EXPERIMENTAL INVESTIGATION ON THE OXIDATION CHARACTERISTICS OF DIESEL PARTICULATES RELEVANT TO DPF REGENERATION

H. S. Chong, S. K. Aggarwal | University of Illinois at Chicago
K. O. LEE | Argonne National Laboratory

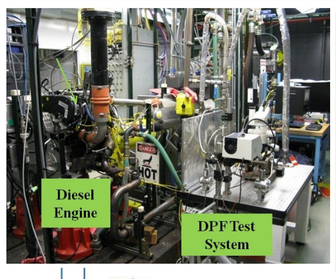
ABSTRACT

Diesel engines generally require diesel particulate filter (DPF) systems to meet increasingly stringent emissions regulations. The development of optimum methodologies for DPF regeneration requires detailed information on the oxidation characteristics of diesel PM accumulated on the DPF in realistic engine conditions. We report herein an experimental investigation on the oxidation of behavior of diesel PM collected from a DPF test system, which was connected to the exhaust stream of a 1.9-L, 4-cylinder light-duty diesel engine. The experimental investigation is firstly concerned with measuring the instantaneous rate of heat generation as well as the total amount of heat released during the oxidation of diesel PM containing different concentrations of soluble organic fraction (SOF). The experimental approach was to measure directly, by means of a differential scanning calorimeter (DSC), the amount of heat release during the thermal reactions of diesel PM with air and to elucidate differences in the heat release characteristics of diesel PM and surrogate soot. And a thermogravimetric analyzer (TGA) was also used to measure the instantaneous sample mass and the rate of mass loss during its oxidation for a wide range of conditions, which include initial sample mass, amount of volatile components of SOF in the sample, oxygen concentration, and various heat treatment schemes in both the inert and oxidizing environments. The DSC experiments revealed that the amounts of heat released from the oxidation of SOF-containing diesel PM sample, dry diesel soot, and surrogate soot were approximately 14.67 kJ/g, 17.3 kJ/g, and 14.02 kJ/g, respectively, indicating that the largest heat release was obtained from the dry diesel soot sample. Furthermore, the specific heat release from the oxidation of SOFs was found to be 5.47 kJ/g. Results also indicated significant differences in the temporal rates of heat release in the oxidation of SOF-containing diesel PM, dry diesel soot, and surrogate soot. In particular, experiments on the heat release during the oxidation of SOF-containing diesel PM and dry diesel soot (with no SOF) revealed two peaks in heat release rate profiles for the diesel PM, and only one peak for the dry diesel soot. For the diesel PM, the first peak corresponds to exothermic reactions associated with the oxidation of SOFs at temperatures below 400°C, followed by the second peak corresponding to exothermic reactions for soot oxidation at higher temperatures. In the TGA experiment, The global kinetic parameters, i.e., the reaction orders of soot and oxygen, activation energy, and pre-exponential factor, were determined for the diesel PM and surrogate soot samples. Significant differences are observed in the oxidation behavior of surrogate soot and diesel PM. The oxidation rate of surrogate soot decreases continuously as the soot is oxidized, while that of diesel soot is nearly constant until about 80% of the sample mass is oxidized, and then decreases as the sample is completely oxidized. In addition, the oxidation of surrogate soot is essentially independent of the various heat treatment schemes used, while that of diesel soot is strongly influenced by them. These differences may be attributable to changes in soot morphology during heating/oxidation and the presence of surface functional groups and heavier SOF components in the diesel PM. The effects of SOFs and thermal aging on diesel PM oxidation have also been characterized. Results indicate that the PM oxidation is only weakly influenced by the presence of volatile components of SOFs, whereas it is noticeably affected by thermal aging.

