UNIVERSITEIT GENT

FACULTY OF ENGINEERING AND ARCHITECTURE

Detailed experimental and kinetic modeling study of cyclopentadiene pyrolysis and the effect of ethene as co-reactant

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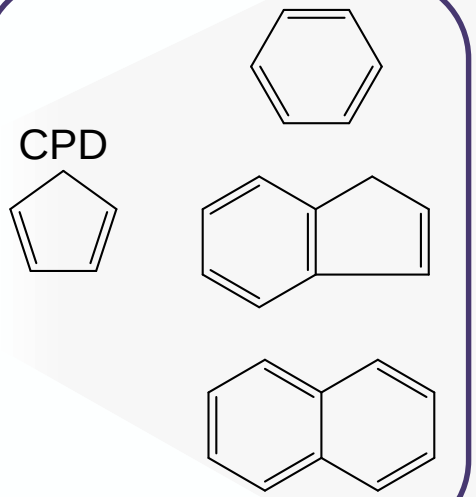
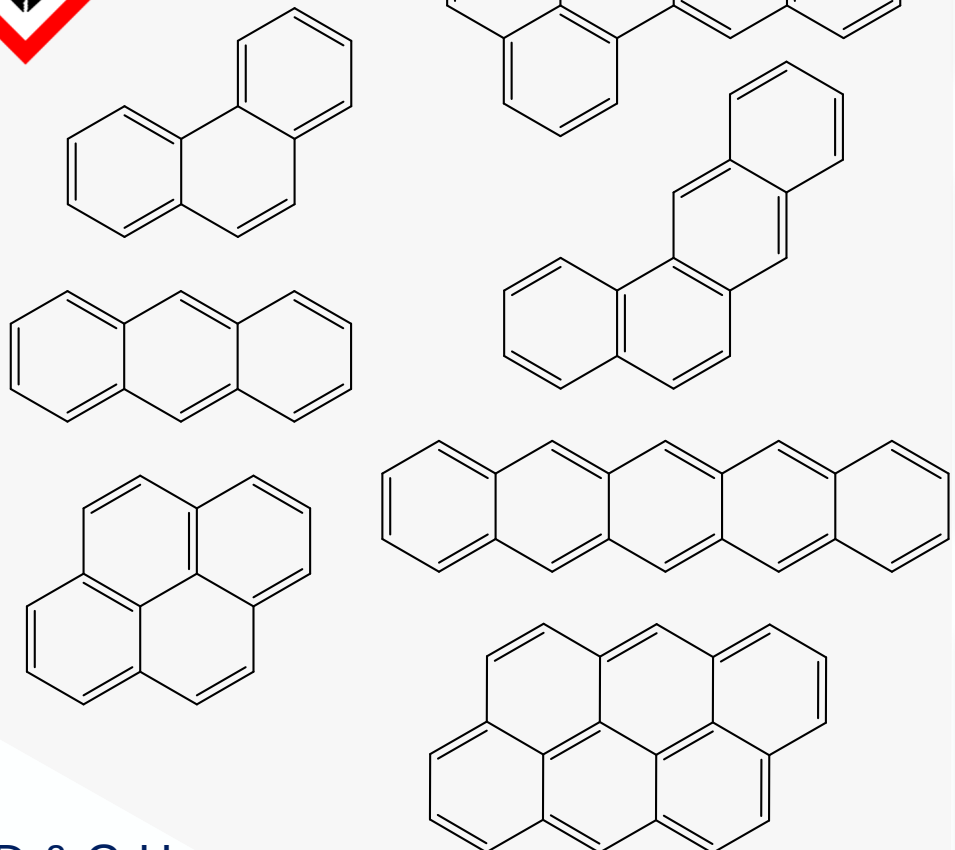
ERIC

Polycyclic aromatic hydrocarbons

Kinetic model

CPD





Validation

Pyrolysis CPD*

Co-pyrolysis CPD & C_2H_4

*Djokic, M. R.; Van Geem, K. M.; Cavallotti, C.; Frassoldati, A.; Ranzi, E.; Marin, G. B., Combustion and Flame, 161 (11), 2739-2751 (2014).

