A Two-Step Reaction Mechanism for Combustion of Polymeric Solids Containing Flame Retardants

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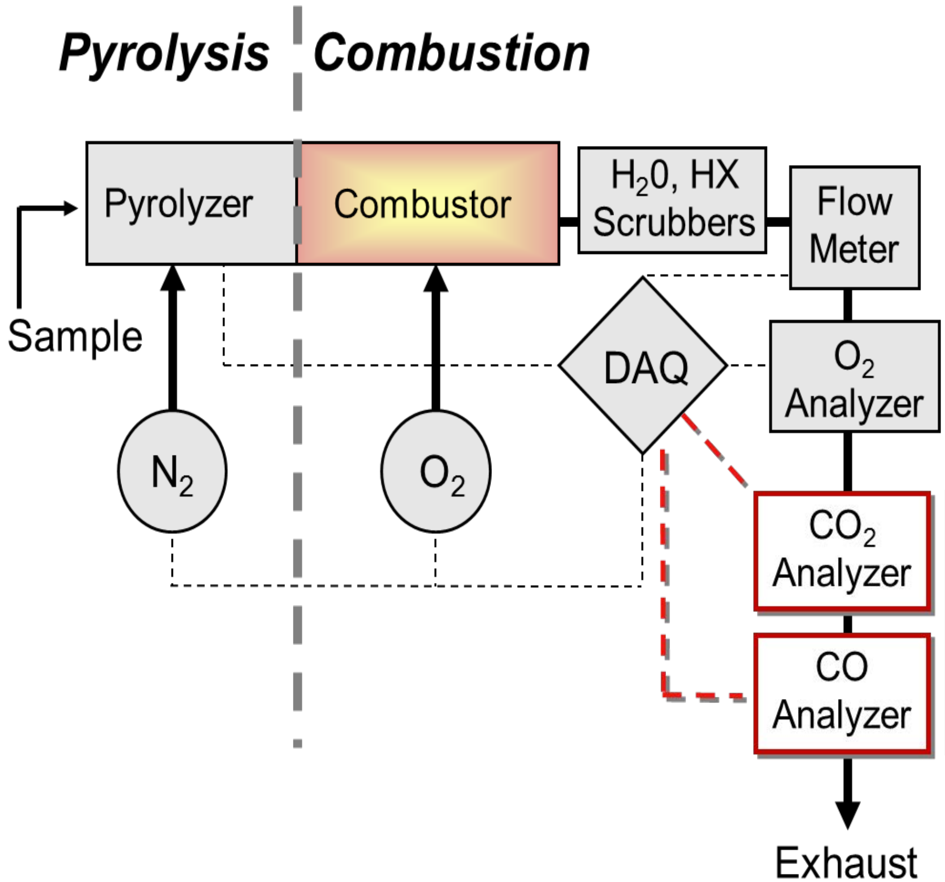
Background

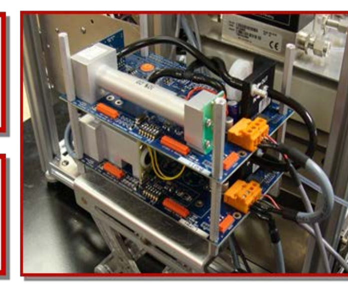
- A ban of highly effective bromine containing flame-retardant compounds that are widely used in aircraft cabins.
- Advance in phosphorous containing flame-retardant compounds as bromine replacement.
- Use of MCC (micro scale combustion calorimeter) as a tool for gas-phase combustion kinetics study (one-step global reaction).
- MCC is modified for measurements of CO and CO_2.

Objectives

- Obtain incomplete combustion of polymeric solids containing flame retardants in MCC by varying the combustor temperature.
- Implement a 2-step reaction mechanism, including a CO generation and a CO oxidation step, to describe the kinetics in the combustor.
- Correlate the kinetics from MCC test with cone calorimeter test results.

