GAS PHASE COMBUSTION STUDIES IN THE MICROSCALE COMBUSTION CALORIMETER

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Objective

Develop a lab-scale screening test for gas phase activity of halogen-replacement flame retardants.

Approach

- **Use ASTM D 7309 microscale combustion calorimeter (MCC) to generate fuel pulse and control combustion gas temperature, oxygen concentration, and residence time.**
- **Use carbon monoxide (CO) and carbon dioxide (CO_2) analyzers to quantify CO_x in the combustion gases.**
- **Obtain fuel oxidation kinetic parameters from experiments using a global reaction model.**
- **Correlate gas phase activity in flame with MCC data for FR polymers and plastics.**

Experimental Methods

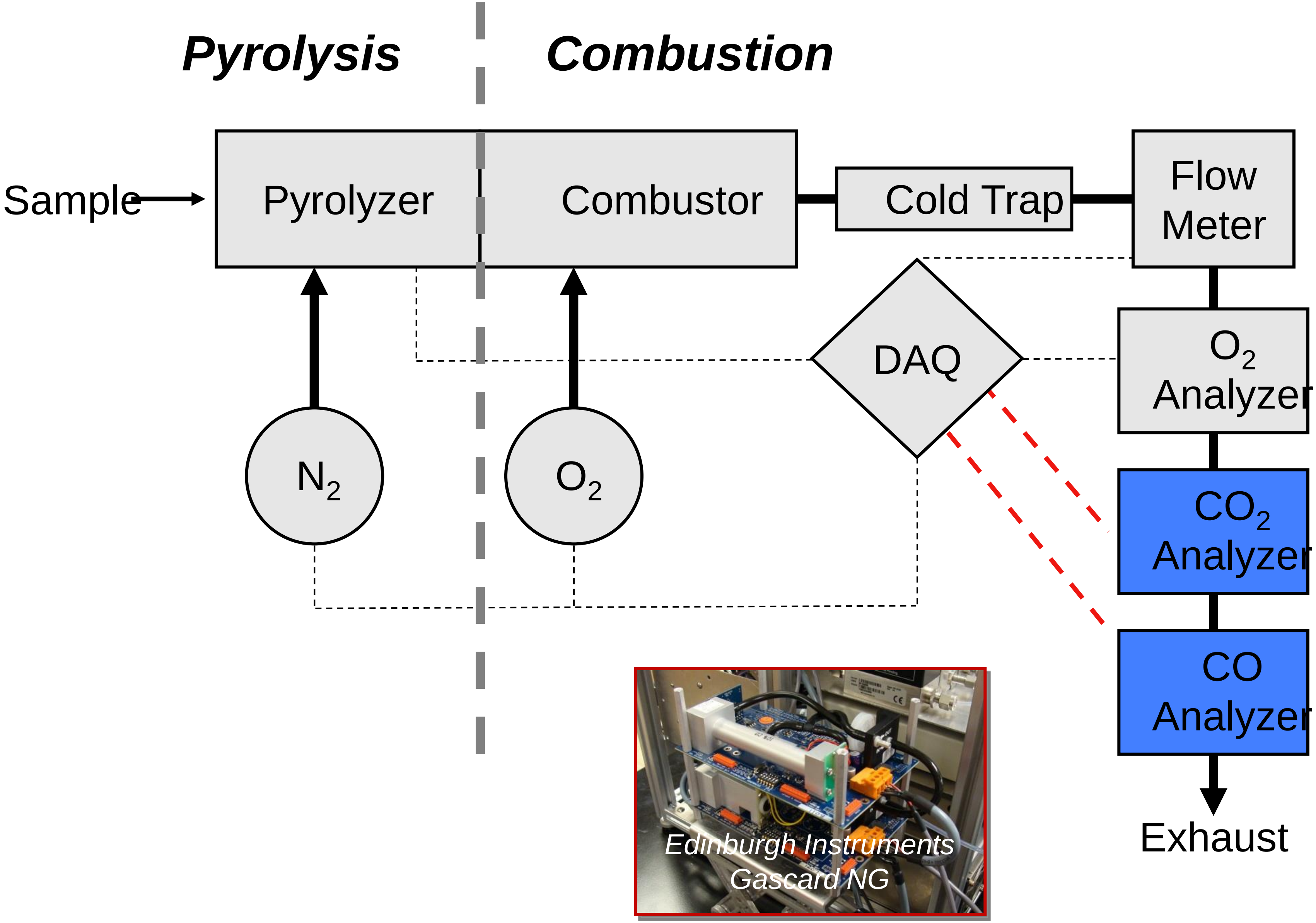
Premixed, Non-flaming Combustion

ASTM D 7309 Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry, American Society for Testing and Materials (2007).

Non-Premixed, Flaming Combustion

ASTM E 1354 Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter, American Society for Testing and Materials (2004).

