

# An experimental and theoretical study of cyclopentadiene-ethene co-pyrolysis: Growth of polycyclic aromatic hydrocarbons

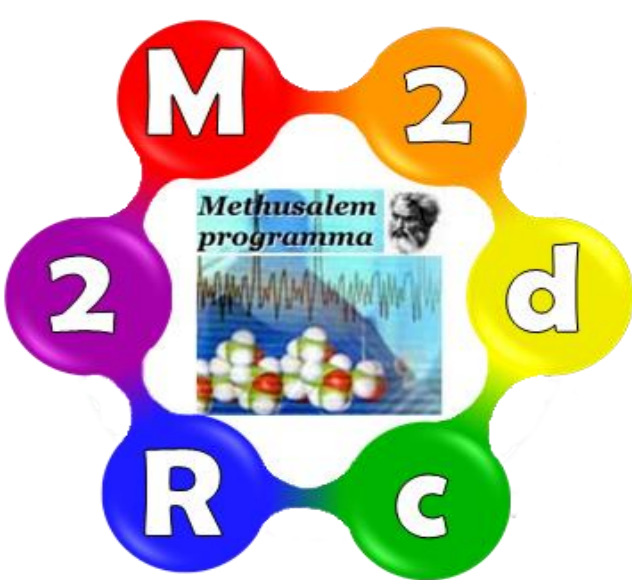
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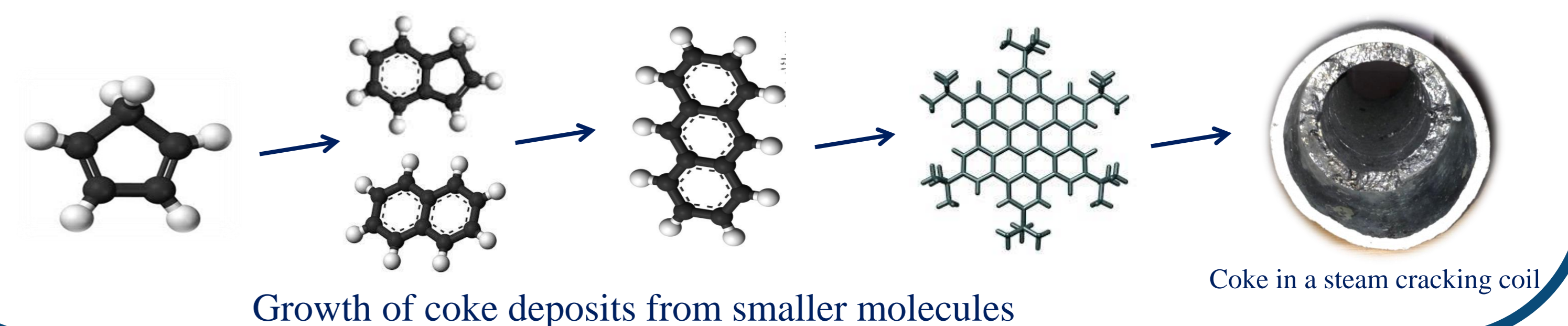


