5	0.22
Isopropanol	C_3H_7OH	2.4	0.17
Propane	C_3H_8	1.8	0.23
Propene	C_3H_6	1.6	0.20
Hexane	C_6H_{14}	1.6	0.20
Toluene	C_7H_8	0.7	0.11
Polyethylene	$-CH_2-$	3.0	0.19
PMMA	$-C_5H_7O_2-$	3.0	0.19
Ponderosa Pine	$C_{0.95}H_{2.4}O$	3.2	0.14

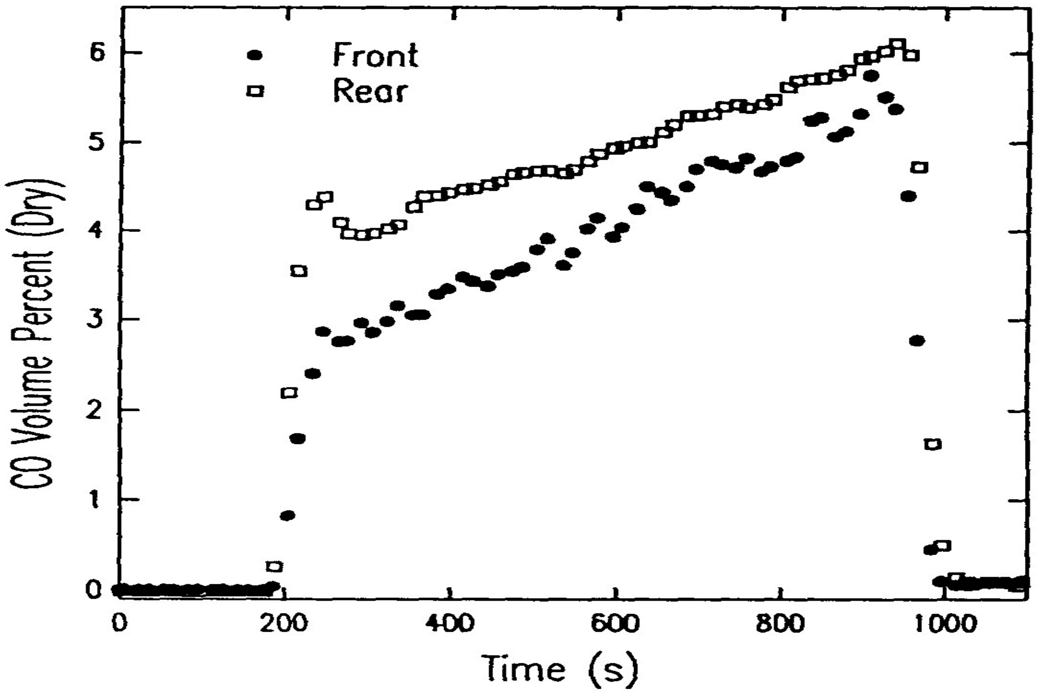
Beyler, C. (1983) PhD thesis, Harvard Uni.