MCC Modification

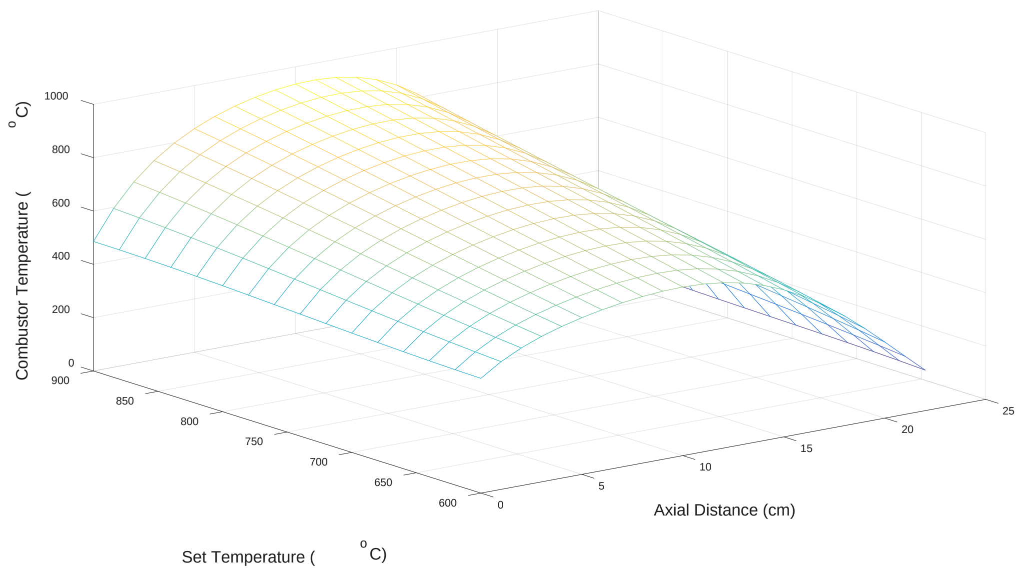




Edinburgh Instruments Gascard NG

Combustor Temperature

- ❑ Combustor temperature is not perfectly uniform at each set point.
- ❑ Surface fitting was performed with the measured temperatures at varied locations and temperature set points.
- ❑ Pyrolyzer temperature is maintained at 430 °C.



2-Step Reaction Kinetics

- The kinetics in the MCC combustor involves a 2-step reaction mechanism.

$$Fuel + O_2 \xrightarrow{k_1} CO + H_2O + product$$

$$CO + \frac{1}{2}O_2 \xrightarrow{k_2} CO_2$$

- Both reactions are second-order: first-order dependent on the fuel and the oxidizer concentration.

- Wall effect is negligible.

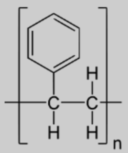
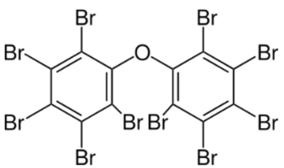
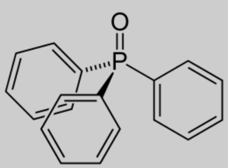
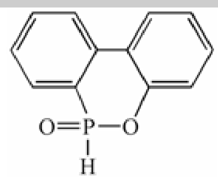
- Heat release through chemical reaction does not affect combustor temperature.

- The molar number change in the combustor is neglected.

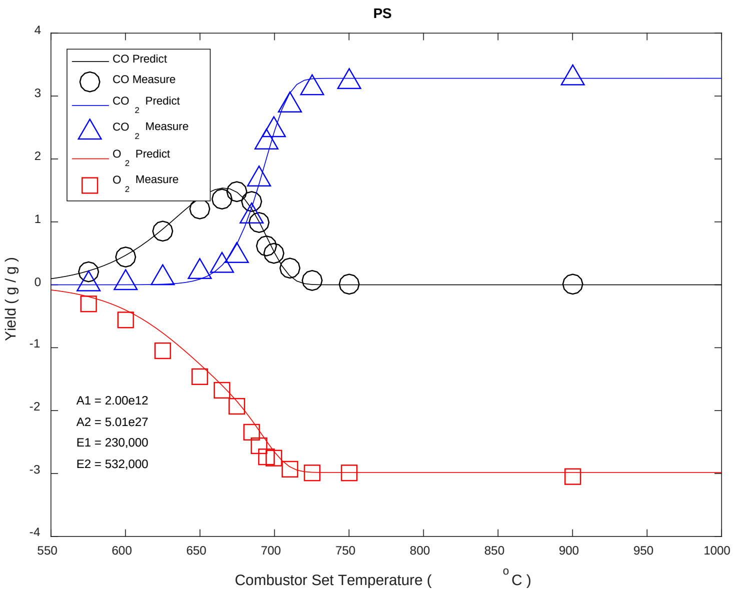
2-Step Reaction Kinetics

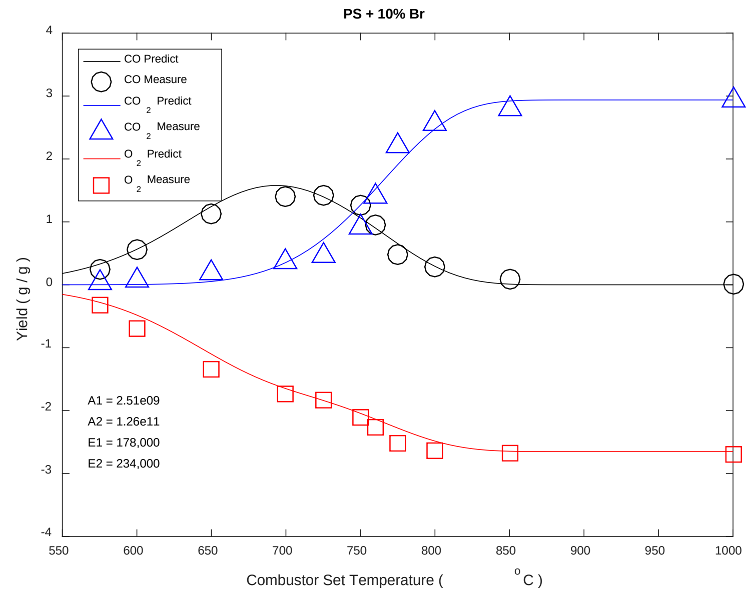
- MCC measures species (O_2, CO and CO_2) molar fraction in a dry-basis. Water is corrected based on molar balance.
- The combustor is divided into 200 elements and the residence time in each element is evaluated with the bulk velocity at ambient temperature and corrected with local temperature.
- The initial fuel concentration into the combustor is estimated with the CO_2 measurement at the complete combustion condition.
- Species concentration in the next time step is updated with d[*i*]/dt and also accounts for temperature-related volume change.
- Evolution of the species within the combustor are simulated following the 2-step mechanism using MATLAB.
- The appropriate value for the pre-exponential factor (A) and the activation energy (E) are obtained by minimizing the error in fitting the measured and the simulated species concentrations (i.e., O_2, CO, and CO_2)