Steam cracking

Endothermic

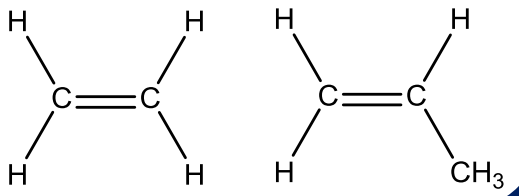
Temperature: 700 – 900 °C

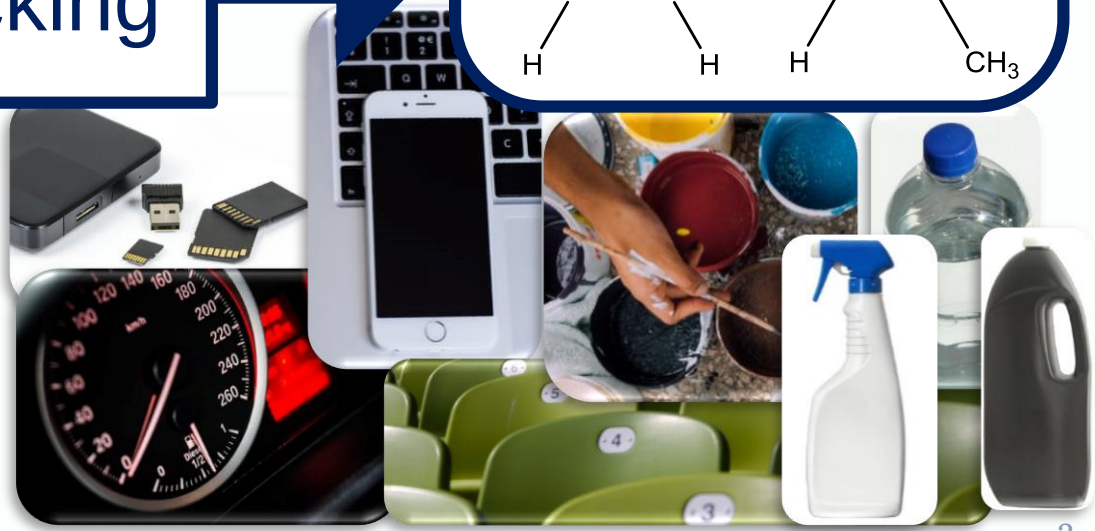
Residence time: 0.1 – 0.5 s

1.5 10^6 t/a ethene per plant

Steam Cracking

Base Chemicals





H. Zimmermann and R. Walzl, "Ethylene," Ullmann's Encyclopedia of Industrial Chemistry, 2009.

Coke formation

- × Decreased thermal efficiency
- × Increased tube metal temperatures
- × Increased pressure drop
- × Decoking procedure

Estimated annual cost to industry: $ 2 billion

Optimization

- Feed additives
- Metallurgy & surface technology
- 3D reactor technology

} Need to understand and describe the formation of coke and its **precursors**

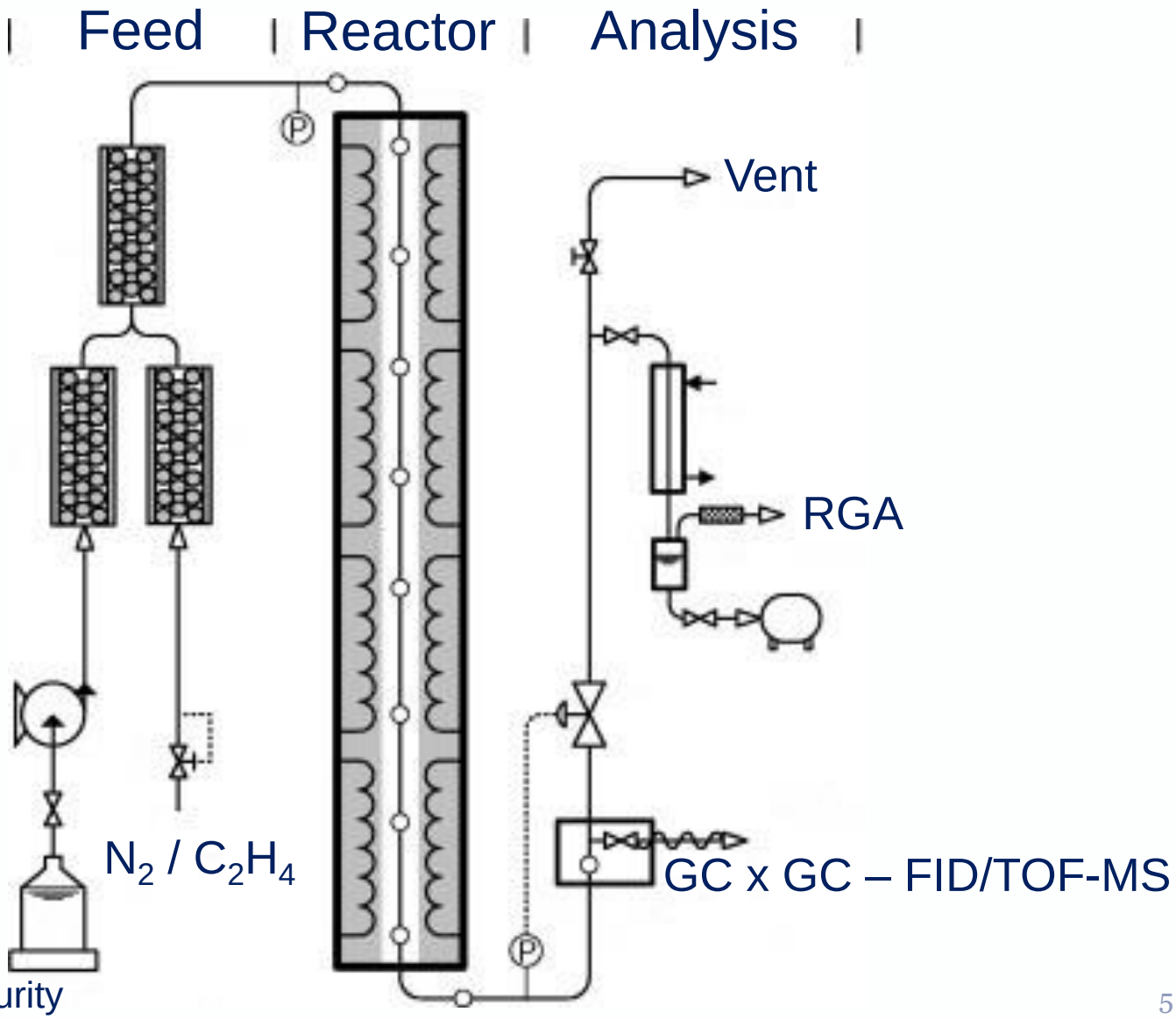
Kolmetz, K.; Kivlen, J.; Gray, J.; Sim, C.; Soyza, C. Refining Technology Conference, Dubai, 14-18 Dec, 2002.

