SAND2023-06875C

Chemical Kinetics and Thermal Properties of Ablator Pyrolysis Products during Atmospheric Entry

Mitchell Gosma*, Caleb Harper, Lincoln Collins, Kelly Stephani, Jeffrey Engerer

Center for Hypersonics and Entry System Studies

University of Illinois at Urbana-Champaign

AIAA Aviation Forum, 12-16 June 2023

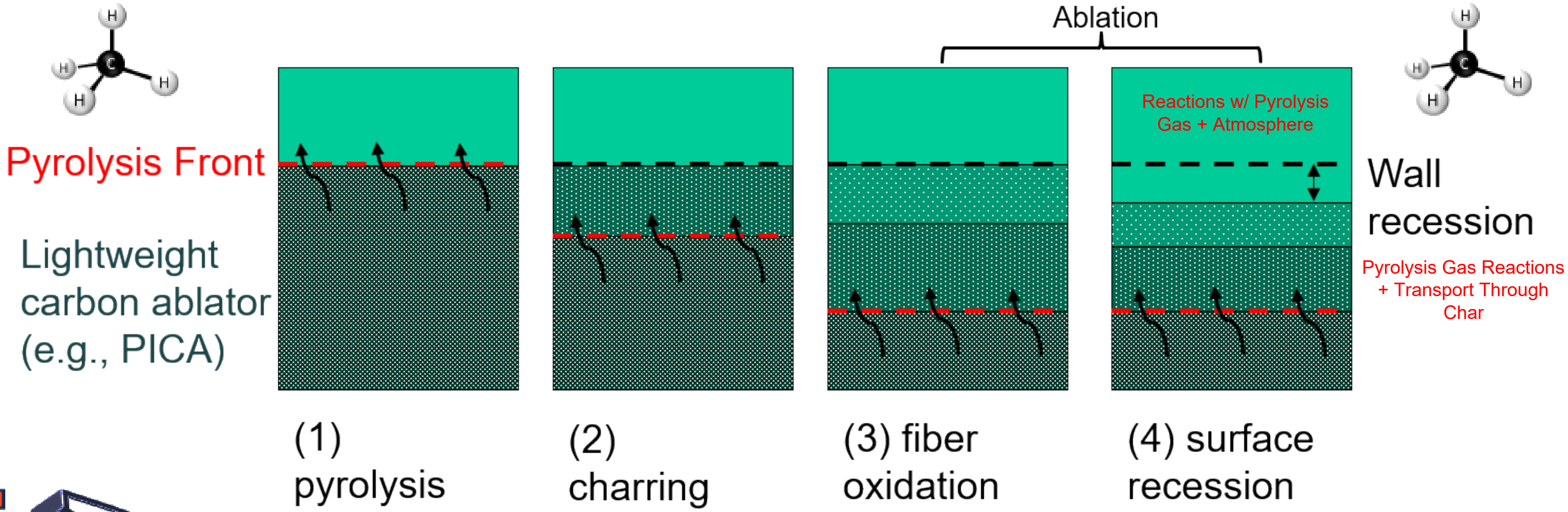
Sandia National Laboratories

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

CHESS

Background – Thermal Protection System Modeling

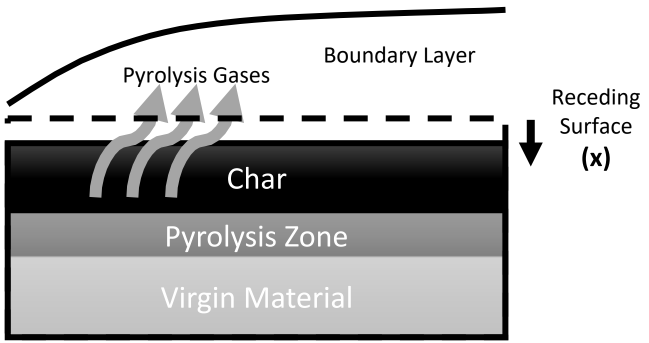
- Interest in modeling thermochemical response of ablative TPS materials
  - Focus: Modeling of reacting pyrolysis gas in char layer; Surface reactions with pyrolysis gas + atmospheric species
  - Interests: **thermal transport, gas-phase chemistry**



Credit: V. Arias, CHESS

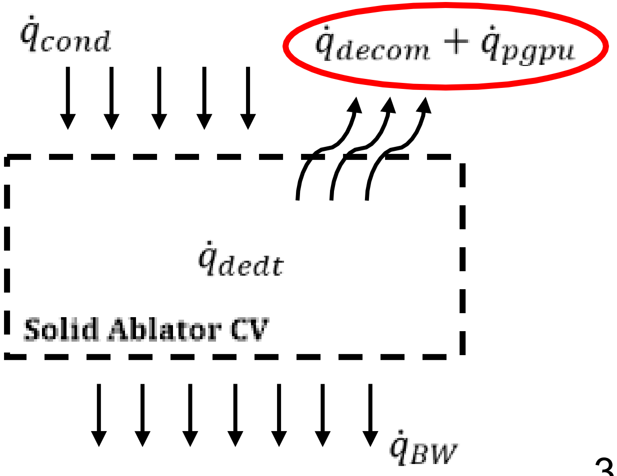
Modeling Ablator Energy Balance

- **Pyrolysis gas enthalpy is critical**
  - Different composition -> Different thermal response



