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Vapor Liquid Equilibrium in Pressurizing Porous Media Systems

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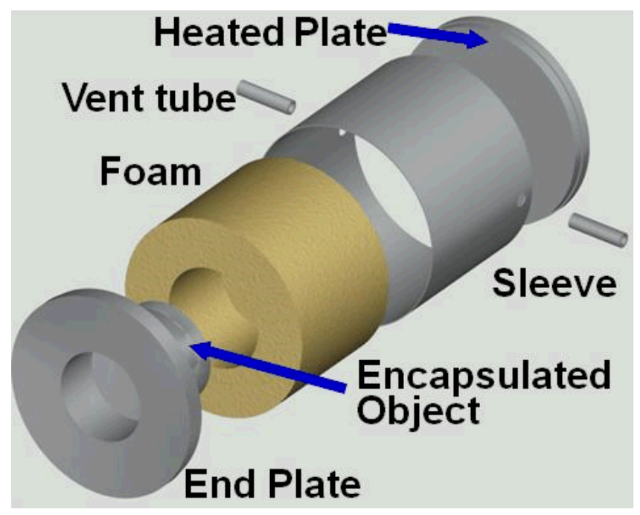
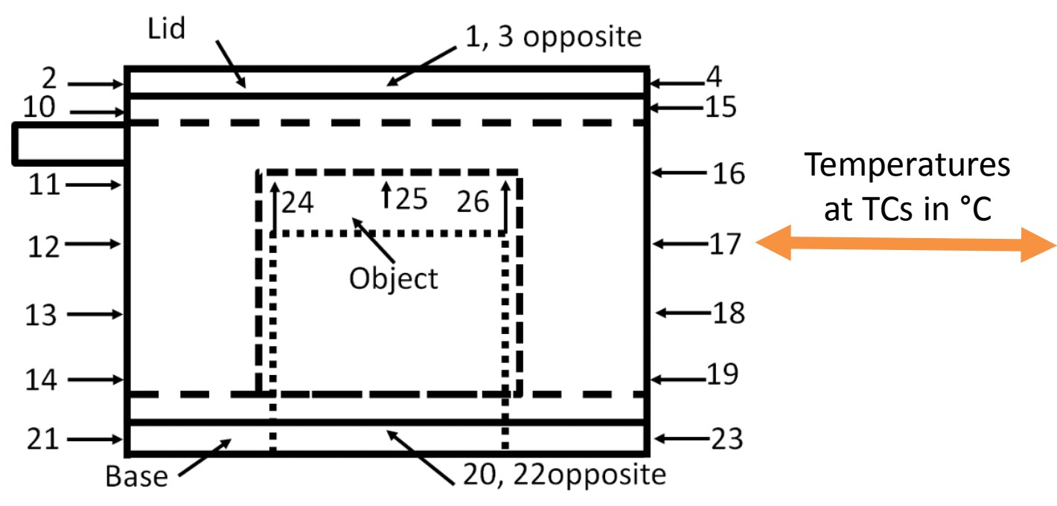
Background

Polymer foam encapsulants provide mechanical, electrical, and thermal isolation in engineered systems. When heated, foams thermally decompose and create gaseous products. In fire environments, a sealed container filled with foam will pressurize and may result in mechanical failure. Accurately modeling organic materials in fire environments is therefore crucial for system safety analyses, but it is challenging due to complex physics. **A finite element model including conservation equations and models for porous flow, thermal decomposition, and vapor liquid equilibrium (VLE), was developed to simulate the physics of the decomposing foam problem.**