Hood experiments - continued

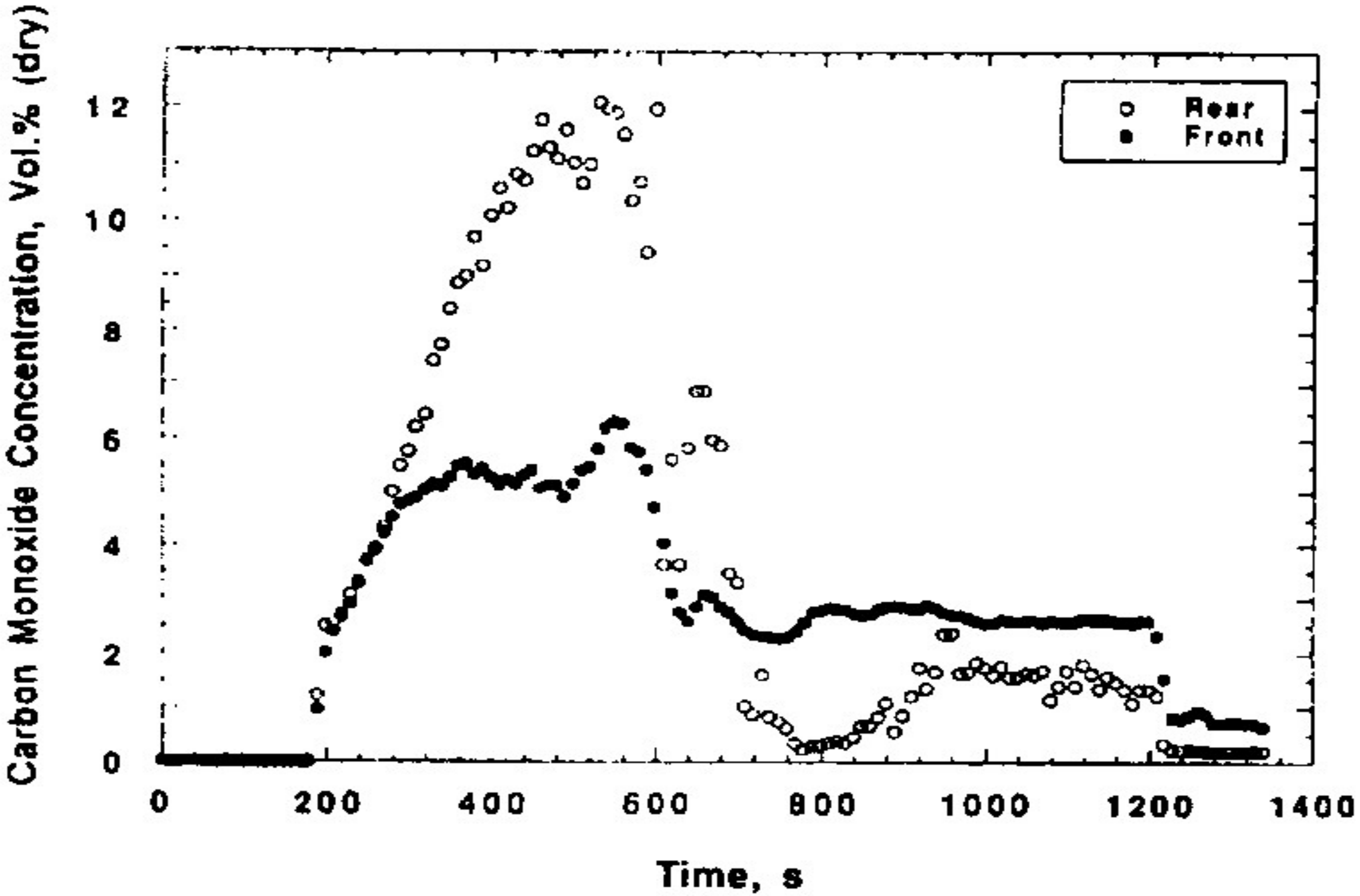


Compartment fires

- **Reduced scale enclosures**
  - Rasbash & Stark (1966)
    - 0.9m cubic enclosure, cellulosics
    - CO concentrations ≈ 10%
  - Bryner, Pitts, et al.
    - Reactions in layer
      - O_2 mixing
      - Residence time
        - Scale!
      - Equilibrium



Solid-phase pyrolysis



Essential CO mechanisms

- **Formation in plume, quenched**
  - Function of fuel
  - Affected by temperature
- **Reaction with entrained air**
- **Continued reaction in layer**
- **Pyrolysis**
  - e.g. wood in a rich upper layer
- **Smoke interaction**
- **Other species**
  - Affect toxicity in general