Experimental setup

Temperature:
873 K – 1163 K

CPD conversion:
1.2 % - 92.4 %

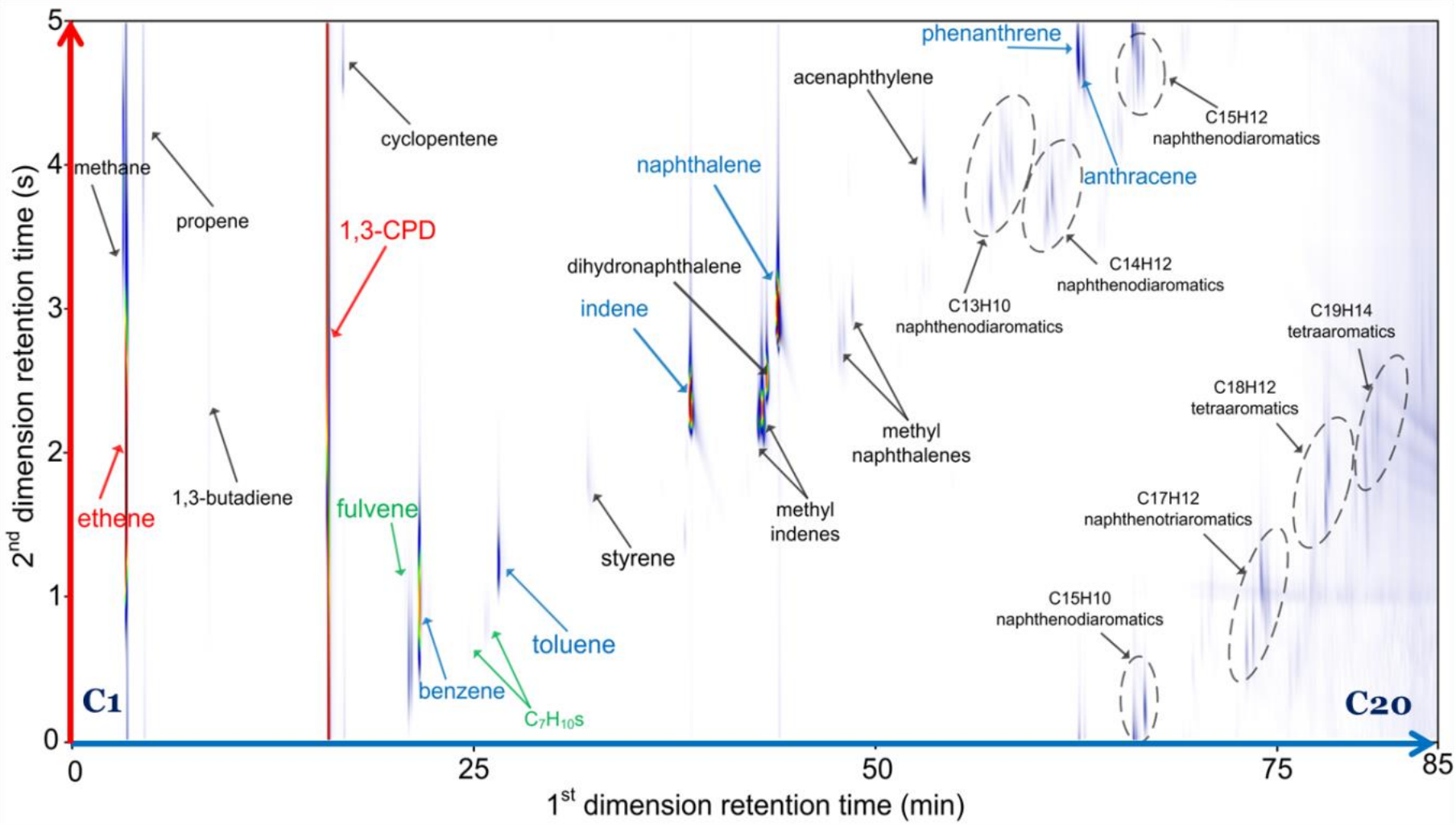
Flow rates:
$F_{0,CPD}$ = 13.6 mg/s
$F_{0,C2H4}$ = 5.8 mg/s
$F_{0,N2}$ = 57.2 mg/s