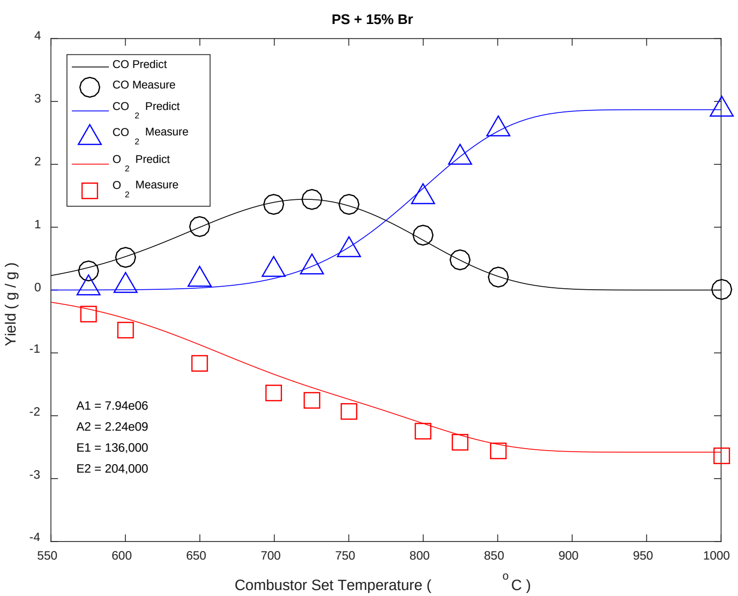
Materials

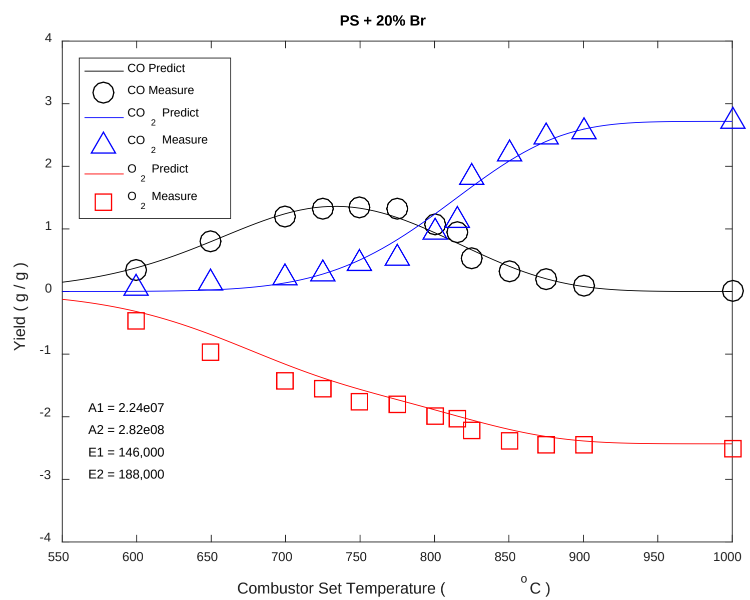
Sample	Formula	Structure
Polystyrene	PS C_8H_8	
Decabromodiphenyl oxide	DBDPO $C_{12}Br_{10}O$	
Triphenylphosphine oxide	TPPO $C_{18}H_{15}PO$	
9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide	DOPO $C_{12}H_9PO_2$	

