Depletion of Soot Precursors in a Rich Ethylene Flame by Addition of Dimethoxymethane (DMM) : Experimental and Kinetic Modeling

Task 2.4F

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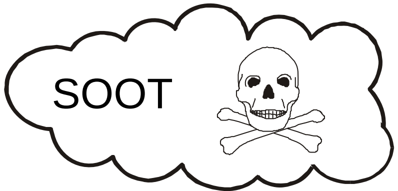
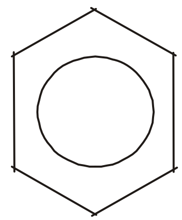
Aim of this work



PAH ←  $= C_6$ ← **Precursors**

Effect of dimethoxymethane (DMM) « methylal » : $C_3H_8O_2$

Experimental

Modeling

$C_2H_4/O_2/Ar$ flame

(ϕ = 2.50)

Flames composition - Experimental conditions

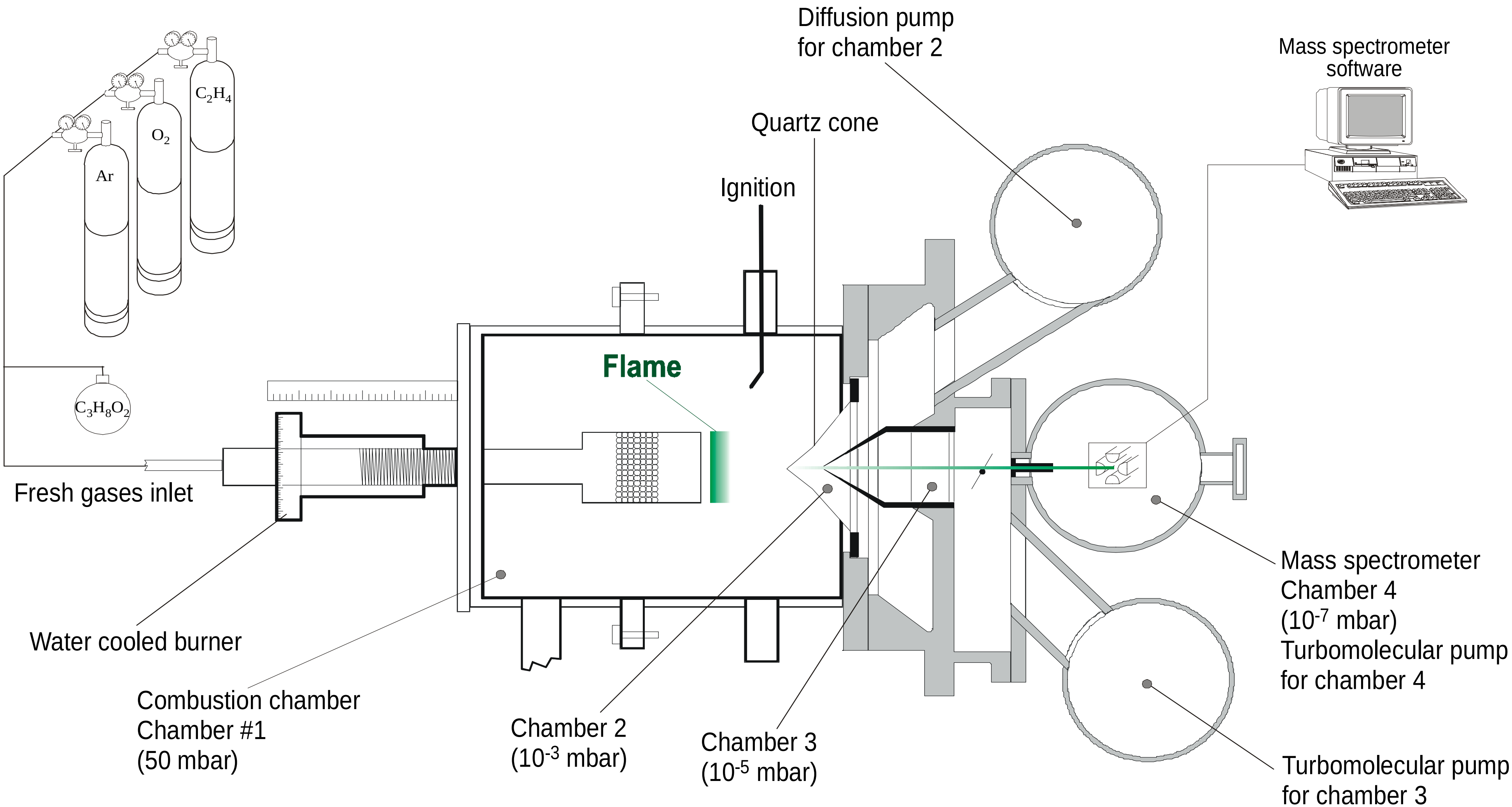
2 flames studied

- **without DMM** → **F2.50**
- **with DMM** → **F2.50M**

Flame	X C_2H_4	X O_2	X Ar	X DMM	ϕ	C/O	V_0	P_T
F2.50	0.330	0.400	0.270	-	2.50	0.83	40.31	50
F2.50M	0.273	0.400	0.284	0.043	2.50	0.76	40.31	50

ϕ : equivalence ratio V_0 : initial flow velocity (cm/s) P_T : working pressure (mbar)

Experimental setup



Molecular Beam Mass Spectrometry

Kinetic model

Original reaction mechanism : **416 reactions - 78 chemical species (C_1 to C_{10})**

validated against premixed $C_2H_4/O_2/Ar$ (ϕ = 1.00 to 2.50), $CH_4/O_2/Ar$ (ϕ = 1.94), $C_2H_2/O_2/Ar$ (ϕ = 2.00) and $C_2H_6/O_2/Ar$ (ϕ = 2.00) flames, by Dias et al. (2003)

DMM reaction sub-mechanism : **46 reactions - 10 chemical species**

built by taking into account oxygenated species involved in the methylal combustion

$\Rightarrow$ **New reaction mechanism :** **462 reactions - 88 chemical species**

for a rich $C_2H_4/O_2/Ar$ flame with some $C_3H_8O_2$ added

- **Simulation of the kinetic mechanism by using of PREMIX, code of the CHEMKIN package**

- **Validation of the new mechanism by comparing simulated mole fraction profiles with MBMS experimental results**

DMM reaction sub-mechanism (1)

$k = A\,T^n \exp(-E_a/RT)$ in $cm^3\,mol^{-1}\,s^{-1}$

Reactions	A	n	E_a (cal)
DMM consumption			
$DMM = CH_3 + CH_3OCH_2O$	2.62E+16	0	83797
$DMM = CH_3O + CH_3OCH_2$	2.51E+15	0	87876
$DMM + OH = DMM1 + H_2O$	1.40E+08	1.61	-35
$DMM + OH = DMM2 + H_2O$	1.00E+12	0	-668
$DMM + H = DMM1 + H_2$	9.70E+13	0	6210
$DMM + H = DMM2 + H_2$	3.70E+12	0	3239
$DMM + CH_3 = DMM1 + CH_4$	2.26E-05	5.35	5810
$DMM + CH_3 = DMM2 + CH_4$	5.00E+12	0	9749
$CH_3OCH_2O + M = CH_2O + CH_3O + M$	6.48E+12	-0.13	14870
$CH_3OCH_2O + M = CH_3OCHO + H + M$	2.39E+14	0	23400
$CH_3OCH_2 + M = CH_2O + CH_3 + M$	1.60E+13	0	25500
$DMM1 + M = CH_2O + CH_3OCH_2 + M$	1.00E+14	0	32500
$DMM2 + M = CH_3OCHO + CH_3 + M$	1.00E+14	0	32500
$CH_3OCHO = CH_3O + HCO$	4.38E+11	0	48100
$CH_3OCHO + OH = CH_3OCO + H_2O$	2.35E+10	0.73	-1113
$CH_3OCHO + H = CH_3OCO + H_2$	4.10E+09	1.16	2405
$CH_3OCO + M = CH_3O + CO + M$	8.64E+15	0	26091

DMM: $CH_3OCH_2OCH_3$ DMM1: $CH_3OCH_2OCH_2$ DMM2: $CH_3OCHOCH_3$

DMM reaction sub-mechanism (2)