- **Thermal QoIs:**

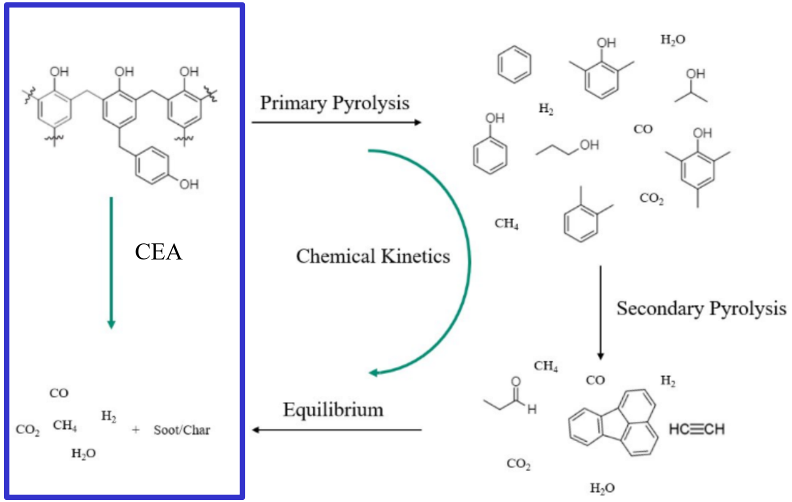
- **$\dot{q}_{decom}$ = Heat of Decomposition**
  - $\dot{q}_{decom} = h_{decom}\dot{\omega}_g = (h_{g,\omega} - \bar{h})\dot{\omega}_g$



- **$\dot{q}_{pgpu}$ = Pyrolysis Gas Pick Up (Transpiration Cooling)**
  - $\dot{q}_{pgpu} = -\frac{\partial h_g}{\partial}\bar{m}_g'' = (h_{g,o} - h_{g,\omega})\dot{\omega}_g + \frac{h_{g,o}-h_{g,i}}{}\dot{m}_{g,i}''$

Pyrolysis Gas Chemistry – Legacy Assumption

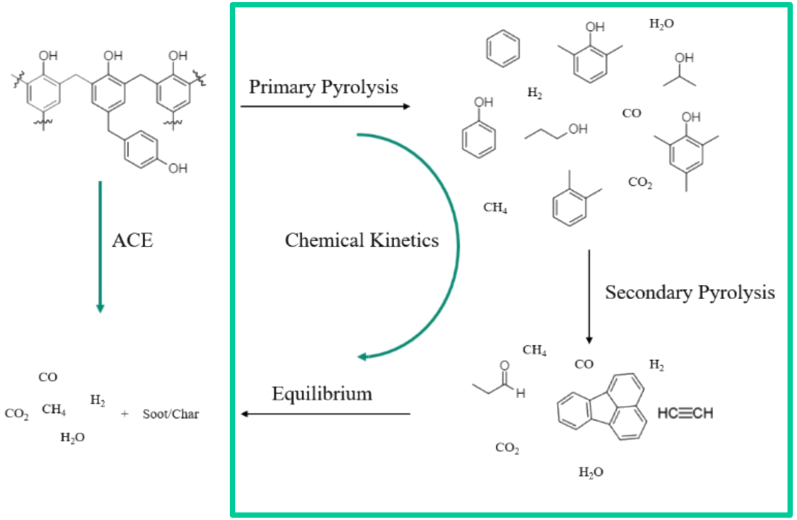
- In modeling of pyrolysis gas in ablation codes, two assumptions are common:
  - **Equilibrium Chemical Composition**
  - **Uniform Elemental Composition**

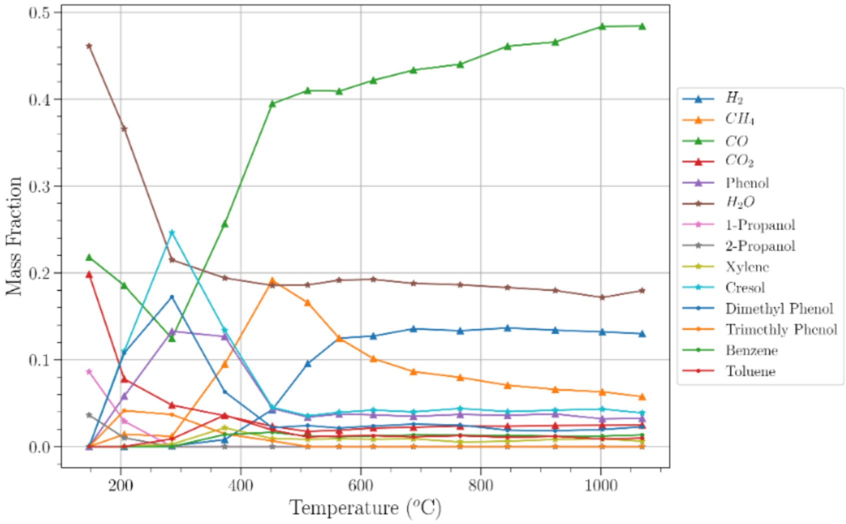


- **Advantage: Significantly easier to simulate in Material Response Codes**

Pyrolysis Gas Chemistry – Legacy Assumption

- **Is this assumption accurate?**
  - Experimental results show large variation in Primary Pyrolysis elemental composition
  - **We will examine the kinetics of these species with a coupled simulation approach**





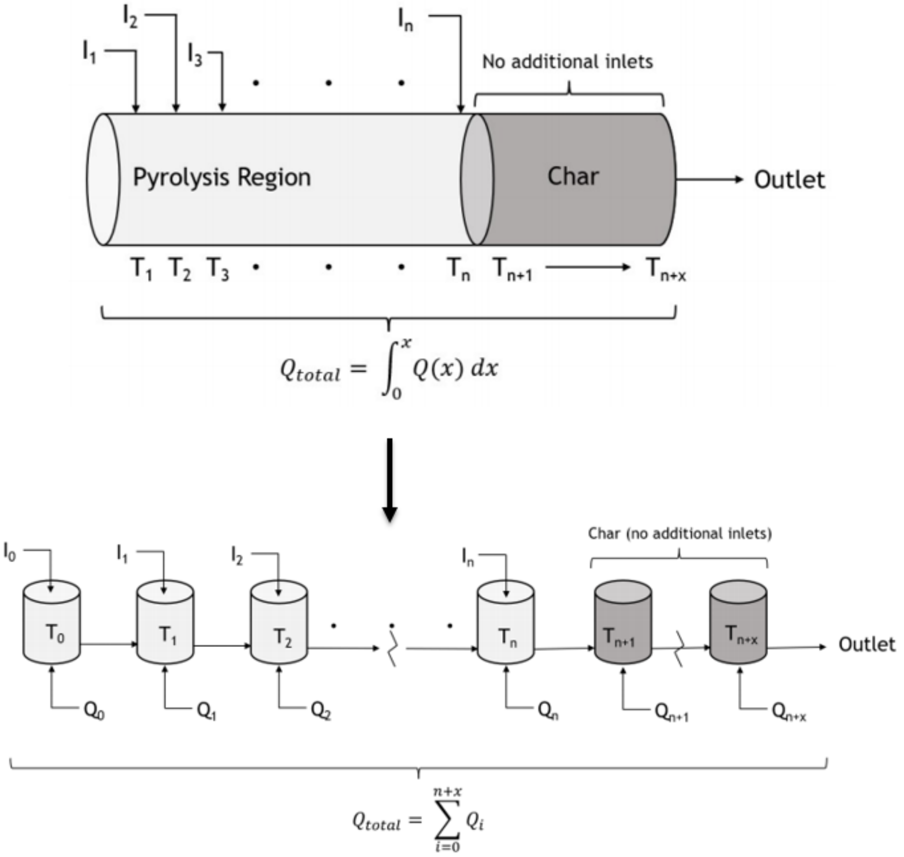
Source: Brody K. Bessire and Timothy K. Minton. Decomposition of phenolic impregnated carbon ablator (pica) as a function of temperature and heating rate. ACS Applied Materials & Interfaces, 9(25):21422–21437, 201