Modelling issues

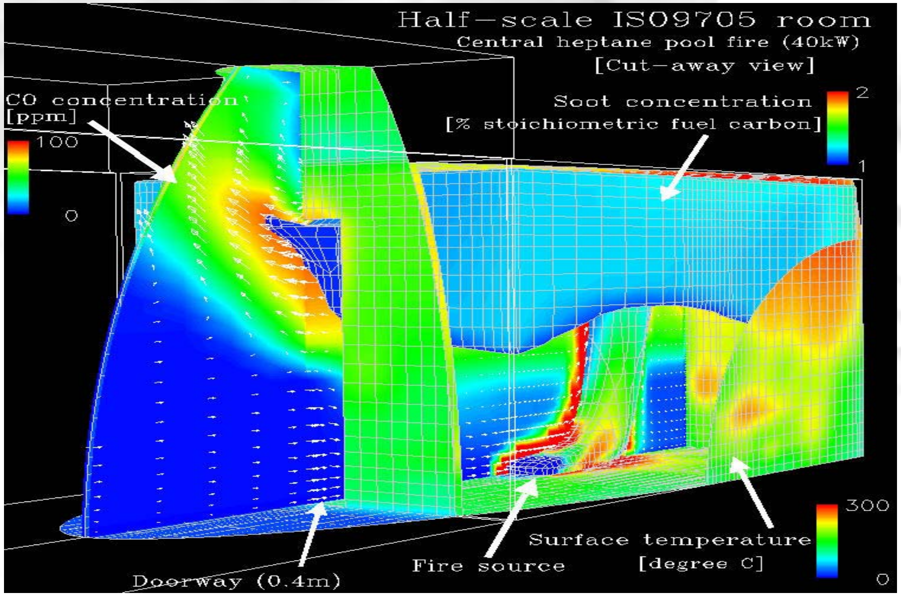
- **Air entrainment into rich upper layer**
  - Correlations for yield will fail
  - Need sufficient grid resolution near interface
- **Solid-phase cellulosic pyrolysis**
  - Couple with a flame spread model
  - Multi-fuel issue is a problem!
- **Approach to equilibrium chemistry**
  - Long time-scales require explicit finite-rate chemistry
- **Smoke, etc.**
  - Engineering models needed

CFD-based models

- **Array of proposed approaches**
  - Review of models
    - Complexity
    - Empiricism
    - Computational costs

    } Huge range!

  - Comprehensive
    - Turbulence
    - Combustion
    - Chemistry
    - Soot
    - Radiation



#	Model name/description	Chemistry	CFD code	Computational cost	Test cases	Advantages	Disadvantages
1.	LER (Local Equivalence Ratio) model Wang *et al*., University of Greenwich (1)	None (EDM)	SMARTFIRE CFX 4.2 (RANS)	• Low	Range of reduced-scale and full-scale fire experiments (including corridors)	• Simple extension of GER concept • Includes a crude temperature dependency	• Parametric approach • Requires extensive calibration
2.	Constrained equilibrium flamelets Huang & Wen, Kingston University (2)	Detailed	CFX-FLOW3D	• Moderate	Jet fire test, 135m³	• Detailed CO chemistry is included	• Cannot handle real fuels (e.g. wood) • CO chemistry is instantaneous • Not thoroughly validated
3a.	Two-step eddy breakup Hyde & Moss, Cranfield University (3, 4)	Simple	SOFIE (RANS)	• Low	Steckler compartment	• Simple	• CO chemistry is crude • Not thoroughly validated
3b.	Flamelet-based CO model Hyde & Moss, Cranfield University (4)	Detailed	SOFIE (RANS)	• Moderate • Flamelet library is precomputed	Steckler compartment	• Detailed CO chemistry is included	• Cannot handle real fuels (e.g. wood) • CO chemistry is instantaneous • Not thoroughly validated
4.	Flamelet-based HCN/CO model Tuovinen, SP Swedish National Testing and Research Institute (5)	Detailed GRI 1.2	SOFIE (RANS)	• Moderate • Flamelet library is precomputed	ISO Room corner test	• Accounts detail chemistry	• Not general fuels • CO chemistry is instantaneous • Vitiation level has to be prescribed • Complex and time-consuming pre-processing
5.	CO/HC mass model Hu, Trouve *et al* University of Maryland (6)	Fast	FDS 4.05 (LES)	• Low • Solves 1 extra transport equation for fuel	RSE experiments at Univ. of Maryland	• Simple and general model • Extinction effects	• Provides CO+ HC predictions • Poor extinction treatment – either fully burning or fully extinguished.
6.	CO yield McGrattan, NIST Hu *et al*. USTC, Rinne *et al*. VTT (8, 9)	None	FDS 4.0	• Low	Tunnel fires	• Simple	• Crude predictions
7.	CO production (Two-step reaction with extinction). Floyd & McGrattan, NIST (7, 10, 11)	Fast	FDS 5.0 (LES)	• Low • Solves 3 extra transport equations	Slot burner, Beyler Hood and RSE experiments	• Does not require detailed chemistry information • Consistent HRR • Extinction effects	• Formation step not yet generalised (EDC to be explored) • Validated ongoing
8.	CMC modelling of CO formation, Cleary *et al*. University of Sydney (6)	Detail GRI 3.0, CER	In-house code (RANS)	• High	Toner's hood fire cases	• Accurate combustion modelling • Promising CO predictions	• Computationally expensive • Requires detailed chemistry • Not thoroughly validated
9.	CO production (dedicated CO transport equation), Paul & Welch, The University of Edinburgh (13, 14)	Simple	SOFIE (RANS)	• Low • Solves at least 1 extra transport equation	VTT 10x10m compartment (9)	• Simple and general model • Facilitates linkage to flame spread (13)	• Less appropriate for turbulent conditions • Not thoroughly validated