## Introduction

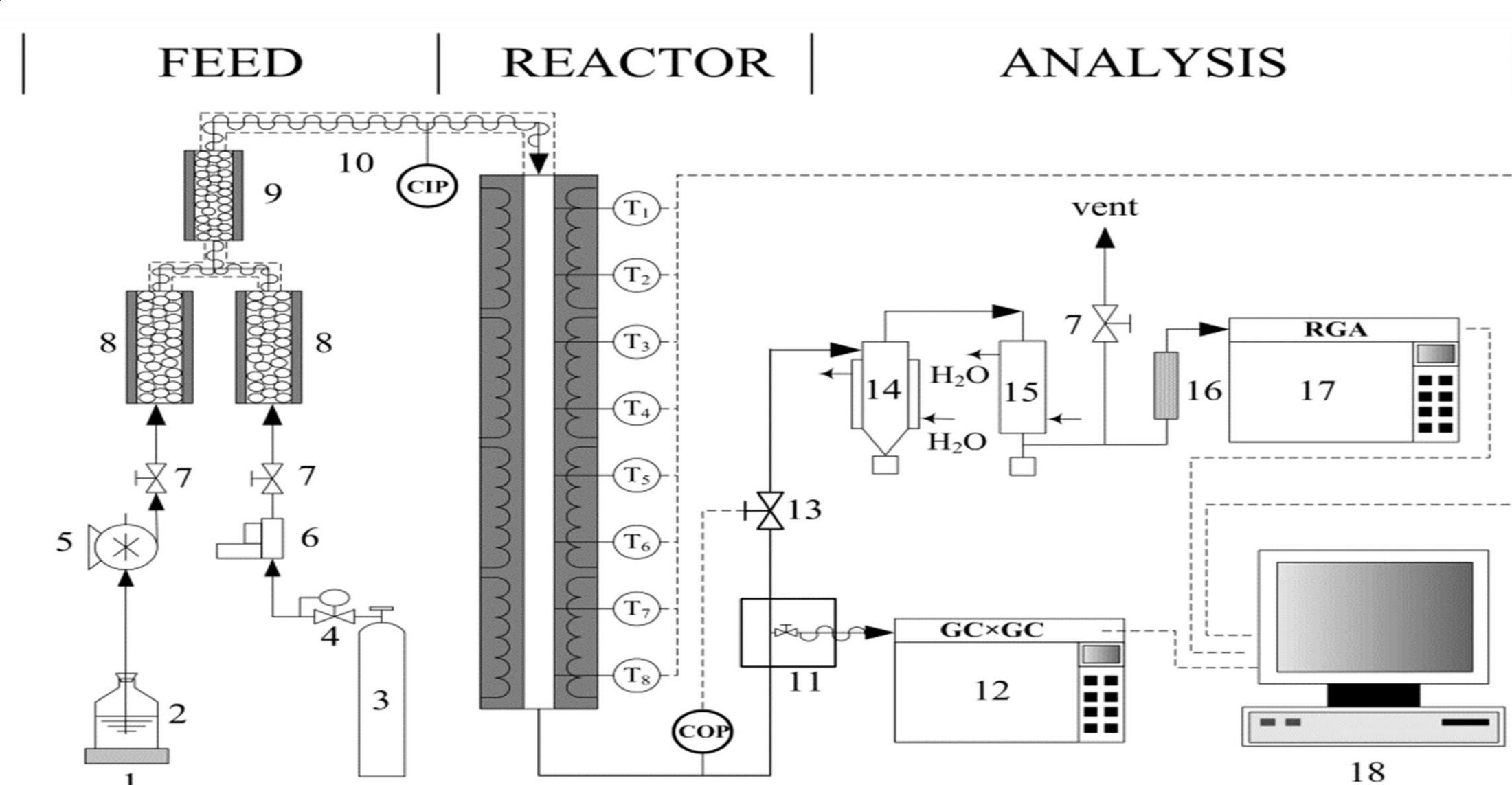
- Polycyclic aromatic hydrocarbons (PAHs) are a group of more than 100 chemicals that can be produced from various anthropogenic sources, such as the incomplete combustion of heating fuels, oil refining processes and the combustion of diesel fuels
- Many PAHs are known to be **carcinogenic** or **mutagenic** and important precursors to **soot**, which has been linked to **human morbidity** and **global warming**
- Among many potential soot precursors' reactions those involving the cyclopentadiene (CPD) and its corresponding cyclopentadienyl (CPDyl) radical are considered to be one of the most important contributors to PAHs and soot formation

## Role of CPD and CPDyl

- The CPDyl radical is a resonance-stabilized, ambident, i.e. containing multiple reactive centers, radical that may undergo self-recombination reactions
- Due to its importance significant amount of experimental and theoretical data has been published on the gas phase chemistry involving CPDyl and CPD in the growth of PAHs
- This work deals both **experimentally** and **theoretically** with the growth of PAHs starting from CPD and CPDyl



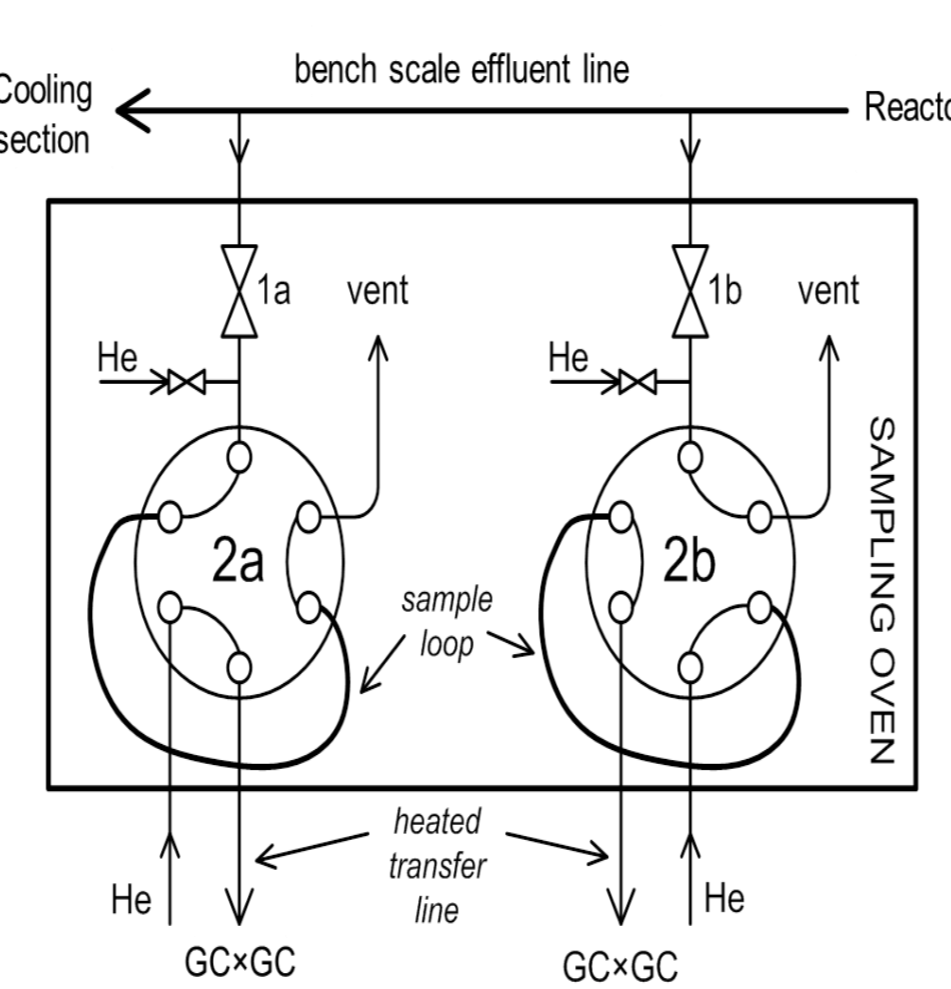
## Bench scale set-up for (steam) pyrolysis