Analysis – Coupled Aria/Cantera Simulation

Material Response Code (Aria)
- Temperature/Pressure
- Mass Flow Rate
- Primary Pyrolysis Rate
- Recession

Update Every Timestep

Chemistry Solver (Cantera)
- Pyrolysis Speciation
- Finite-Rate Kinetics
- Species/Element Mole Fractions
- Thermal Properties

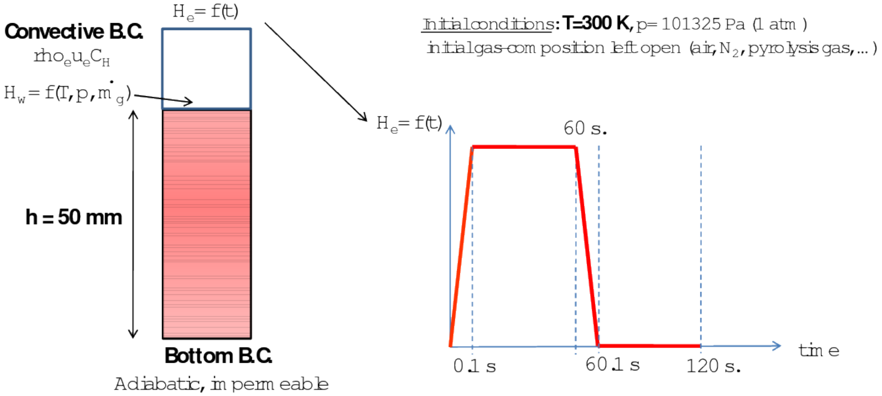


Aria Model Assumptions
- **TACOT** Ablator Material
- Equilibrium Chemistry
- Constant Element Comp.
- Legacy Pyrolysis Model
  - **Goldstein**

Cantera Model Assumptions
- Neglect porous flow, GSI effects
  - No coking
- Neglect Transport
- Pyrolysis Speciation
  - **Bessire-Minton (6.1 C°/s) Data**
- Kinetics
  - **Blanquart Mech.**
  - **148 species, 1600+ reactions**

Aria – Ablation Workshop Test Cases 2.2 & 2.3

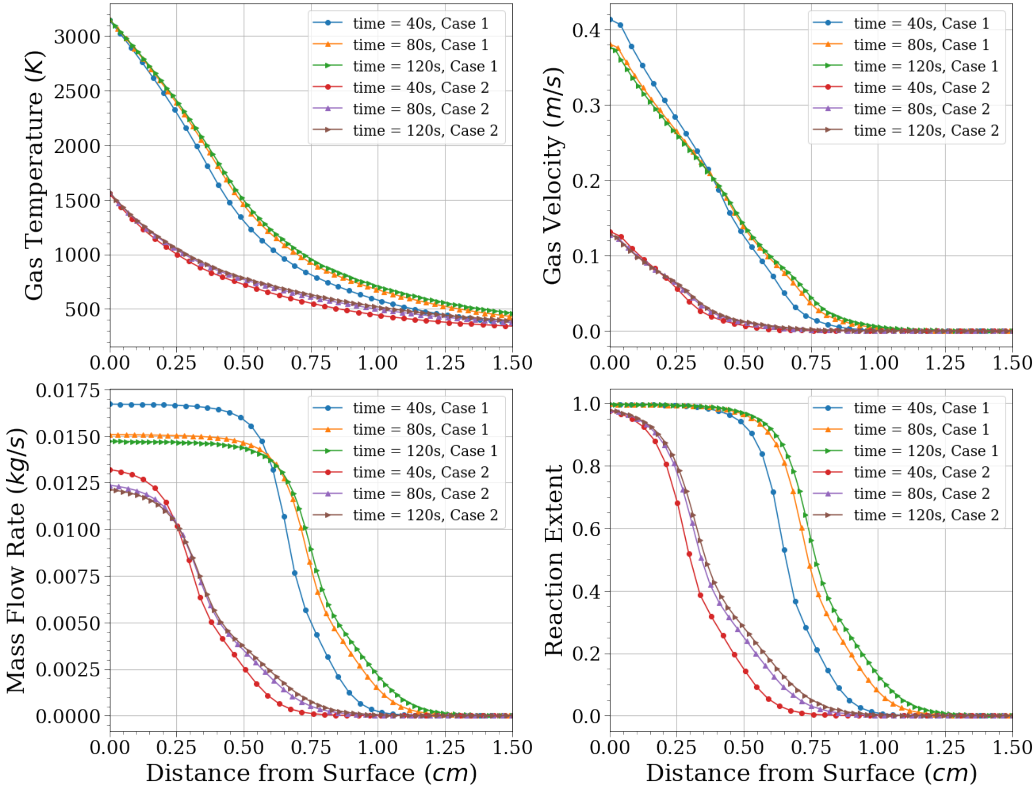
- Aria – Galerkin finite element porous flow solver
  - Part of Sandia's SIERRA Multitool
  - Used to run Lachaud's 1D Ablation Test Cases using the TACOT Material:



Case	Time, s	T_∞, K	T_{surf}, K	$h_r\rho_e u_e C_H$, Wm^{-2}
1	120.1	300	3200	7.5×10^6
2	120.1	300	1600	4.5×10^5

Source: "Sierra Multimechanics module: Aria User Manual - Version 5.8.," 2022.
Source: Lachaud, Jean R.; Martin, Alexandre; van Eekelen, Tom; and Cozmuta, Ioana, "Ablation Test-Case Series #2. Numerical Simulation of Ablative-Material Response: Code and Model Comparisons" (2012).