Product Analysis: GC x GC

ONLINE effluent analysis

1073 K

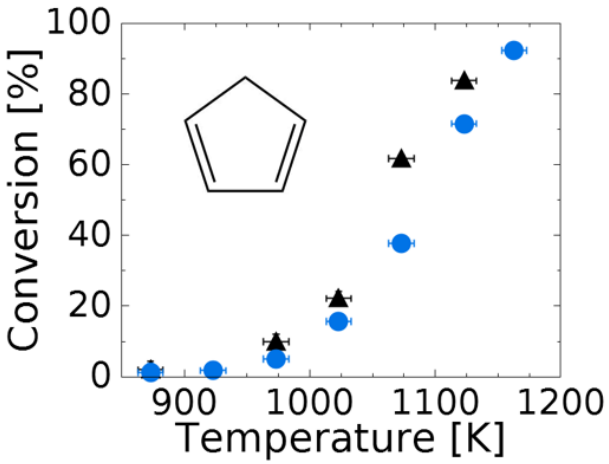


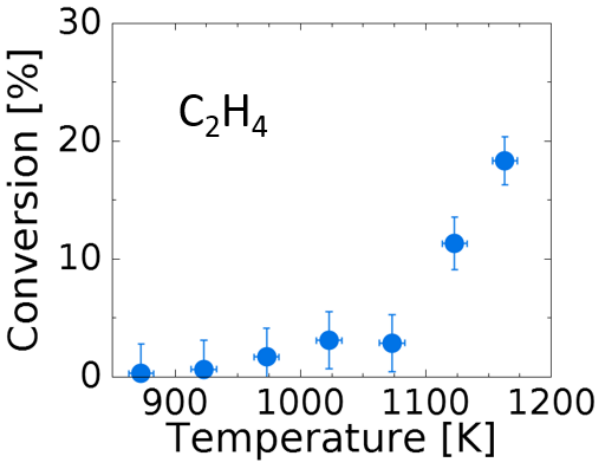
Experimental results

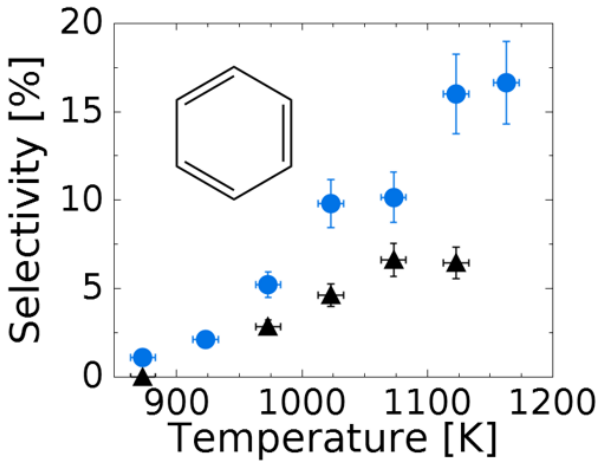
P = 1.7 bar

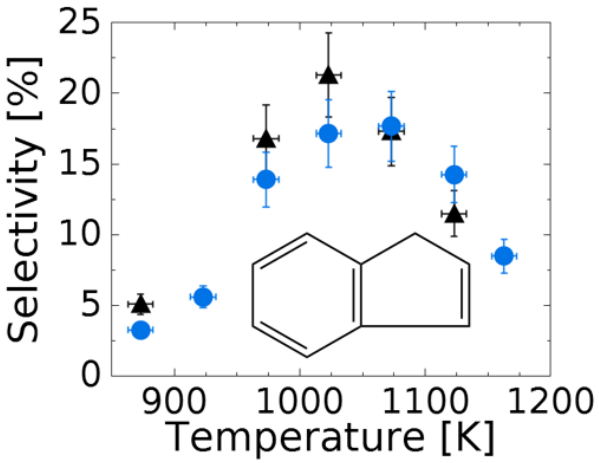
▲ Pyrolysis CPD*
$F_{0,CPD}$ = 27 mg/s
1 mol CPD / 5 mol N_2

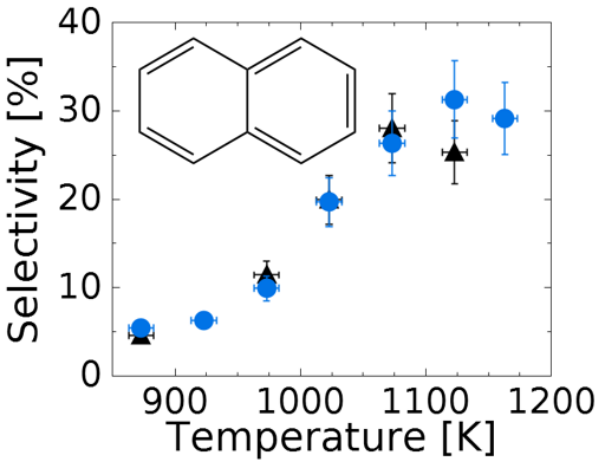
● Co-pyrolysis CPD & C_2H_4
$F_{0,CPD}$ = 13.6 mg/s
1 mol CPD / 1 mol C_2H_4 / 10 mol N_2