Schematic diagram of the experimental set-up indicating process gas temperatures (Ti) and pressure measurements (CIP & COP) (1-electronic balance; 2-liquid feed reservoir (DCPD); 3-gaseous diluent/internal standard (nitrogen/ethene); 4-pressure reducing valve; 5-coriolis flow meter controlled pump; 6-coriolis mass flow controller; 7-valve; 8-evaporator/heater; 9-mixer; 10-heater; 11-heated sampling oven; 12-GC×GC-FID/TOF-MS for C5+; 13-outlet pressure restriction valve; 14-cyclone separator; 15-condenser; 16-dehydrator; 17-Refinery Gas Analyzer (RGA) for C4-; 18-data acquisition system)

•Djokic et al. *Combust. Flame.* 2014

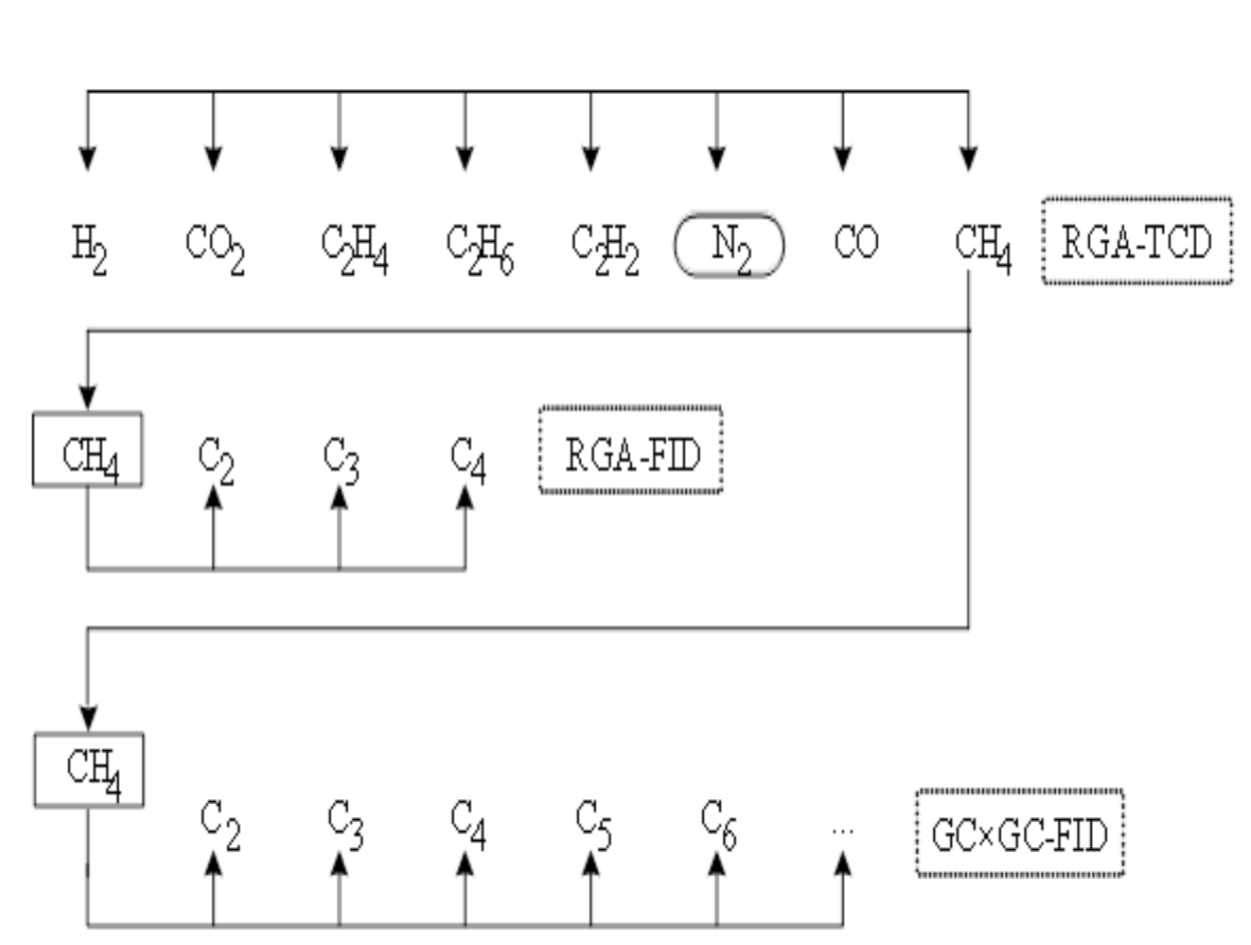