Modified MCC to Measure CO & CO_2



Pyrolysis

Combustion

Sample

Pyrolyzer

Combustor

Cold Trap

Flow Meter

DAQ

O_2 Analyzer

CO_2 Analyzer

CO Analyzer

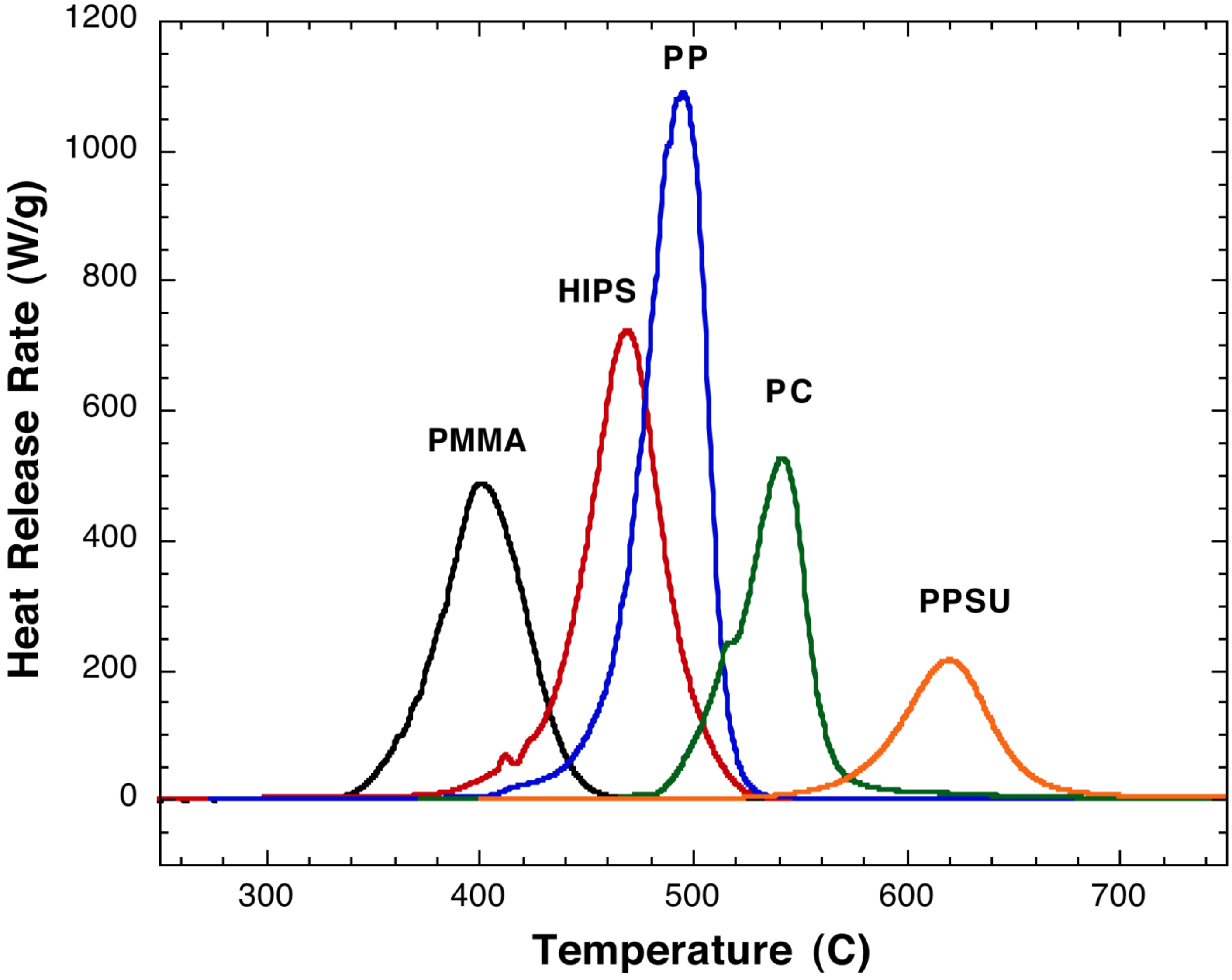
Exhaust

N_2

O_2

Edinburgh Instruments Gascard NG

Sample Heat Release Rates



Combustion Gas Analysis

Mass flow rate of gas

$$\dot{m}_i = F X_i \rho_i$$

Where i = O_2, CO, CO_2

Time integral for total amount of gas consumed/produced

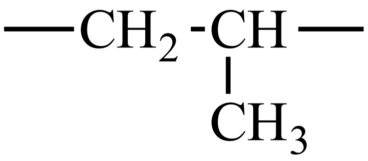
$$m_i = \int_0^{\tau} \dot{m}_i dt + \int_{\tau}^{\infty} \dot{m}_i dt = \int_0^{\infty} (\dot{m}_i + 0) dt = \int_0^{\infty} \dot{m}_i dt = \int_0^{\infty} F X_i \rho_i dt$$

Yield of gas per mass of volatile fuel in sample

$$y_i = \frac{m_i}{m_F}$$

Maximum Gas Yields

Polypropylene



$$-CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$$

Stoichiometry

$$1\ C_3H_6 + 4.5\ O_2 \longrightarrow 3\ CO_2 + 3\ H_2O$$

$$-y_{O_2}^{\infty} = r_0 = \frac{(4.5\,moles\,O_2)(32g/mole\,O_2)}{(1\,mole\,PP)(42.1g/mole\,PP)} = 3.42\,\frac{g\,O_2}{g\,PP}$$

$$y_{CO_2}^{\infty} = f_0 = \frac{(3\,moles\ CO_2)(44g/mole\ CO_2)}{(1\,mole\,PP)(42.1g/mole\ PP)} = 3.14\,\frac{g\ CO_2}{g\ PP}$$

$$y_{CO}^{\max} \le \frac{(3\,moles\ CO)(28g/mole\ CO)}{(1\,mole\,PP)(42.1g/mole\ PP)} = 2.00\,\frac{g\ CO}{g\ PP}$$

Gas Yields

Polymer	**Formula**	**MW** (g/mol)	**Total HR** (kJ/g)	**Char** (%)	**O2 Yield**		**CO Yield**		**CO2 Yield**		
					Theory	Expt.	Theory	Expt.	Theory	Expt.	
PP	C_3H_6	42.1	42.5	0.0	3.42	3.24	2.00	1.09	3.14	3.06	Non-Charring
PMMA	$C_5H_8O_2$	100.1	24.6	0.0	1.92	1.88	1.40	0.78	2.20	2.16	
FEP	C_5F_{10}	214.0	4.5	0.0	0.75	0.34	0.65	0.06	1.03	0.66	
POM	CH_20	30.0	14.2	0.1	1.07	1.08	0.93	0.75	1.47	1.41	
HDPE	C_2H_4	28.1	42.9	0.2	3.42	3.27	2.00	1.14	3.14	3.01	
ABS	$C_{15}H_{17}N$	211.3	36.6	0.7	2.92	2.79	1.99	0.98	3.12	3.03	
PA66	$C_{12}H_{22}O_2N_2$	226.3	28.7	1.0	2.33	2.19	1.49	0.54	2.33	2.17	
HIPS	$C_{12}H_{14}$	158.2	38.8	2.4	3.13	2.96	2.12	1.29	3.34	3.25	Charring
PET	$C_{10}H_8O_4$	192.2	17	12.8	1.67	1.30	1.46	0.53	2.29	1.73	
PVC	C_2H_3Cl	62.5	11.2	18.5	1.41	0.85	0.90	0.34	1.41	0.78	
PC1	$C_{16}H_{14}O_3$	254.3	21.9	20.2	2.27	1.67	1.76	0.43	2.77	1.92	
PC2	$C_{16}H_{14}O_3$	254.3	20.3	22.9	2.27	1.55	1.76	0.43	2.77	1.85	
PPS	C_6H_4S	108.2	15.2	40.9	2.07	1.16	1.55	0.39	2.44	1.03	
PPSU	$C_{24}H_{16}O_4S$	400.4	13.1	41.2	2.08	1.00	1.68	0.39	2.64	1.06	
PEI	$C_{37}H_{24}O_6N_2$	592.6	10.4	52.0	2.16	0.79	1.75	0.21	2.75	0.88	

Mass Balance - Non-Charring

Repeat Unit Structure

Complete Combustion Products

Measured Values

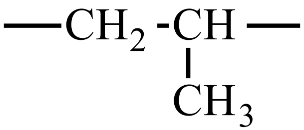
POM $—CH_2-O—$ $+ 1\ O_2 \longrightarrow 1\ CO_2 + 1\ H_2O$