Results _ Bromine Containing

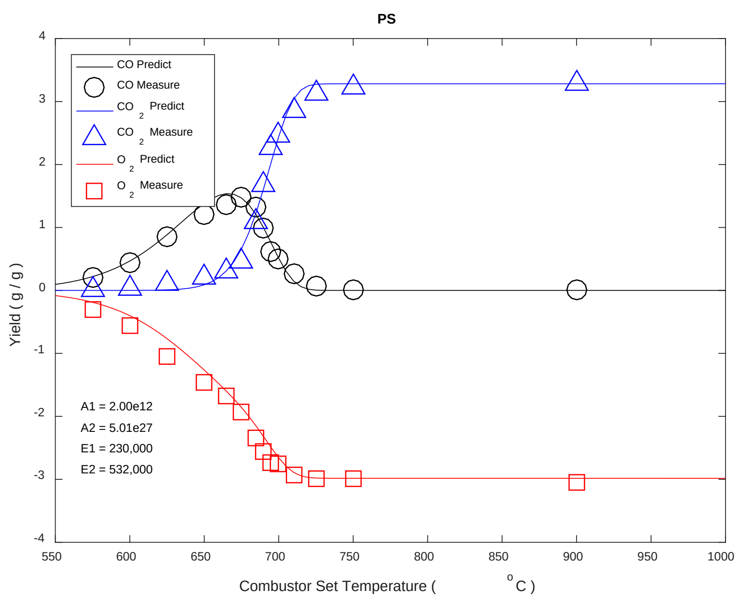


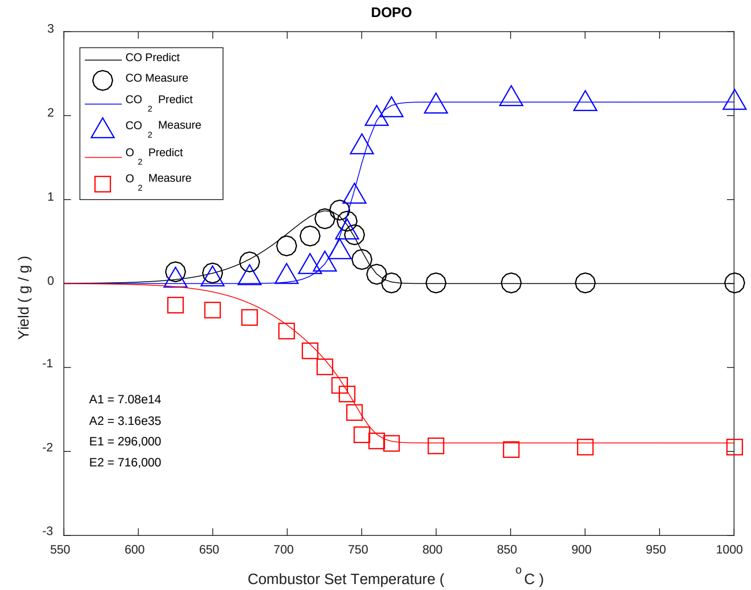


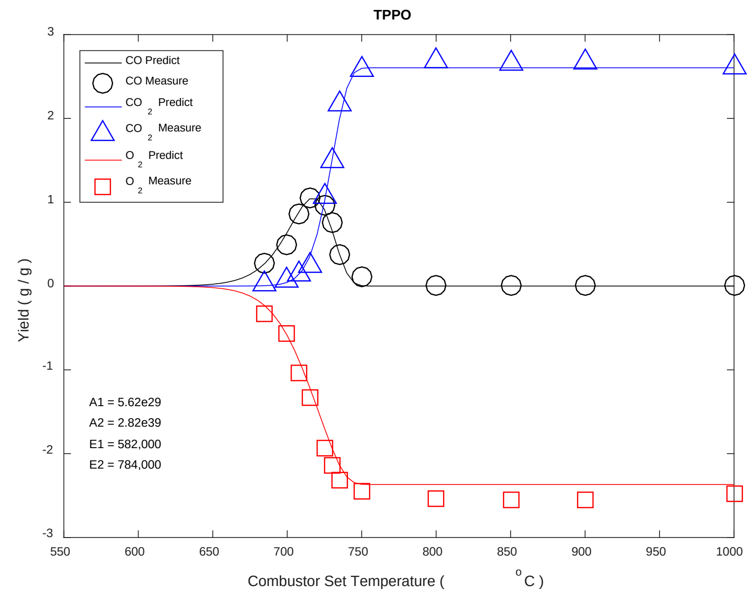




Results _ Phosphorous Containing

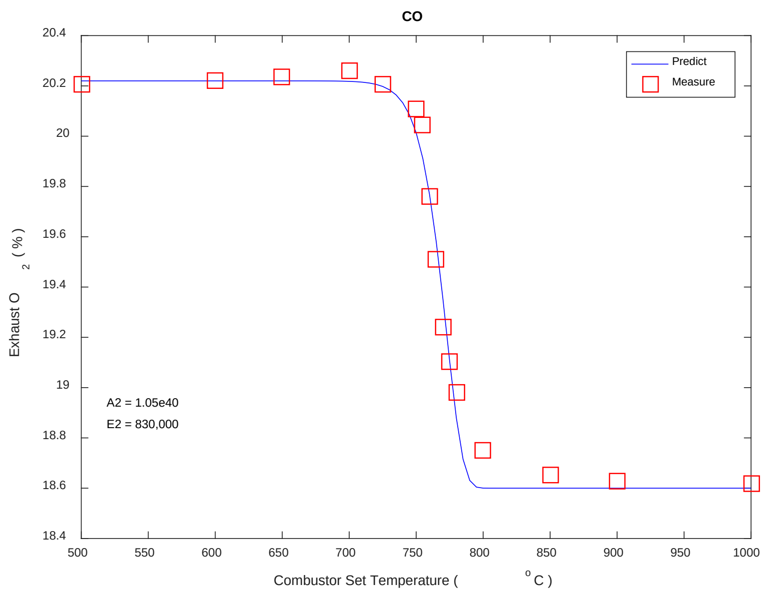