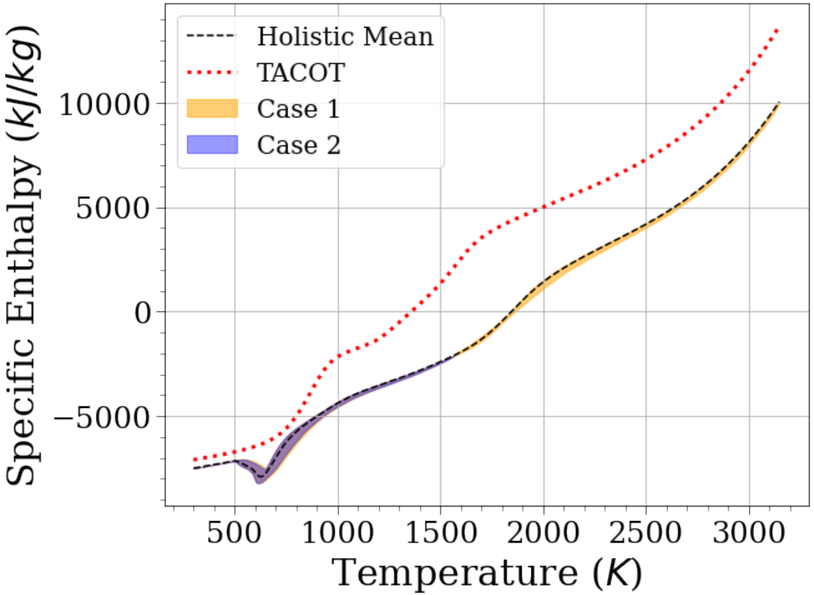
Aria Simulation Results

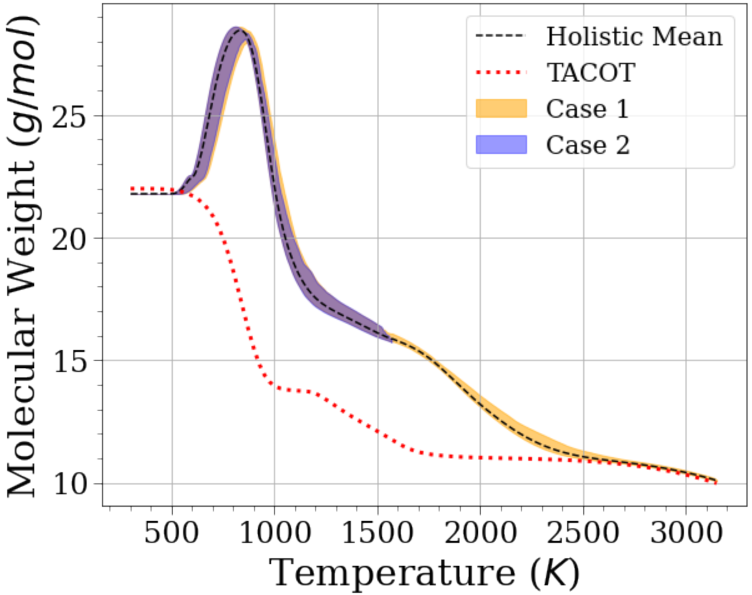


- ➢Resulting temperature and recession profiles are nominal to published PATO results of Lachaud
- ➢**Results are then used to run Cantera reactor network**

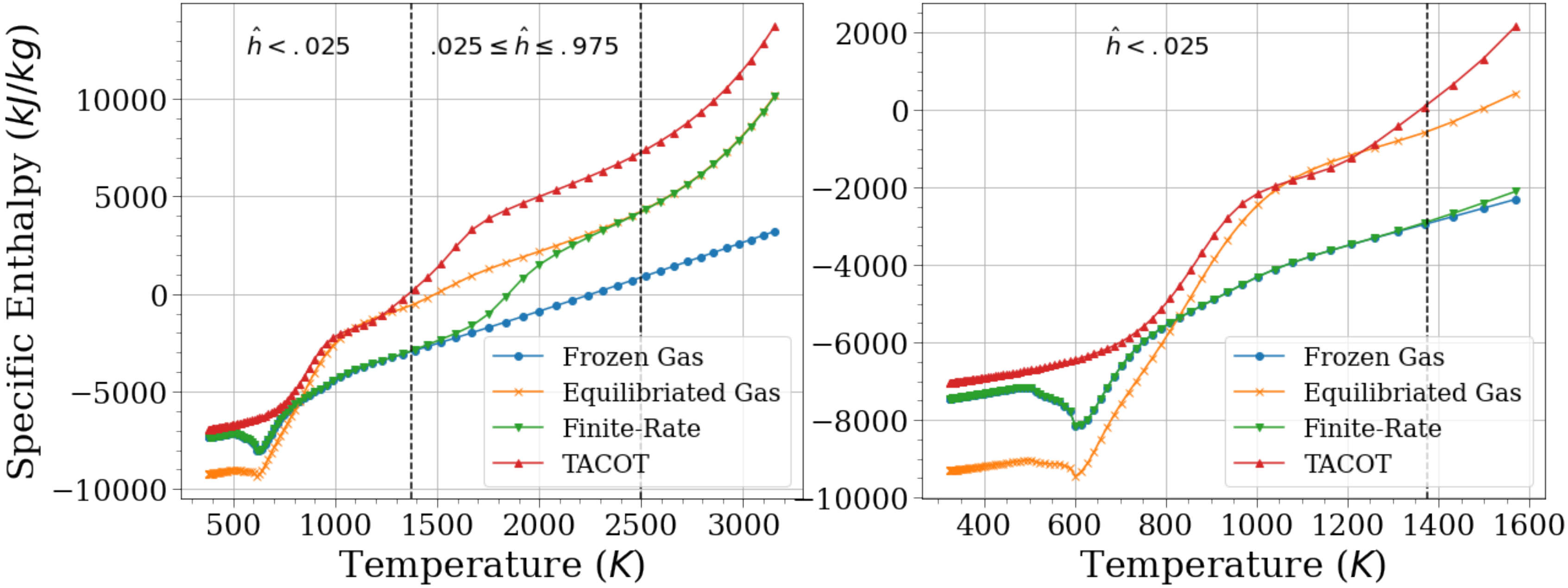
Holistic Cantera Results – Gas Enthalpy over T & Time