$k = A\,T^n \exp(-E_a/RT)$ in $cm^3\,mol^{-1}\,s^{-1}$

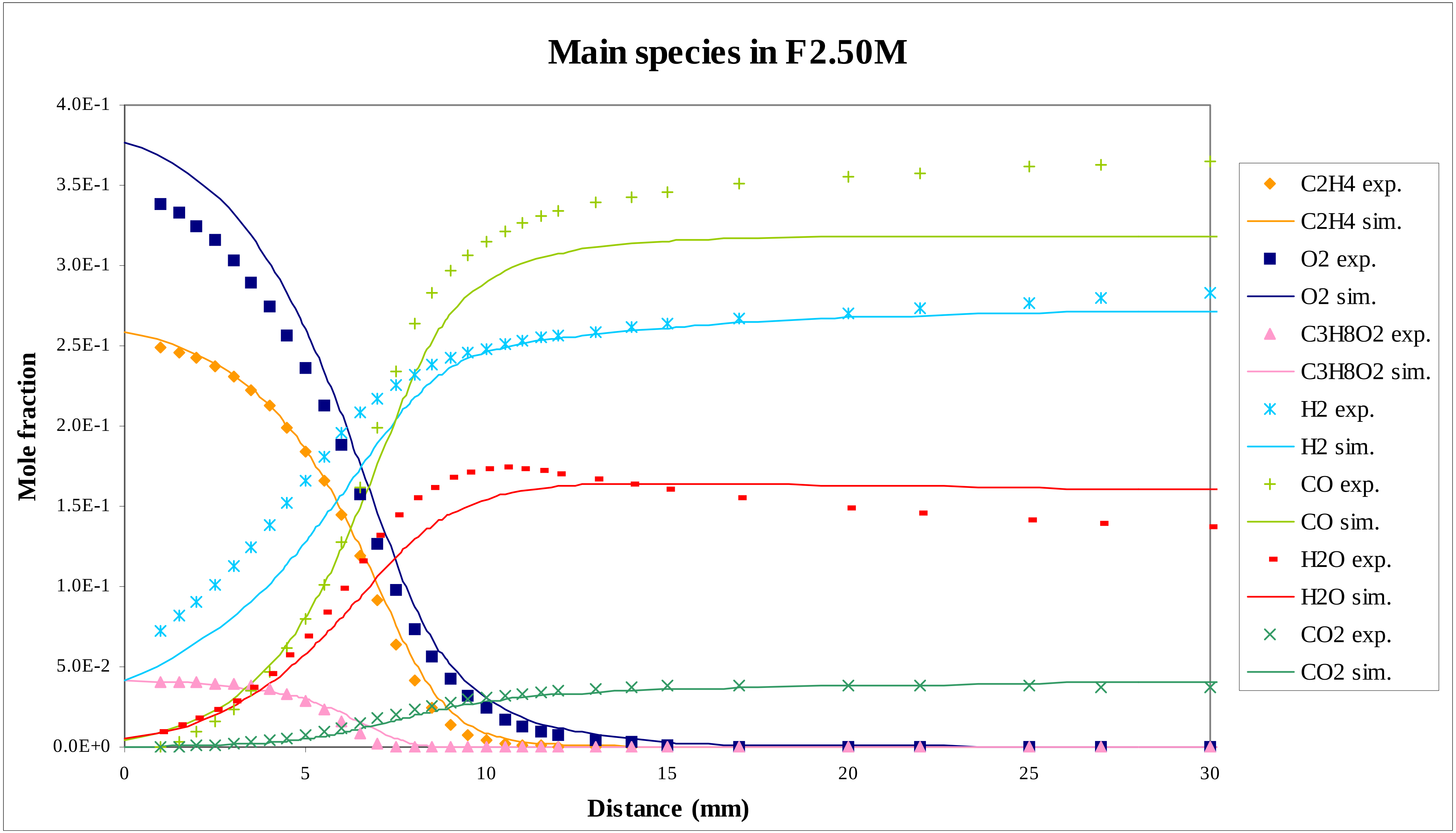
Reactions	A	n	E_a (cal)
CH_3O			
$CH_3 + HO_2 = CH_3O + OH$	3.78E+13	0	0
$CH_3 + O_2 = CH_3O + O$	2.05E+18	-1.57	29229
$CH_3O + H = CH_3 + OH$	3.20E+13	0	0
$CH_3O + M = CH_2O + H + M$	1.00E+14	0	25000
$CH_3O + H = CH_2O + H_2$	2.00E+13	0	0
$CH_3O + OH = CH_2O + H_2O$	5.00E+12	0	0
$CH_3O + O = CH2O + OH$	1.00E+13	0	0
$CH_3O + O_2 = CH_2O + HO_2$	6.30E+10	0	2600
$CH_3 + CH_3OH = CH_3O + CH_4$	1.00E+07	1.5	9940
$CH_3O + H = CH_2OH + H$	3.40E+06	1.6	0
$CH_3OH + OH = CH_3O + H_2O$	5.30E+03	2.65	-884
$CH_3OH + O = CH_3O + OH$	1.30E+05	2.5	5000
$CH_3OH + H = CH_3O + H_2$	4.00E+13	0	6100
$CH_3 + CH_3O = CH_2O + CH_4$	2.41E+13	0	0
$CH_3O + CH_3OH = CH_2OH + CH_3OH$	3.01E+11	0	4073

DMM reaction sub-mechanism (3)

$k = A\,T^n \exp(-E_a/RT)$ in $cm^3\,mol^{-1}\,s^{-1}$

Reactions	A	n	E_a (cal)
CH_3OH			
$CH_3 + OH (+M) = CH_3OH (+M)$	6.30E+13	0	0
LOW / 2.700E+38 -6.300 3100.00 /			
TROE / 0.2105 83.50 5398.00 8370.00 /			
H_2/2.0/ H_2O/6.0/ CH_4/2.0/ CO/1.5/ CO_2/2.0/ C_2H_6/3.0/			
$CH_3 + CH_3OH = CH_2OH + CH_4$	3.00E+07	1.5	9940
$O + CH_3OH = OH + CH_2OH$	3.88E+05	2.5	3100
$H + CH_3OH = CH_2OH + H_2$	1.70E+07	2.1	4870
$OH + CH_3OH = CH_2OH + H_2O$	4.80E+13	0	4500
$CH_3OH + H = CH_3 + H_2O$	5.25E+12	0	5340
$CH_3OH + HO_2 => CH_2OH + H_2O_2$	6.31E+12	0	19360
CH_2OH			
$CH_2OH + H = CH_3 + OH$	1.20E+13	0	0
$CH_2OH + M = CH_2O + H + M$	1.00E+14	0	25000
$CH_2OH + H = CH_2O + H_2$	2.00E+13	0	0
$CH_2OH + OH = CH_2O + H_2O$	1.00E+13	0	0
$CH_2OH + O = CH_2O + OH$	1.00E+13	0	0
$CH_2OH + O_2 = CH_2O + HO_2$	1.00E+14	0	5000
$CH_3 + CH_2OH = CH_2O + CH_4$	2.41E+12	0	0

Results : Mole fraction profiles



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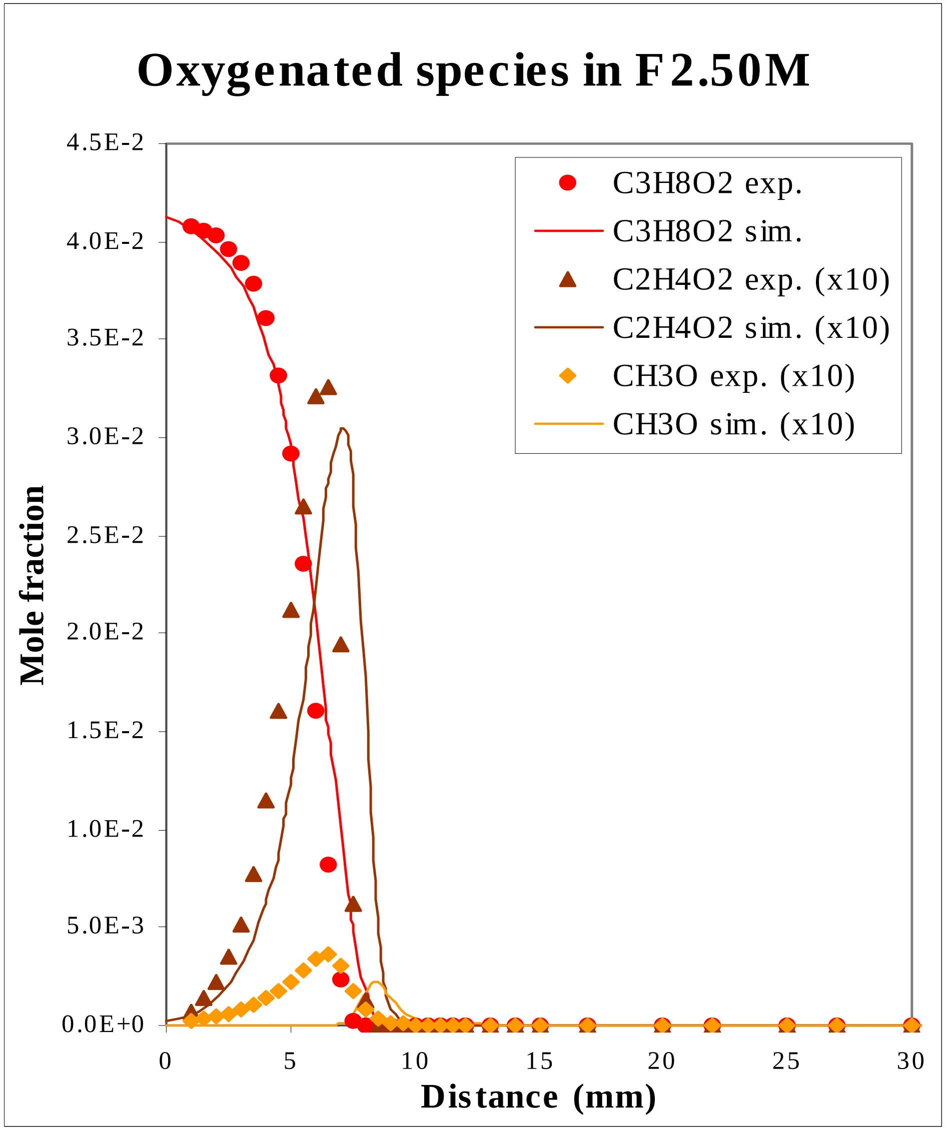