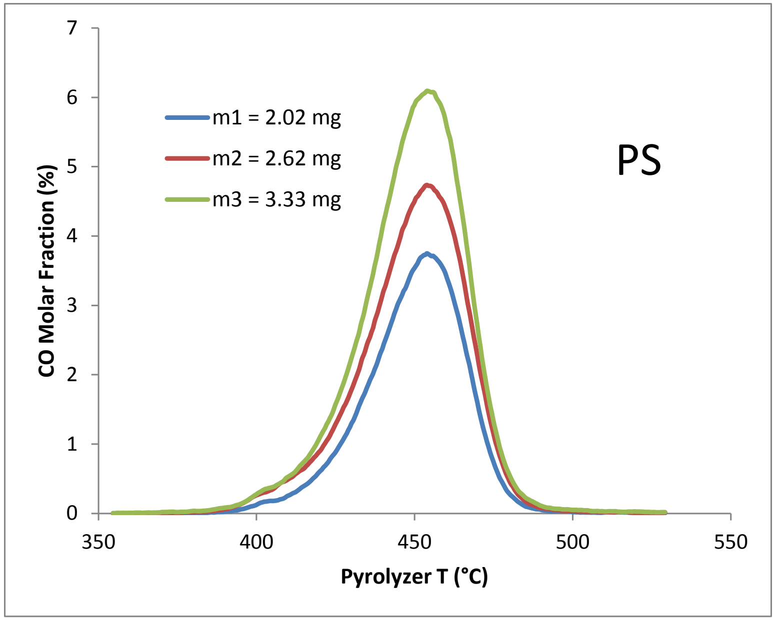
Results _ CO Oxidation

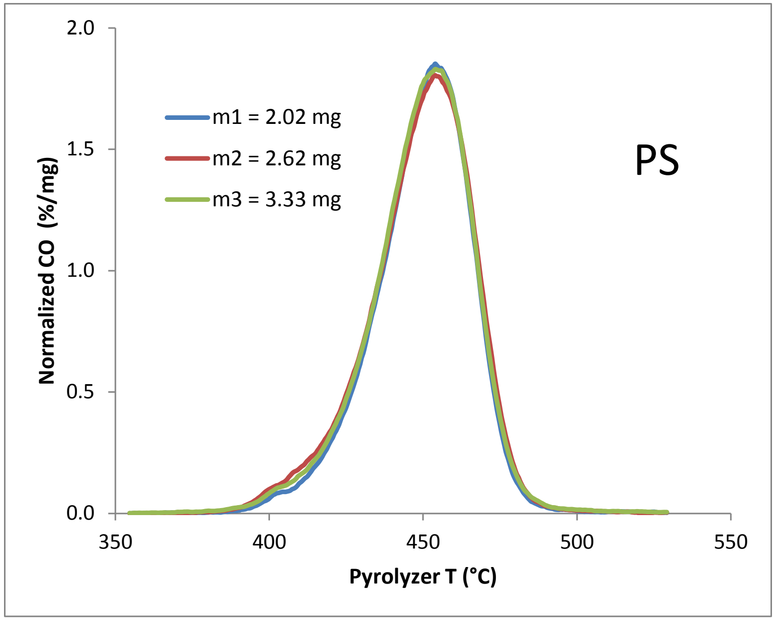
- The second reaction is examined with pure CO burning in the combustor.
- N_2 line was replaced 4.06% CO mixed in N_2 balance.