1 1

Polyethylene $—CH_2-CH_2—$ $+ 3\ O_2 \longrightarrow 2\ CO_2 + 2\ H_2O$

2.9 1.9

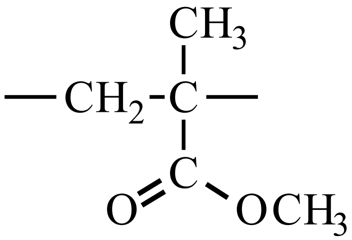
Polypropylene



$—CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}—$ $+ 4.5\ O_2 \longrightarrow 3\ CO_2 + 3\ H_2O$

4.3 2.9

PMMA



$+ 6\ O_2 \longrightarrow 5\ CO_2 + 4\ H_2O$

5.9 4.9

Char Composition from CO_2 Measurements

$$C_C = C_P - C_G \qquad C_G = \left[MW_P * \left(\frac{y_{CO_2}}{MW_{CO_2}} \right) \right]$$

$$C_C = C_P - \left[MW_P * \left(\frac{y_{CO_2}}{MW_{CO_2}} \right) \right]$$

$$Char(\%) = 100 * \frac{\left[\left(C_C * MW_C \right) + \left(H_C * MW_H \right) + \left(O_C * MW_O \right) + \left(X_C * MW_X \right) \right]}{MW_P}$$

Char Composition C_5H_2

$$H_C = {}^{2}\!/_{5}\, C_C \qquad Char(\%) = 100 * \frac{\left[\left(C_C * MW_C \right) + \left({}^{2}\!/_{5}\, C_C * MW_H \right) \right]}{MW_P}$$

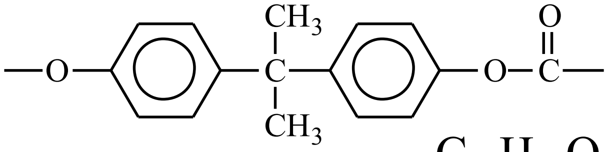
Mass Balance - Charring

Repeat Unit Structure

Complete Combustion Products

Char

PC



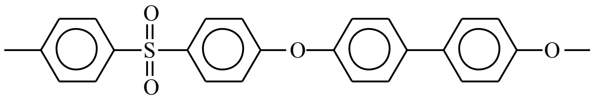
$C_{16}H_{14}O_3$

~~$+ 18\ O_2 \longrightarrow 16\ CO_2 + 7\ H_2O$~~

21.6 %

$+ 12.8\ O_2 \longrightarrow 10.9\ CO_2 + 6\ H_2O + C_5H_2$

PPSU



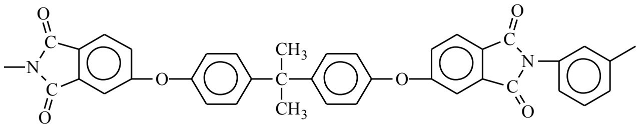
$C_{24}H_{16}O_4S$

~~$+ 27\ O_2 \longrightarrow 24\ CO_2 + 8\ H_2O + 1\ SO_2$~~

41.2 %

$+ 12.5\ O_2 \longrightarrow 9.6\ CO_2 + 5\ H_2O + 1\ SO_2 + 3\ C_5H_2$

PEI



$C_{37}H_{24}O_6N_2$

~~$+ 38.5\ O_2 \longrightarrow 37\ CO_2 + 9\ H_2O + 1\ N_2$~~

52 %

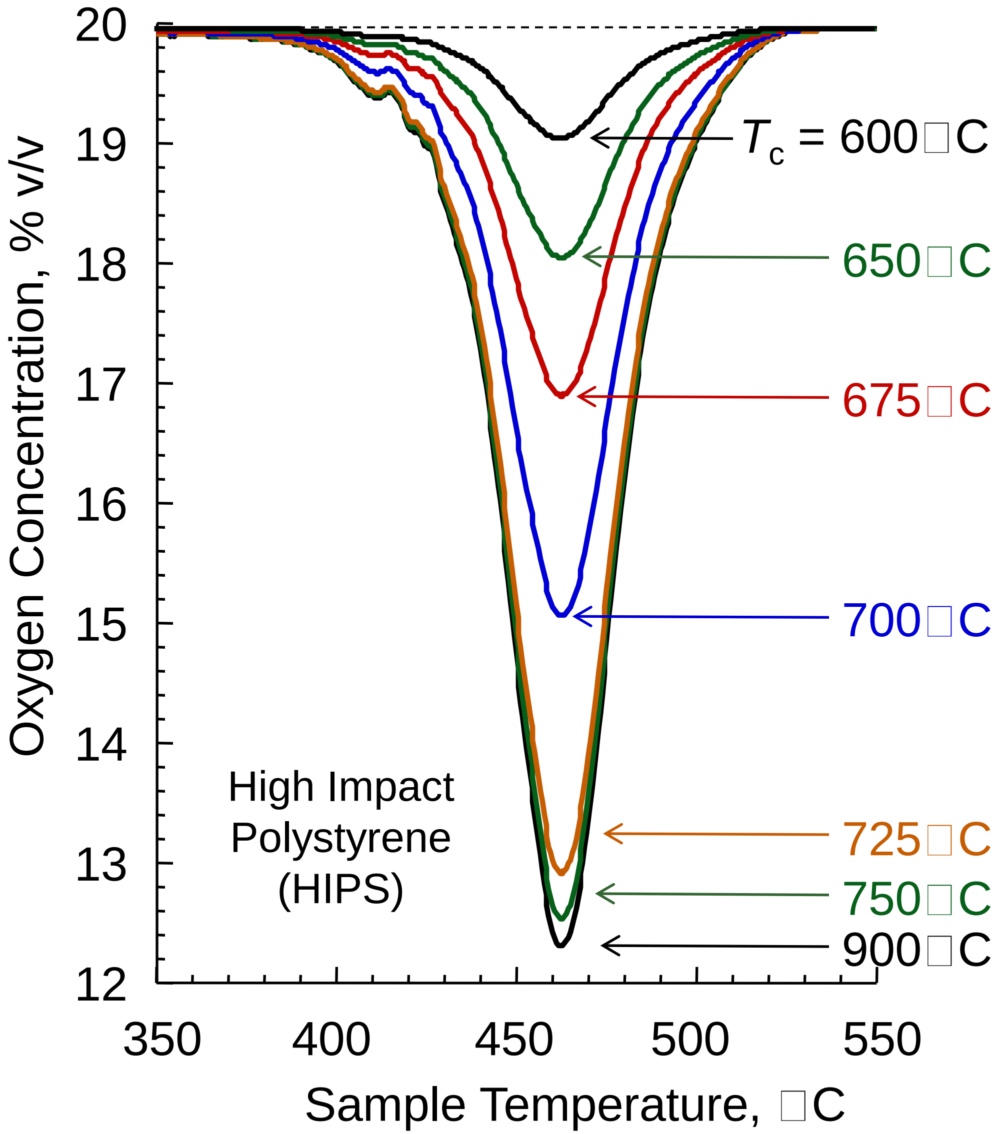
$+ 14.7\ O_2 \longrightarrow 11.8\ CO_2 + 4\ H_2O + 1\ N_2 + 5\ C_5H_2$