Experiments



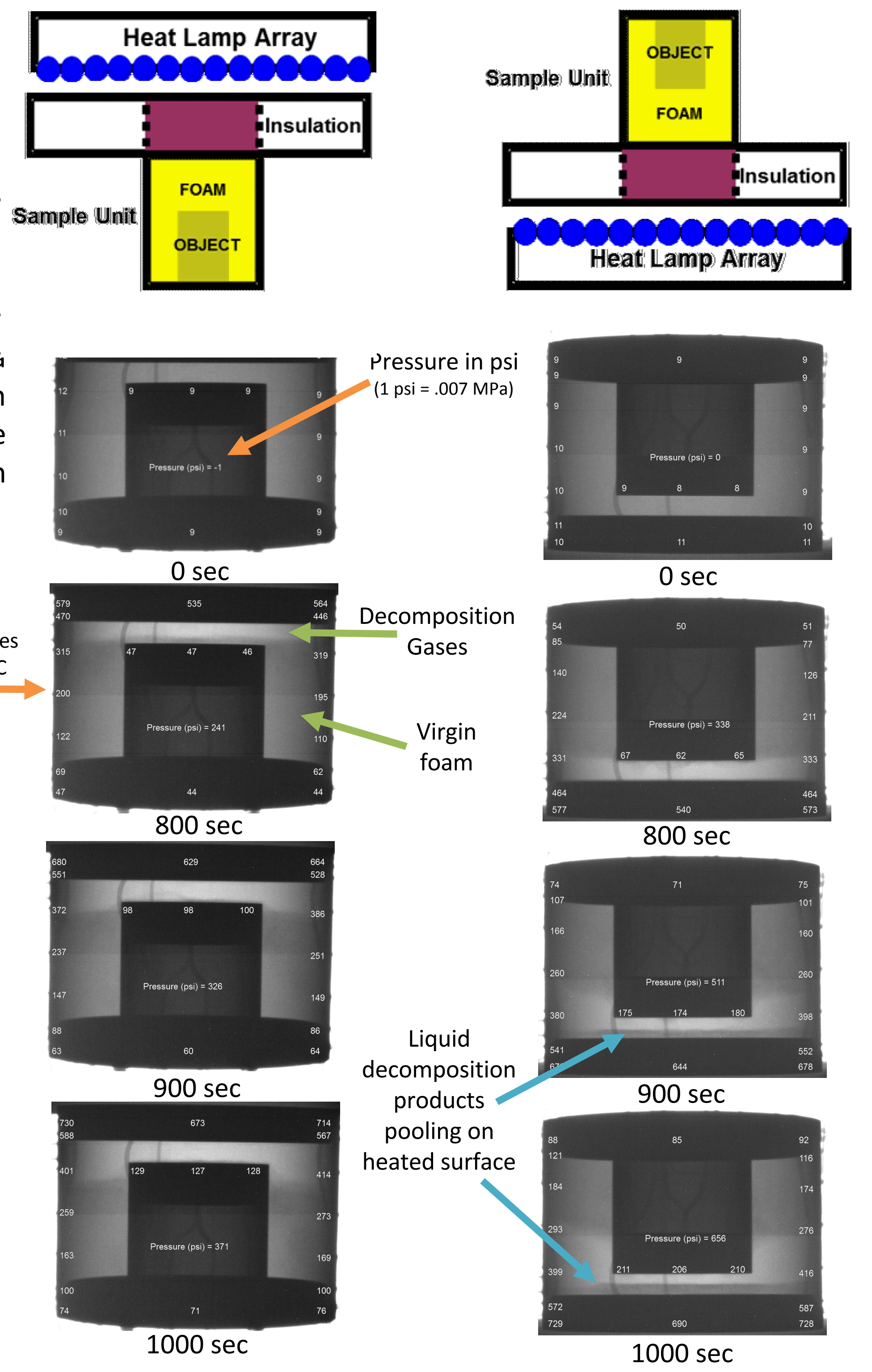
The Foam in a Can (FIC) experiments were performed in a stainless steel can filled with 320 kg/m^3 PMD polyurethane foam and containing an embedded metal object. Overall can dimensions are 9cm diameter, 6.5cm tall, 0.5mm wall thickness. A radiant heat flux from a heater array heats the lid to 800°C at a rate of 50°C/min and causes the polymer to decompose and the container to pressurize. The experiment is performed in the upright and inverted orientations.



Temperature is monitored on the top, along the sides, and on the bottom of the can as well as on an embedded object. The internal pressure is also monitored.

The experiments display the complicated nature of the physics of decomposing foam. The rate of pressurization in the inverted cases is faster than in the upright cases due to the liquefaction and flow of the decomposition products. In the inverted orientation the liquid products flow towards the heated surface, thus gasifying at a faster rate.