Fuel Dependence

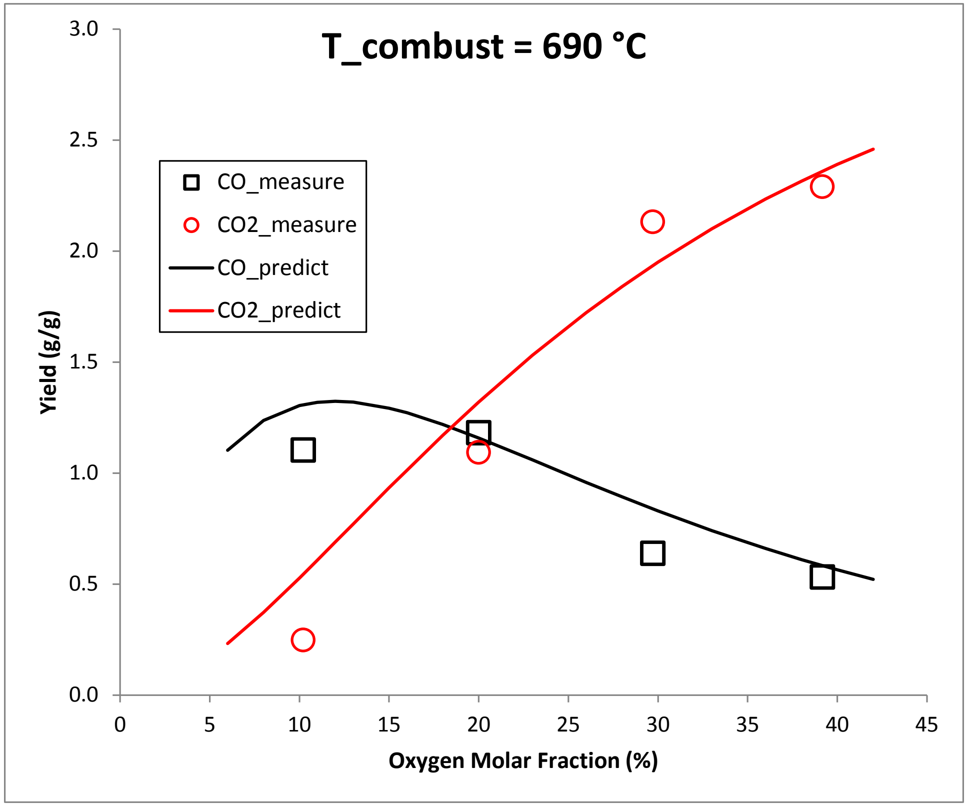
- The measured CO molar fraction should be proportional to the initial sample mass if the proposed 1st order fuel dependence is satisfied.
- Combustor temperature is fixed at 675 °C





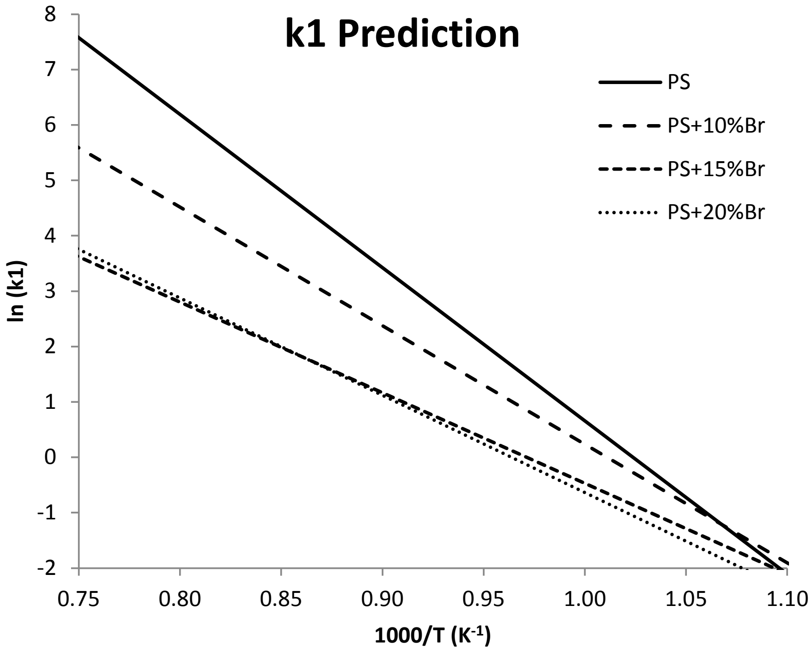
Oxygen Dependence

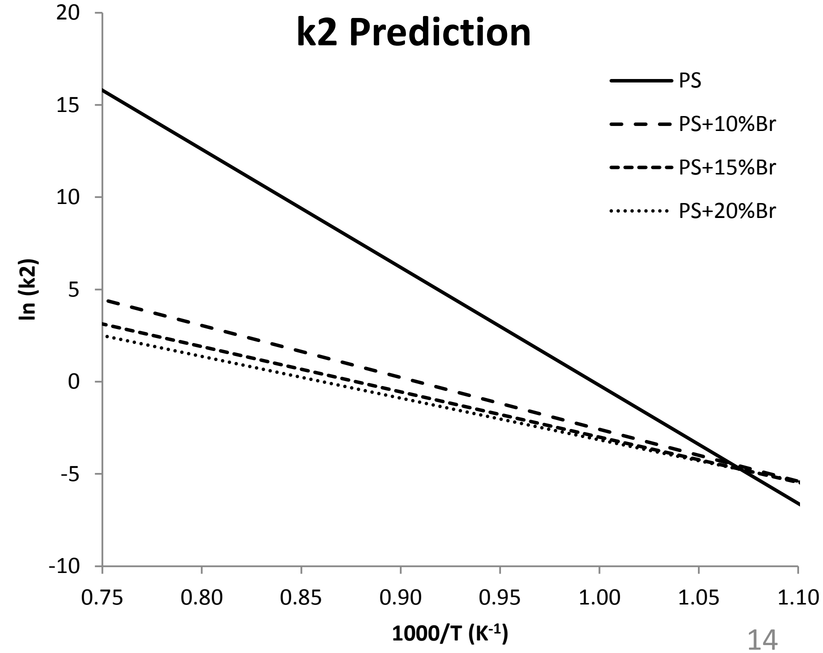
- PS was tested at T=690 °C with varied initial O_2 molar fraction.
- Reasonable agreement was observed.