Methylal consumption: Main pathways

$$CH_3OCH_2OCH_3 + R \xrightarrow{90\%} CH_3OCH_2OCH_2 + RH \quad (a1)$$

$$\xrightarrow{10\%} CH_3OCHOCH_3 + RH \quad (b1)$$

76% 22% 2% (a1)

where R is a radical H or OH or CH_3

75% 16% 9% (b1)

$$CH_3OCH_2OCH_2 \xrightarrow{M} CH_3OCH_2 + CH_2O \quad (a2)$$

$$CH_3OCH_2 \xrightarrow{M} CH_3 + CH_2O \quad (a3)$$

$$CH_3OCHOCH_3 \xrightarrow{M} \underbrace{CH_3OCHO}_{\text{methyl formate}} + CH_3 \quad (b2)$$

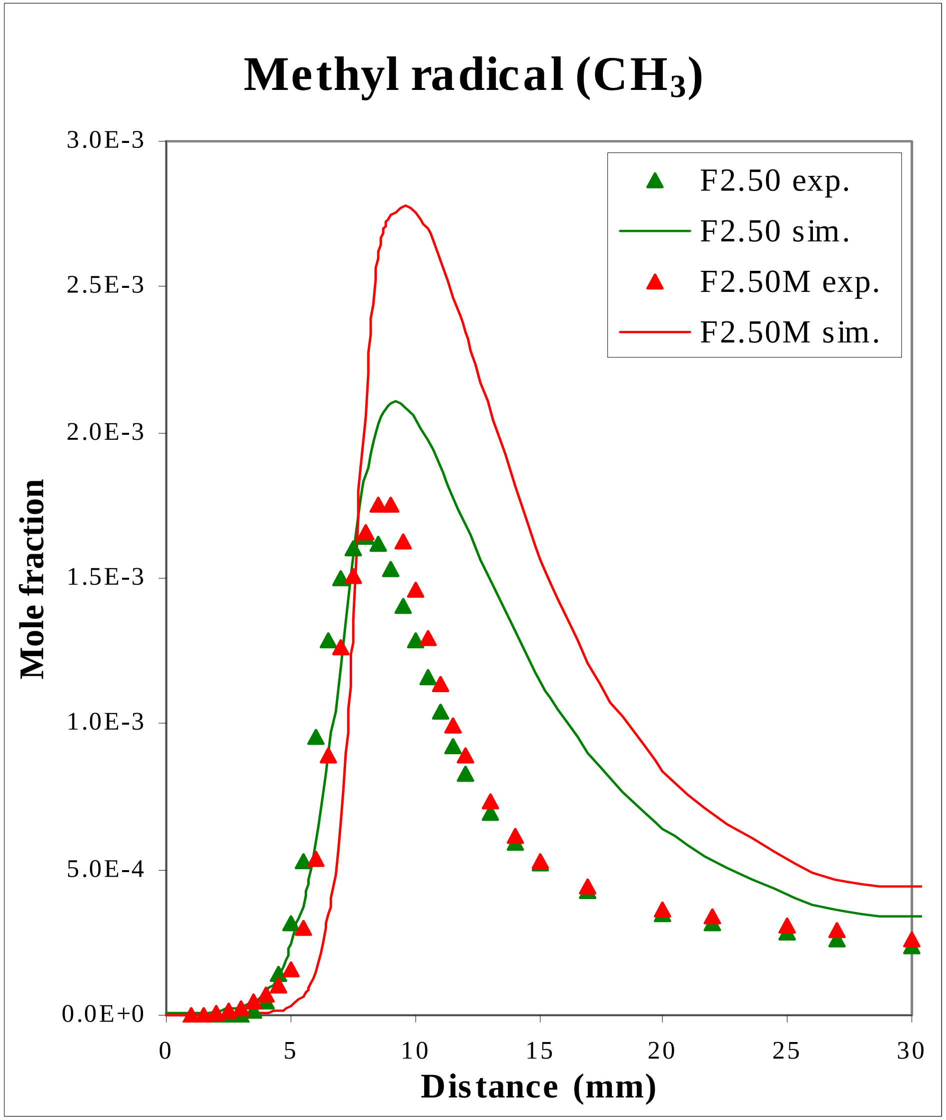
$$CH_3OCHO + R \rightarrow CH_3OCO + RH \quad (b3)$$