Char from Mass Balance

Polymer	Formula	MW (g/mol)	Total HR (kJ/g)	Char Yield		
				Expt.	Theory	
PP	C_3H_6	42.1	42.5	0.0	2.1	Non-Charring
PMMA	$C_5H_8O_2$	100.1	24.6	0.0	1.0	
FEP	C_5F_{10}	214.0	4.5	0.0	10.2	
POM	CH_20	30.0	14.2	0.1	1.7	
HDPE	C_2H_4	28.1	42.9	0.2	3.5	
ABS	$C_{15}H_{17}N$	211.3	36.6	0.7	2.7	
PA66	$C_{12}H_{22}O_2N_2$	226.3	28.7	1.0	4.6	
HIPS	$C_{12}H_{14}$	158.2	38.8	2.4	2.4	Charring
PET	$C_{10}H_8O_4$	192.2	17	12.8	15.9	
PVC	C_2H_3Cl	62.5	11.2	18.5	17.8	
PC1	$C_{16}H_{14}O_3$	254.3	21.9	20.2	23.9	
PC2	$C_{16}H_{14}O_3$	254.3	20.3	22.9	26.0	
PPS	C_6H_4S	108.2	15.2	40.9	39.8	
PPSU	$C_{24}H_{16}O_4S$	400.4	13.1	41.2	44.6	
PEI	$C_{37}H_{24}O_6N_2$	592.6	10.4	52.0	52.7	

Theoretical yield assumes char composition is C_5H_2

Polystyrene Oxygen Consumption



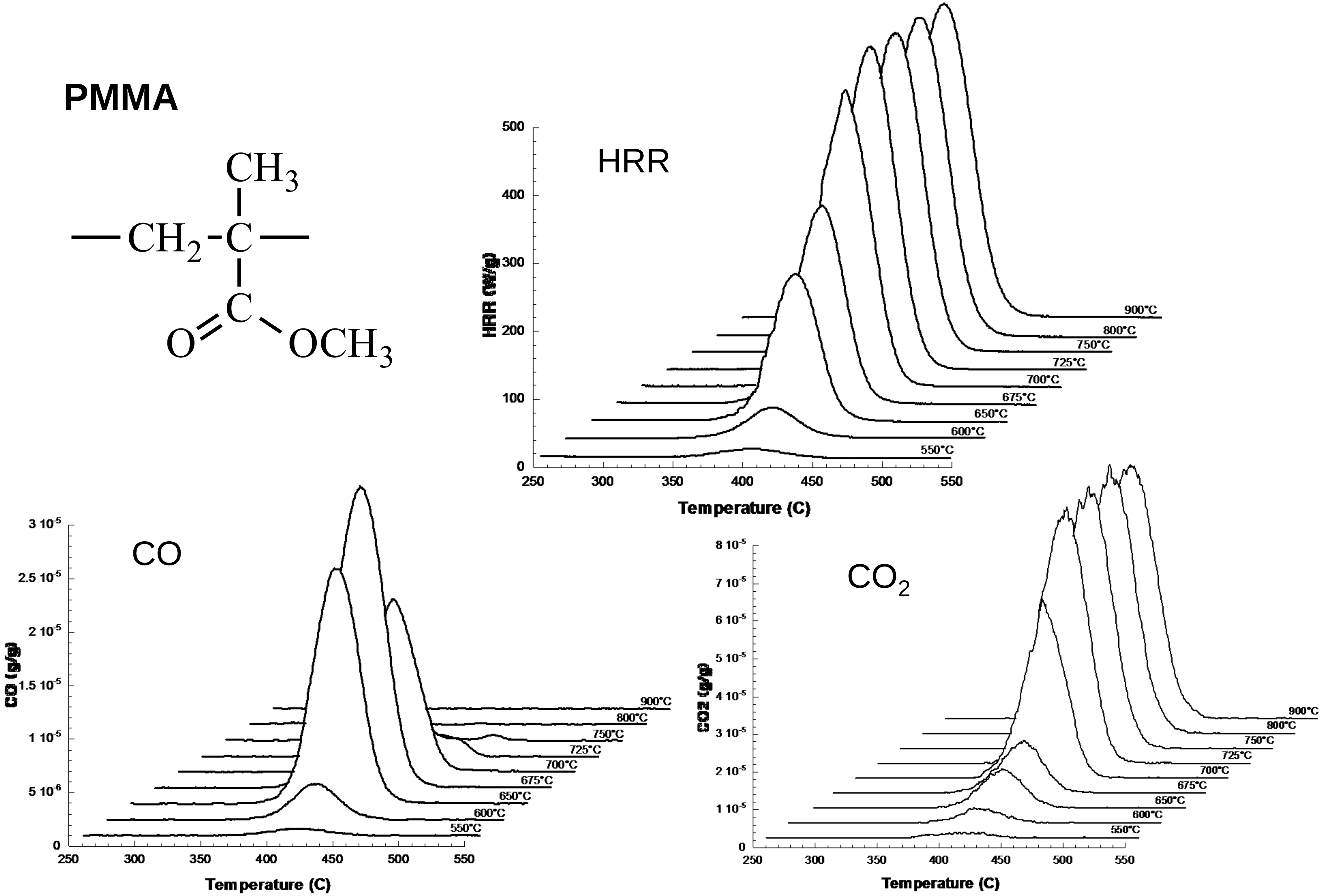
Extent of Oxidation (α) at Combustor Temperature, T_c =

$$\alpha(T_c) = \frac{\left(\int \Delta X_{O_2} dT\right)_{T_c}}{\left(\int \Delta X_{O_2} dT\right)_{T_c = 900°C}}$$

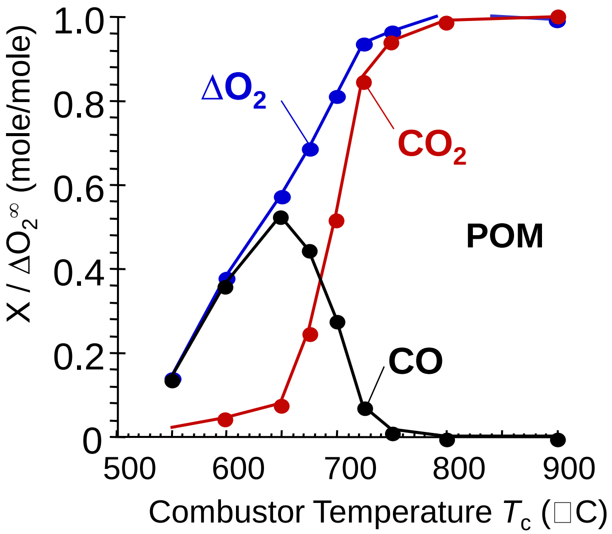
$$= \frac{\Delta O_2(T_c)}{\Delta O_2(900°C)}$$