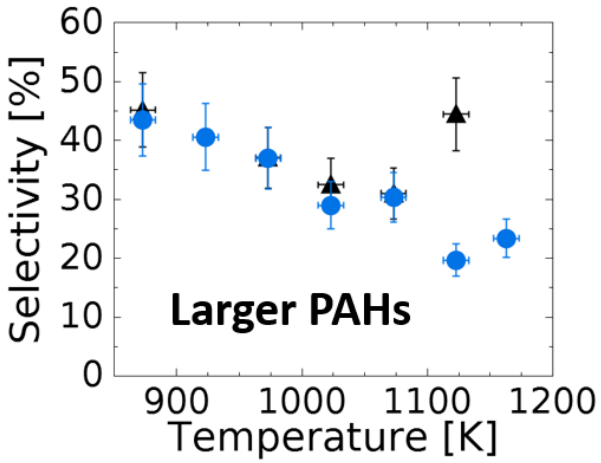












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Kinetic model

Reaction Mechanism Generator

- Rate based
- Libraries: Reactions, kinetic data and thermodynamic data
- Estimation methods

Generated kinetic model

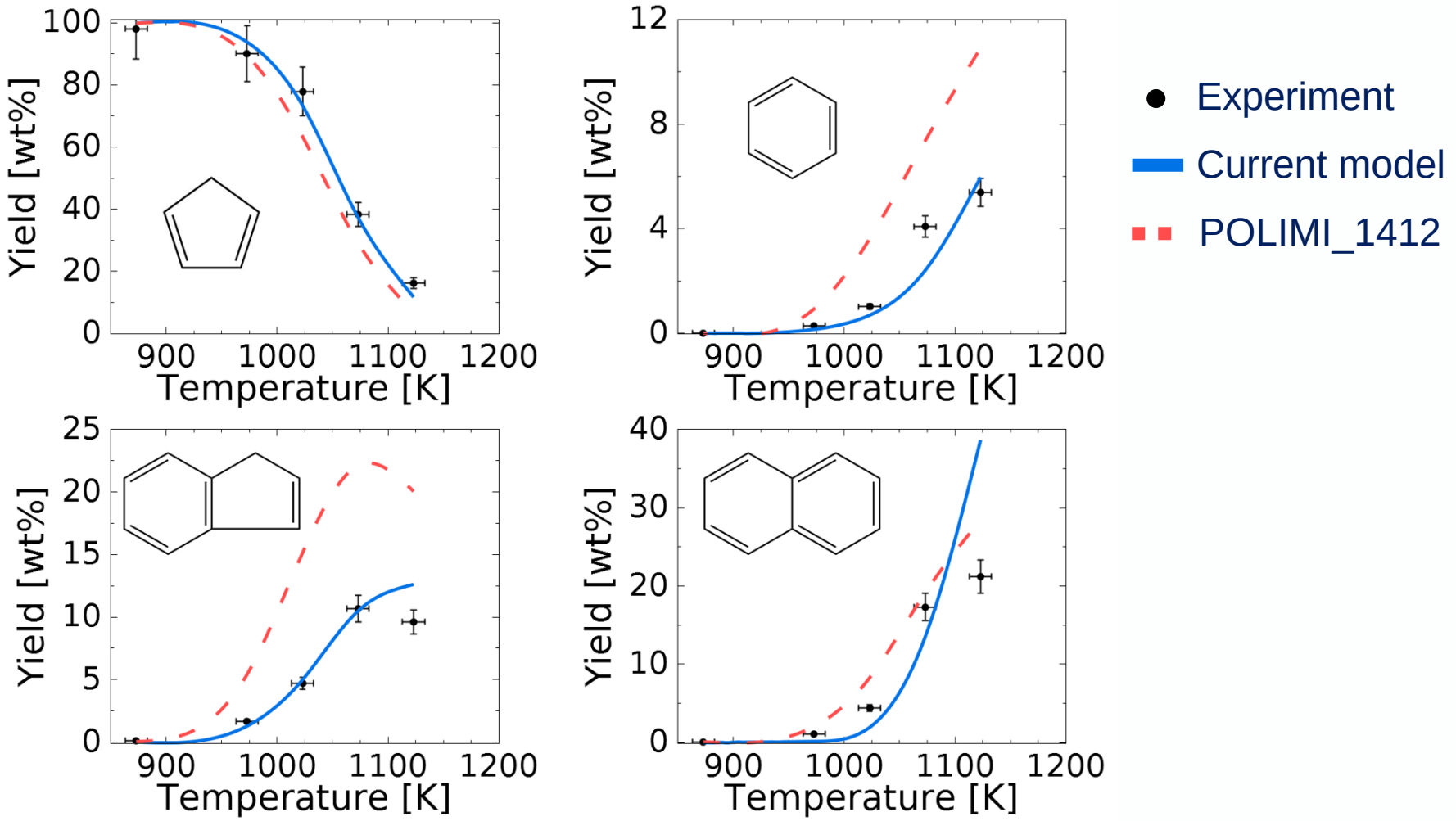
462 Species

6337 Reactions

Gao, C. W.; Allen, J. W.; Green, W. H.; West, R. H., *Computer Physics Communications,* 203, 212-225 (2016).