Reaction Rates _ Bromine

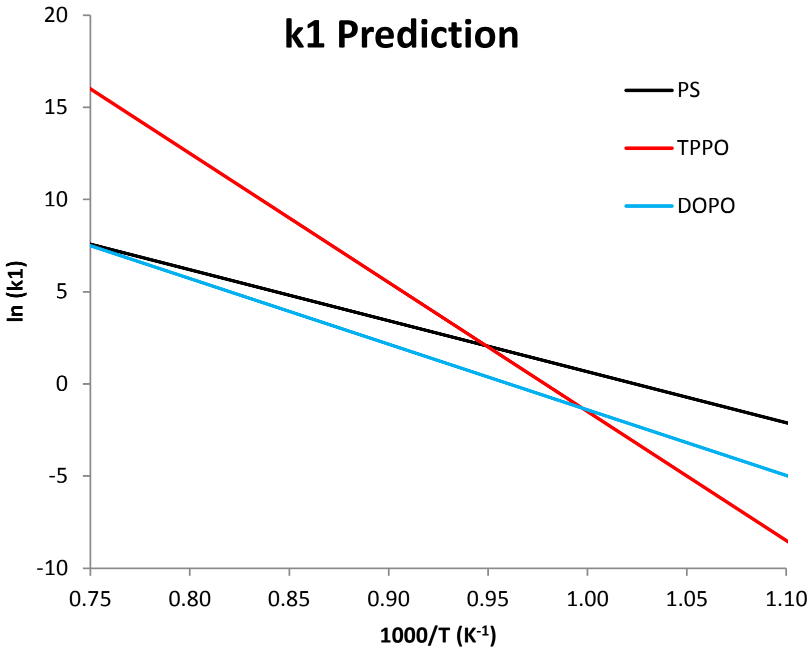
- Presence of bromine suppresses both reactions.
- The effect on the 2nd reaction is larger.
- The bromine becomes less efficient with the increase of additive concentration.

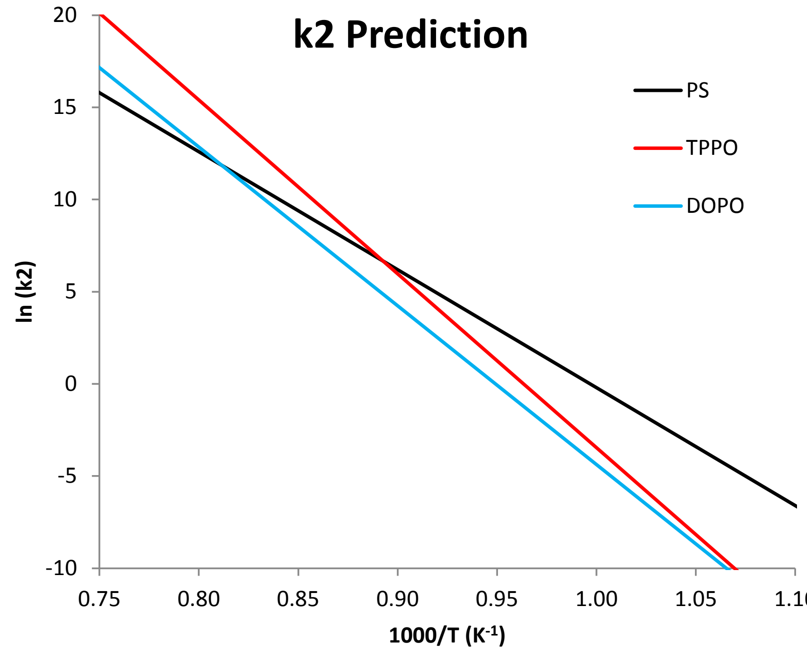




Reaction Rates _ Phosphorous

- Phosphorous containing materials' reaction rates are comparable to that of the pure PS.
- TPPO has a much faster reaction rate on the 1st reaction at higher temperatures.