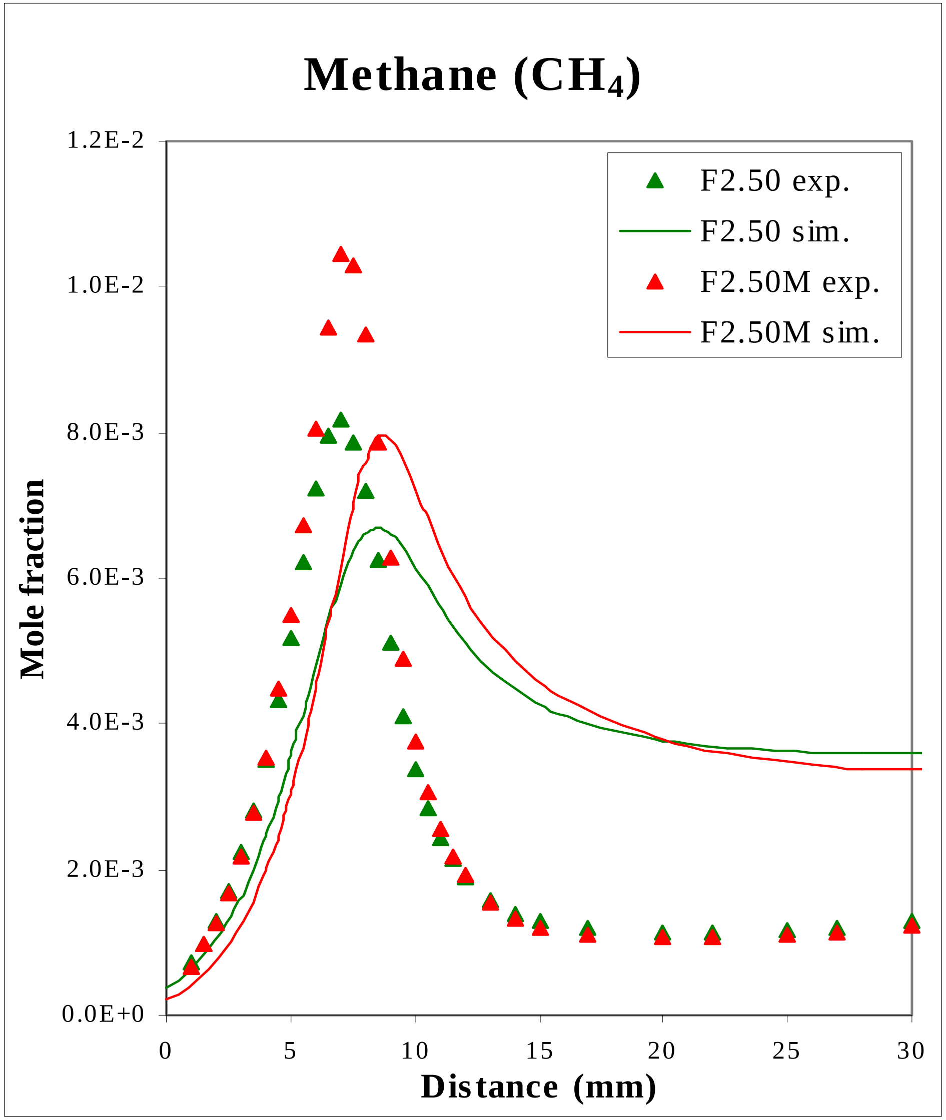
83% 17%

where R is a radical H or OH

$$CH_3OCO \xrightarrow{M} CH_3O + CO \quad (b4)$$

Results : Mole fraction profiles