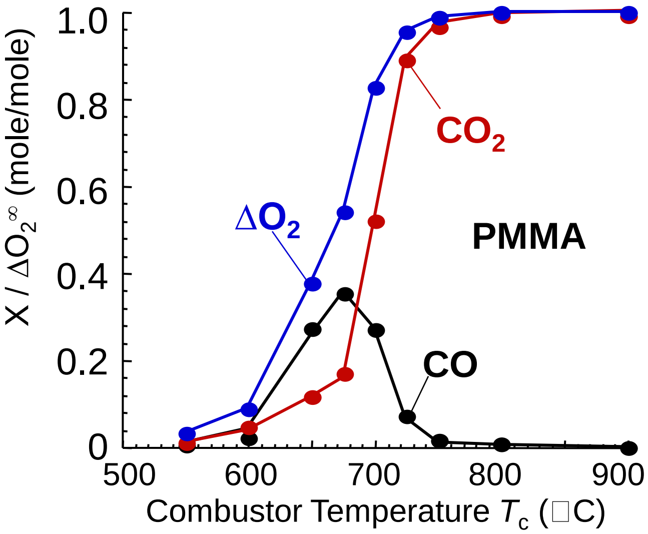
Heat Release Rate & CO/CO_2 Generation

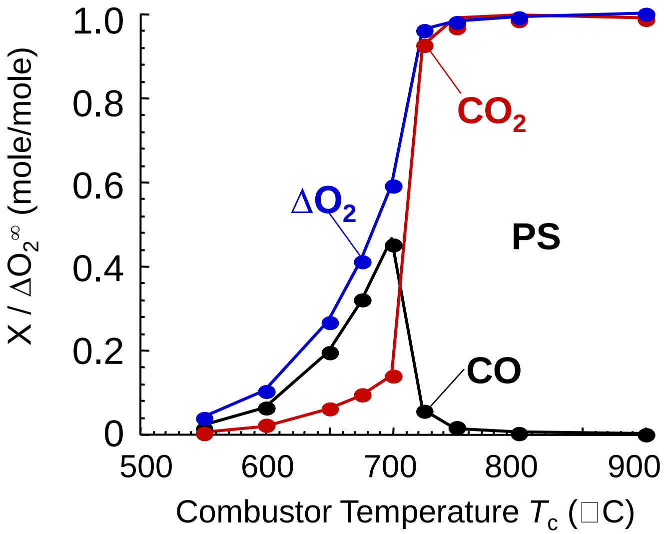
PMMA

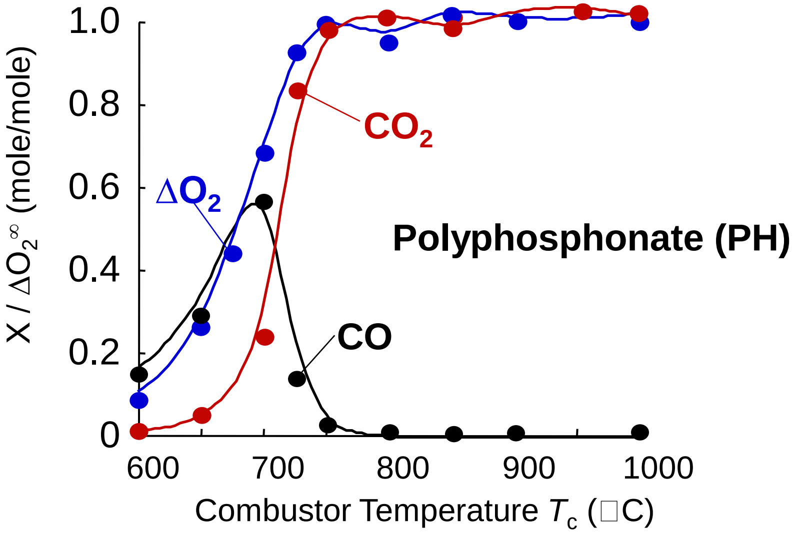


Hydrocarbon Polymers

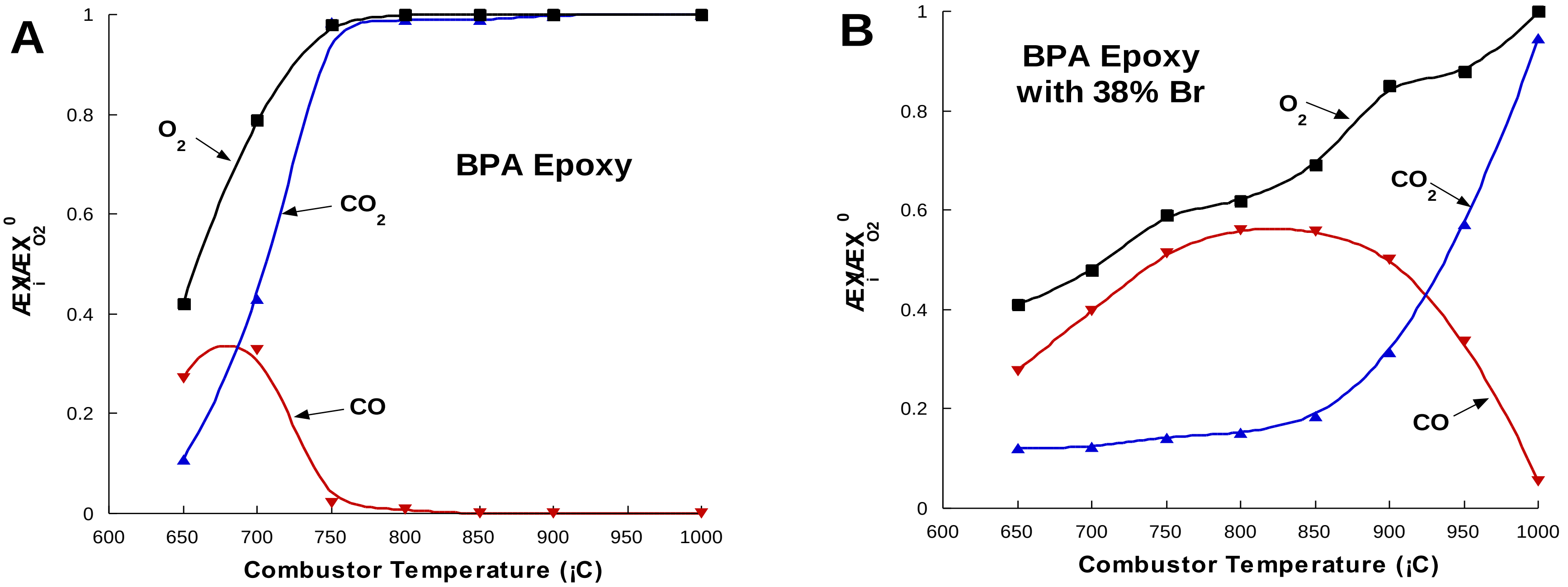








Bromine Effect on Combustion



Bromine slows down the CO → CO_2 reaction by scavenging the necessary H and OH radicals: $Br_2 + 2OH \rightarrow 2HBr + O_2$ and $H + HBr \rightarrow H_2 + Br$.