Model validation: Pyrolysis CPD

P = 1.7 bar $F_{0,CPD}$ = 27 mg/s 1 mol CPD / 5 mol N_2



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Model validation: Co-pyrolysis CPD & C_2H_4

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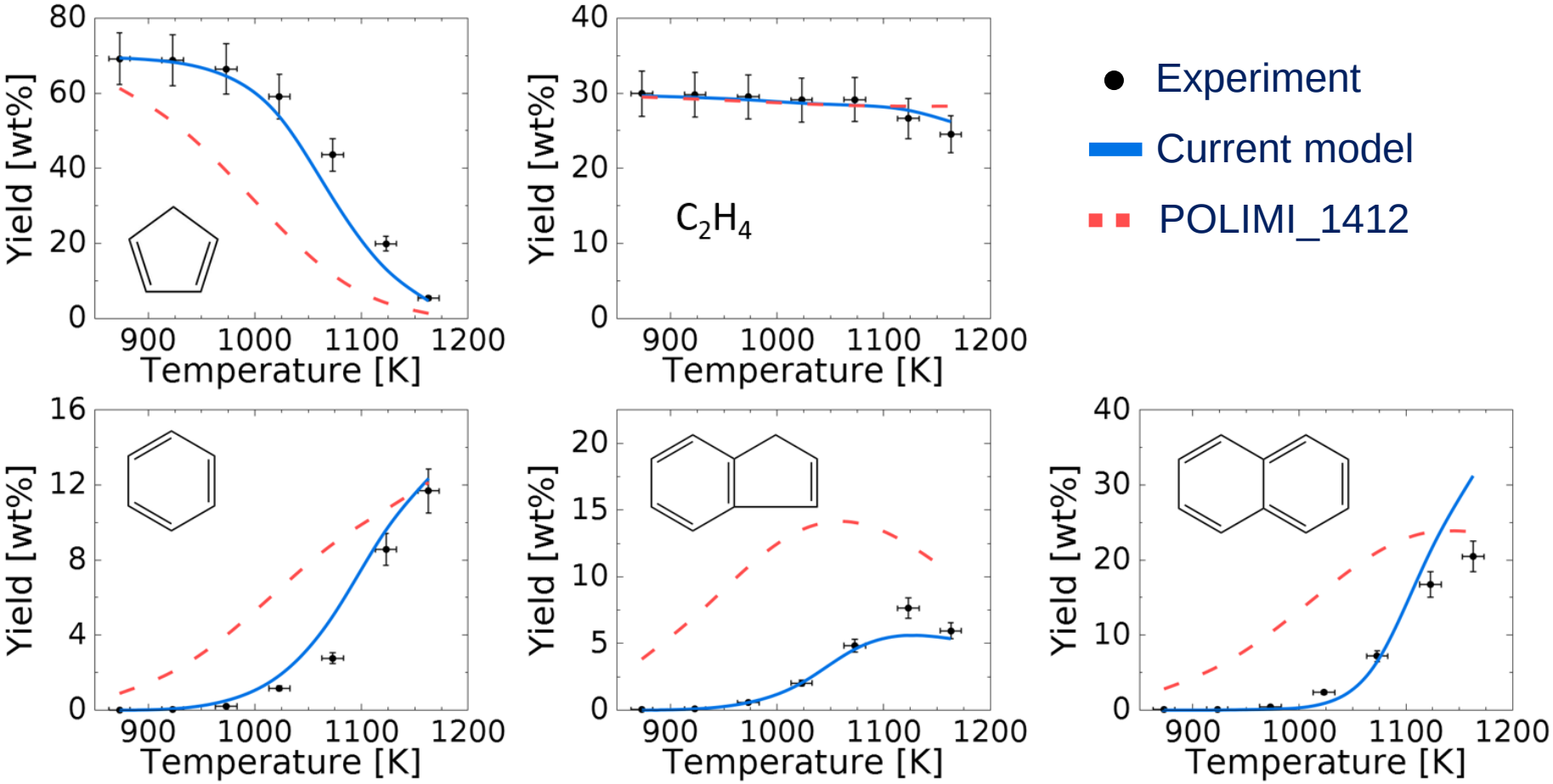