Upright



Pressure in psi (1 psi = .007 MPa)

0 sec

0 sec

Decomposition Gases

Virgin foam

800 sec

800 sec

Liquid decomposition products pooling on heated surface

900 sec

900 sec

1000 sec

1000 sec

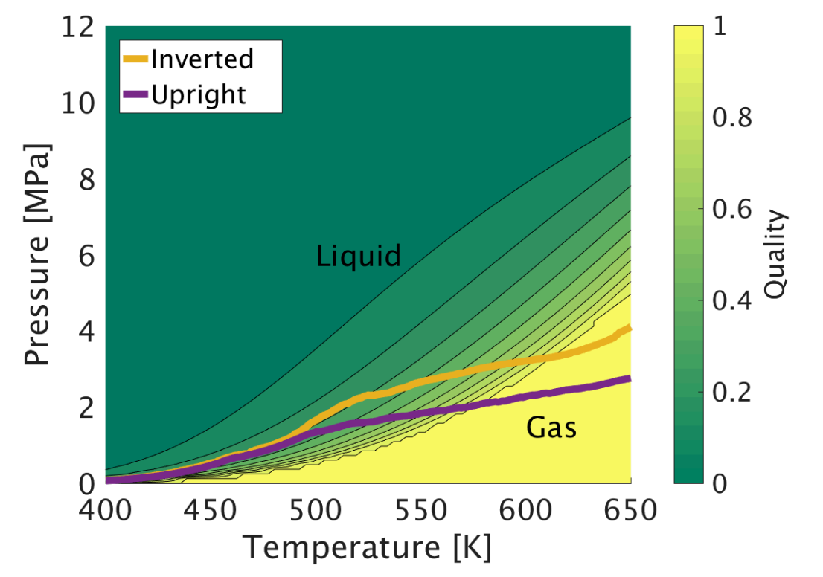
Vapor Liquid Equilibrium Motivation

The use of separate gas/vapor splits for the inverted and upright orientations illustrates the need for a more sophisticated method for determining the phase of the decomposition products. For the temperatures and pressures in question (up to 800°C and 8 MPa), the mid- and high-molecular weight decomposition products can exist in both the gas and liquid phases.

Molecule	Molecular Weight	Critical Temperature [K]	Critical Pressure [MPa]	Antoine Coefficients A [$\log_{10}$(Pa)]	B [K]	C [K]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Aniline	93	698	4.89	9.34541	1661.858	-74.048
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
Propylene glycol	76	624	6.1	11.07936	2692.187	-17.94

The table to the left shows the major decomposition products, along with the critical temperatures and pressures. The critical temperatures and pressures are all within the range of the experiments.

The graph to the right shows the phase diagram for aniline. The pressure-temperature curves trace the inverted and upright experiments. They pass through the vapor dome, indicated by the quality, where 1 means the mixture is in the gas phase and 0 means it is in the liquid phase. **This means that there will be liquid products as the foam decomposes, which will change the pressure and heat transfer.** Including a methodology for determining the vapor liquid split will improve the predictiveness of the model.



Vapor Liquid Equilibrium Model

The vapor liquid equilibrium model is an addition to the porous media model. The foam still decomposes through a three step mechanism into CO$_2$, high and low weight organics, and char. However, now the mass fraction of organics in the gas and condense are determined through a vapor liquid equilibrium equations. Equilibrium is defined as, for a constant temperature and pressure, the change in the Gibb's free energy is equal to zero. By the Gibbs-Duhem equation, this means that the chemical potential of the vapor and liquid phases are equal to each other. This leads to two equations: Raoult's Law and Henry's Law

Raoult's Law

$$K_i = \frac{x_{vapor,i}}{x_{liquid,i}} = \frac{P_i^{sat}(T)}{P}$$

Ratio of the vapor to liquid mole fractions of the i^{th} decomposition product

Ratio of the saturation pressure of the i^{th} product to the total pressure

Henry's Law

$$K_i = \frac{x_{vapor,i}}{x_{liquid,i}} = \frac{H_i(T)}{P}$$

Ratio of the Henry's constant i^{th} product to the total pressure

The saturation pressure can be solved for through the Antoine equation: $\log_{10}(P_{sat}) = A - \frac{B}{T+C}$. Raoult's law cannot be used above the critical temperature, since $P_i^{sat}(T)$ is no longer defined. Henry's law can be used above the critical temperature, however the Henry's constant, which is experimentally measured, must be known for the two substances in question.