- Shaded regions are bounded by recorded maximum and minimum values.
  - Little variation is seen transiently or between the two test cases.



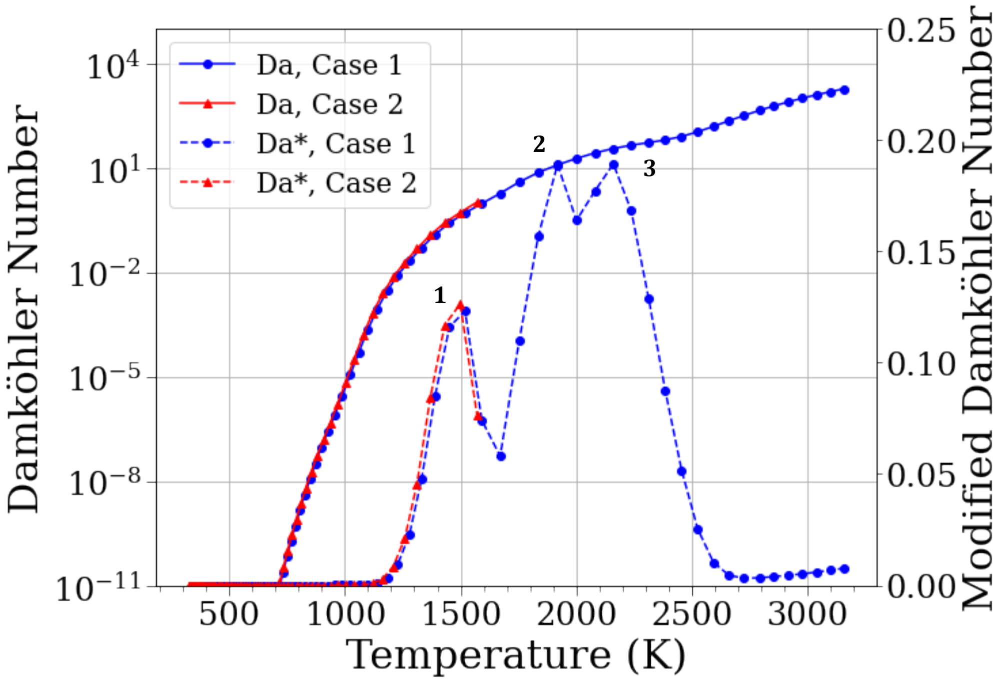


Case 1 (Left) & 2 (Right) – T = 120 seconds



$$\hat{h} = \frac{|h - h_{frzn}|}{|h_{equil} - h_{frzn}|}$$

Case 1 – T = 120 seconds



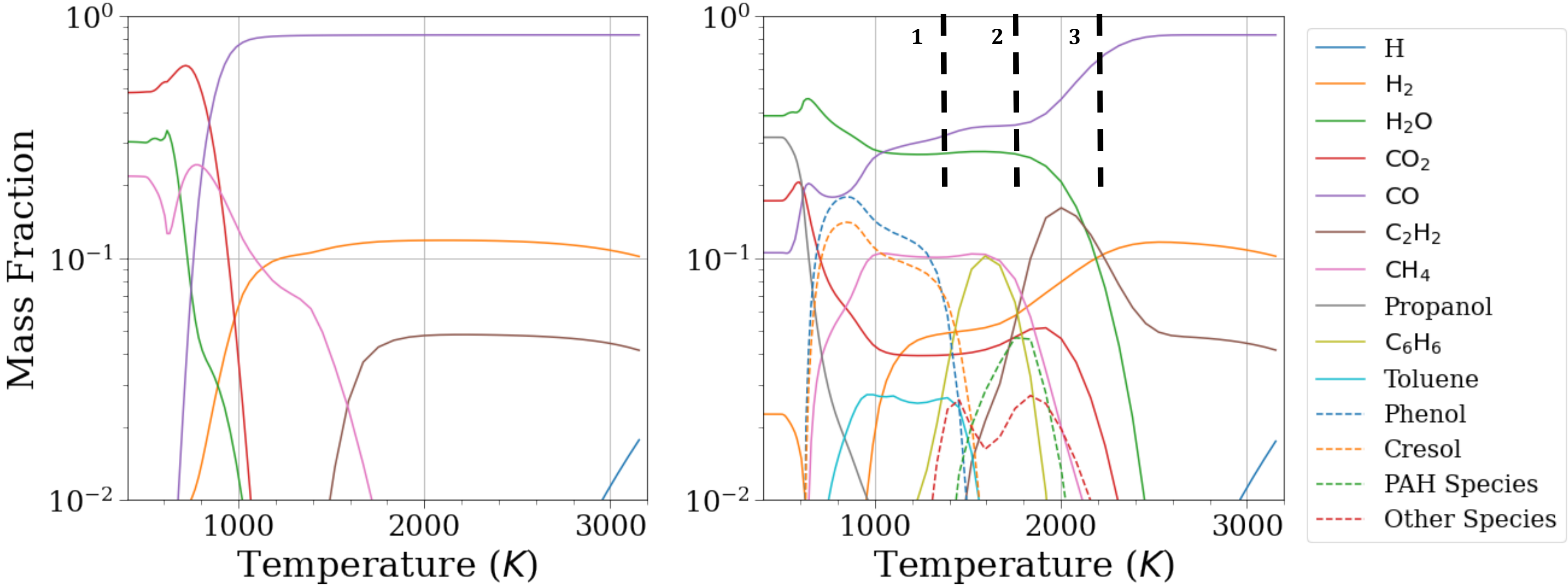
$$Da = \frac{Rate\ of\ Reaction}{Rate\ of\ Advection} = \frac{\tau_R \sum_{i=0}^{n} r_i^+}{\rho}$$