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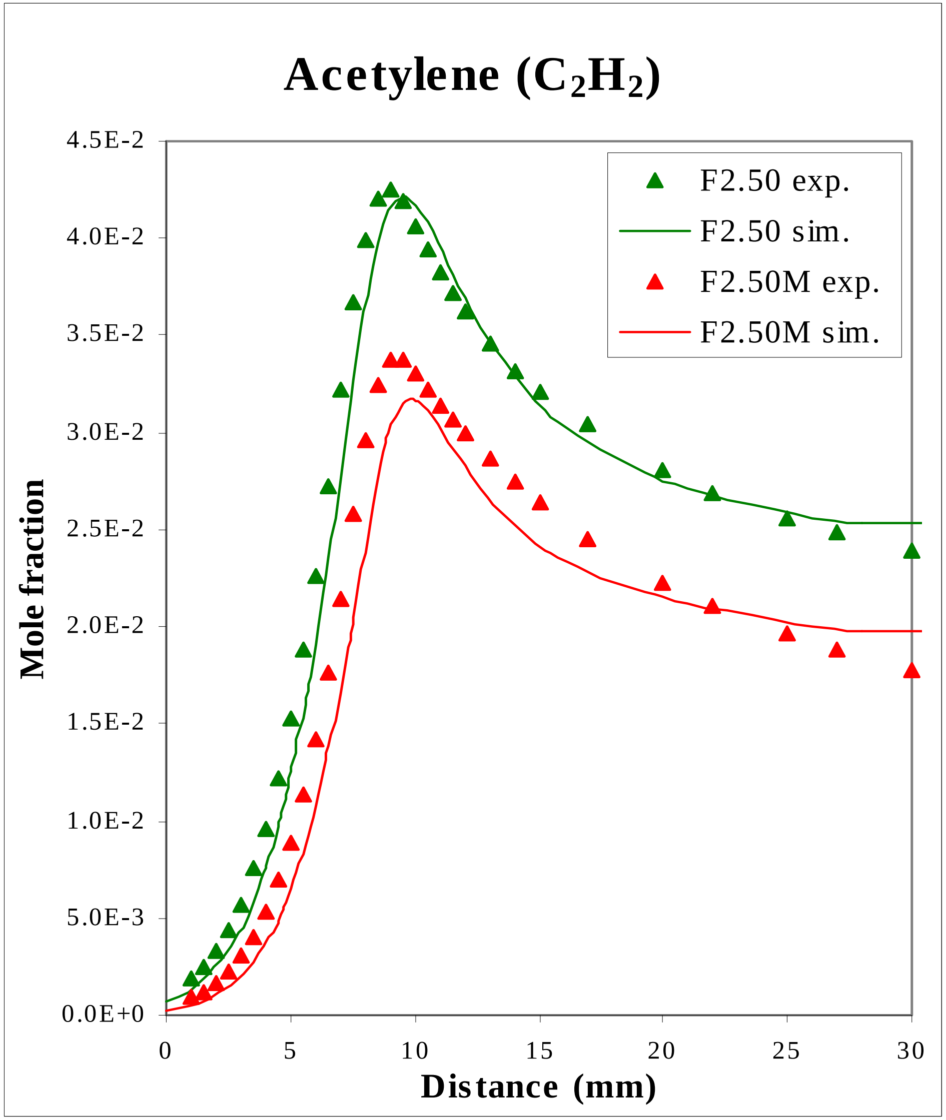
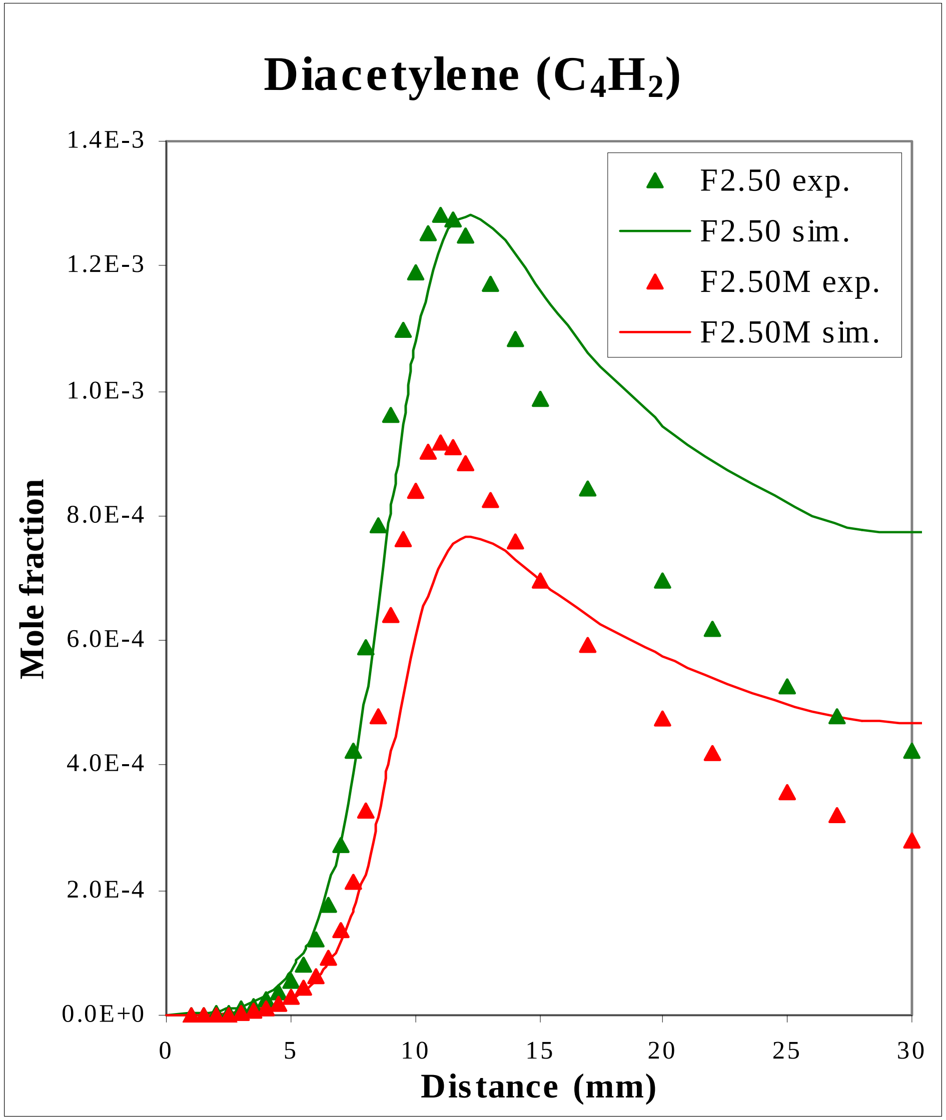
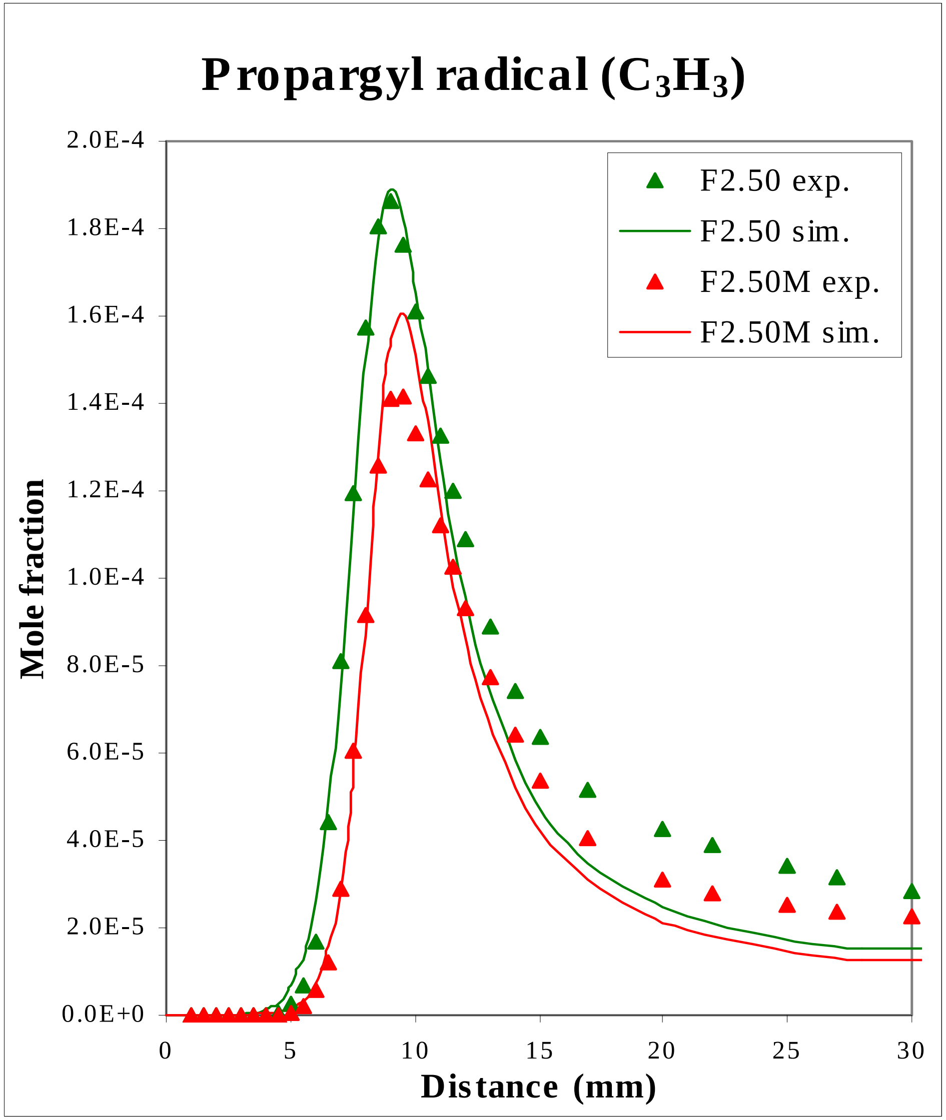
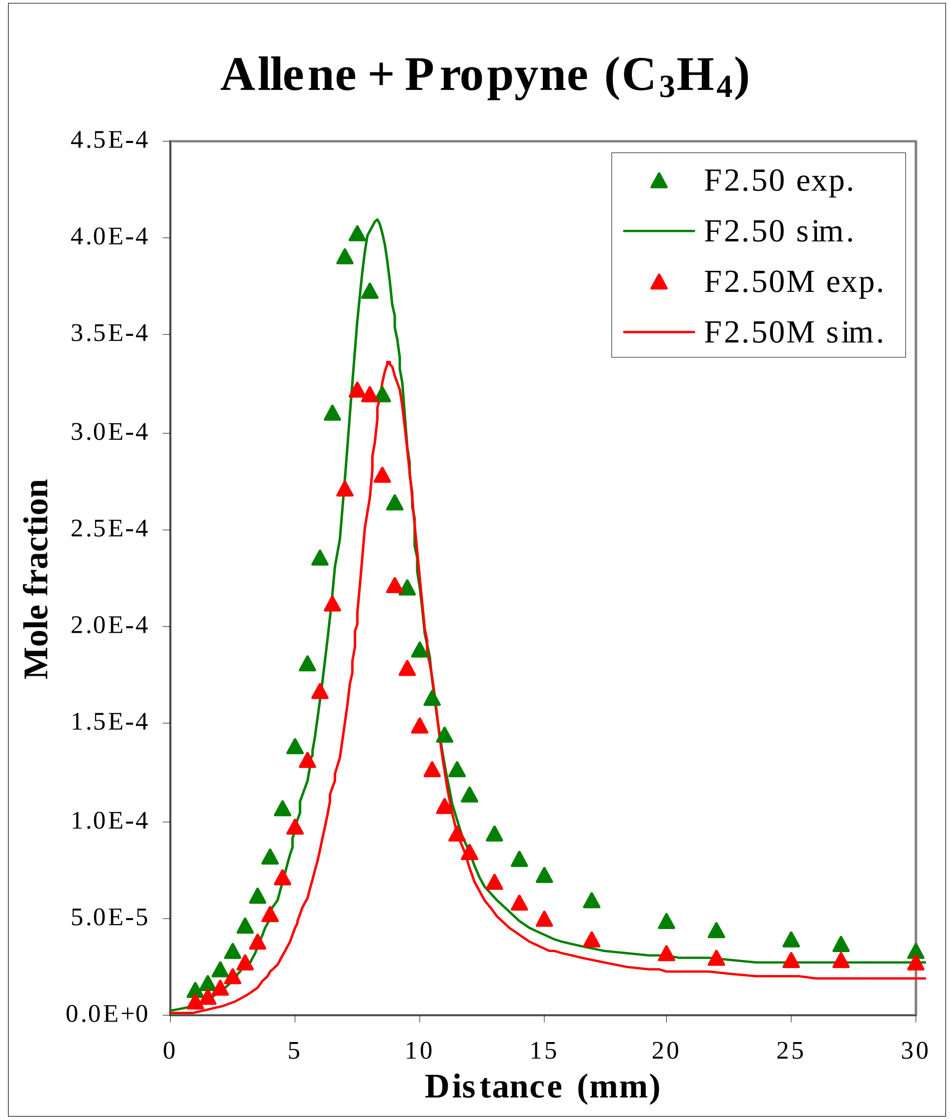




