Journée « Bio-carburants » Franco-Brésilienne

EM2C

23/01/2019

Luc-Sy TRAN

CNRS Research Scientist

PC2A

CNRS-Univ. Lille

Outline:

Summarization of the research on the combustion of biofuels at PC2A

Influence of the structure of biofuels on combustion

Research on the combustion of biofuels at PC2A

PC2A-Lille

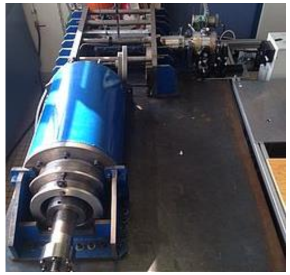
Three research teams:

1. PhysicoChemistry of Combustion
2. PhysicoChemistry of the Atmosphere
3. Chemical kinetics, Combustion, Reactivity: Nuclear Safety

Research on the combustion of biofuels at PC2A

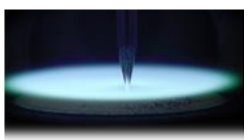
Biofuels

(2nd and 3rd generations)



Rapid compression machine (high P, low T)

Premixed flames (P=1atm, high T)



Premixed flames (P<1atm, high T)

Non-premixed flames (P=1atm, high T)

GC (TCD, FID, MS)
PEPICO (Soleil Synchrotron)
ToF-SIMS
Jet-Cooled LIF

LII/CRDS
SMPS

Kinetic model

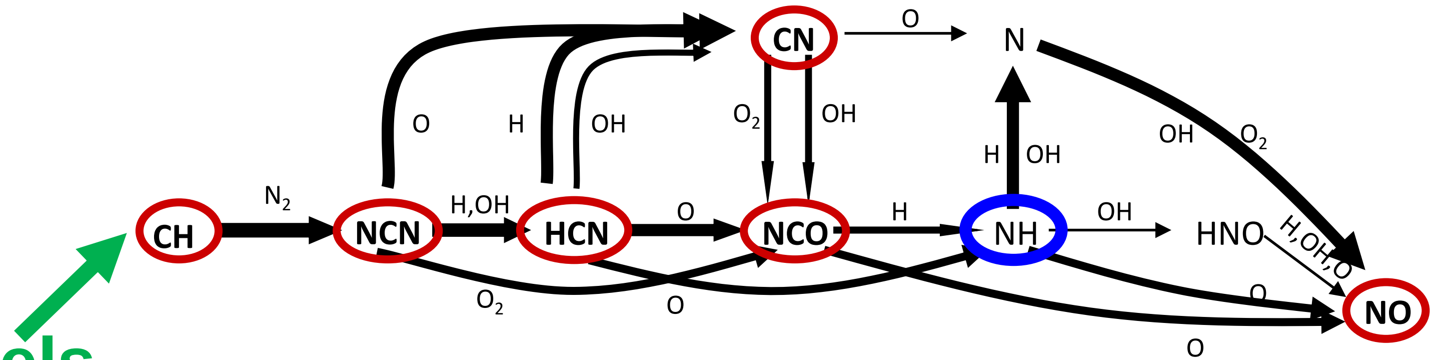
- **Low T high P ignition delay times**
- **Low T speciation**
- **Chemical structure of flames**
- **Pollutant formation:**
  PAHs, soot
  NOx
  Aldehydes, etc.

Open for national and international collaborations

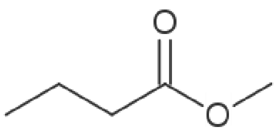
GC: Gas Chromatography
PEPICO: PhotoElectron-PhotoIon Coincidence spectroscopy
ToF-SIMS: Time of Flight Secondary Ion Mass Spectrometry
Jet-Cooled LIF: Jet-Cooled Laser-Induced Fluorescence
LII: Laser-Induced Incandescence
CRDS: Cavity Ring-Down Spectroscopy
SMPS: Scanning Mobility Particle Sizer

Research on the combustion of biofuels at PC2A

Effect of Biofuels on the formation of prompt-NO



Biofuels



Methyl butanoate

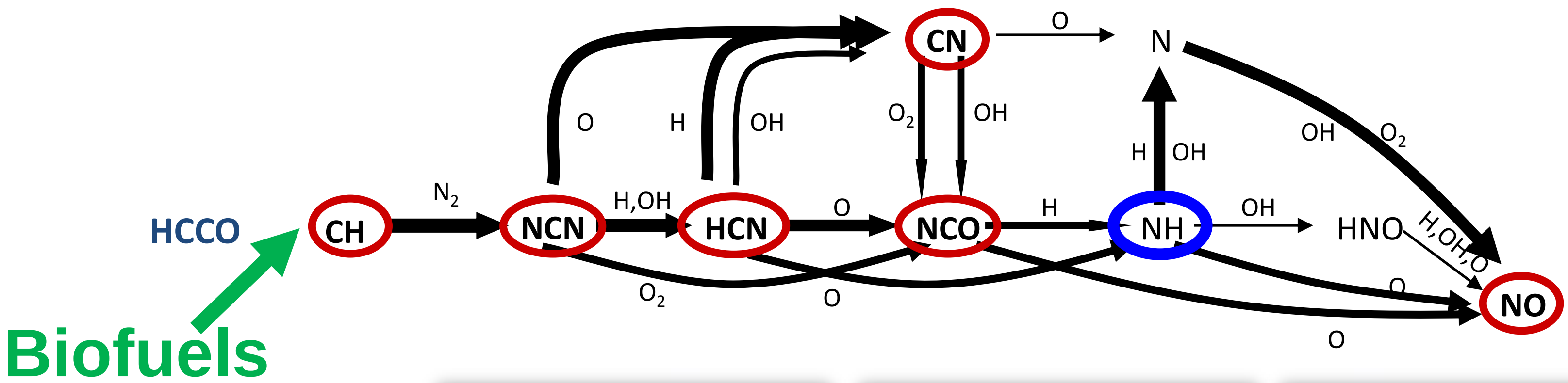
- Mole fraction species profiles in flames
  - Challenging due to trace concentrations
    Ex.: NH mole fraction: few tenth of ppb
  - By using spectroscopic laser-based techniques
- Mechanism “NOMecha2.0”

By N. Lamoureux, P. Desgroux, L. Gasnot and coworkers

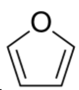
Refs: [Lamoureux et al. Combust. Flame 2016]
[Sylla, Lamoureux et al. Fuel 2017]

Research on the combustion of biofuels at PC2A

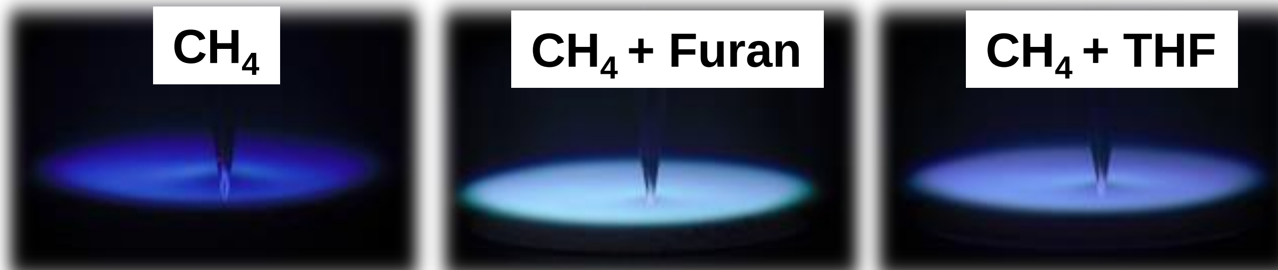
Effect of Biofuels on the formation of prompt-NO



Tetrahydrofuran (THF)



Furan



Influence of furanic fuels on the prompt-NO formation in CH_4 flames

(Ongoing work at PC2A)

By N. Lamoureux, P. Desgroux, L. Gasnot and coworkers

Refs: [N. Lamoureux et al. Combust. Flame 2016]
[Thesis of L. Giarracca 2018]

Influence of biofuels on PAHs and Soot in Swirled turbulent jet flames

Diesel flame

n-Butanol flame

Mixture flame
(50% diesel + 50% *n*-butanol)

(Ongoing work at PC2A)

By E. Therssen, X. Mercier and coworkers

- Butanol forms less soot than the diesel (about 2500 times).
- Mixture flame forms 3 times less soot than the diesel flame
- Analytical techniques: laser-based and Tof-SIMS

Ref: [Thesis of L.D NGO, ongoing]

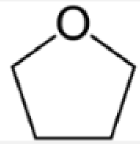
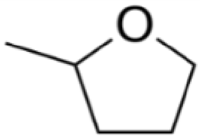
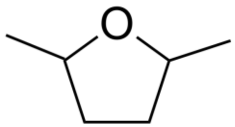
Influence of the structure of biofuels on combustion performance and emissions

Example 1: Tetrahydrofuranic biofuels (saturated cyclic ethers)

Example 2: Furanic biofuels (unsaturated cyclic ethers)

Example 3: Acyclic biofuels (acyclic ether<->acyclic alcohol)