### 11: On-line effluent sampling



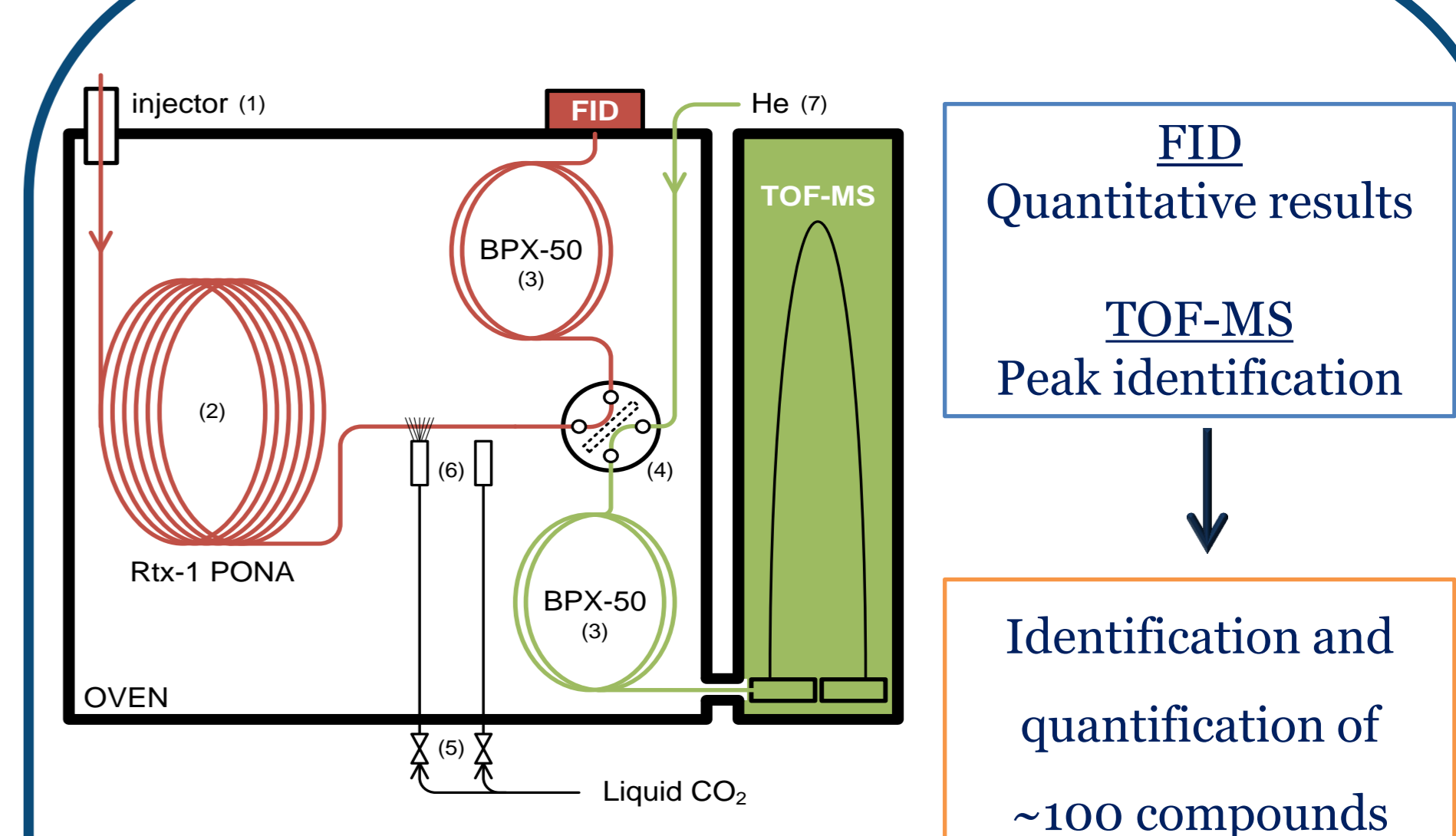
Experimental conditions:

- Co-pyrolysis of CPD-ethene mixture
  - ✓ A tubular continuous flow reactor (Incoloy 800HT; 1.5 m L.; 6 mm I.D.)
  - ✓  $T_{\text{reactor}} = 873 - 1163 \text{ K}$ , nearly **isothermal**, COP=1.7 bara,
- Nitrogen was used as a diluent and primary **Internal standard**
  - ✓ **Dilution** of 1 mol CPD/ 1 mol C<sub>2</sub>H<sub>4</sub>/ 10 mol N<sub>2</sub>, F<sub>0,CPD</sub>=13.6 mg/s
  - ✓ **Argon** was used as additional (as a double-check) internal standard
- On-line sampling of the effluent using **heated transfer lines (573 K)**
  - ✓ Dedicated analysis section: GC×GC-FID/TOF-MS + RGA(FID, TCD)