Results : Mole fraction profiles





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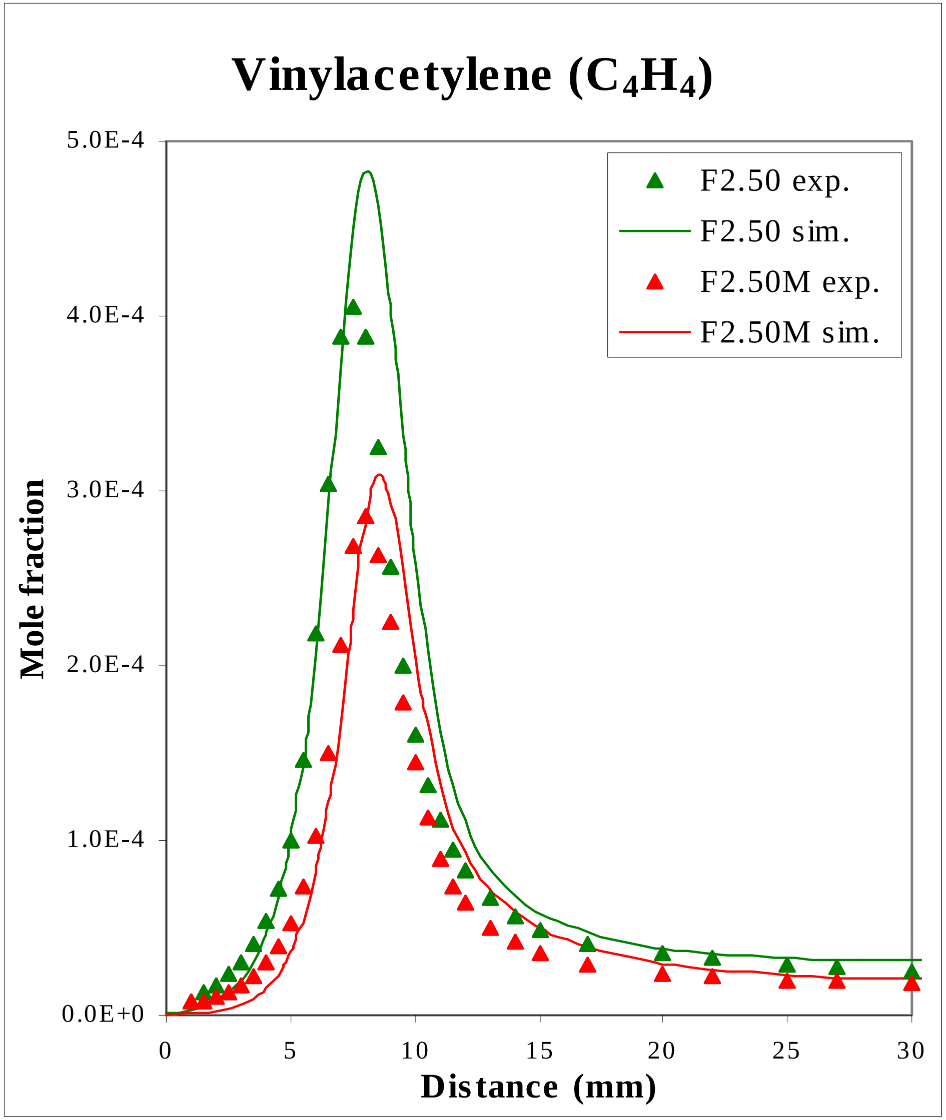
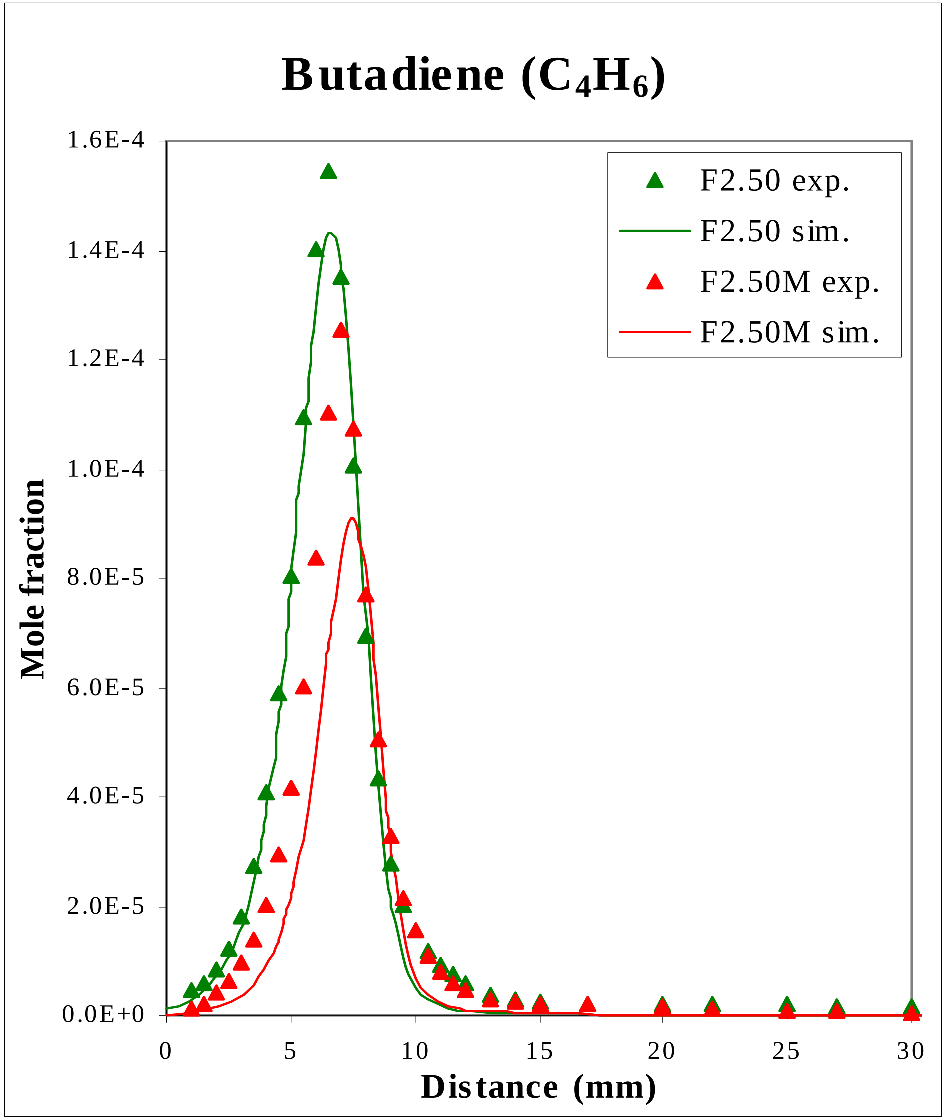
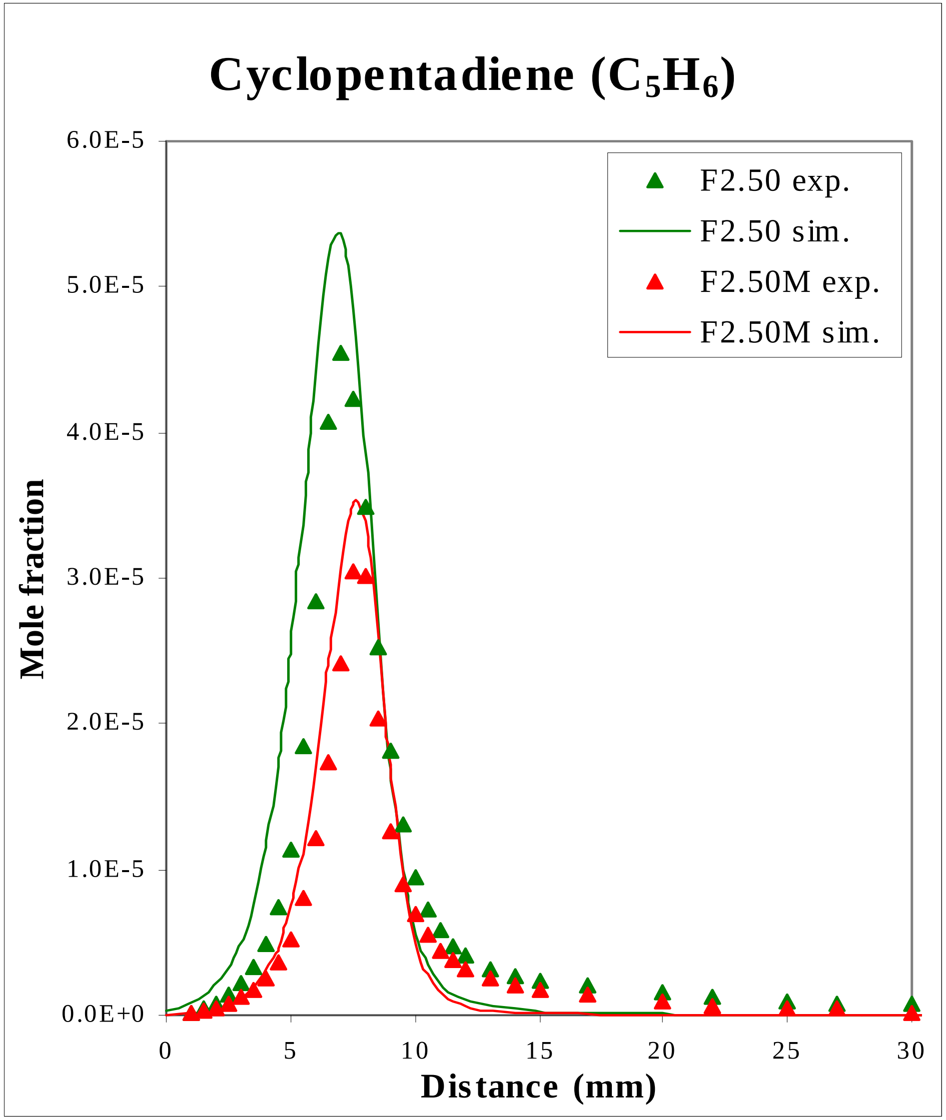
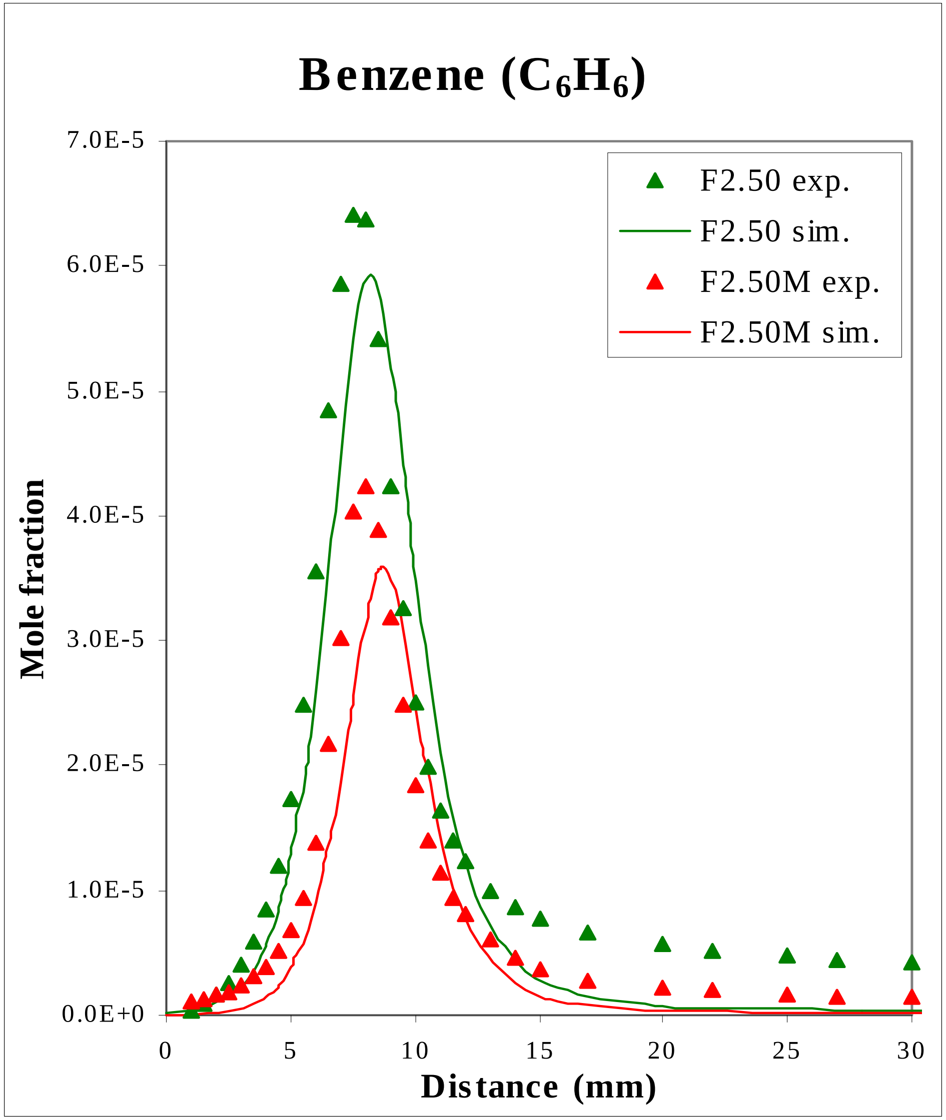