Example 1: Tetrahydrofuranic biofuels

Molecular structure					
Name	**THF**	**2-MTHF**	**2,5-DMTHF**	Gasoline	Ethanol
Formula	C_4H_8O	$C_5H_{10}O$	$C_6H_{12}O$	mixture	C_2H_5OH
Lower Heating Value (MJ/L)	28.1	28.2	29.5	30–33	21.4
Research Octane Number	73	86	92	88–98	109
Motor Octane Number	65	73	80	80–88	90

THF: Tetrahydrofuran

2-MTHF: 2-MethylTetrahydrofuran

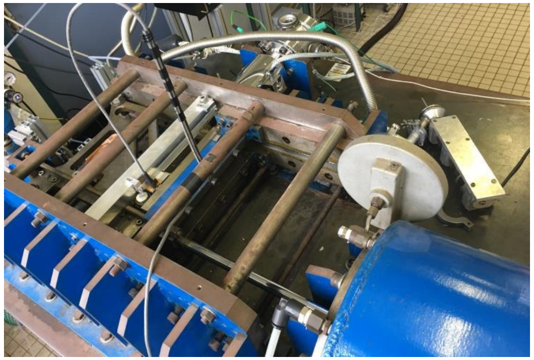
2,5-DMTHF: 2,5-DiMethylTetrahydrofuran

Data from:
NREL technical report NREL/TP-5400-50791, 2011
L-S. Tran et al., 8th U.S. National Combustion Meeting, 2013
ASTM Special Technical Publication No. 225, 1958

Ref: [G. Vanhove et al. 2019 (personal communication)]

Example 1: Tetrahydrofuranic biofuels

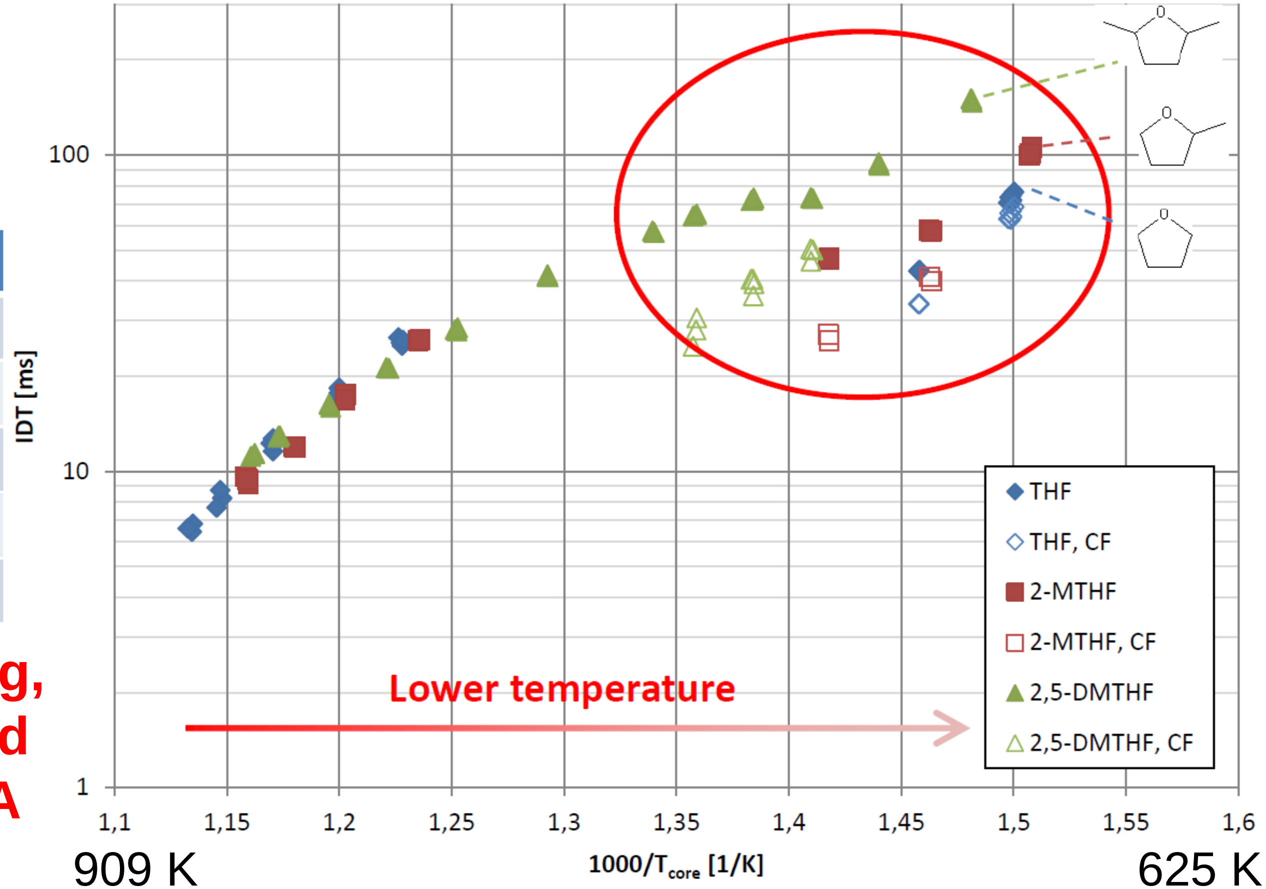
LOW TEMPERATURE ignition delay time (IDT) measurements with RCM at PC2A



Specifications	
Peak press.	Max. 30 bar
Core gas temp.	600–1000 K
Compression time	60 ms
Sampling	Immediate expansion
Analyzing	GC/MS (TCD, FID)

By G. Vanhove, H. Song, C. Mergulhao, Y. Fenard and coworkers at PC2A

THF < 2-MTHF < 2,5-DMTHF
=> THF is more reactive at low T range.

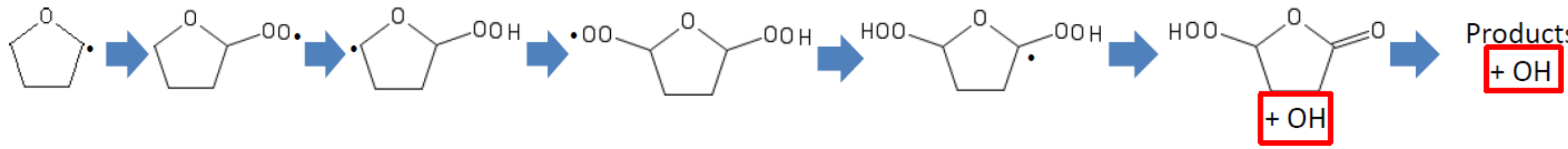


Ref: [G. Vanhove et al. 2019 (personal communication)]

Example 1: Tetrahydrofuranic biofuels

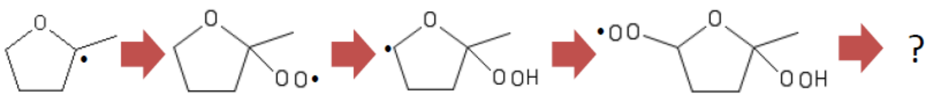
2^{nd} O_2 addition to THF radical: favored pathway with chain branching

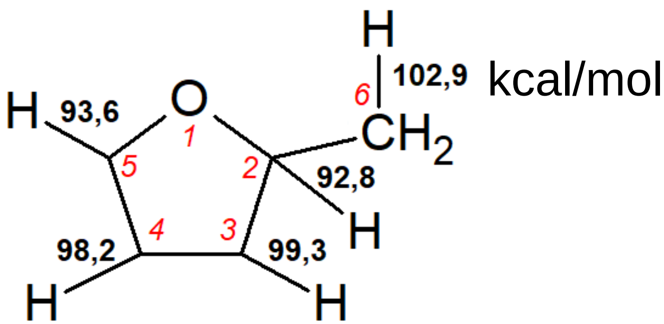
THF →



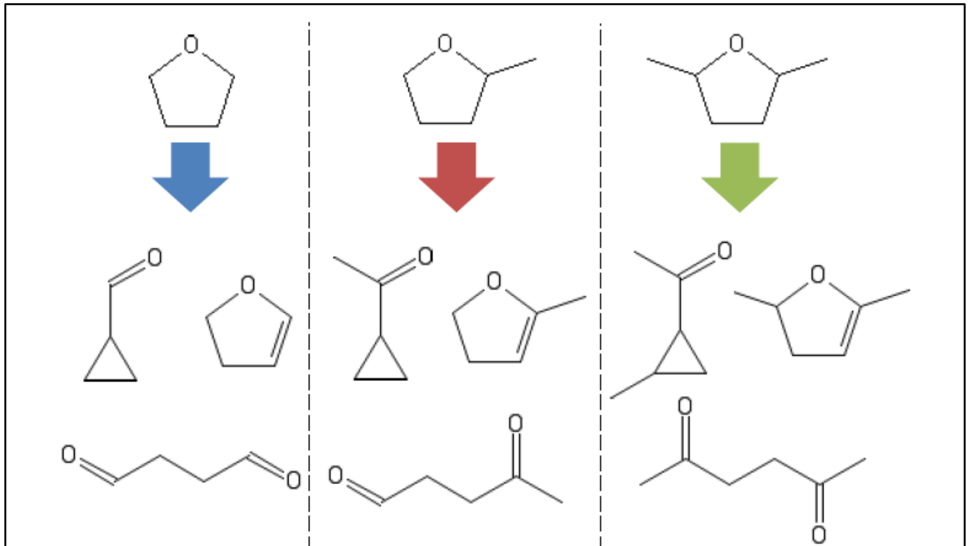
2^{nd} O_2 addition to MTHF: Unfavored pathway