### Use of reference components in the product analysis section (RGA, GC×GC)



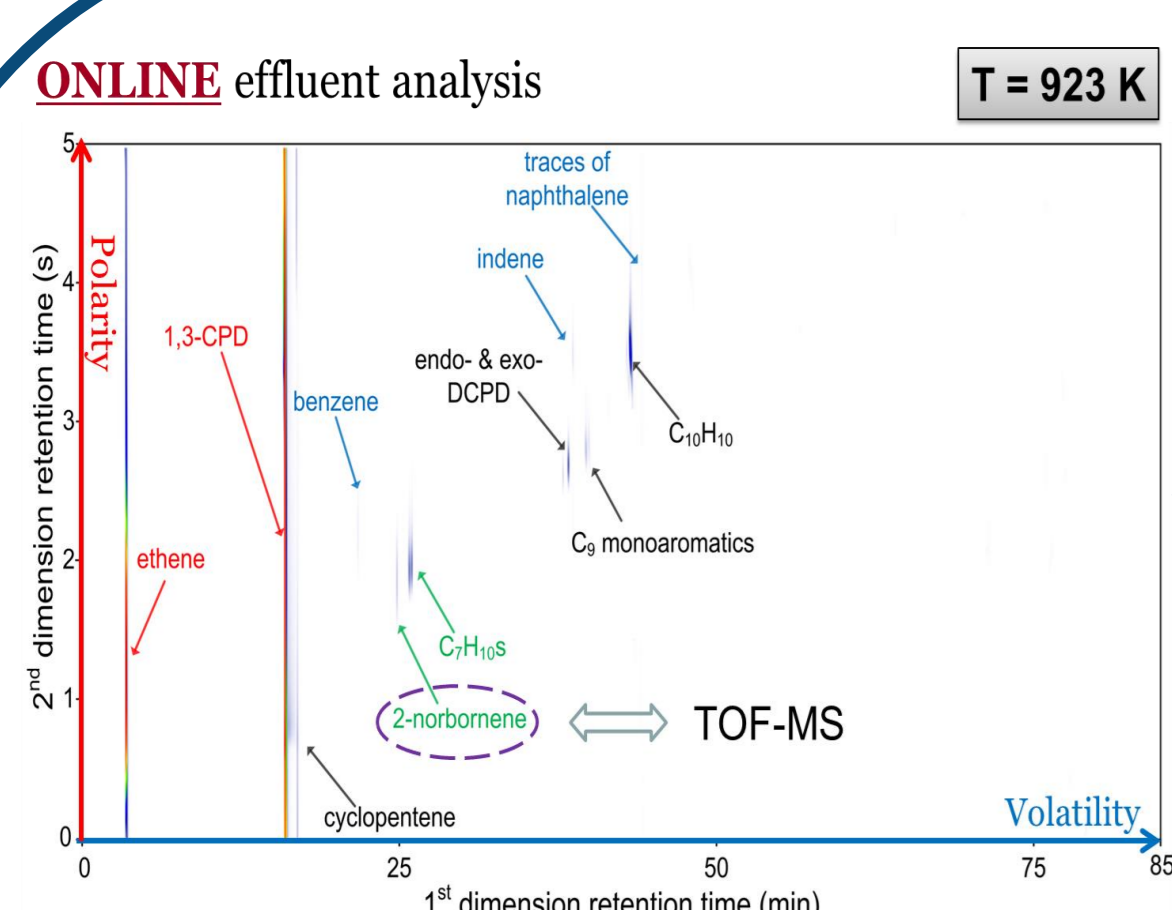
### GC×GC-FID/TOF-MS



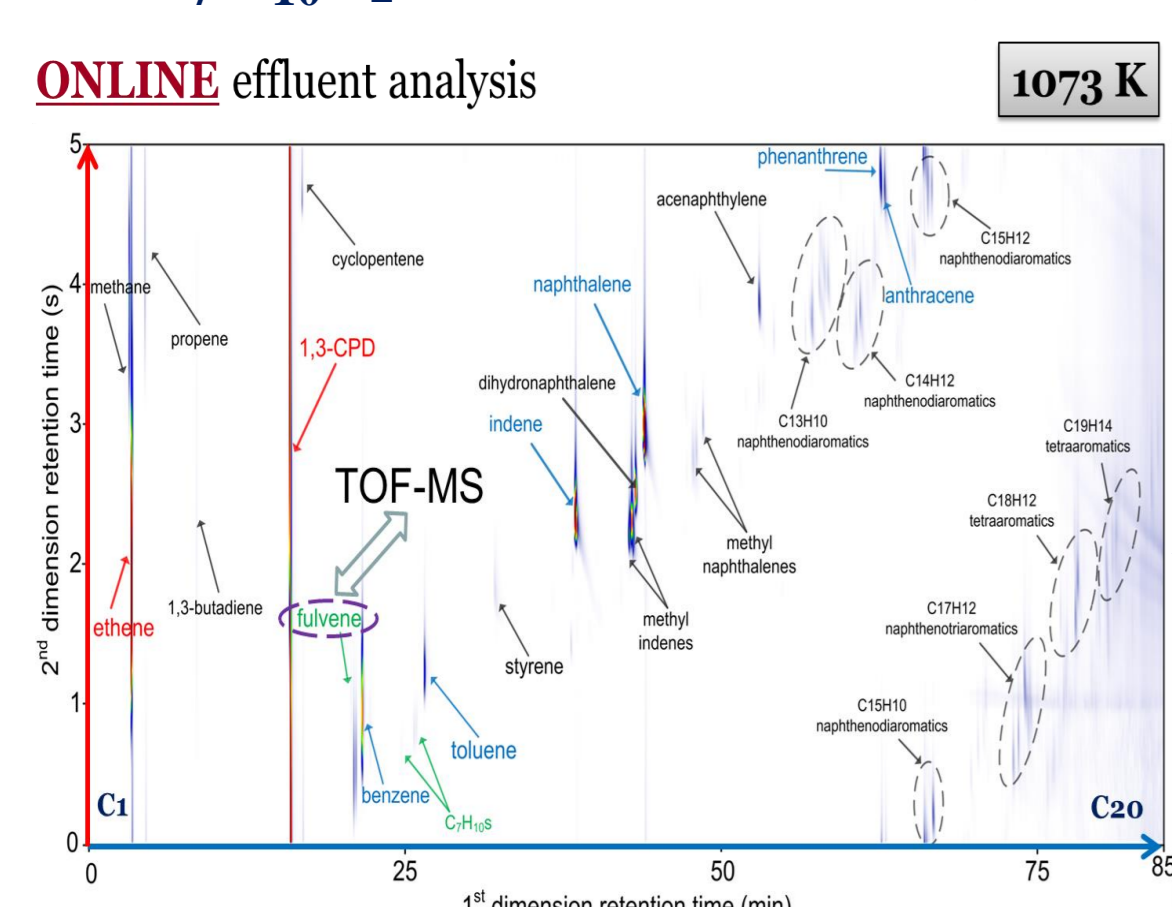
TOF-MS		
Sampling rate	30 Hz	• Thermo Scientific TRACE GC×GC (FID)
EI	70 eV	• Thermo Scientific Tempus TOF-MS
T <sub>source</sub>	473 K	