Results : Mole fraction profiles





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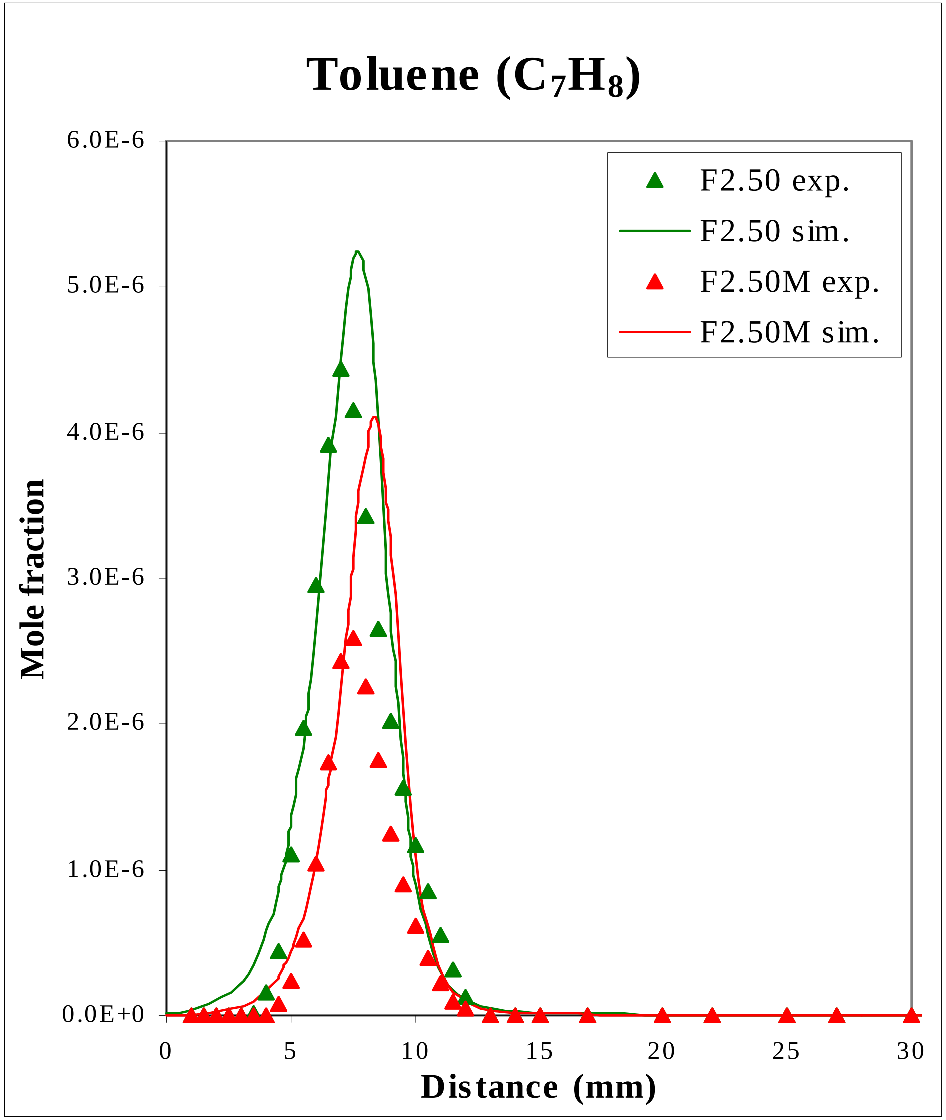

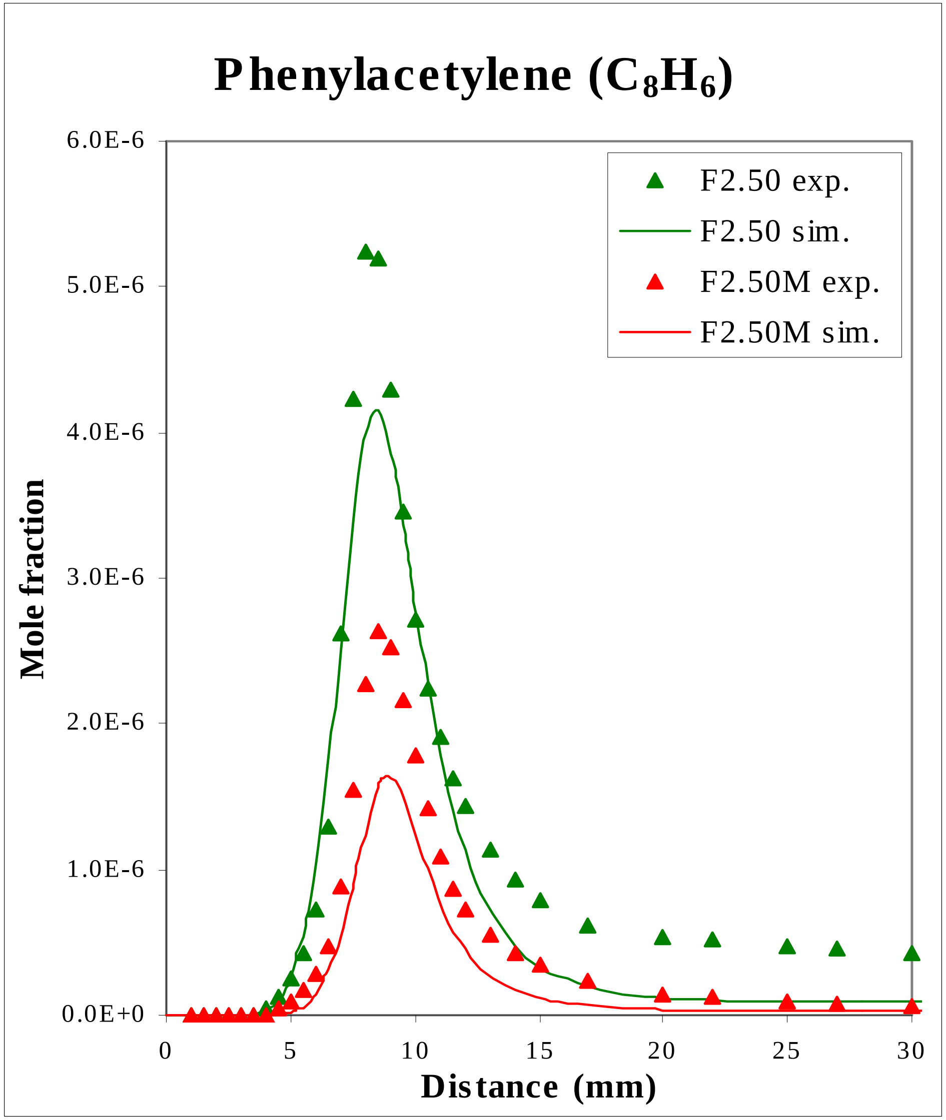

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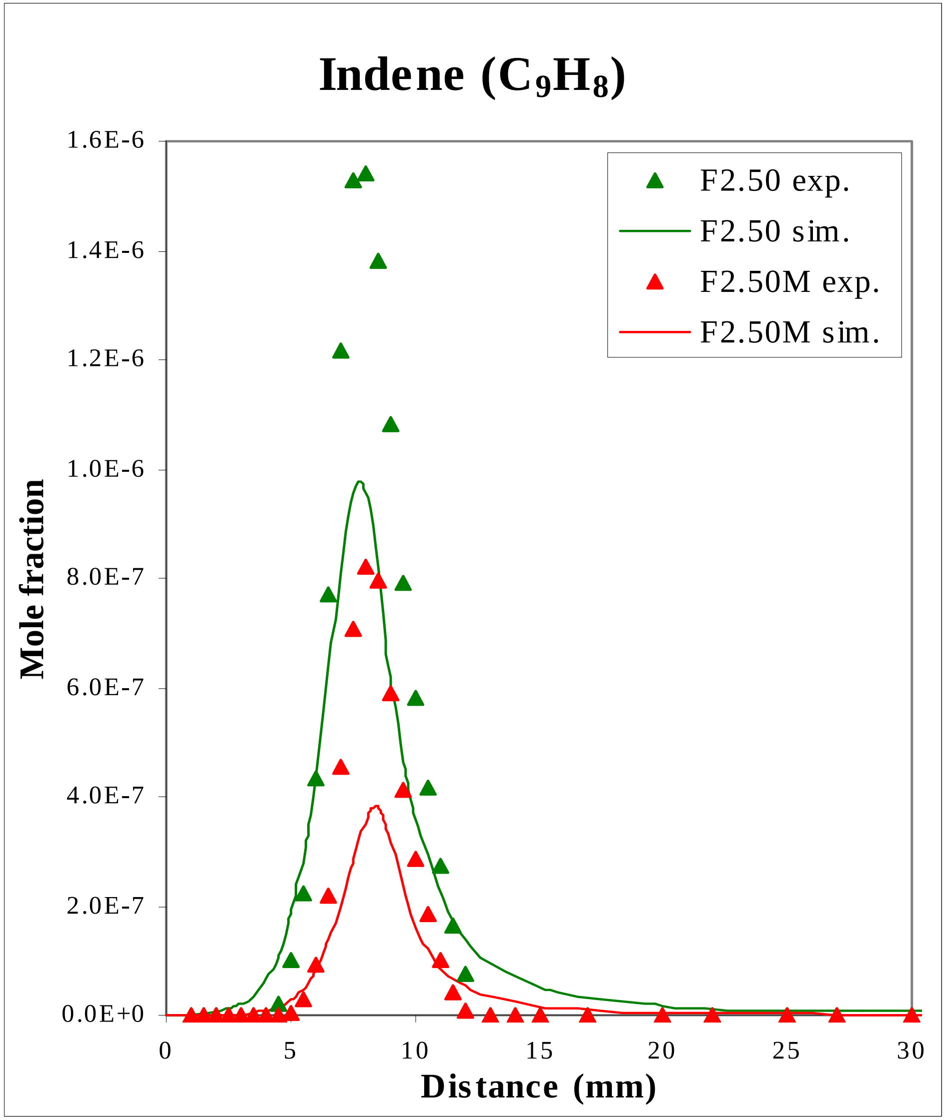
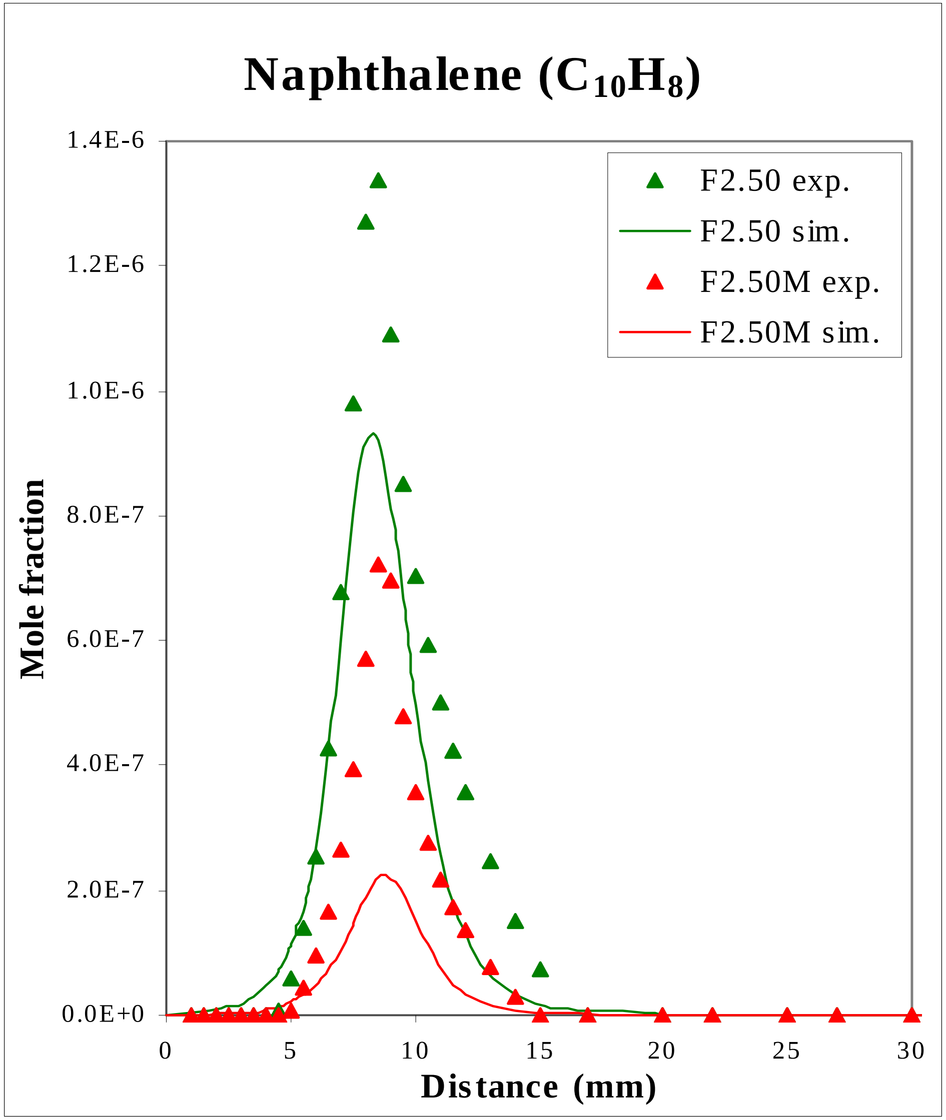