MTHF →





(MTHF)



Examples of intermediates during the reaction pathway of THFs

Kinetic modeling of **2,5-DMTHF** in progress at PC2A

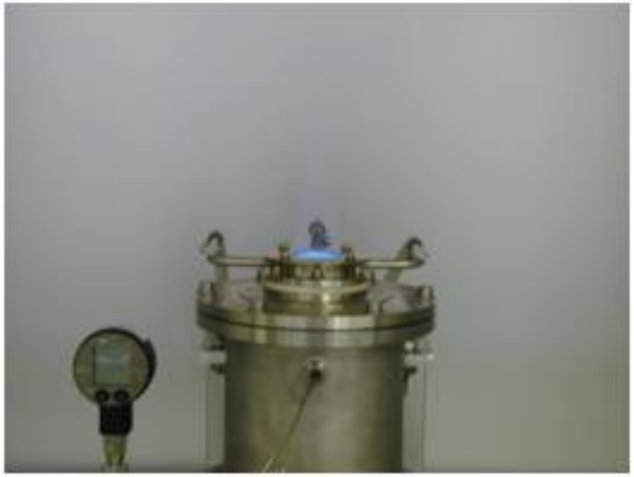
By G. Vanhove, H. Song, C. Mergulhao, Y. Fenard and coworkers at PC2A

Ref: [G. Vanhove et al. 2019 (personal communication)]

Example 1: Tetrahydrofuranic biofuels

Flame speeds (HIGH TEMPERATURE chemistry)

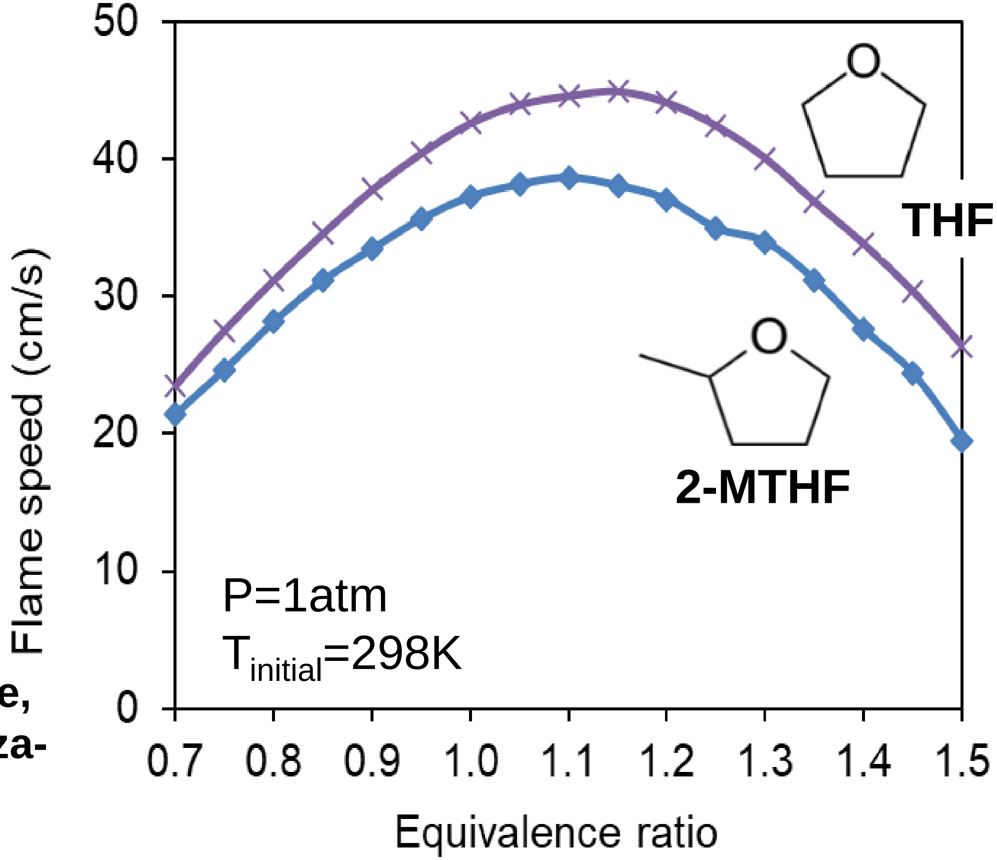
Heat flux method applied to a flat flame adiabatic burner



(at LRGP, Nancy)

(collaboration Nancy-France, Ghent-Belgium, and Zaragoza-Spain)

THF > 2-MTHF
=> THF is also more reactive at high T

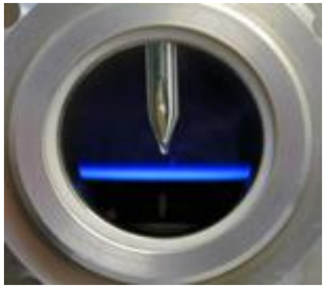


The structure of biofuel influences strongly their reactivity

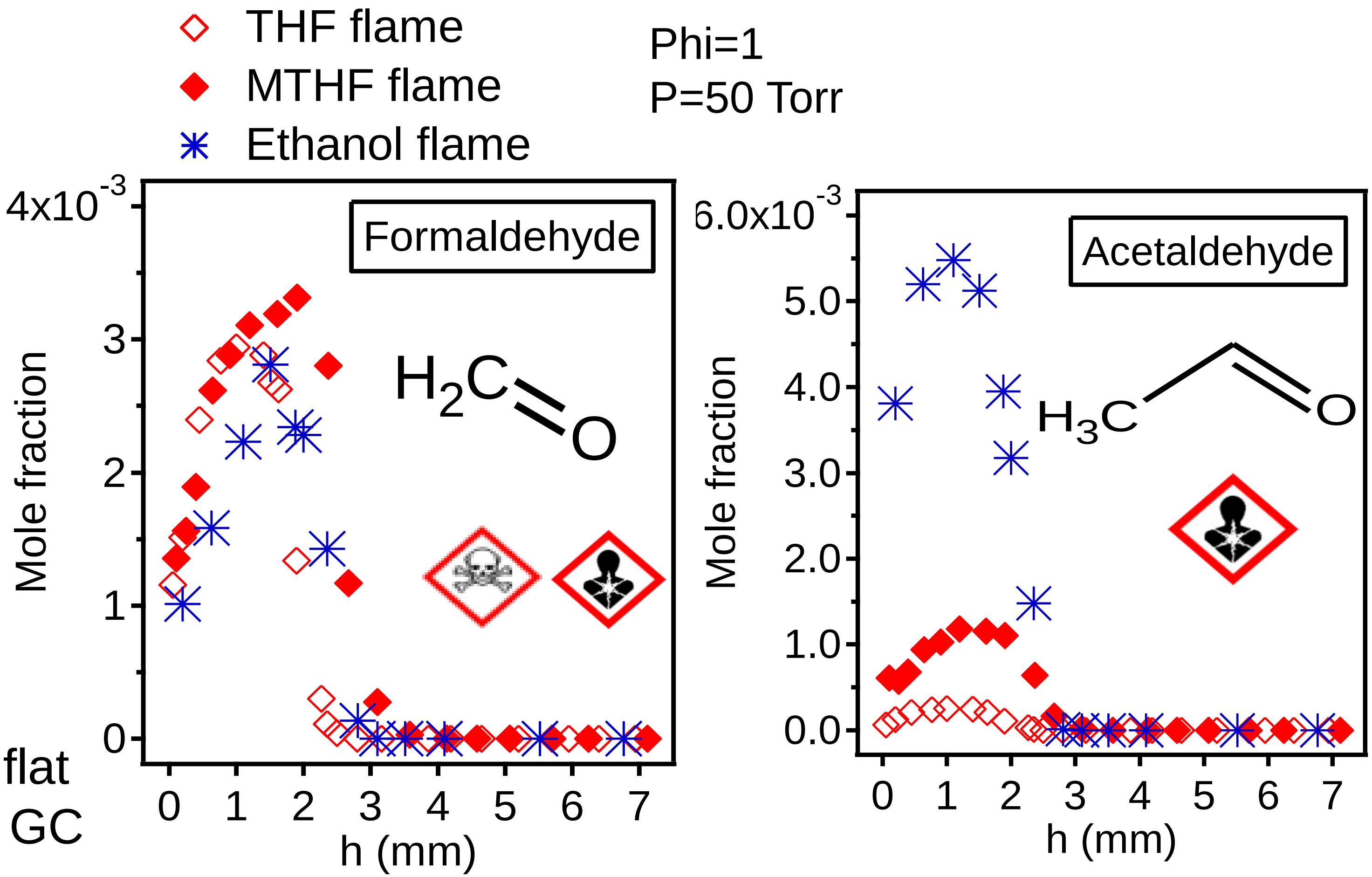
Refs: [Tran et al. Combustion and Flame 2015]
[De Bruycker, Tran et al. Combustion and Flame 2017]