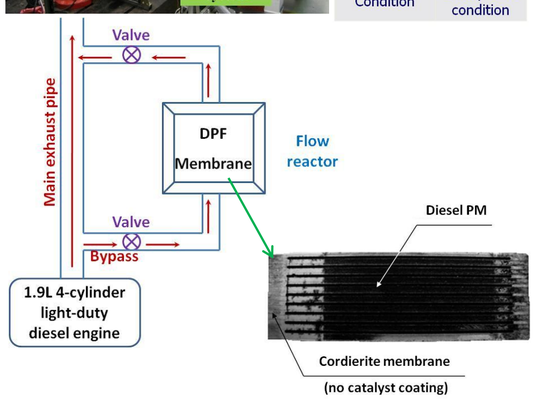
Collection of diesel PM sample

Lab scale DPF test system connected to 1.9-L, 4-cylinder light-duty diesel engine

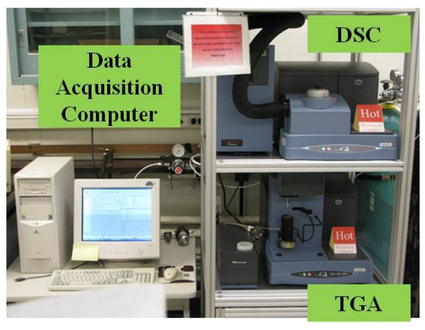
Experimental setup for collection of diesel PM samples



Engine Type	Light-duty Diesel Engine
Number of Cylinder	4
Displacement	1.9L
Compression Ratio	17.5:1
Operation Condition	Multiple steady state condition



Instrumentation for oxidation experiments



Measurement of the amount of heat released during the oxidation

- Differential scanning calorimeter (DSC)
- Samples:
  - ✓ SOF-containing diesel PM
  - ✓ Dry diesel soot
  - ✓ Surrogate soot

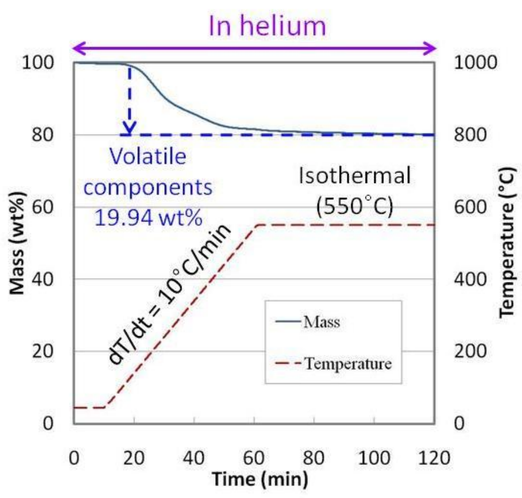
Measurement of the rates of oxidation

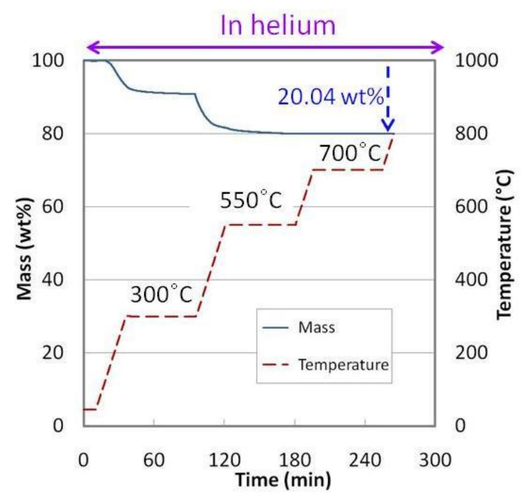
- Thermogravimetric analyzer (TGA)
- Samples:
  - ✓ SOF-containing diesel PM
  - ✓ Dry diesel soot
  - ✓ Thermal aging diesel PM
  - ✓ Surrogate soot

Investigation for developing optimum DPF regeneration strategies

- Measurement of the instantaneous rate of heat generation as well as the total amount of heat released during the oxidation of surrogate soot and diesel PM containing different concentrations of SOF
- Determination of the global kinetic parameters, i.e., the reaction orders of soot and oxygen, activation energy, and pre-exponential factor, for surrogate soot and diesel PM
- Investigation on the effects of SOFs and thermal aging on the oxidation behavior of surrogate soot and diesel PM