From continuity: $Fx_i = Lx_{liquid,i} + Vx_{vapor,i}$

Total moles of the decompositions products

Mole fraction of the i^{th} product

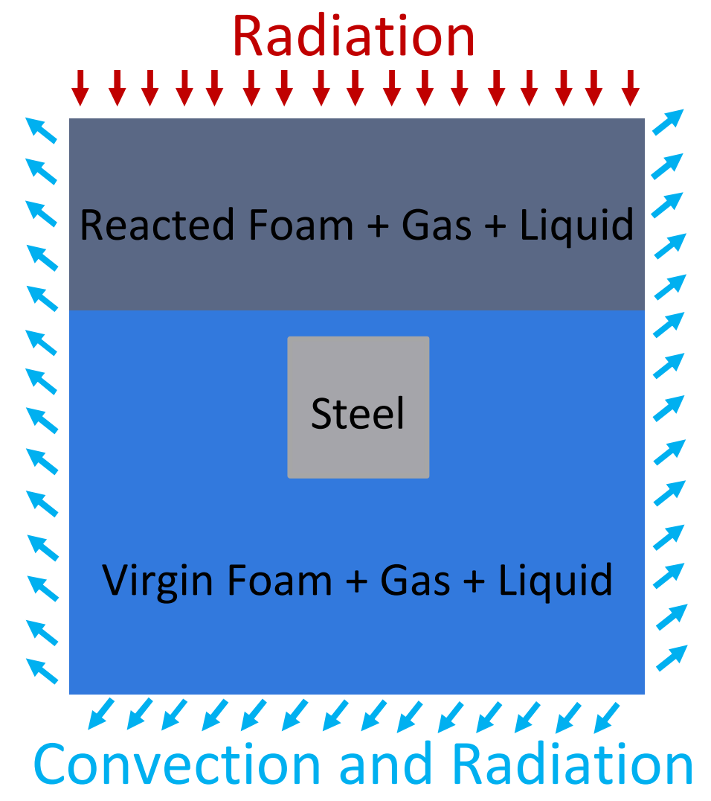
Moles of liquid

Moles of vapor

Rearrange and use the fact: $\sum y_i - x_i = 0$

$$\sum \frac{z_i(K_i - 1)}{1 + \frac{V}{F}(K_i - 1)} = 0$$

Known as the Rachford-Rice equation, this can be solved for V/F, the fraction of vapor, using either Raoult's or Henry's law.



$$FOAM \xrightarrow[k_1]{} [0.44]organics_{light} + [0.56]CO_2$$
$$FOAM \xrightarrow[k_2]{} [1]organics_{heavy}$$
$$FOAM \xrightarrow[k_3]{} [0.5]organics_{heavy} + [0.5]char$$

Decomposition mechanism determined via TGA at atmospheric pressure.