Example 1: Tetrahydrofuranic biofuels

Species formation in flames (high temperature chemistry)



Low-P premixed flat flame coupled to GC at LRGP, Nancy



THF ~ MTHF ~ Ethanol **THF < MTHF << Ethanol**

The structure of biofuel influences strongly the formation of aldehydes

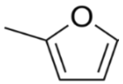
Ref: [Tran et al. The 8th U.S. National Combustion Meeting 2013]

Example 2: Furanic biofuels

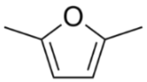
LHV: ~ 28-30 (MJ/L)
RON: > 100

(collaboration Bielefeld-Germany and Ghent-Belgium)

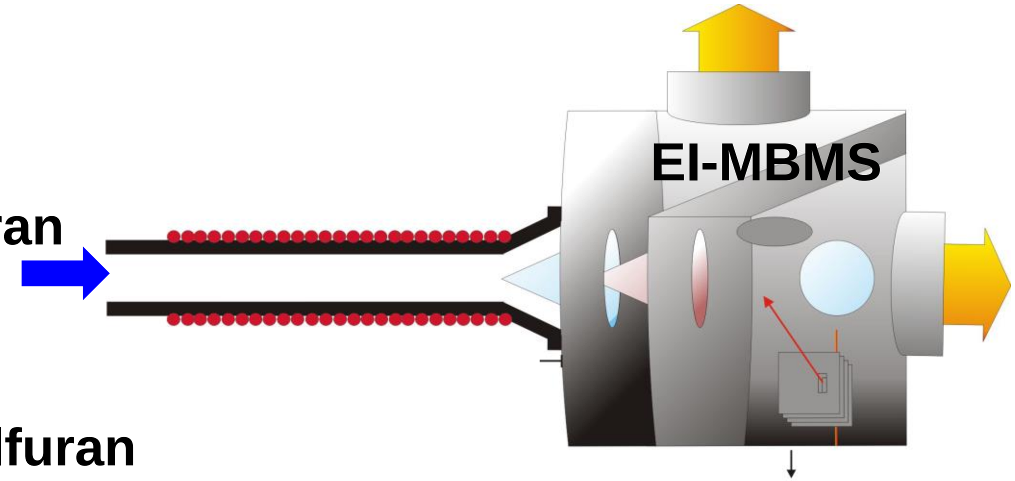
Furan



2-Methylfuran (MF)



2,5-Dimethylfuran (DMF)



Species profiles

- Oxidation in a flow reactor

(at Bielefeld-Germany, team of K. Kohse-Höinghaus)

L=0.84 m, D = 8 mm

P=1.0 bar, T=700-1200 K

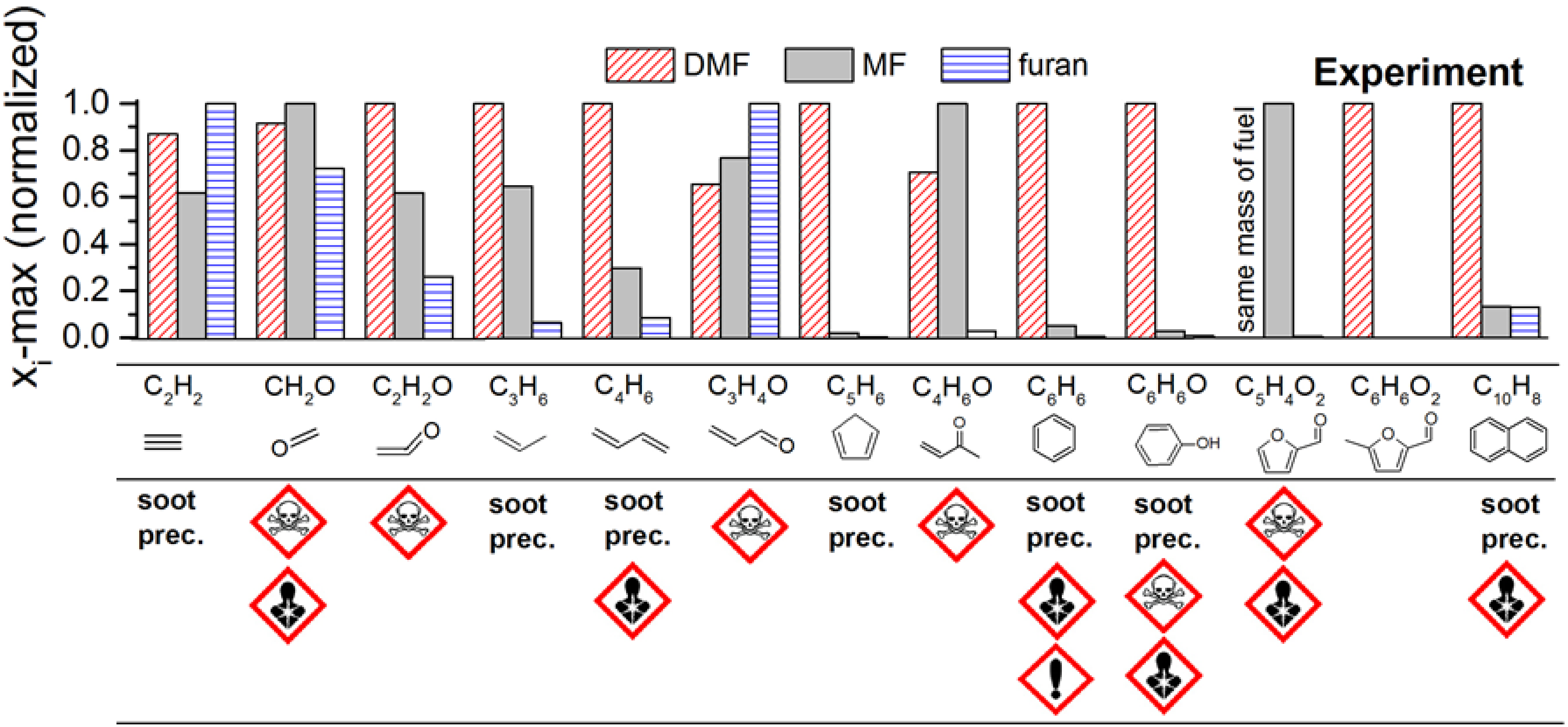
- ϕ=0.5, 1.0, 2.0

EI-MBMS: Electron Ionization Molecular-Beam Mass Spectrometry

Ref: [Tran et al. Combustion and Flame 2017]

Example 2: Furanic biofuels

Several toxic species and soot precursors are formed.

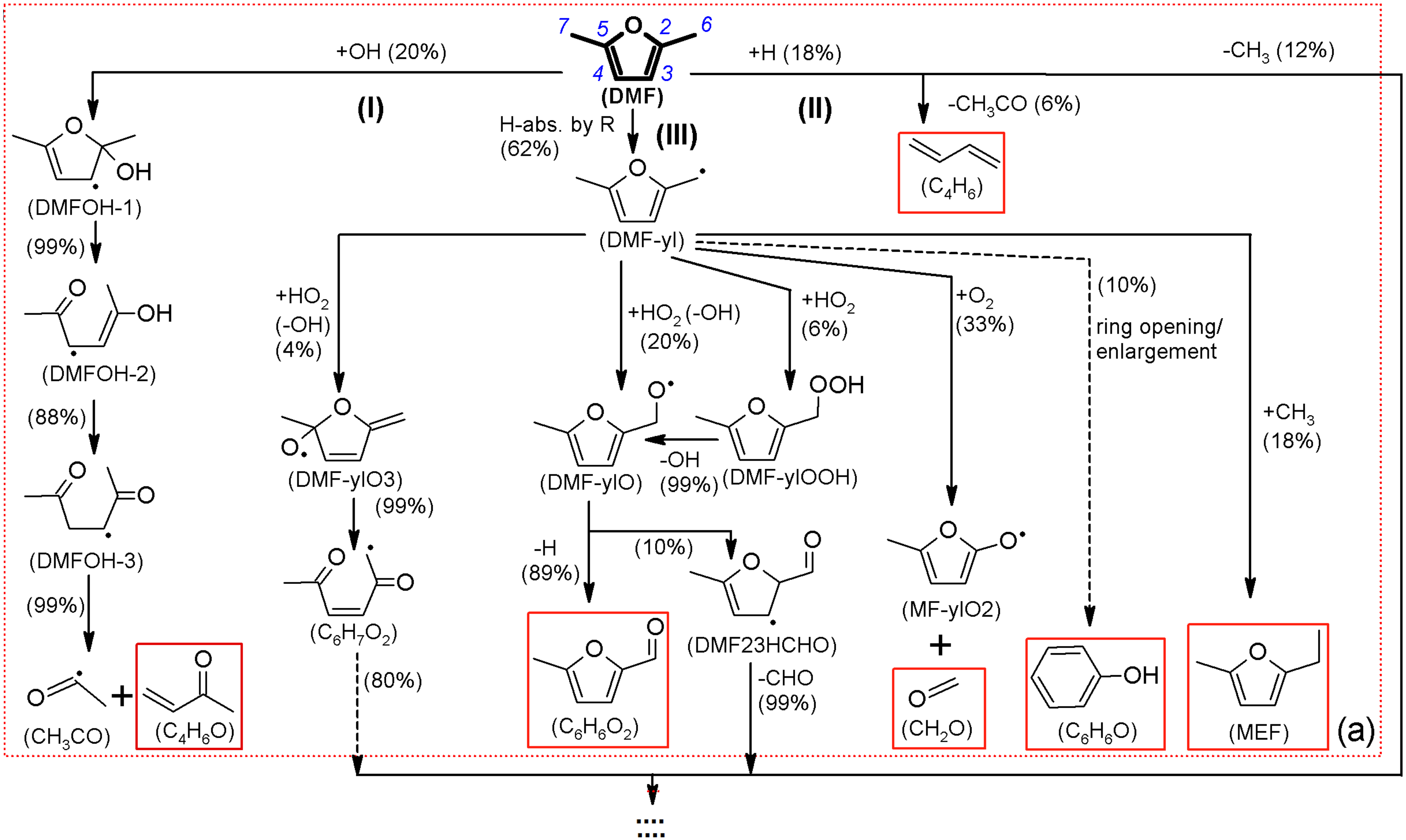


A detailed kinetic model (524 species, 3145 reactions) was developed to predict the consumption of these biofuels and the formation of pollutants.