Measurement of the amount of volatile components of SOF adsorbed in diesel PM

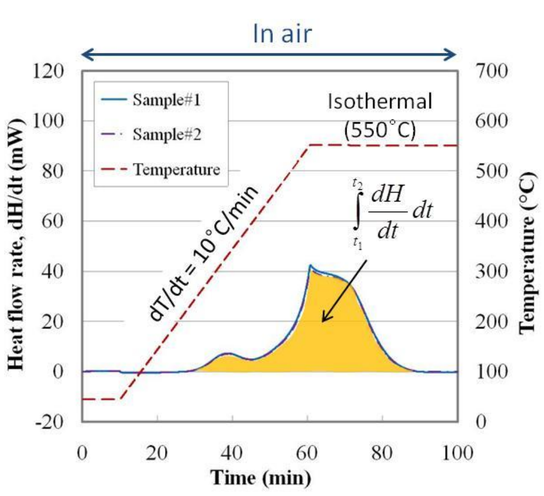




- The diesel PM sample was heated to 550°C at a rate of 10°C/min, and then maintained at 550°C for an hour. The volatile components of SOFs adsorbed in the PM sample were completely removed during this time. The reduction of PM mass or the mass of SOFs evaporated from the sample was found to be 19.94% of the initial mass.
- The PM sample was subjected to the same heating rate of 10°C/min, but three different isothermal conditions were applied for an hour each at 300°C, 550°C, and 700 °C, respectively. The mass profile for this case is significantly different, indicating fraction vaporization of SOF components depending upon volatility. the total amount of SOFs evaporated for this case was 20.04 % of the initial mass.

Measurement of the amount of heat released during the oxidation

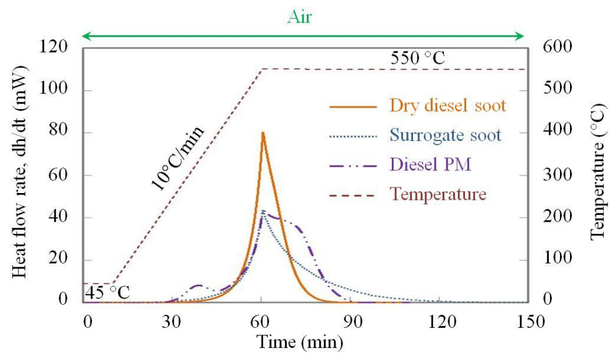
SOF-Containing diesel PM

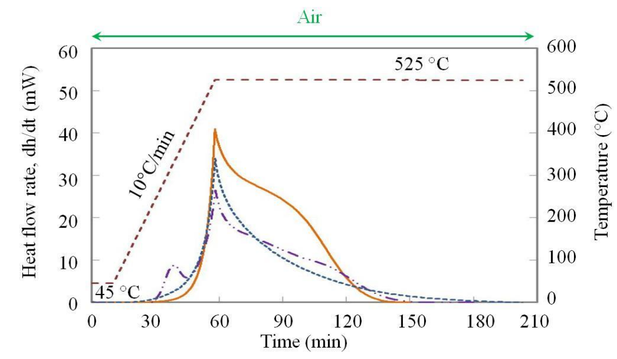


Sample	M_0 (mg)	M_r (mg)	M_0-M_r (mg)	Total heat release per mass (kJ/g)
#1	4.197	0.323	3.874	14.67
#2	4.081	0.363	3.718	14.61

$$\text{Heat release (kJ/g)} = \left[\int_{t_1}^{t_2} \frac{dH}{dt}\,dt\right] \cdot \left(\frac{1}{M_0 - M_r}\right)$$

dH/dt: Heat flow rate (mW)
t: Time (s)
M_0: Initial mass (mg)
M_r: Residual mass (mg)