References (from "Fire toxicity")

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2. Wen, J. & Huang, L.Y. (2000) CFD modelling of confined jet fires under ventilation-controlled conditions, *Fire Safety J.*, 34(1), pp. 1-24.
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13. Welch, S., Collins, S., Odedra, A. & Paul, S.C. (2008) Toxic species yield – the role of the solid phase, Poster presentation, *IAFSS 9*, University of Karlsruhe, Germany, 21-26 September 2008.
14. Paul, S.C. & Welch, S. (2010) Prediction of CO formation in fires, 6th Int. Sem. Fire & Explosion Hazards, University of Leeds, 9-16 April 2010

Multi-mixture fraction model

- **Under development in FDS**
  - Validation cases
    - Slot burner, hood and RSE
      - Range of fire sizes and 7 diverse fuels in RSE (IAFSS9)
  - FDS road map* outlines further work
    - Formation rate linked to Magnusson's EDC
    - Decouple soot
    - Asphyxiants: CO, HCN, Low O_2, CO_2
    - Irritants: HCL, HBr, HF, SO_2, NO_2, CH_2CHO (acrolein), CH2O (formaldehyde), X(user defined)

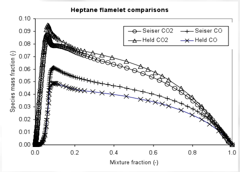
* http://code.google.com/p/fds-smv/wiki/FDS_Road_Map

Flamelet-derived models

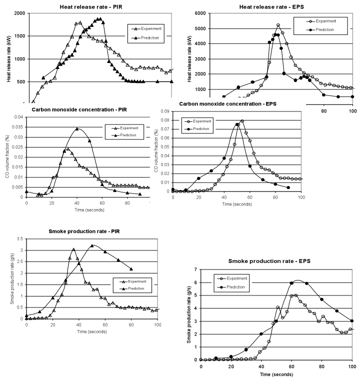
- **Arbitrarily complex chemistry**
  - Done offline
    - Modelled, or experiment
- **Steady Laminar Flamelet Model (SLFM)**
  - "Instantaneous"
  - Only partial relaxation of fast chemistry assumption
- **Demonstrated for well-ventilated fires**
    - Half-scale ISO room (Pierce & Moss)
    - Flame spread over corner wall (Marshall & Welch)

Heptane flamelet

- **SOFIE laminar flamelet modelling**
  - Heptane mechanisms
    - Held (Princeton)
      - 41 species
      - 274 reactions
    - Seiser (UCSD)
      - 160 species
      - 1540 reactions