Ref: [Tran et al. Combustion and Flame 2017]

Example 2: Furanic biofuels

Consumption paths of DMF (based on our kinetic model) at 900-950 K, 0-10% fuel conversion



Refs: Low T sub-model [Tran et al. Combust. Flame 2017],
High T sub-model [Sirjean et al J. Phys. Chem. A 2013] [Togbé et al. Combust. Flame 2014]

Impact of the oxygenated function of biofuels on the formation of soot precursors in premixed flames

Diethylether (DEE) $C_4H_{10}O$

- Cetane number: ~125 (45 for diesel)
- Heating value: ~34 MJ/kg (~28: Dimethyl ether (DME), ~43: diesel)

[Rakopoulos et al. J Energy Eng. 2015]

n-Butane C_4H_{10}

Soot precursors ?

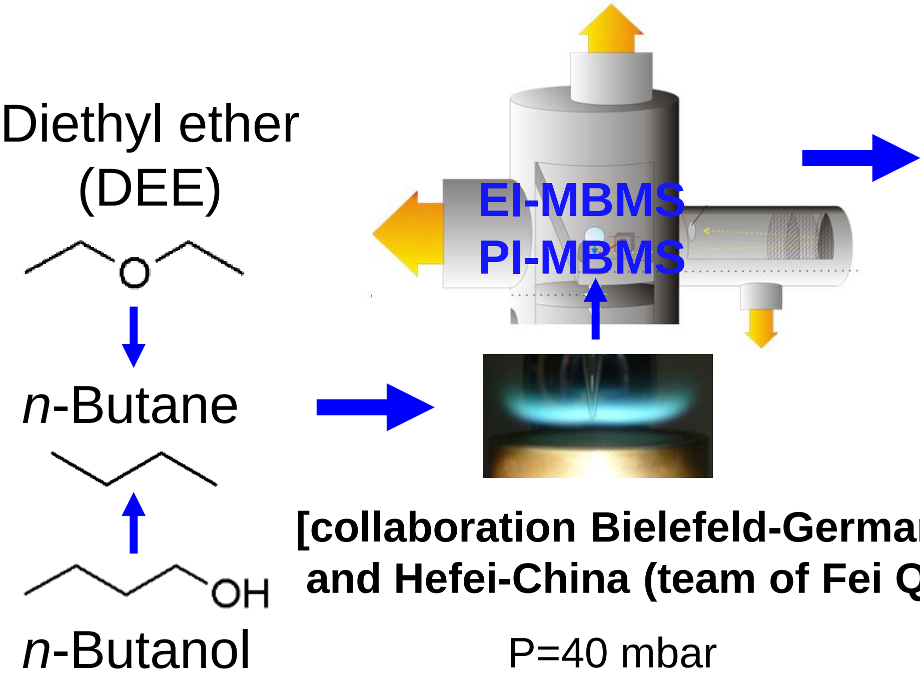
n-Butanol $C_4H_{10}O$

- Cetane number: ~25
- Heating value: ~33 MJ/kg

Ref: [Tran et al. Combustion and Flame 2016]

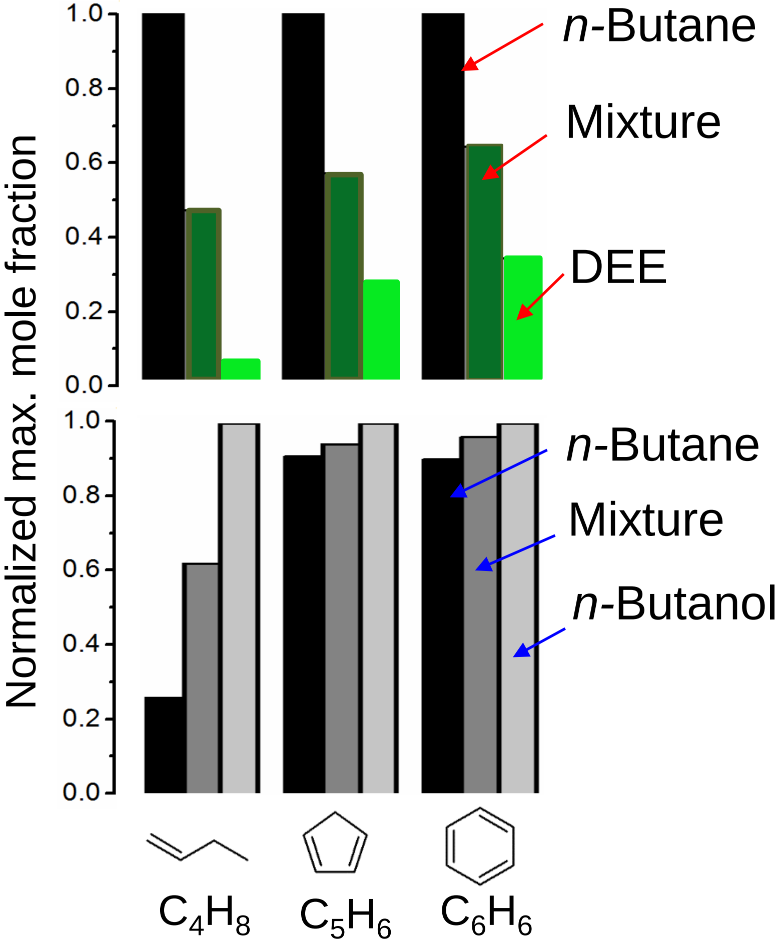
Example 3: Acyclic biofuels

Impact of the oxygenated function of biofuels on "small" soot precursors in premixed flames



[collaboration Bielefeld-Germany and Hefei-China (team of Fei Qi)]

P=40 mbar
Phi=1.7-1.8
C/O=0.52



The structure of biofuel influences strongly the formation of soot precursors

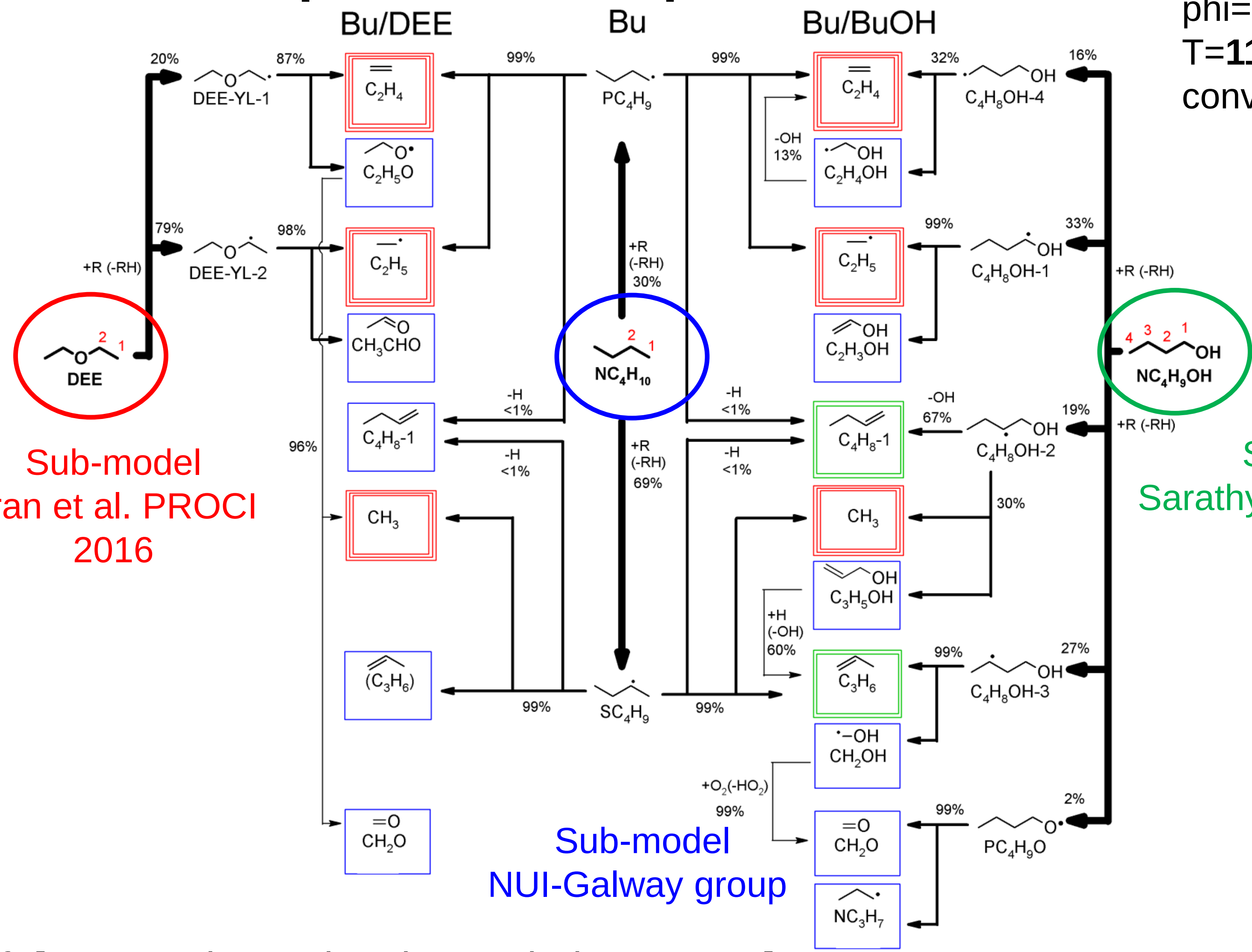
EI-MBMS: Electron Ionization Molecular-Beam Mass Spectrometry
PI-MBMS: PhotoIonization Molecular-Beam Mass Spectrometry