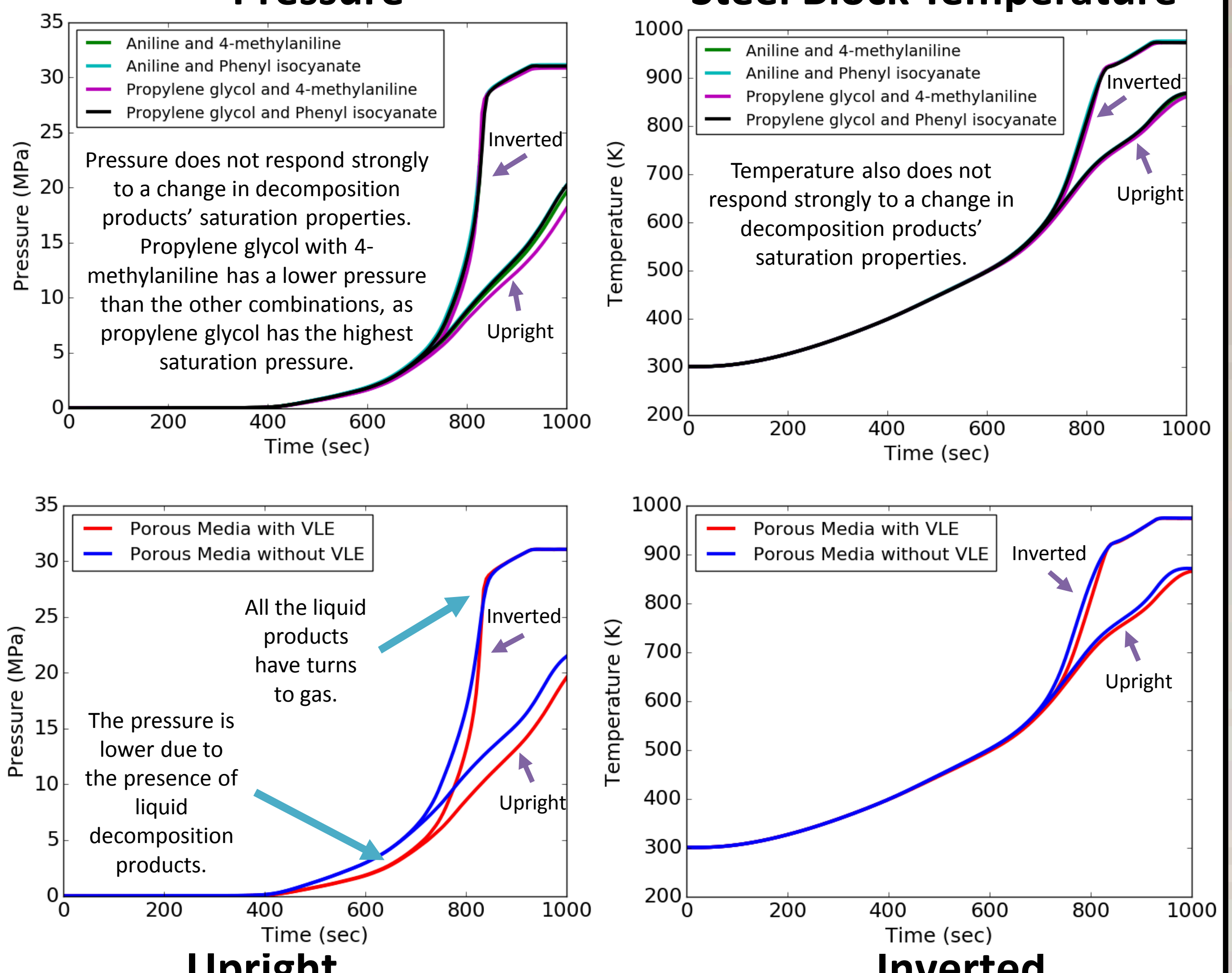
A 2D model of PMDI polyurethane foam surrounding a block of steel was created. The heating rate was 50°C/min. The simulation was run using the properties of the major decomposition products, where propylene glycol and aniline were 'light' organics and 4-methylaniline and phenyl isocyanate were 'heavy'. **The graphs to the right show that the pressure or the temperature are generally independent of the decomposition product properties.**

The addition of the VLE to the porous media equations changes both the pressure and the temperature predictions. Adding the liquid phase lowers the pressure early in time, and, in the inverted, agrees with the VLE late in time when all the liquid has vaporized.

The images to the right show the temperature and the progression of the creation of the gaseous and liquid aniline. **The amount of liquid aniline varies with temperature, where hotter areas are in the gas phase and cooler areas are in the liquid phase.**

Pressure

Steel Block Temperature



Pressure does not respond strongly to a change in decomposition products' saturation properties. Propylene glycol with 4-methylaniline has a lower pressure than the other combinations, as propylene glycol has the highest saturation pressure.