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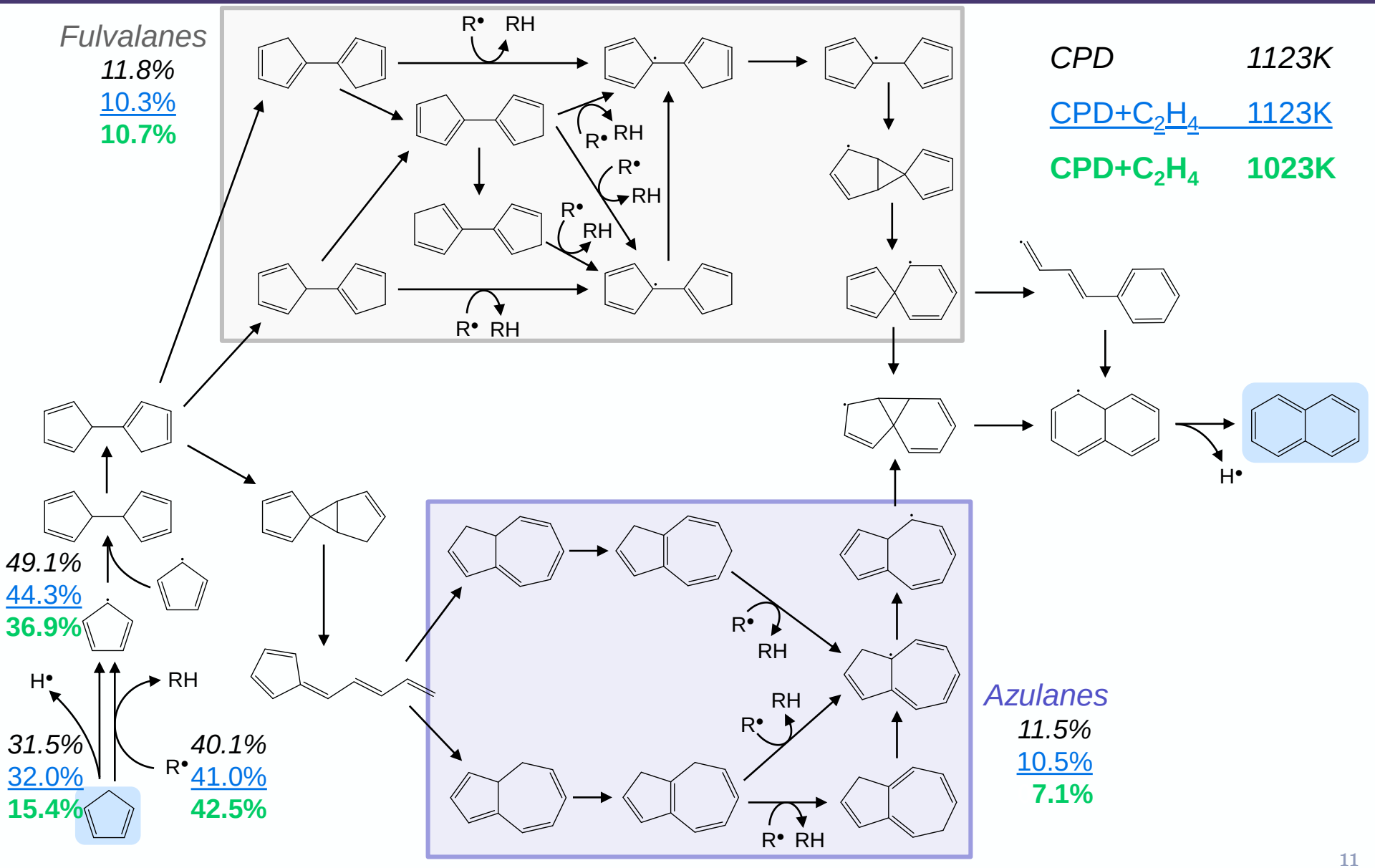
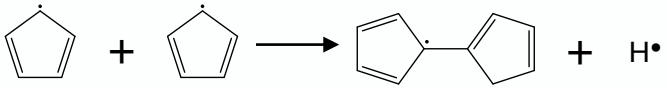
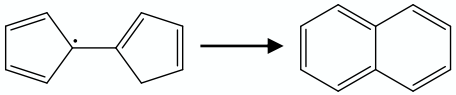
Reaction pathways: Naphthalene