Ref: [Tran et al. Combustion and Flame 2016]

Example 3: Acyclic biofuels

STRONG impact of the oxygenated function of biofuels on “small” soot precursors in premixed flames

phi=1, P=40mbar, T=**1100K**, à un taux de conversion 78%



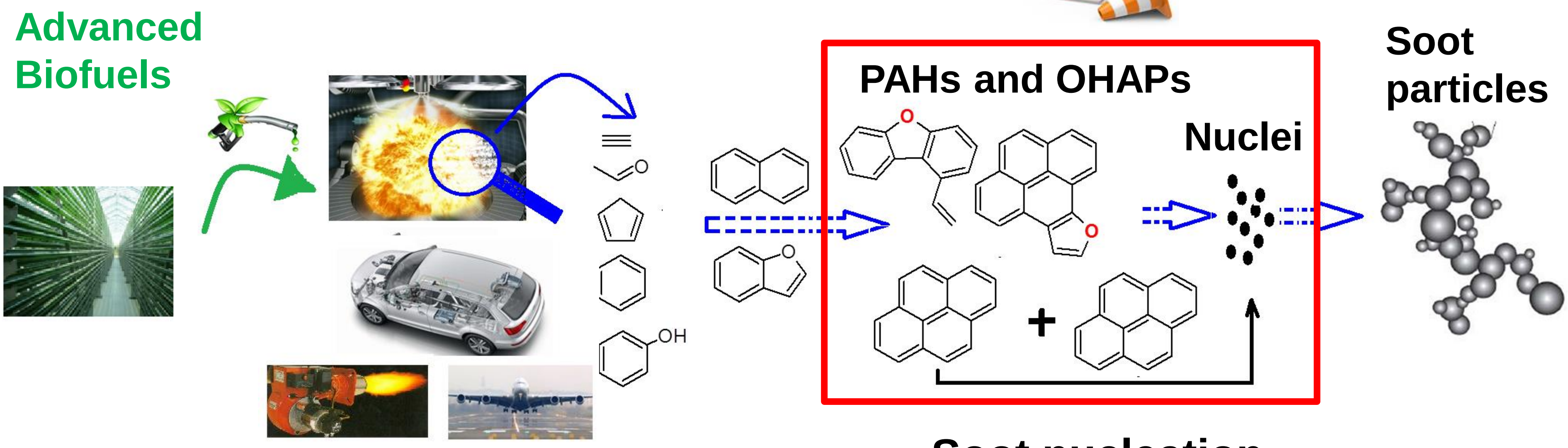
Ref: [Tran et al. Combustion and Flame 2016]

One of perspectives

Impact of the combustion of biofuels on “heavy” soot precursors (PAHs*, OPAHs*) in the soot nucleation process.

=> Very important but very poorly known.

Open for national and international collaborations.



Soot nucleation
(Central step of the soot formation process)

** PAH: Polycyclic Aromatic Hydrocarbons*
** OPAHs: Oxyganated Polycyclic Aromatic Hydrocarbons*

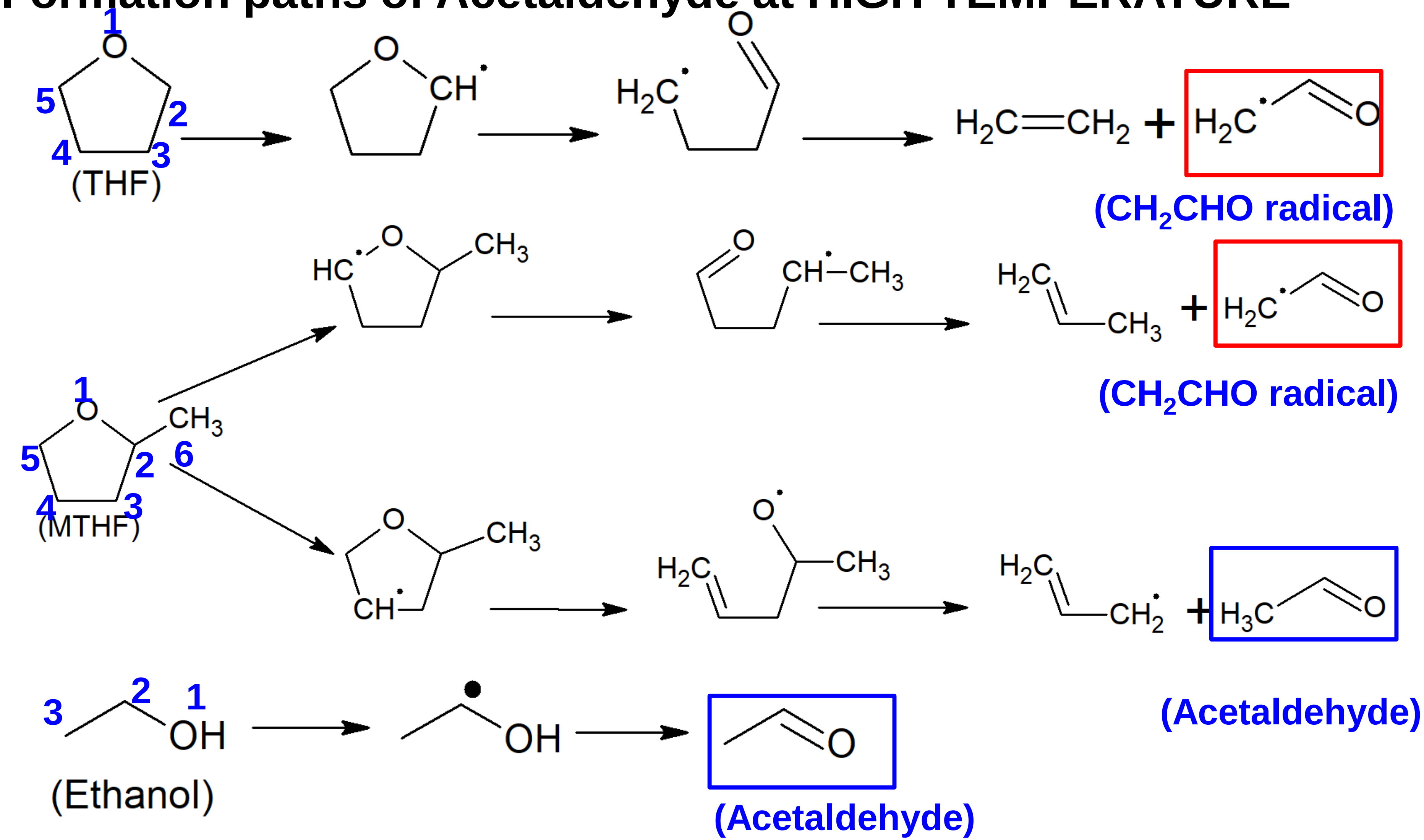
Thank you for your attention

Contributors to the presented studies:

Funding:

Example 1: Tetrahydrofuranic biofuels

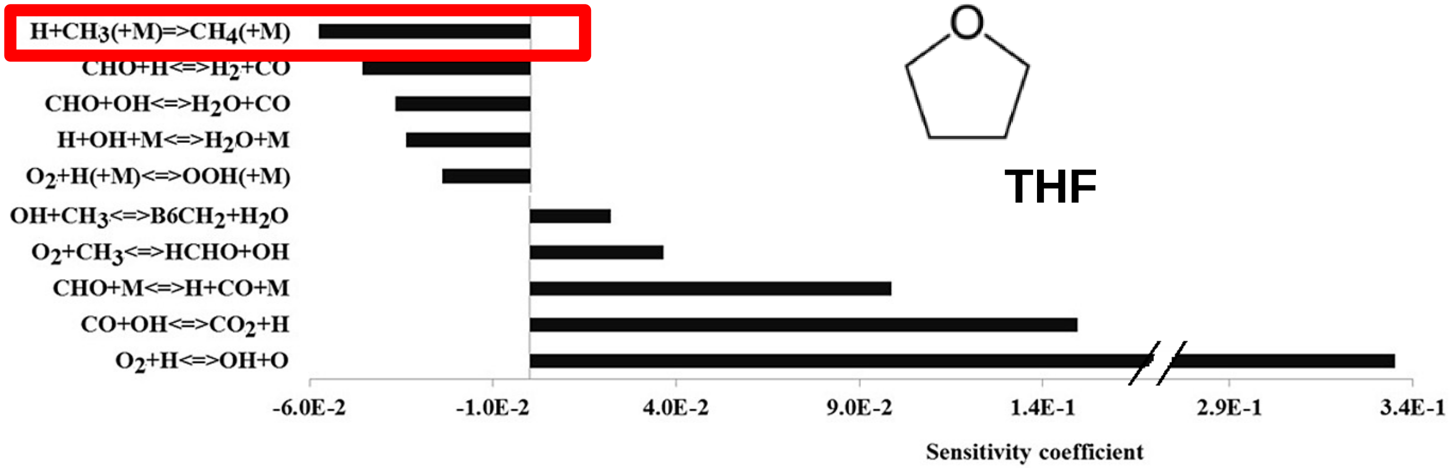
Formation paths of Acetaldehyde at HIGH TEMPERATURE



The structure of biofuel influences strongly the formation of aldehydes

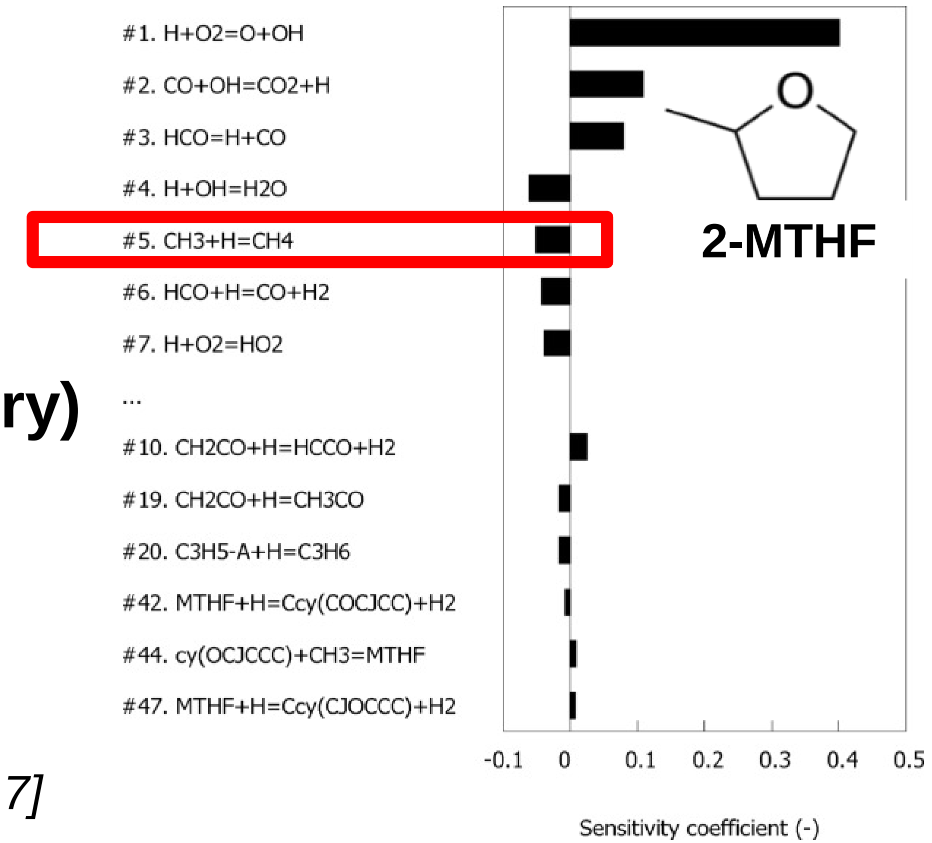
Ref: [Tran et al. The 8th U.S. National Combustion Meeting 2013]

Example 1: Tetrahydrofuranic biofuels



Ref: [Tran et al. CnF 2015]

Flame speeds (HIGH TEMPERATURE chemistry)



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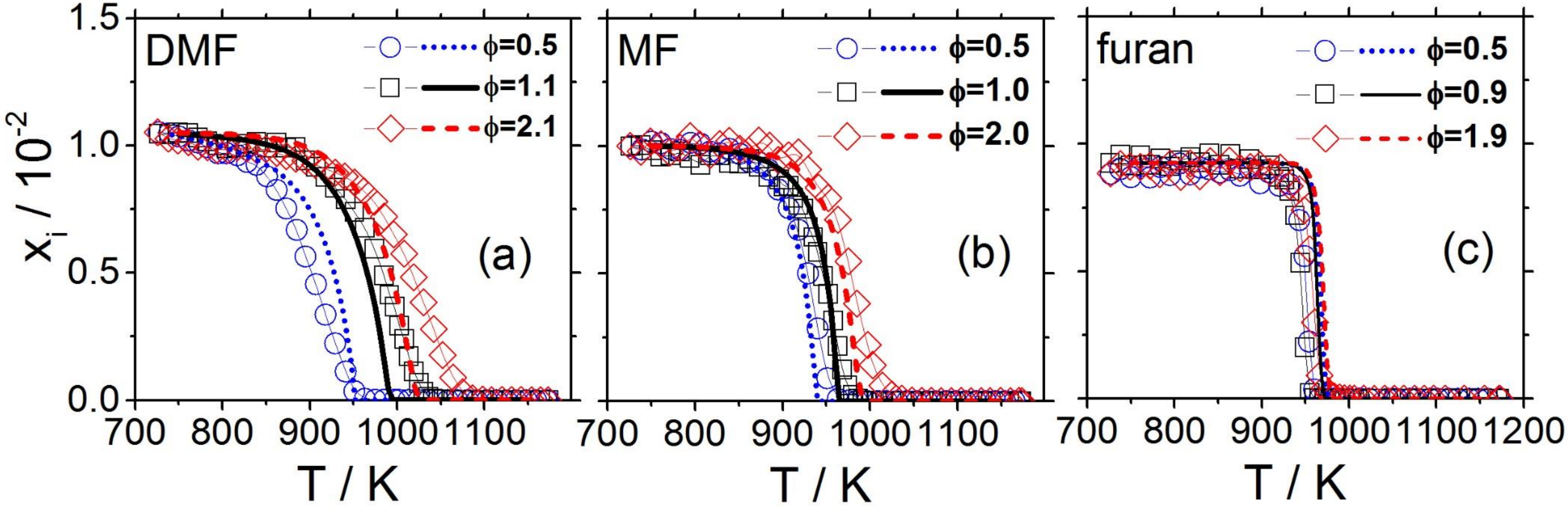
Example 2: Furanic biofuels