•Van Geem, Pyl, et al. *J. Chromatogr. A.* 2010

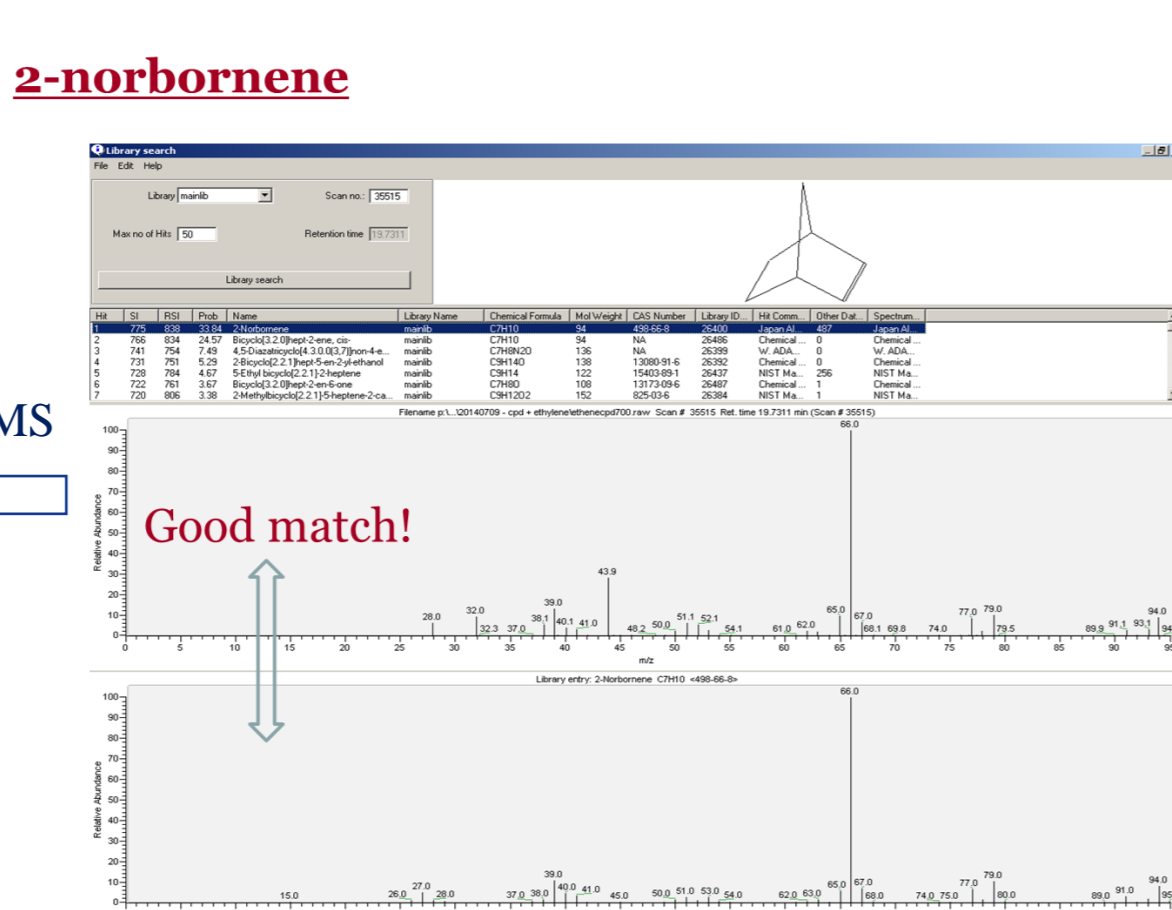
## Experimental and Kinetic Modeling Results