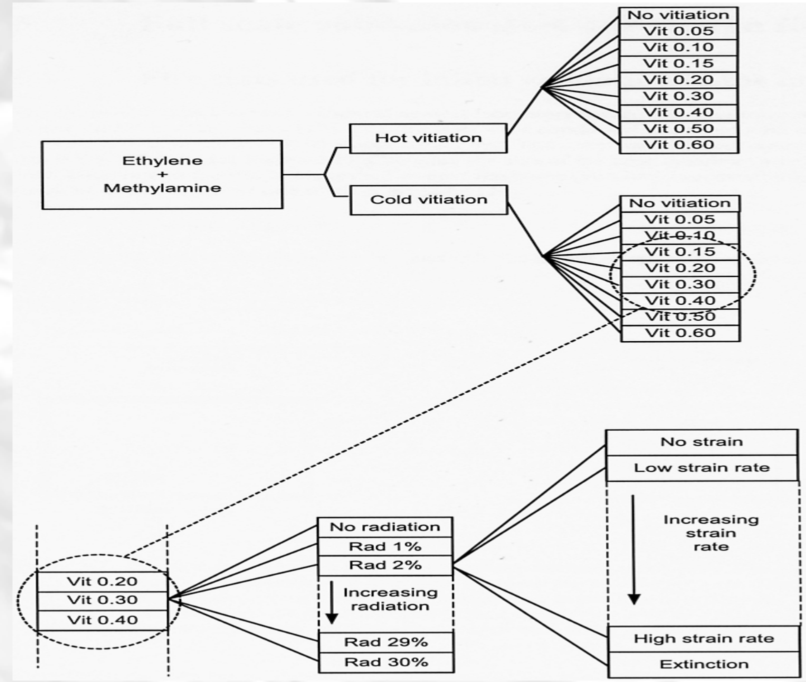


Corner façade: FR-EPS


Heat release rate - PIR
Heat release rate - EPS
Heat release rate (kW)
Carbon monoxide concentration - PIR
Carbon monoxide concentration - EPS
Smoke production rate - PIR
Smoke production rate - EPS
Smoke production rate (g/s)
Experiment
Prediction
Time (seconds)

Vitiated flamelets

- **Vitiated fires**
  - Tuovinen
    - 100 species, 2000 reaction
    - Over 30,000 flamelets
  - Moss & Hyde
    - Vitiated flamelets for ethylene
    - Demonstrated in under-ventilated Steckler



Single vitiation level!

New modelling strategy

- **Decouple finite-rate CO chemistry**
  - CO regarded as trace (mainly)
  - Additional weakly-coupled balance equations and link to solid-phase pyrolysis

$$\frac{\partial\left(\overline{\rho}\tilde{Y}_{CO}\right)}{\partial t}+\frac{\partial\left(\overline{\rho}\tilde{u}_j\tilde{Y}_{CO}\right)}{\partial x_j}=\frac{\partial}{\partial x_j}\left(\Gamma\frac{\partial\left(\tilde{Y}_{CO}\right)}{\partial x_j}-\overline{\rho u_j''Y_{CO}''}\right)+\overline{\rho}\tilde{S}\left(Y_{CO}\right)$$

  - Implemented in SOFIE3
    - Fire specific RANS code (1990-)
    - Existing non-adiabatic flamelets

Post-processed CO chemistry

- **Hybrid SLFM and quasi-laminar**
  - Partitioned via turbulent mixing timescale
    - $\tau_{mix} \propto k/\varepsilon$
  - Hot layer is distinguished
    - Homogenous regions
    - Can couple solid-phase release
  - Exploit simple chemistry
    - Two-step reaction mechanisms for range of (simple!) fuels
- **Rate flamelets**
  - Piggy-backed on SLFM
  - Explicit representation of finite-rate chemistry
  - Can be parameterised
    - Heat loss, vitiation, strain rate

Modelling strategy

- **CO transport equation**

$$\frac{\partial\left(\overline{\rho}\widetilde{Y}_{CO}\right)}{\partial t}+\frac{\partial\left(\overline{\rho}\widetilde{u}_j\widetilde{Y}_{CO}\right)}{\partial x_j}=\frac{\partial}{\partial x_j}\left(\Gamma\frac{\partial\left(\widetilde{Y}_{CO}\right)}{\partial x_j}-\overline{\rho u''_j Y''_{CO}}\right)+\overline{\rho}\widetilde{S}\left(Y_{CO}\right)$$