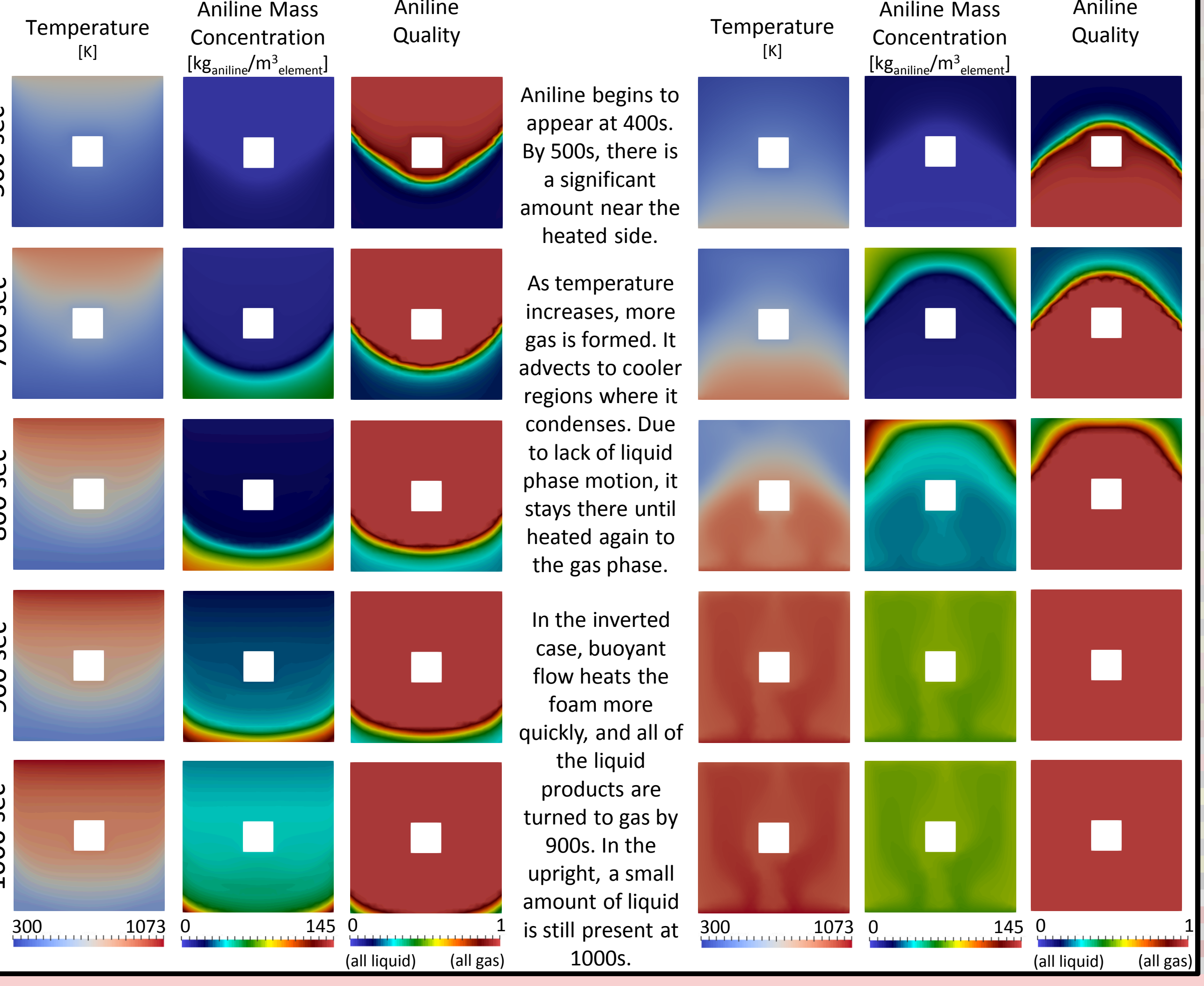
Temperature also does not respond strongly to a change in decomposition products' saturation properties.

All the liquid products have turns to gas.

The pressure is lower due to the presence of liquid decomposition products.