$$Da^* = \frac{\tau_R \sum_{i=0}^{n} \left(r_i^+ - r_i^-\right)}{\rho}$$

- ➢The standard Damköhler Number shows the onset of chemical kinetics, but not equilibrium
- ➢The modified Da* shows finite-rate/equilibrium transition

Case 1 – T = 120 seconds

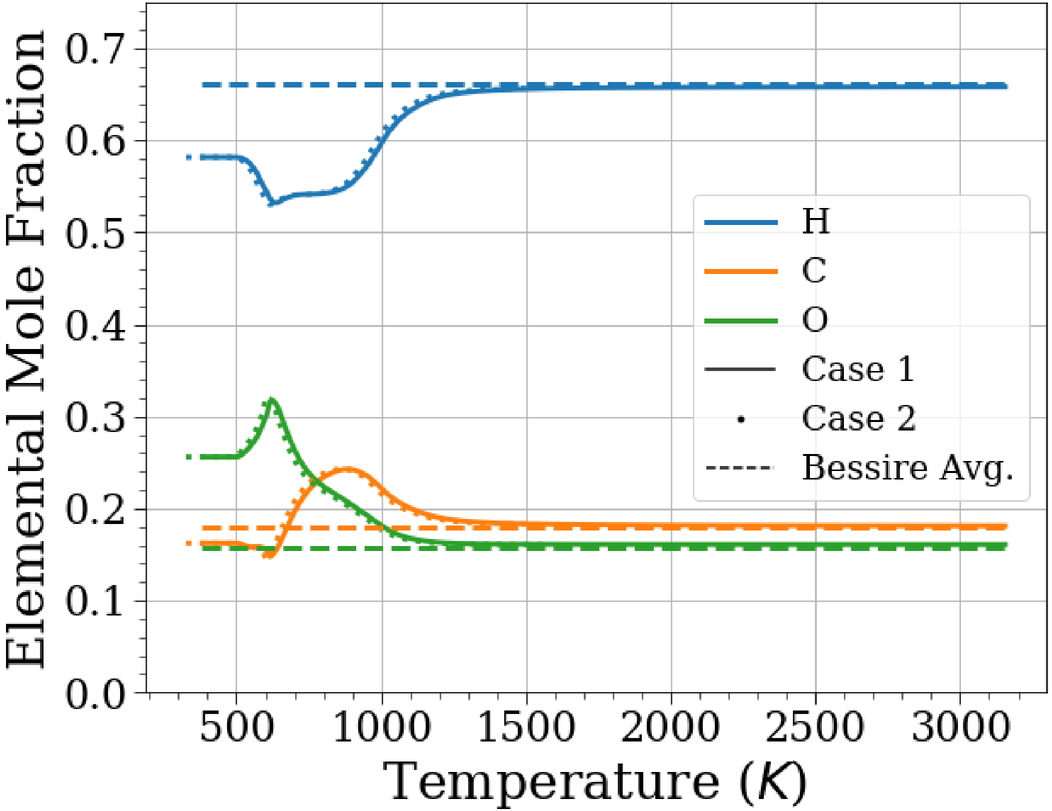
➢Strong variations in chemical composition seen, only approaching equilibrium at very high temperatures; PAH peaks at around 5% mass fraction



Low Temperature + Low Free Oxygen = **Non-Equilibrium**

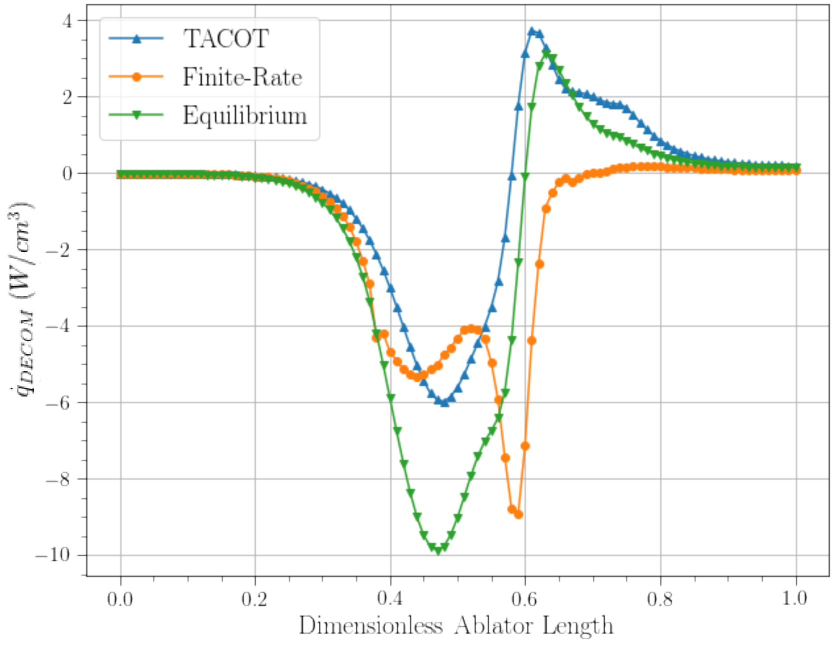
Case 1 – T = 120 seconds

- Elemental composition is seen to stabilize at around 1400K, once primary pyrolysis is mostly completed
- **Molar Ratios: 18.2% carbon, 16.1% oxygen, 65.7% hydrogen**