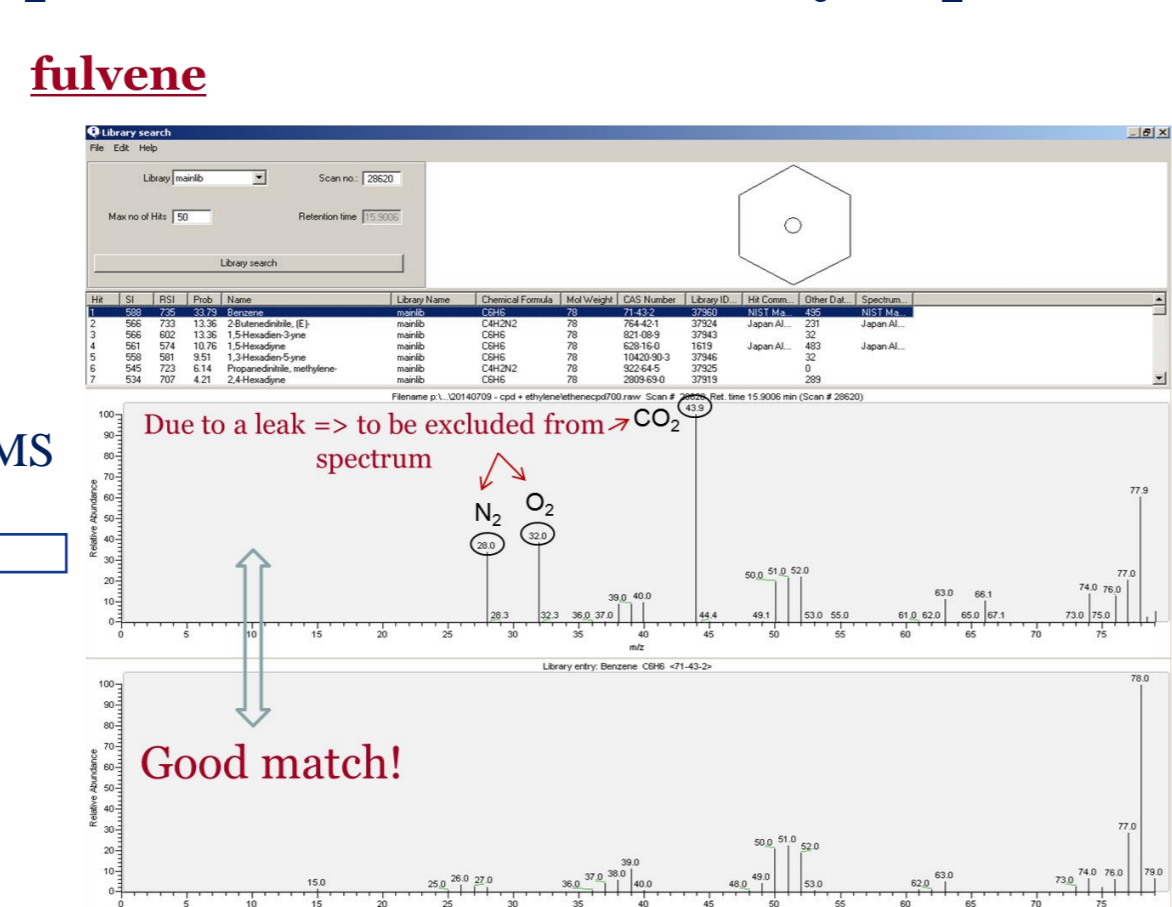
- A **very complex** product spectrum strongly depending on the temperature
- At **923 K** only limited number of pyrolysis products can be detected such as C<sub>7</sub>H<sub>10</sub> species, norbornene, indene, naphthalene, benzene and cyclopentene



- At **1073 K** the reactor effluent is significantly more complex, containing on the order of up to **hundred different compounds** at the highest temperature
- At the most severe conditions, **92% of CPD** is converted yielding almost **44 wt%** of PAHs with a carbon number up to C<sub>20</sub>