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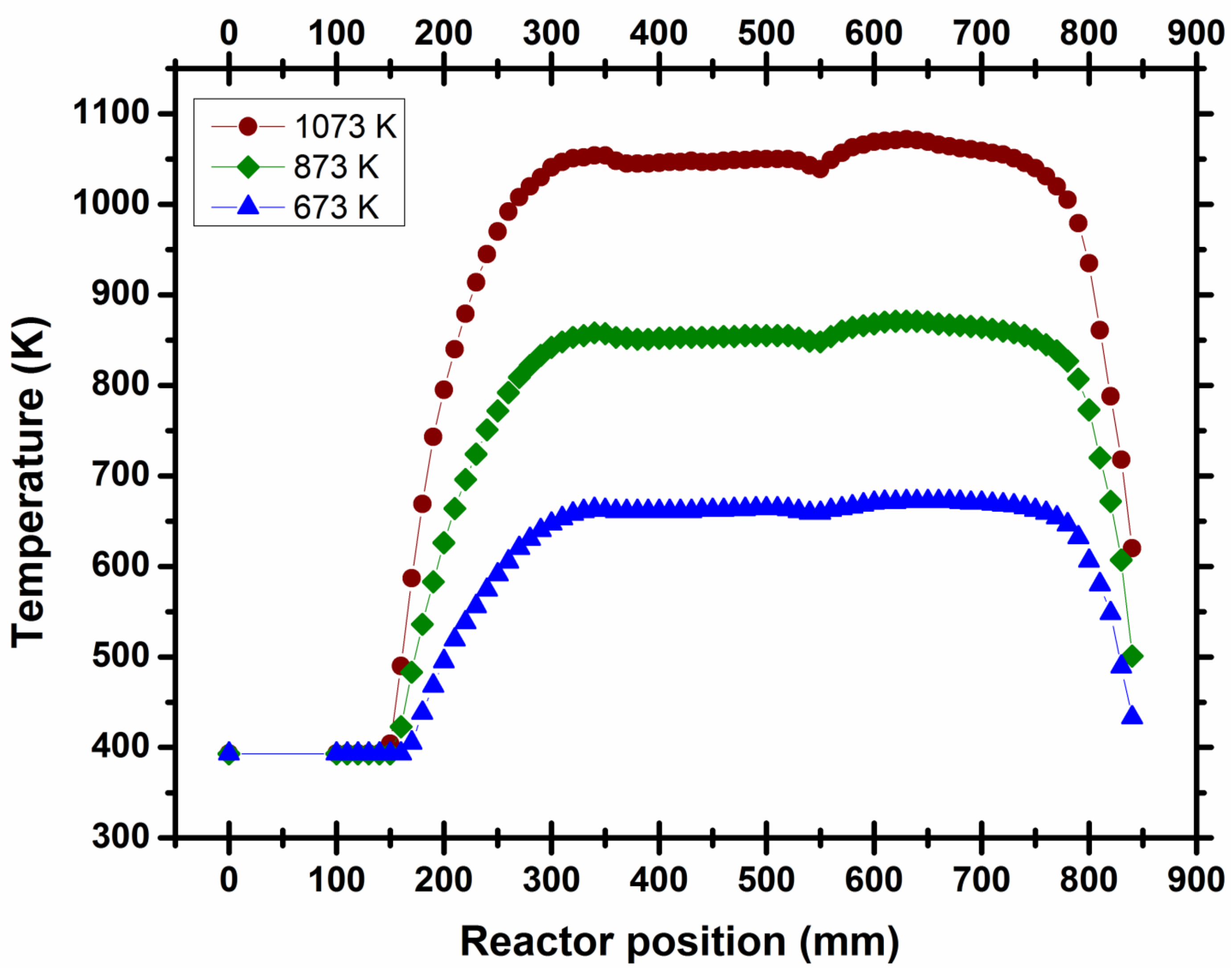
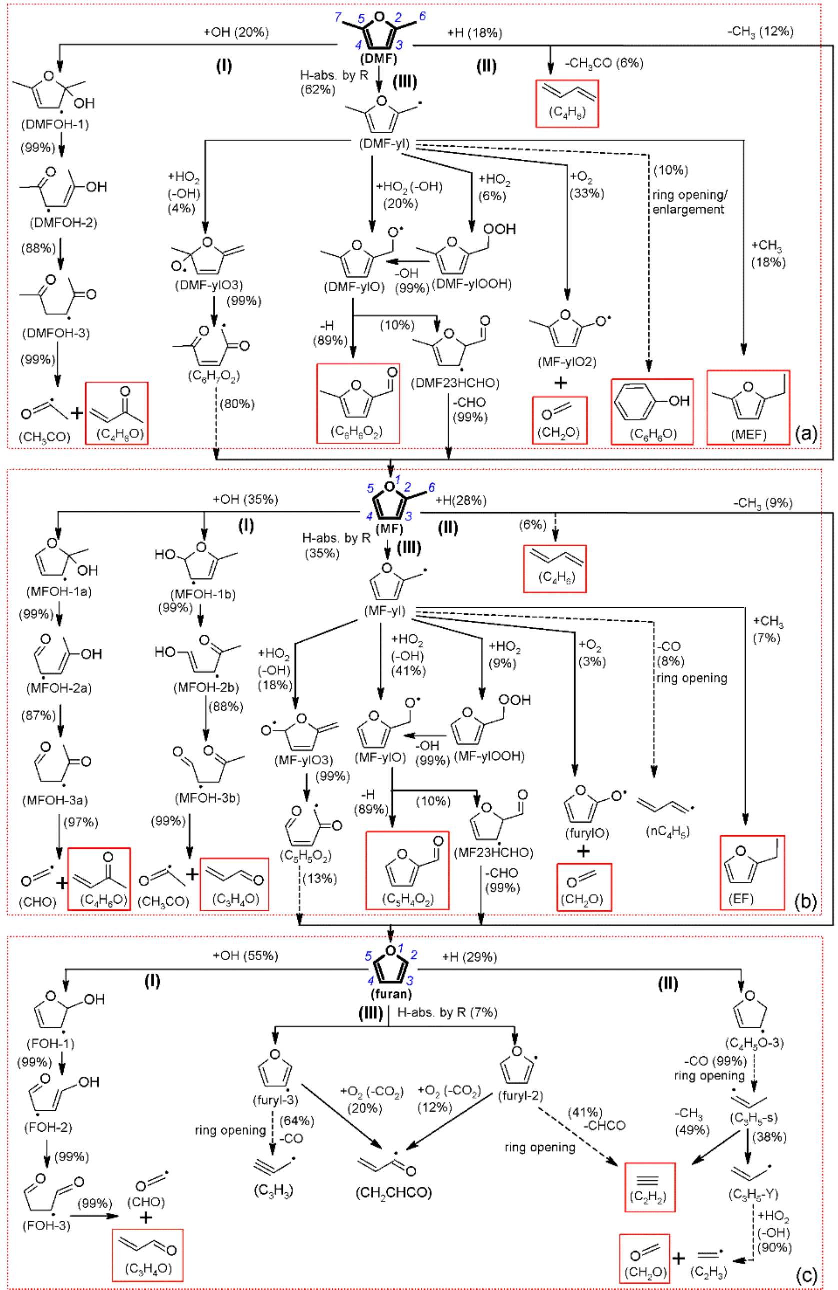


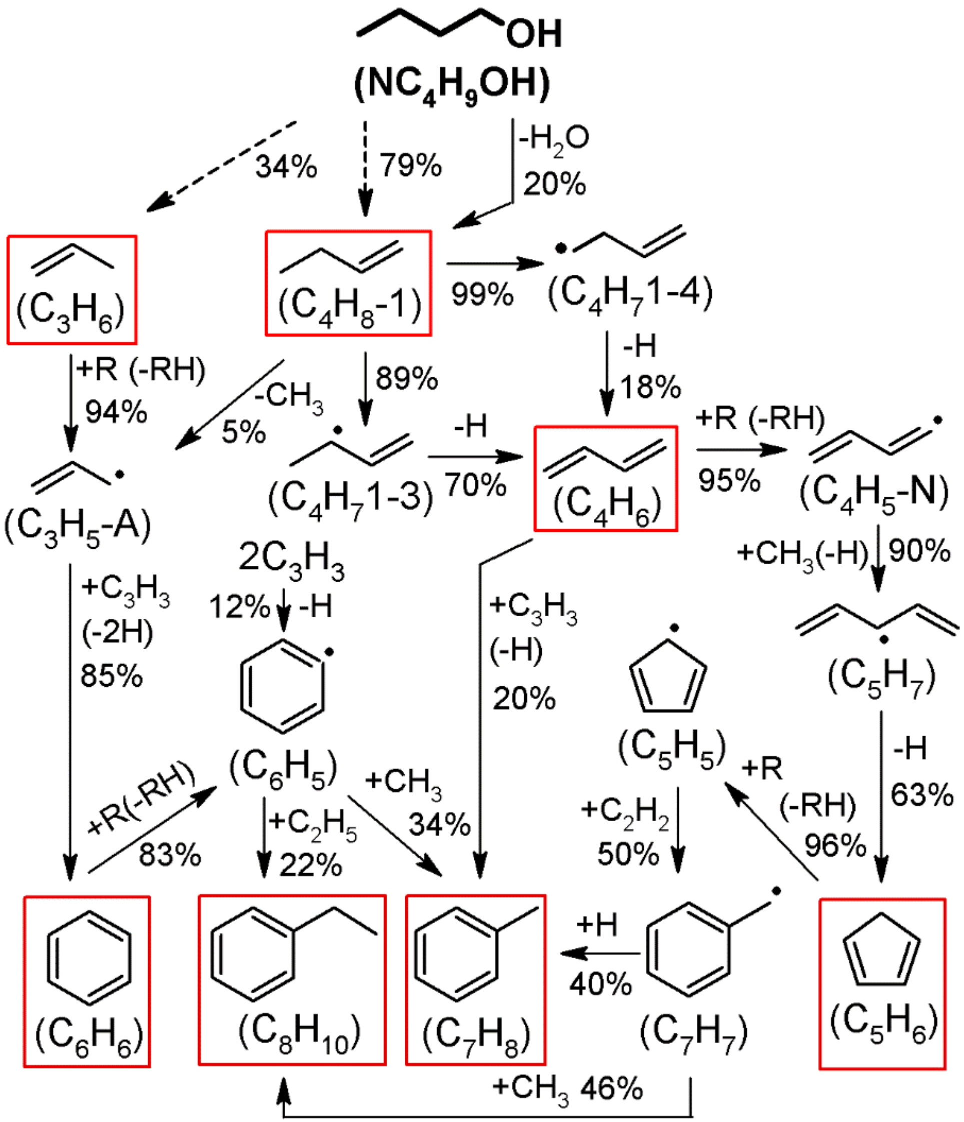
Ref: [Tran et al. Combustion and Flame 2017]

Example 2: Furanic biofuels



Example 3: Acyclic biofuels

Impact on soot precursors in premixed flames



Ref: [Tran et al. Combustion and Flame 2016]