As a result, complete combustion of Br-containing fuel gases not attained in 9 seconds until T_c > 1000°C.

Kinetic Parameters from MCC

$$1-\alpha = \exp[-k_{app}t]$$

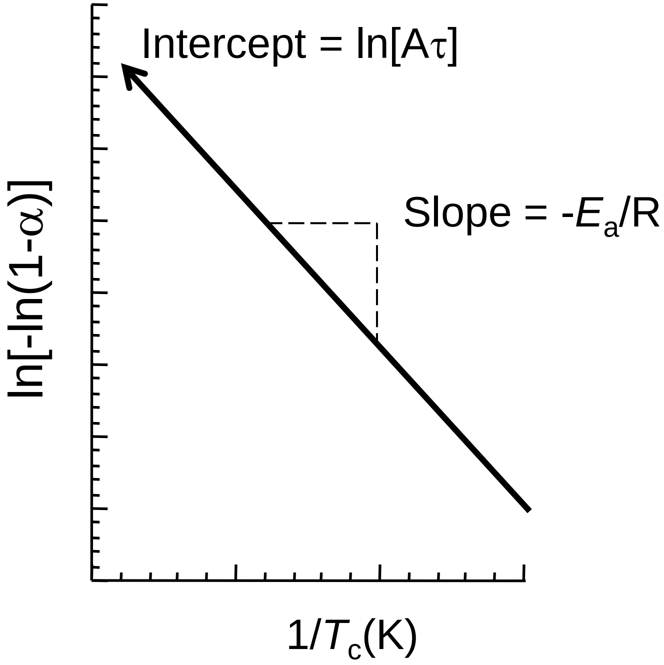
Pseudo-First Order,
Isothermal ($T = T_c$), Isochronal ($t = \tau = 9s$)
Oxidation Kinetics