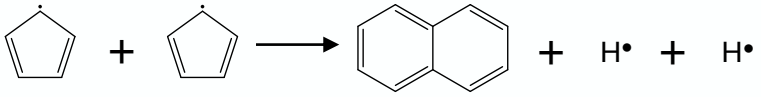


Naphthalene pathway

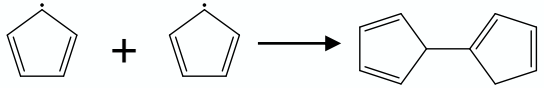
High Temperature

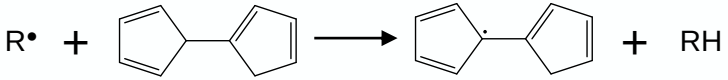


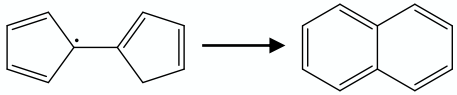


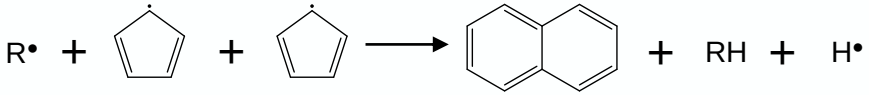


Low Temperature



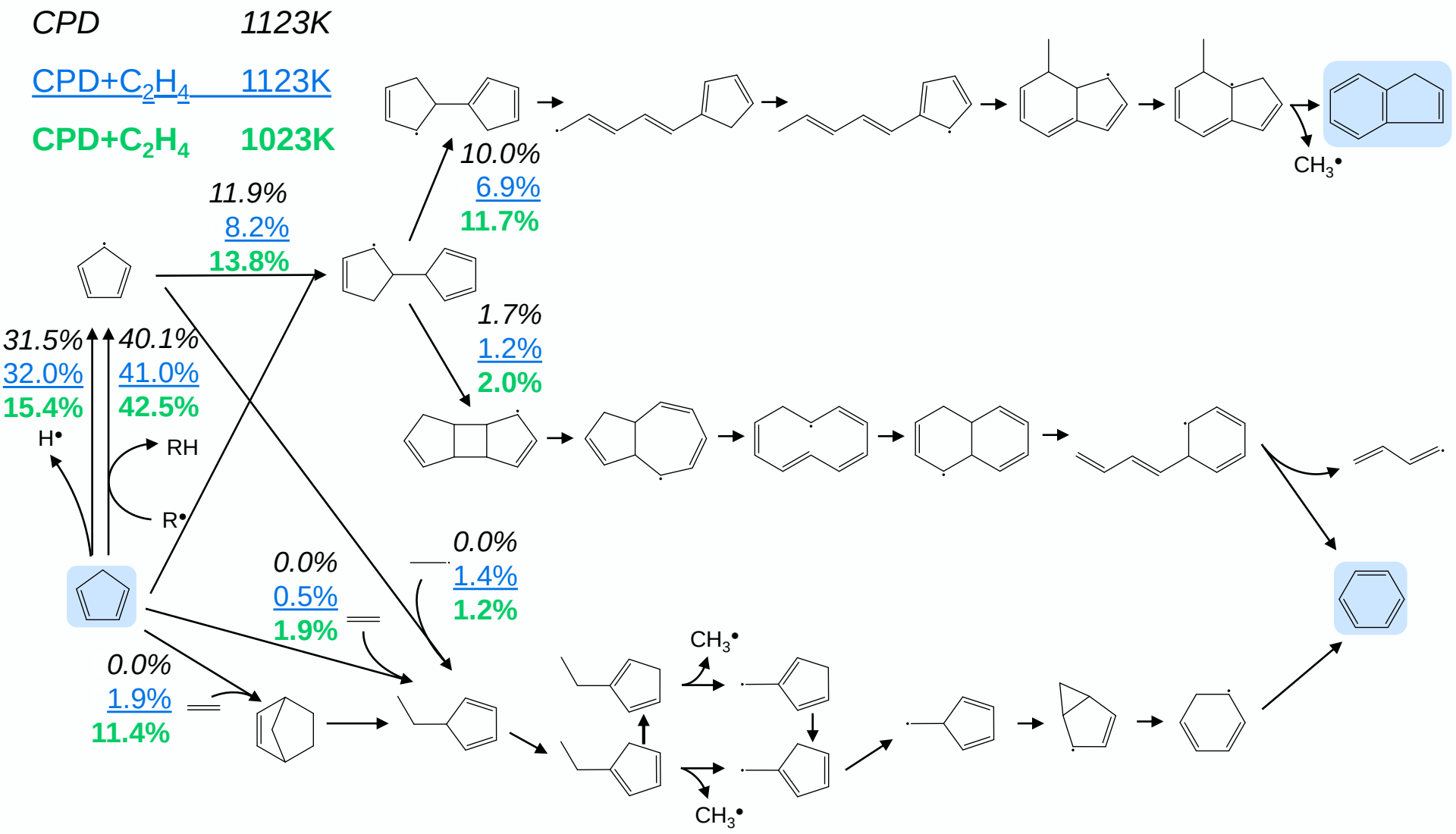






Long, A. E.; Merchant, S. S.; Vandeputte A. G.; Carstensen H.-H.; Vervust, A. J.; Marin, G. B.; Van Geem, K. M.; Green, W. H., Submitted to Combustion and Flame (2017)

Reaction pathways: Benzene & Indene



Conclusion

Polycyclic aromatic hydrocarbons (PAHs) are detrimental to human health and precursors to soot and coke.

Pyrolysis of cyclopentadiene (CPD) produces a lot of polycyclic aromatic hydrocarbons (PAHs). Indene and naphthalene are the major PAH products.

Developed an accurate kinetic model using the reaction mechanism generator (RMG) and validated it with experimental data for the pyrolysis of CPD and the co-pyrolysis of CPD and ethene.

Under the studied conditions, hydrogen abstraction reactions are important for naphthalene formation

The addition of ethene as co-reactant, aside from increasing benzene formation, has little influence on CPD pyrolysis.

Acknowledgment

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Methusalem programma

The Combustion Energy Frontier Research Center

U.S. DOE COMBUSTION ENERGY FRONTIER RESEARCH CENTER

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