;

$$\overline{\rho}\widetilde{S}(Y_{CO})=MW_{CO}[\widetilde{R}_{CO,form}-\widetilde{R}_{CO,cons}]$$

$$C_7H_{16}+\frac{15}{2}O_2\xrightarrow{R_{CO,form}}8H_2O+7CO$$

$$CO+\frac{1}{2}O_2\xrightarrow{R_{CO,cons}}CO_2$$

Modelling strategy

- **Rate expressions (heptane)**

$$R_{CO,form} = 6.3\times10^{11}\times exp(-30/RT)\times\left[C_7H_{16}\right]^{0.25}\times\left[O_2\right]^{1.5}$$
$$+5\times10^{8}\,exp\left(-40/RT\right)\left[CO_2\right]^{1.0}$$

;

$$R_{CO,cons} = 10^{14.6}\times exp\left(-40/RT\right)\times\left[CO\right]\times\left[H_2O\right]^{0.5}\times\left[O_2\right]^{0.25}$$

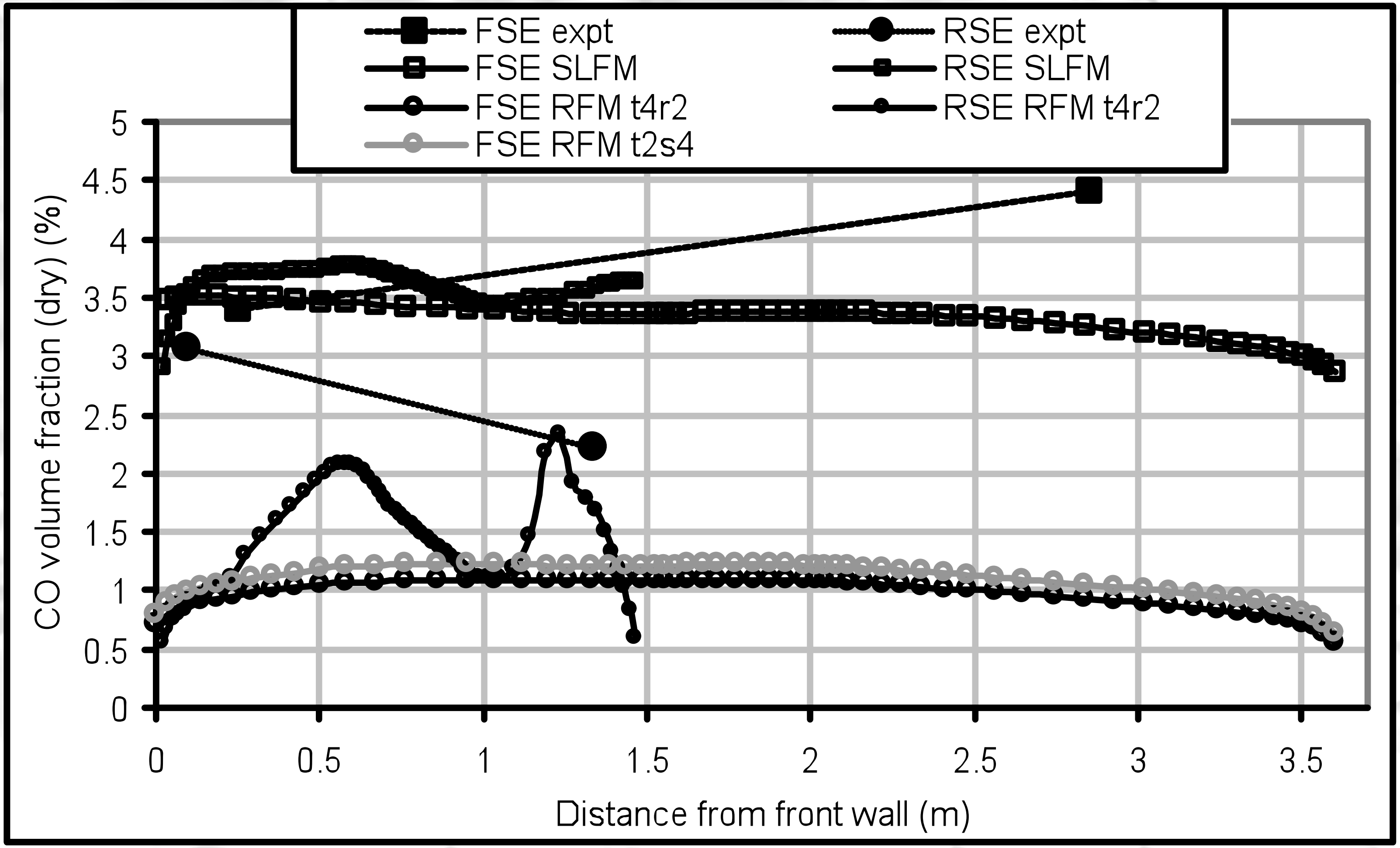
- **Source term closure**
  - Mean properties $\quad \overline{\dot{\omega}} = \dot{\omega}(\overline{T},\overline{c}_i)$
  - Rate flamelet $\quad \widetilde{R}\left(\widetilde{\xi}\right) = \int_0^1 R(\xi)\widetilde{P}\left(\xi,\widetilde{\xi}\right)d\xi$