Upright

Inverted

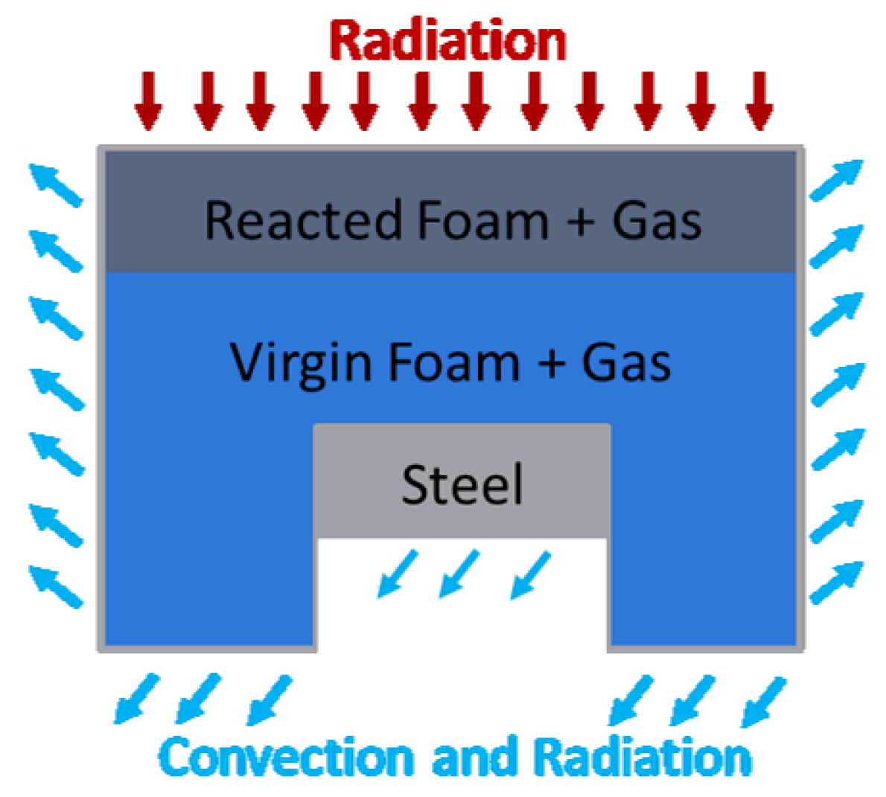


Aniline begins to appear at 400s. By 500s, there is a significant amount near the heated side.

As temperature increases, more gas is formed. It advects to cooler regions where it condenses. Due to lack of liquid phase motion, it stays there until heated again to the gas phase.

In the inverted case, buoyant flow heats the foam more quickly, and all of the liquid products are turned to gas by 900s. In the upright, a small amount of liquid is still present at 1000s.

Porous Media Model



The porous media model tracks both the condensed and the gas phases. The ideal gas equation of state is used to relate pressure and density, and Darcy's equation is used to model advection. In the condensed phase, the species and enthalpy conservation equations are solved, and the gas phase is coupled to the condensed phase through source terms in the species equations and a volumetric heat transfer term in the enthalpy equations. The foam decomposes through a three step mechanism into CO$_2$, high and low weight organics, and char. In this model, the mass fraction of organics in the gas and condensed phases are constant and determined through calibration.

In the original calibration, a 3D FEM model was used to calibrate the gas vs condensed mass fractions. The same value was used for both the inverted and upright orientations

$$FOAM \xrightarrow[k_1]{} [0.11]organics_{light} + [0.33]char + [0.56]CO_2$$
$$FOAM \xrightarrow[k_2]{} [0.34]organics_{heavy} + [0.66]char$$
$$FOAM \xrightarrow[k_3]{} [0.17]organics_{heavy} + [0.83]char$$

In a second calibration, separate values were used for the inverted and upright orientations, leading to better agreement. However, this requires prior knowledge of orientation. In addition, adding to the char phase is non-physical.