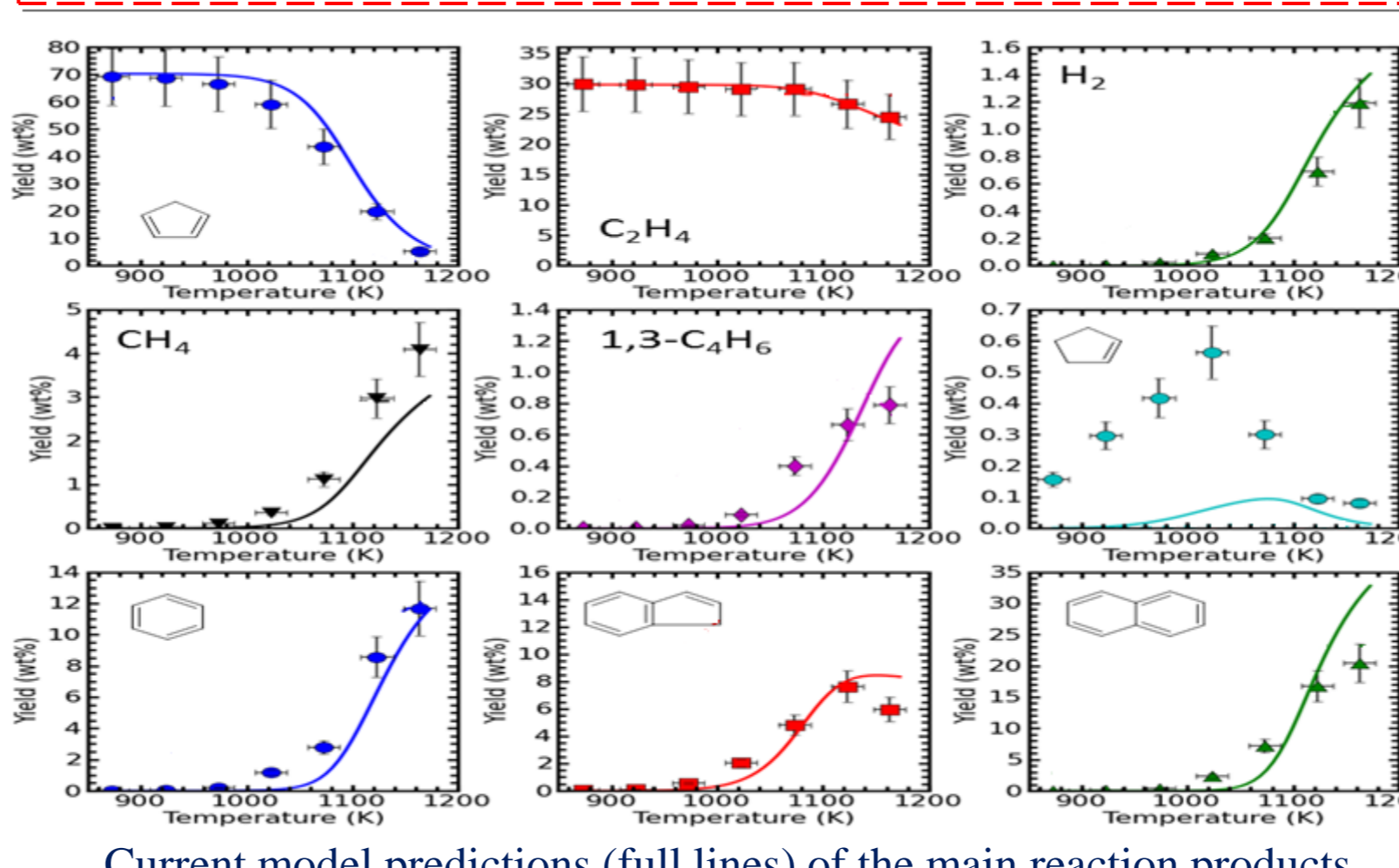


Due to a leak => to be excluded from -CO<sub>2</sub> spectrum



Summary of the measured product yields at the reactor outlet

Conditions	873	923	973	1023	1073	1123	1163
Temperature (K)	873	923	973	1023	1073	1123	1163
CPD flow rate (g/h)	49	49	49	49	49	49	49
Ethene flow rate (g/h)	21	21	21	21	21	21	21
N <sub>2</sub> flow rate (g/h)	206	206	206	206	206	206	206
CPD Conversion (%)	1.2	1.8	5.0	15.6	37.8	71.6	92.4
Yield (wt%)							
<b>Permanent gases</b>							
H <sub>2</sub>	0.00	0.01	0.02	0.09	0.20	0.69	1.19
CH <sub>4</sub>	0.00	0.02	0.11	0.36	1.13	2.97	4.09
<b>Alkenes</b>							
Ethene	29.92	29.81	29.50	29.08	29.14	26.61	24.50
Cyclopentadiene	69.16	68.76	66.47	59.09	43.57	19.88	5.35
<b>Aromatics</b>							
Benzene	0.01	0.03	0.21	1.16	2.77	8.56	11.68
Toluene	0.02	0.00	0.03	0.18	0.43	1.98	3.74
Styrene	0.00	0.00	0.01	0.00	0.17	0.92	2.43
Indene	0.03	0.08	0.56	2.03	4.82	7.63	5.95
Naphthalene	0.05	0.09	0.40	2.33	7.19	16.74	20.44
Phenanthrene	0.00	0.00	0.00	0.44	1.29	1.29	1.39
Anthracene	0.00	0.00	0.00	0.03	0.37	0.81	2.35
<b>Total PAHs</b>	<b>0.48</b>	<b>0.77</b>	<b>2.47</b>	<b>7.82</b>	<b>20.36</b>	<b>35.18</b>	<b>43.55</b>



## Kinetic Modeling

- A **single-event** microkinetic model was generated using an automated reaction network generator, **RMG**
- Parameters requiring refinement are identified through **sensitivity analysis**
- No fitting** of the parameters to the experimental data
- Individual reactions are subjected to an increased level of theoretical analysis
- Thermodynamics and kinetic data of sensitive species and reactions were calculated using quantum chemistry calculations at the **CBS-QB3** level using Gaussian 03

## Conclusions

- Dedicated **GC×GC** setup combining **FID** and **TOF-MS**
- Implemented in an **on-line** analysis section of a bench scale set-up for (steam) **co-pyrolysis of CPD/C<sub>2</sub>H<sub>4</sub>**
- Detection of **PAHs** up to carbon number **C<sub>20</sub>**
- Excellent agreement between **experiments** and **theory**

## Acknowledgment

- The work at the LCT was supported by the 'Long Term Structural Methusalem Funding by the Flemish Government'
- The work at the MIT was supported by the Combustion Energy Frontier Research Center, funded by the U.S. Department of Energy, Office of Basic Energy Sciences under award number DE-SC0001198.