Verification & validation

- **Initial *qualitative* examination**
- **Discriminate predictive capabilities**

- **Hood fires (Caltech, 1980's)**
  - Natural gas
- **VTT large room (W66 report, 2004)**
  - 150kW fire
  - Heptane
- **RSE/FSE enclosure fires (NIST, 1993-1995)**
  - Natural gas
  - Range of fires, including significantly under-ventilated

Results – RSE/FSE experiments



Kinetics?!

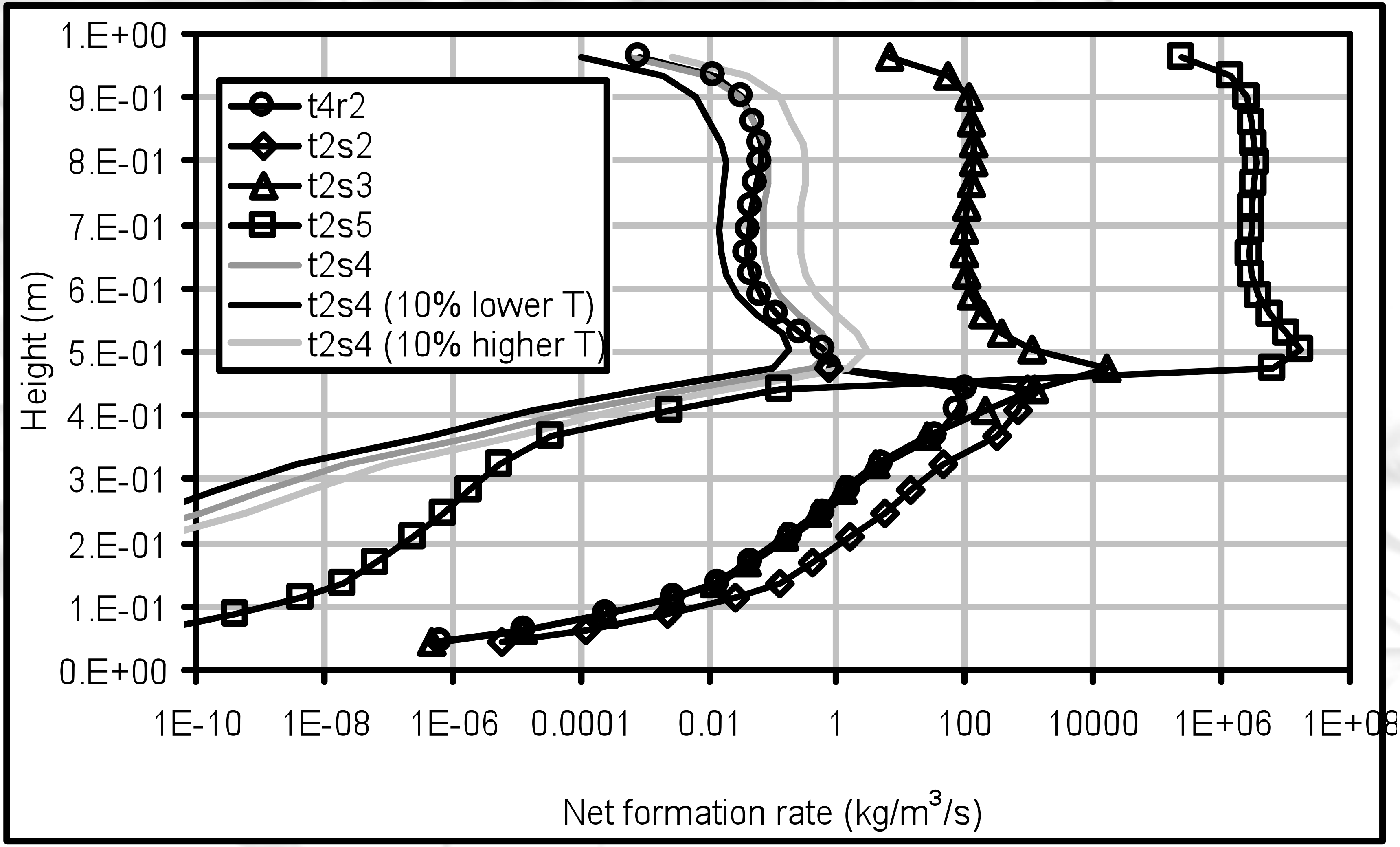
- **How general?**
- **Easily changed**
  - e.g. CH4
    - t4s2
    - t2s2
    - t2s3
    - t2s4
    - t2s5