Upright

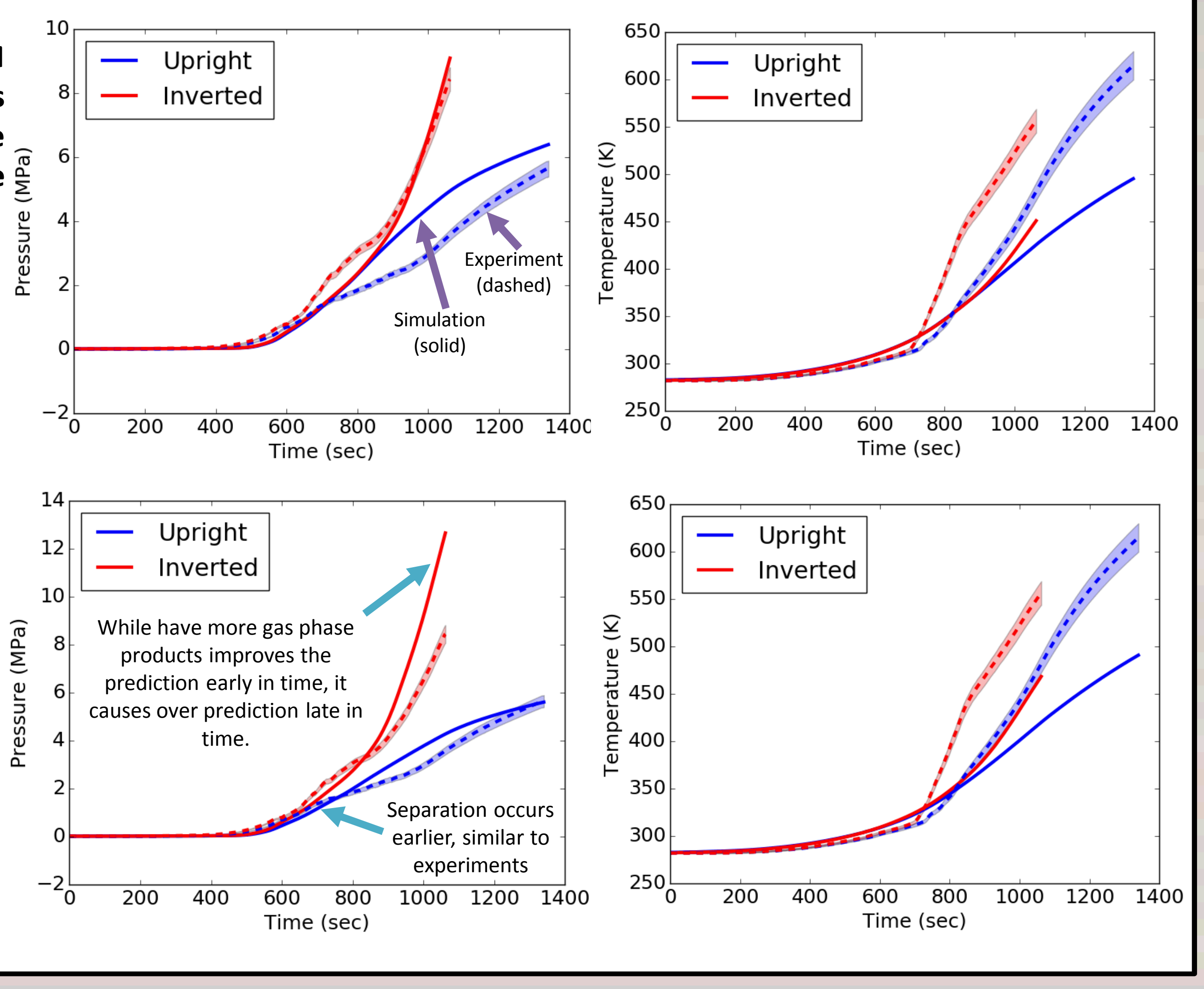
$$FOAM \xrightarrow[k_1]{} [0.01]organics_{light} + [0.43]char + [0.56]CO_2$$
$$FOAM \xrightarrow[k_2]{} [0.14]organics_{heavy} + [0.86]char$$
$$FOAM \xrightarrow[k_3]{} [0.07]organics_{heavy} + [0.93]char$$

Inverted

$$FOAM \xrightarrow[k_1]{} [0.22]organics_{light} + [0.22]char + [0.56]CO_2$$
$$FOAM \xrightarrow[k_2]{} [0.56]organics_{heavy} + [0.44]char$$
$$FOAM \xrightarrow[k_3]{} [0.28]organics_{heavy} + [0.72]char$$

Pressure

TC 25 Temperature



While have more gas phase products improves the prediction early in time, it causes over prediction late in time.

Separation occurs earlier, similar to experiments

Future Work

The vapor liquid equilibrium equations have been successfully implemented into the porous media model, however, there are still many issues to address. First, unlike the gas phase, **the liquid phase lacks motion**, meaning that it does not have gravity dependence. Further, the sensitivity of the responses to the **material properties** outside the vapor liquid equilibrium model need to be examined (e.g. the liquid phase conductivity, specific heat, etc.). Even in 2D, **the model is slow**, so work needs to be performed to decrease the run time. Once the run time is acceptable, **the model needs to be tested in 3D** so that it can be **validated against experimental results at multiple heat fluxes**.

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