Take natural log

$$-\ln[1-\alpha] = kt = A\tau\exp\left[-\frac{E_a}{RT_c}\right]$$

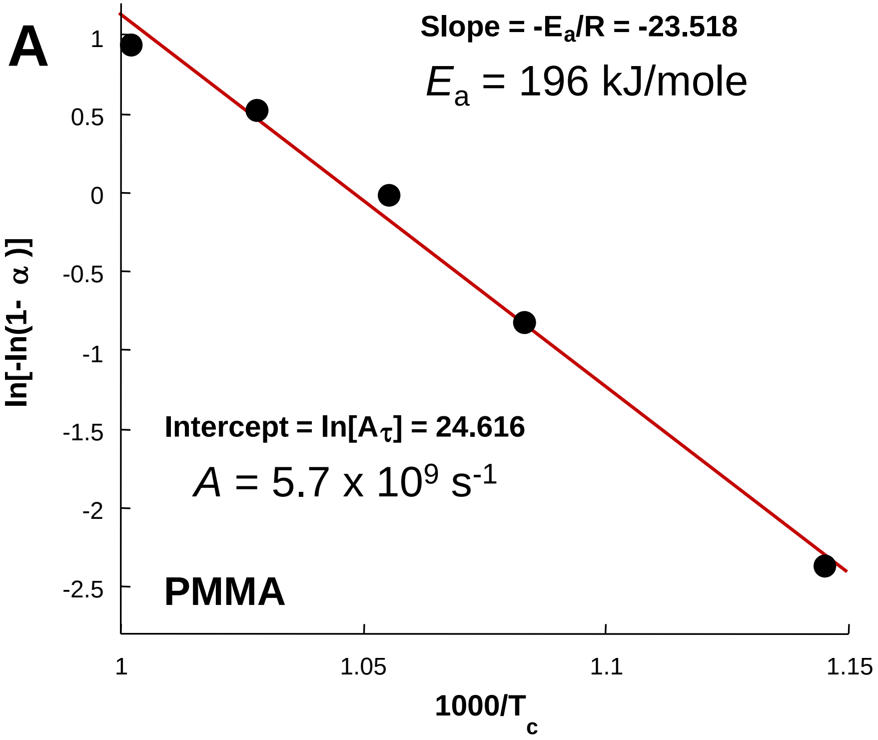
Take natural log again

$$\ln\{-\ln[1-\alpha]\} = \ln[A\tau] - \frac{E_a}{RT_c}$$



Fit to α(□) versus 1/T_c data

Global Oxidation Kinetics

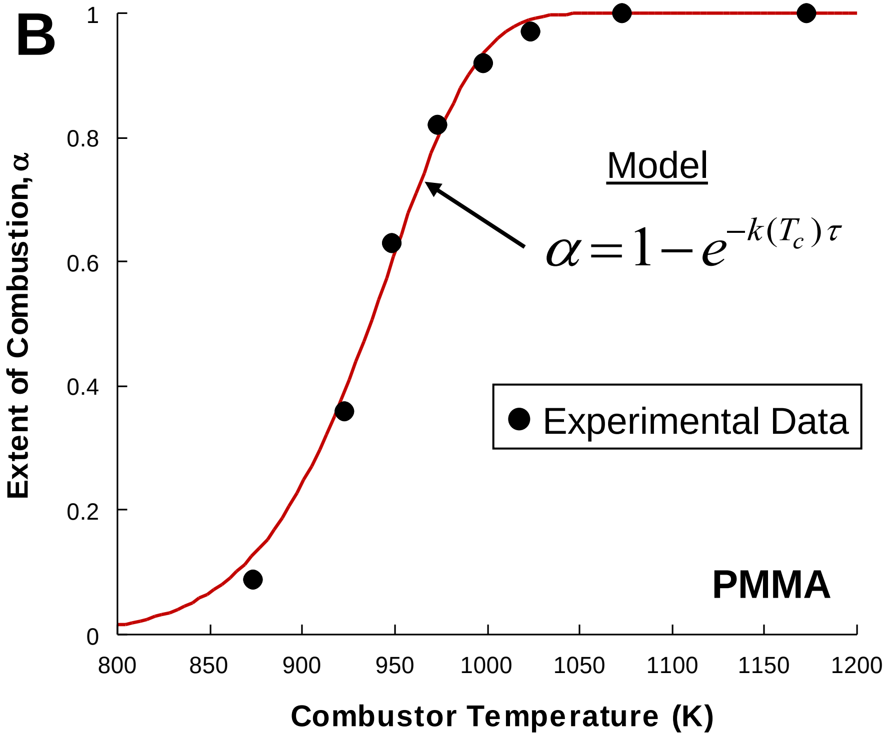


Slope = $-E_a/R$ = -23.518

E_a = 196 kJ/mole

Intercept = ln[$A\tau$] = 24.616

$A = 5.7 \times 10^9\ \mathrm{s}^{-1}$

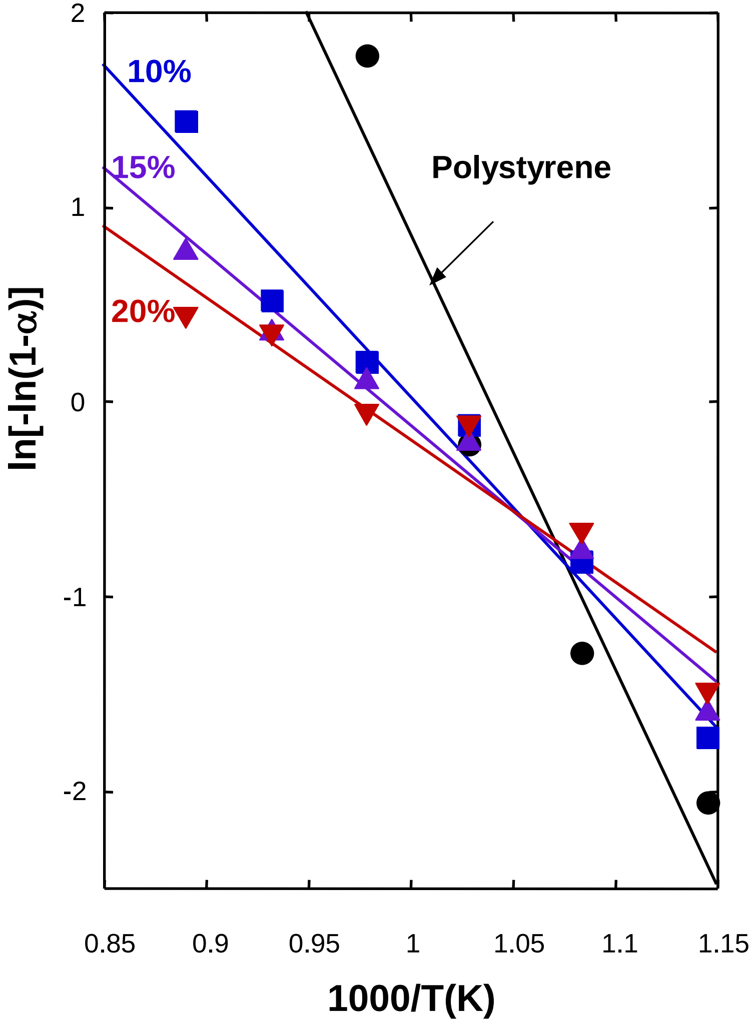


Model

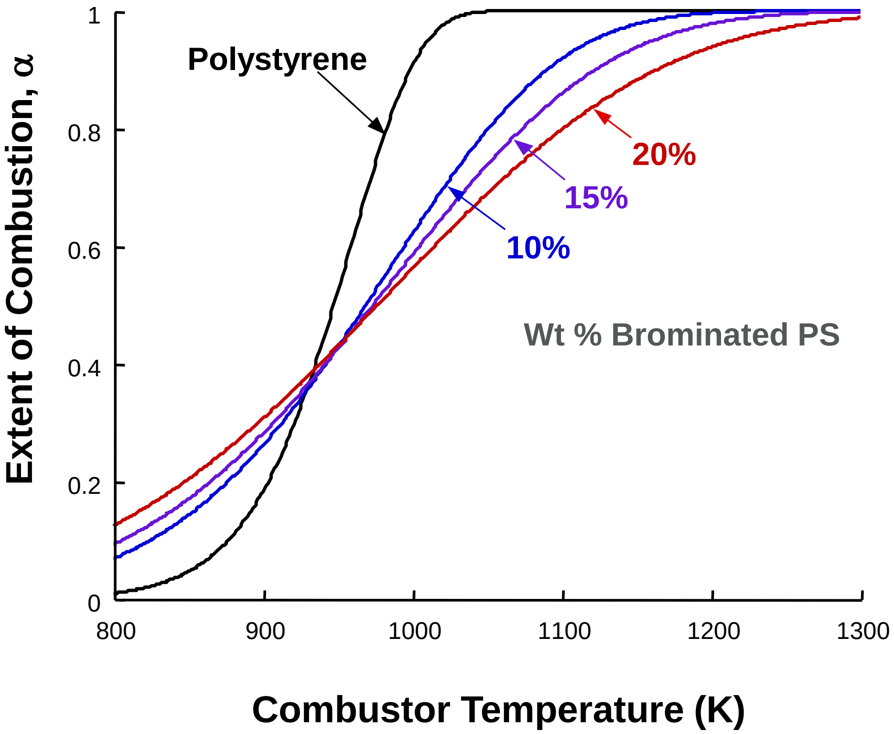
$$\alpha = 1 - e^{-k(T_c)\tau}$$

$$\alpha = 1 - \frac{X_{O_2}}{X_{O_2}^{0}} = \frac{\Delta X_{O_2}}{\Delta X_{O_2}^{\infty}} = 1 - \exp[-k_{app}\tau]$$