$\dot{q}_{decom}$

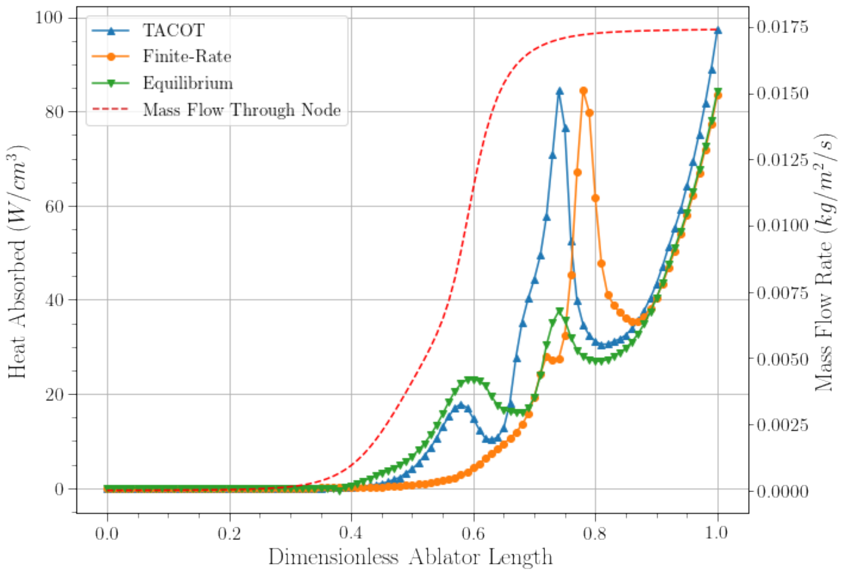
- ➢Both cases are similar, so only **Case 1** is shown here
- ➢As expected, equilibrium and TACOT results behave similarly
- ➢Finite-rate results show exothermic behavior for both reaction peaks



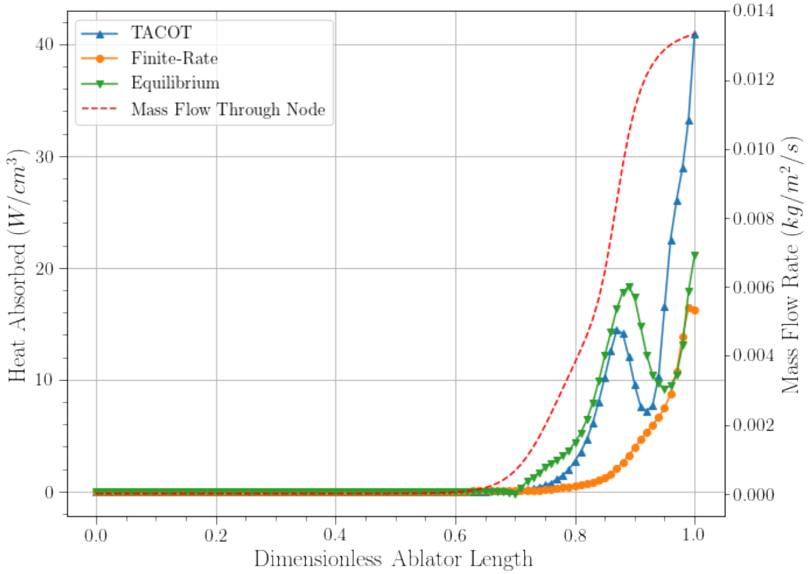
$$\dot{q}_{decom} = h_{decom}\dot{\omega}_g = \left(h_{g,\omega} - \bar{h}\right)$$

$\dot{q}_{pgpu}$

Case 1



Case 2

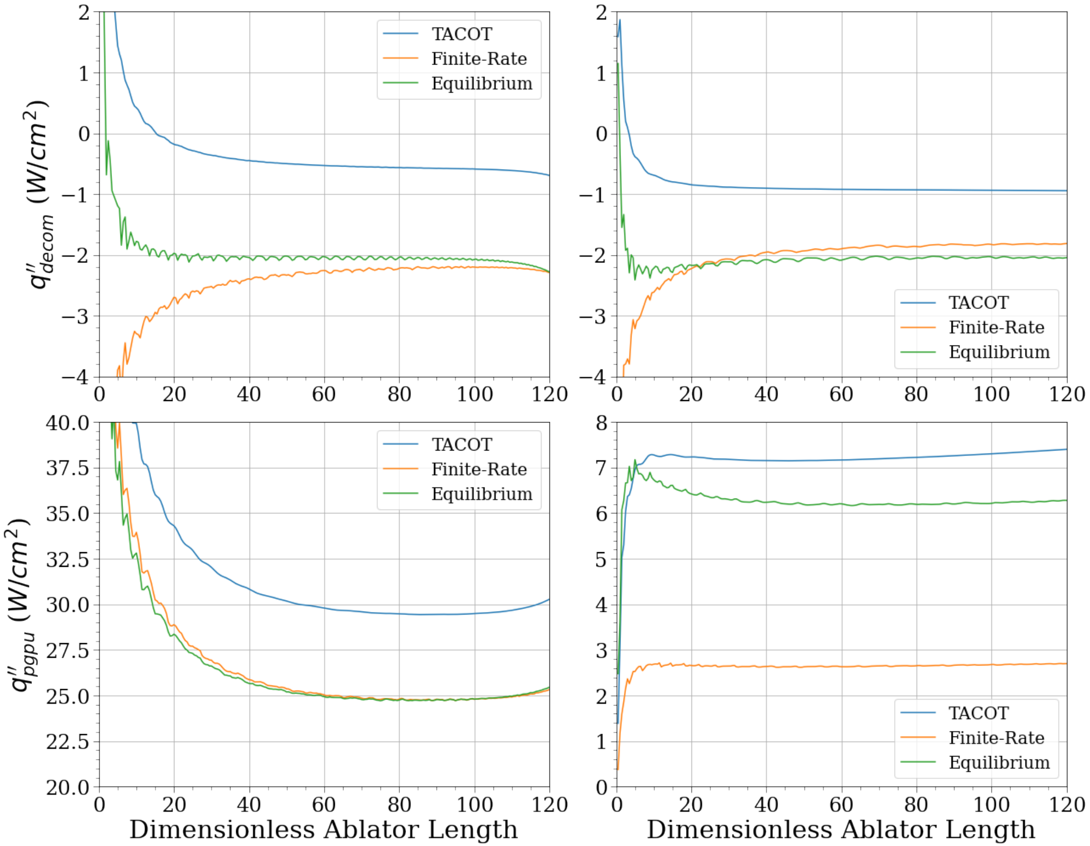


$$\dot{q}_{pgpu} = -\frac{\partial h_g}{\partial x}\bar{\dot{m}}_g'' = (h_{g,o} - h_{g,\omega})\dot{\omega}_g + \frac{h_{g,o} - h_{g,i}}{\Delta x}\dot{m}_{g,i}''$$