Diffusion and Reaction Rates

- Damkohler number (diffusion time scale / chemical reaction time scale) is used to evaluate the condition in fire.
- Diffusion time scale is evaluated with:

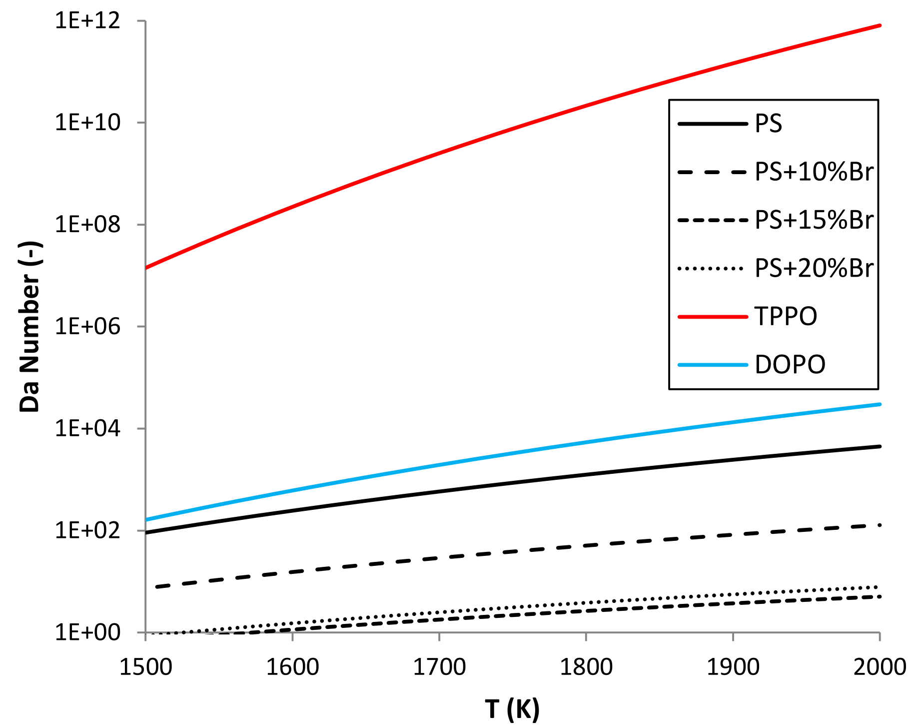
$$\tau_{diff} = \frac{L^2}{D}$$

- For bimolecular reactions where $[O_2]_0$>>$[Fuel]_0$, chemical reaction time scale is evaluated with:

$$\tau_{chem} = \frac{1}{[o_2]k_{chem}}$$

Damkohler Number for Materials

- At typical fire temperatures, the 2nd reaction is much faster than the 1st reaction. The total chemical reaction is limited by the 1st reaction (CO generation).
- *Da* number estimated for the 1st reaction for all materials.
  - Da number is always higher than unity.
  - For brominated materials, *Da* number is close to 1.
  - For Phosphorous containing materials, *Da* number is significantly higher than 1.
  - It is noted the turbulent mixing in real fires should be faster than the diffusion.

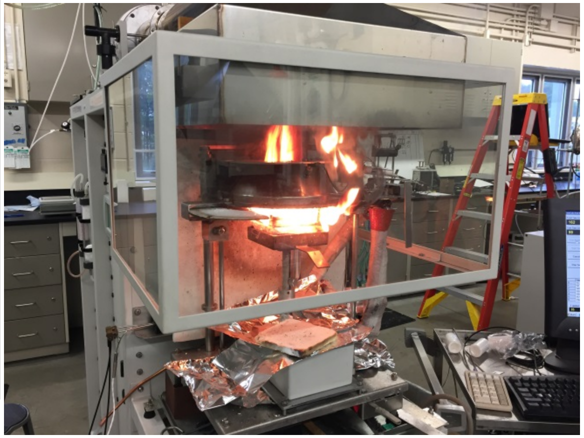


Comparison with Cone Tests

- ❑ Cone test with bromine containing material has a similar CO yield but much more smoke yield.
- ❑ Cone test with phosphorous containing material has a significant increase in incomplete combustion products.

	Smoke Yield (m2/kg)	CO Yield (kg/kg)
PS	1244	0.12
PS+10%Br	1751	0.14
PS+15%Br	1940	0.14
PS+20%Br	1999	0.15
TPPO	> 2369	0.27
DOPO	> 2416	0.37

DOPO



DOPO

Summary

- A MCC was used to study gas phase combustion of phosphorus and bromine containing polymeric materials.
- 2-step reaction kinetics were developed. And appropriate values for *A* and *E* were obtained by optimization.
- Presence of bromine suppresses both reactions with larger effect on the 2nd reaction.
- Presence of phosphorous has a higher temperature dependence.
- The Damkohler number evaluated at typical flame temperature is higher than unity, indicating a oxygen starving condition in fires.
- The cone calorimeter tests show a correlation between Damkohler number and carbon monoxide yield. For materials in which chemical reaction rate is significantly higher than mixing rate, CO yield increases.

Future Work

- Mix phosphorous additives (TPPO / DOPO) with other polymeric materials and study their kinetics. (degrading at the similar temperature)
- Modify current method of MCC testing. Use high-temperature furnace and different oxygen concentrations to achieve flame alike condition.

Acknowledgement

- The authors are grateful to the companies for providing samples used in the current experiments.