Mechanism	***Label***	***A***	***E_a***	***a***	***b***
Table IV Row 2	t4r2	1.5×10^{7}	30	-0.3	1.3
Table II Set 2	t2s2	1.3×10^{8}	48.4	-0.3	1.3
Table II Set 3	t2s3	6.7×10^{12}	48.4	0.2	1.3
Table II Set 4	t2s4	1.0×10^{13}	48.4	0.7	0.8
Table II Set 5	t2s5	2.4×10^{16}	48.4	1.0	1.0

$$R_{CO,form} = 1.5 \times 10^{7} \times exp\left(-30 / RT\right) \times \left[CH_4\right]^{-0.3} \times \left[O_2\right]^{.3}$$

$$R_{CO,form} = 1.0 \times 10^{13} \times exp\left(-48.4 / RT\right) \times \left[CH_4\right]^{0.7} \times \left[O_2\right]^{0.8}$$

Kinetics?!



1.E+00
9.E-01
8.E-01
7.E-01
6.E-01
5.E-01
4.E-01
3.E-01
2.E-01
1.E-01
0.E+00
Height (m)
t4r2
t2s2
t2s3
t2s5
t2s4
t2s4 (10% lower T)
t2s4 (10% higher T)
1E-10
1E-08
1E-06
0.0001
0.01
1
100
10000
1E+06
1E+08
Net formation rate (kg/m3/s)

Comparisons

Issue	FDS v5.0	SOFIE 3 extension
Researchers	Floyd & McGrattan	Paul & Welch
Model basis	LES	RANS
Computational cost	3 extra equations	2 extra equations
Combustion	Fully integrated	Post-processed
Formation	Instantaneous	Finite-rate chemistry
Oxidation	Extinction model	Finite-rate chemistry
Further development	Soot parameter; other toxic gases	Solid-phase pyrolysis; generalise flamelets

Conclusions

- **Some modelling frameworks established**
  - Dedicated treatment of CO
    - Flexibility is attractive
      - Free of constraints of "instantaneous" chemistry
      - Can patch in solid-phase contributions
      - To achieve it we have to resort to *simplified* kinetics!
  - With the freedom comes the responsibility
      - What kinetics?!
        - Database?
      - Gas-phase
        - Pure fuels, better info still needed ☹
      - Solid-phase
        - Will be a much more challenging problem!

References

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Further work

- **Addition of pyrolysis yield**
  - Extension of flame spread model
- **Hybrid models**
  - Quasi laminar/turbulence models
  - Condition on mixture fraction variance
    - Simplified chemistry in layer
    - Flamelet treatment in fire plume
- **Real fuels**
  - Exploit simple tube furnace correlations?
  - Generalisation of CO flamelets