Total Heat Transfer: Case 1 (Left) vs 2 (Right)

Previous curves integrated over length vs simulation time.

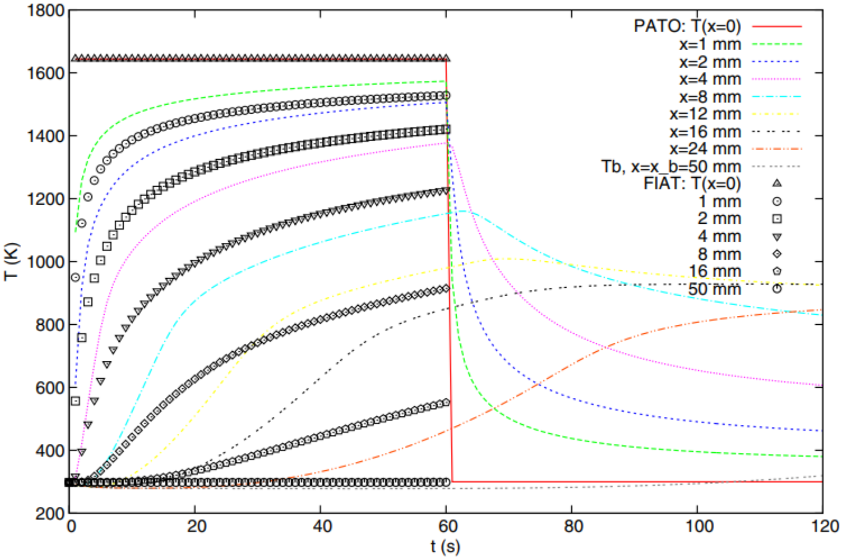
- **Typical surface aeroheating values:**
  - **~550 W/cm² (1)**
  - **~35 W/cm² (2)**



Conclusion

- Non-equilibrium pyrolysis gas conditions in ablator is common <2500K
- Differences between Eq. and Finite-rate gas cause substantial deviations in thermal QoIs
- These QoIs potentially have substantial impact on Ablator Energy Balance
  - **See Lachaud et al ->**

Finite-Rate; 22-species reduced Blanquart mech.



Source: Porous material analysis toolbox based on OpenFoam and applications. J. Lachaud, N. N. Mansour. Journal of Thermophysics and Heat Transfer, 28 (2): 191–202, 2014

Acknowledgements

This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract **DE-NA0003525**. Additional support is provided by a NASA Space Technology Graduate Research Opportunity Fellowship under grant **80NSSC21K1279**.

Sandia National Laboratories

NASA

Questions?

Backup – Batch Reactor Tests

- Used to validate achievement of equilibrium with Blanquart mechanism & identify relevant timescales for chemical kinetics
- Initial mixture: Gas composition taken from Minton 25 C/s experiment at various Ts

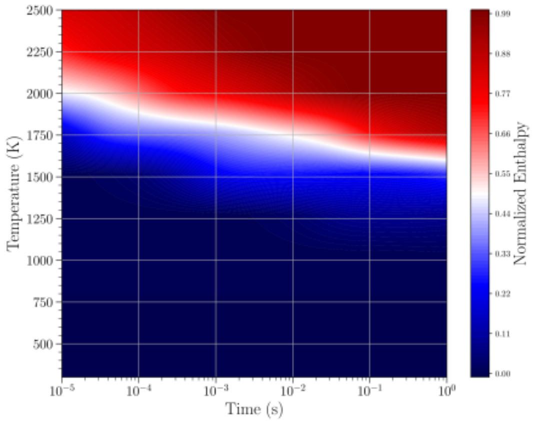
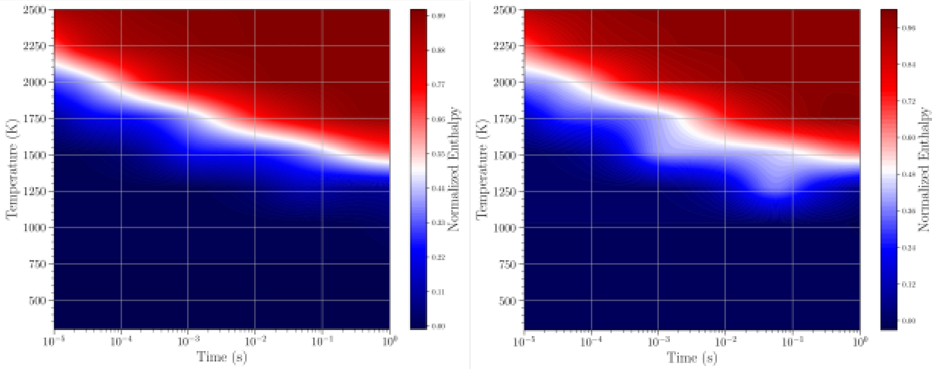


Figure 4-3. Normalized enthalpy of pyrolysis gases with respect to time. Species correspond to Bessire and Minton data at 147.5 °C.



(a) 452.6 °C.

(b) 1068.5 °C.

Figure 4-4. Normalized enthalpy of pyrolysis gases with respect to time. Species correspond to Bessire and Minton data at 452.6 °C and 1068.5 °C

Backup – Heat of Decomposition (Case 1, t=120 seconds)