General Conclusions

Our experimental observations corroborate the impact of methylal blended diesel fuels on soot particulates abatement.

→ **DMM addition** (keeping ϕ = 2.50) **leads to lower concentrations of soot precursors:**

- **already noticeable for C_2 to C_4 intermediates (- 10 % to - 30 %)**
- **more efficient for C_5 to C_{10} species (- 30 % to - 50 %)**

These results have provided data for comparison with numerical modeling of a new combustion mechanism of rich ethylene mixtures involving DMM.

→ **Its good reliability provides more informations about the chemical role played by methylal to deplete soot precursors.**

Financial support of the Région Wallonne is acknowledged under contract # 05/335552

About methylal

Synthesis

$$2\ CH_3\text{-}OH + CH_2O \xrightarrow{\text{acid catalyst}} CH_3\text{-}O\text{-}CH_2\text{-}O\text{-}CH_3$$

→ **production in a continuous process**

Natural gas → **Synthesis gas** → **Methanol**

↓

Formaldehyde

→ **Methylal**

Main uses

→ **solvent and reagent in the production process of ion exchange resins**

→ **solvent for aerosols (cosmetic, pharmaceutical, household, technical, insecticide)**

→ **blowing agent for polyurethanes**

About methylal

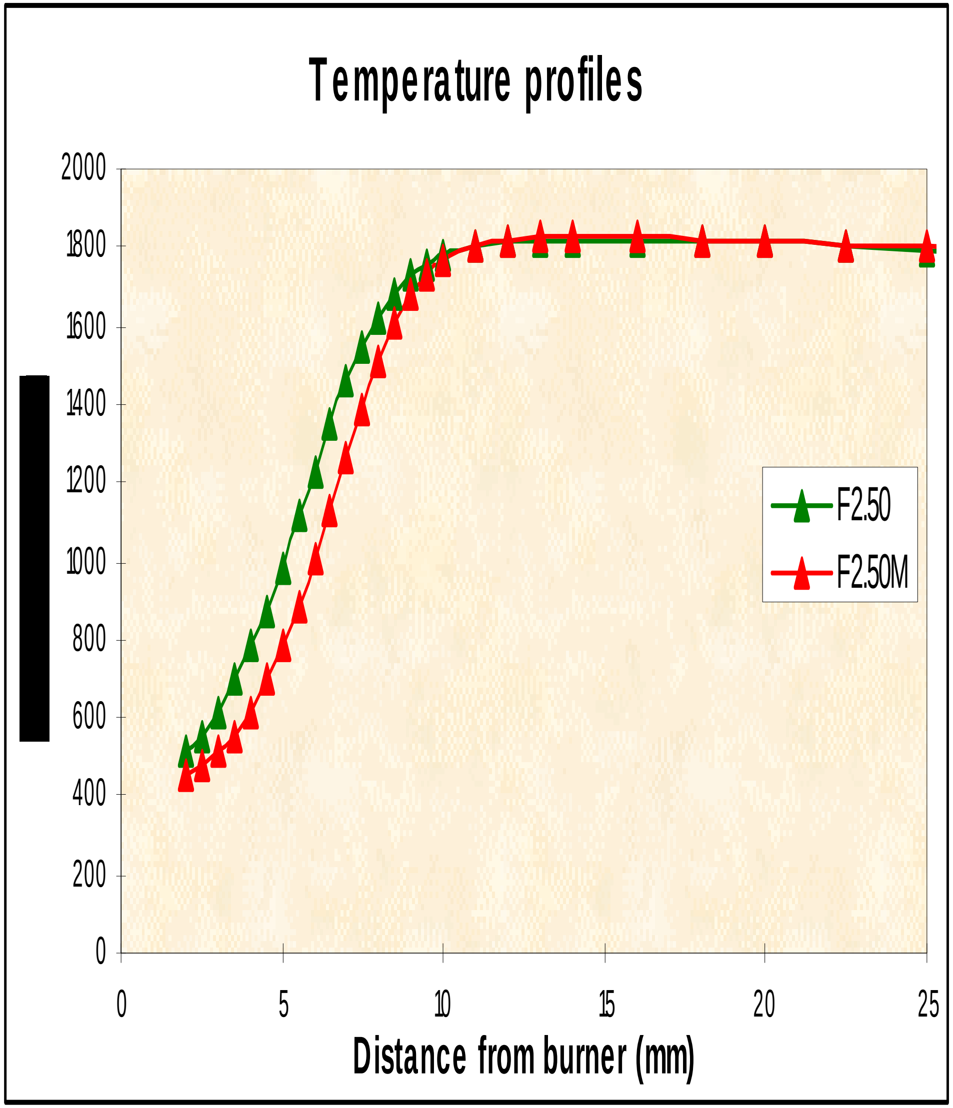
New potential application

→ **use of methylal as diesel fuel component**

Litterature data

Naegeli (1992) Dodge et al. (1994)	Caterpillar diesel engine	20 % methylal blend in diesel fuel	reduction of smoke opacity by about 50 % at start-up and high idle
Sirman et al. (1998).	Daimler-Benz turbodiesel	15 % methylal blend in ultra-low sulfur diesel	52 % lower particulate matter emission 4 % lower oxides of nitrogen emission
Vertin et al. (1999).	unmodified turbocharged diesel engine	10 % to 30 % blends of methylal in diesel fuel	substantial reduction of particulate matter emission
Cheng et al. (2001)	diesel engine	methylal-in-diesel blends	reduction of the total particle mass concentration, as well as the particle number density and the mean particle diameter

Temperature profiles



Pt/PtRh10% coated thermocouple

- 0.1 mm in diameter

- in front of the sampling cone tip (at 0.3 - 0.5 mm distance)

Radiation losses were corrected by the electrical compensation method

The flame temperature profiles have been superimposed with the mole fraction profiles scale by comparison with the water mole fraction profile

Flame	Burner temperature (K)
F2.50	424
F2.50M	403