Bromine Effect on Extent of Combustion in MCC

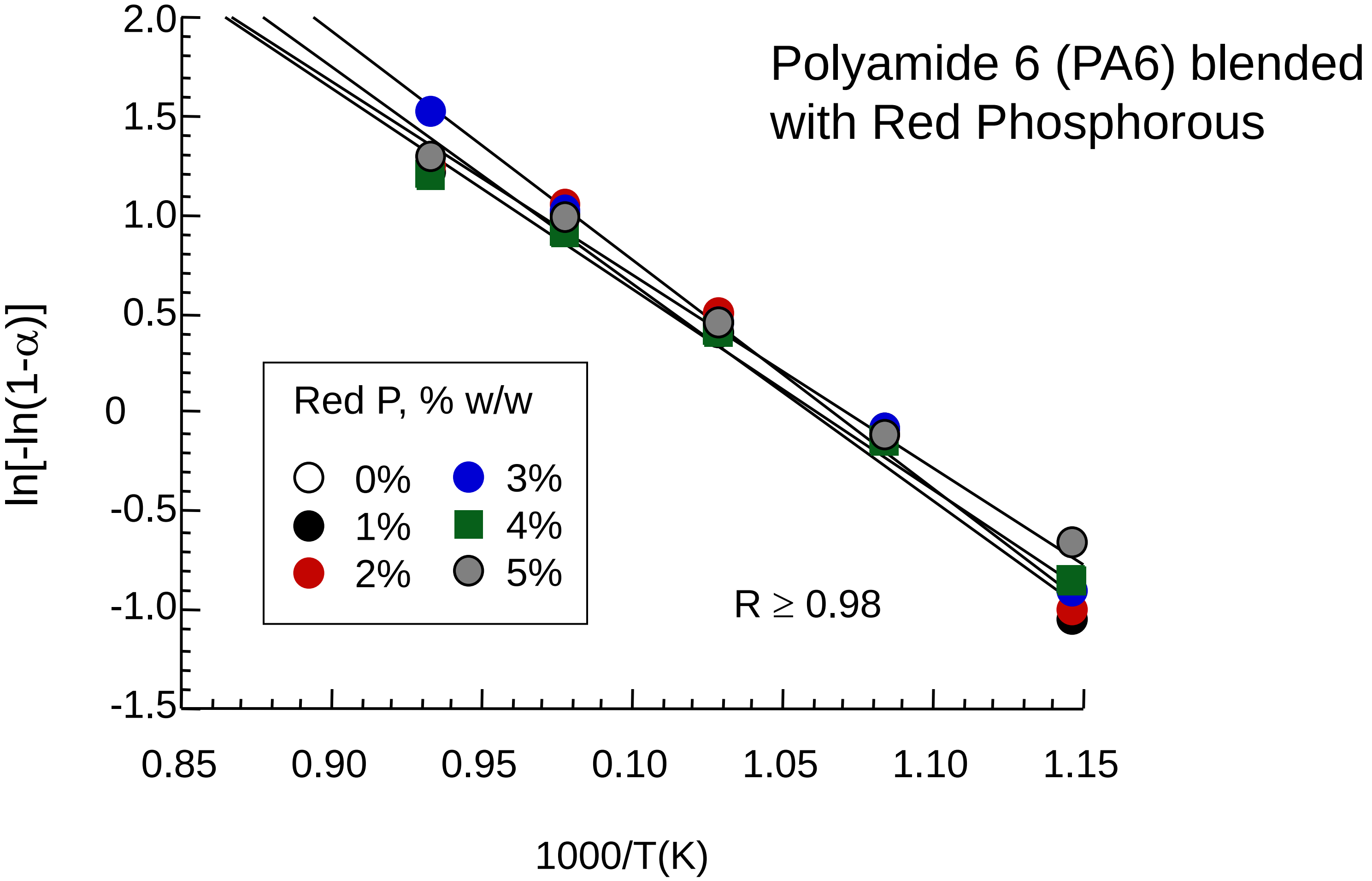


Polystyrene (PS) and Brominated PS Blends



- Kinetic parameters changed with increasing Br

Red Phosphorous Effect on Extent of Combustion in MCC



- Kinetic parameters did not change with increasing P

Combustion Parameters

$\chi = 0.7 \pm 0.2$

$\chi = 0.5 \pm 0.1$

Polymer	E_a (kJ/mol)	A (s^{-1})	χ_{flame} (–)	SEA (m^2/kg)	T_x (K)	τ_{chem} (ms)	
PMMA	195.5	5.74×10^9	0.99	127	1011	0.2	●
Phosphonate (PH)	161.8	5.49×10^7	0.36	951	929	0.3	🟢
PS	163.2	1.09×10^8	0.73	1321	956	0.4	●
PH-PC 60%	162.1	5.99×10^7	0.51	1327	948	0.4	🟢
HIPS	169.2	1.54×10^8	0.74	1236	975	0.5	●
PS FR	154.5	3.34×10^7	0.67	1317	952	0.7	🔴
Polycarbonate (PC)	161.7	7.43×10^7	0.78	698	972	0.7	●
ABS	151.7	3.08×10^7	0.76	1168	951	0.8	●
PH-PC 35%	147.7	9.86×10^6	0.53	1305	951	1.0	🟢
DER 332	153.6	3.05×10^7	0.86	1036	979	1.2	●
PP	151.5	2.53×10^7	0.91	496	986	1.6	●
PC ABS FR	145.7	7.88×10^6	0.70	959	974	1.8	🟢
HDPE	142.2	9.80×10^6	0.97	357	995	3.2	●
PC ABS	135.0	2.95×10^6	0.82	844	975	3.4	●
PEI	112.4	3.02×10^5	0.83	311	942	7.9	●
PVDF	75.2	2.37×10^3	0.22	311	788	13	🔴
PET	106.3	7.81×10^4	0.85	465	988	22	●
PPS	96.8	3.18×10^4	0.82	468	960	27	●
PA66	89.1	1.52×10^4	0.92	153	972	49	●
20% 542	82.4	2.88×10^3	0.56	1581	946	56	🔴
40% 542	75.2	1.21×10^3	0.47	1412	917	64	🔴
POM	98.4	3.51×10^4	0.99	77	1053	72	●
PVC	75.2	1.40×10^3	0.59	714	935	78	🔴
10% BBA	73.8	9.12×10^2	0.66	1385	982	135	🔴
20% BBA	53.5	6.70×10^1	0.49	1667	931	309	🔴
30% BBA	49.1	3.65×10^1	0.43	1738	914	365	🔴
60% 542	45.7	2.10×10^1	0.50	1107	962	619	🔴
40% BBA	35.0	6.57	0.45	1579	898	869	🔴
80% 542	35.6	6.00	0.43	910	919	930	🔴

● Hydrocarbon

🟢 Phosphorus

🔴 Halogen

$$Da = \frac{\tau_{mix}}{\tau_{chem}} > 1$$

$\tau_{mix} \approx 50$ ms

$$Da = \frac{\tau_{mix}}{\tau_{chem}} < 1$$

Conclusions

- Extent of combustion and CO/CO_2 ratios as a function of temperature measured in MCC.

- Mass balance measurements agree with theory

- Char composition calculations agree with theory

- Global kinetic parameters (E_a , A) obtained for thermal oxidation of polymer fuel gases in MCC

- Gas phase mechanism elucidation
  Bromine delays $CO \rightarrow CO_2$ reaction
  Phosphorous has minor effect on gas phase kinetics

Future Work

- Higher temperature/shorter residence time experiments in MCC to simulate flaming combustion experiments

- Recreate flame chemistries in non-flaming test

- Derive combustion kinetics for multi-step oxidation reactions

- Correlate MCC and cone calorimeter gas phase activity with flame retardants