- The amounts of heat released from the oxidation of SOF-containing diesel PM sample, dry diesel soot, and surrogate soot were approximately 14.67 kJ/g, 17.3 kJ/g, and 14.02 kJ/g, respectively. Furthermore, the specific heat release from the oxidation of SOFs was found to be 5.47kJ/g.
- An important observation in the DSC experiment data is that SOF-containing diesel PM sample shows two peak values of heat flow rate, while the dry diesel soot and surrogate soot exhibited one peak. The first peak near 300°C appears due to the exothermic reaction associated with the oxidation of SOFs, while the second peak at the start of isothermal condition is due to the oxidation of soot.

Temperature profile		Sample	M_0 (mg)	M_r (mg)	M_0-M_r (mg)	M_v (mg)	Total heat release (J)	Specific heat release (kJ/g)
Isothermal temperature (°C)	Heating rate (°C/min)							
550	10	Diesel PM	4.521	0.266	4.255	0.904	62.5	14.67
		Dry diesel soot	3.419	0.393	3.026	-	52.2	17.3
		Surrogate soot	3.719	0	3.719	-	52.12	14.02
525	10	Diesel PM	4.912	0.274	4.638	0.982	68.02	14.67
		Dry diesel soot	6.119	0.39	5.729	-	98.84	17.3
		Surrogate soot	4.767	0	4.767	-	66.85	14.02

* Sample mass (M_o), residue mass (M_r), net mass oxidized (M_o-M_r), mass of volatile component of SOF (M_v)

Department of Mechanical & Industrial Engineering
University of Illinois at Chicago

Center for Transportation Research, Argonne National Laboratory

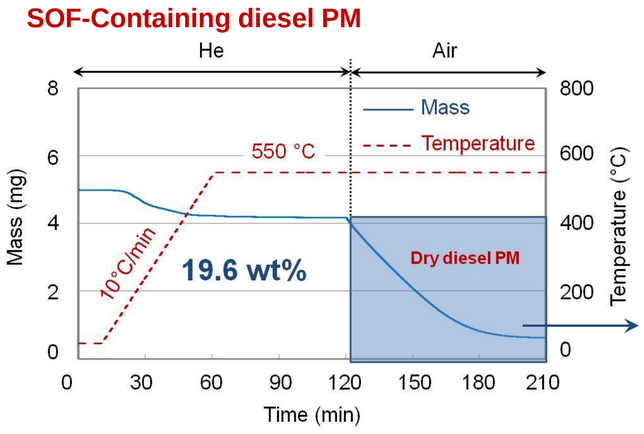
Hwan Soo Chong | hchong@uic.edu

EXPERIMENTAL INVESTIGATION ON THE OXIDATION CHARACTERISTICS OF DIESEL PARTICULATES RELEVANT TO DPF REGENERATION

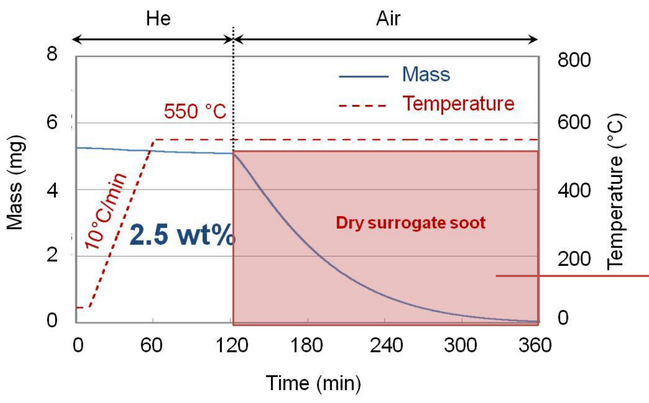
H. S. Chong, S. K. Aggarwal | University of Illinois at Chicago
K. O. LEE | Argonne National Laboratory

Measurement of the rates of oxidation

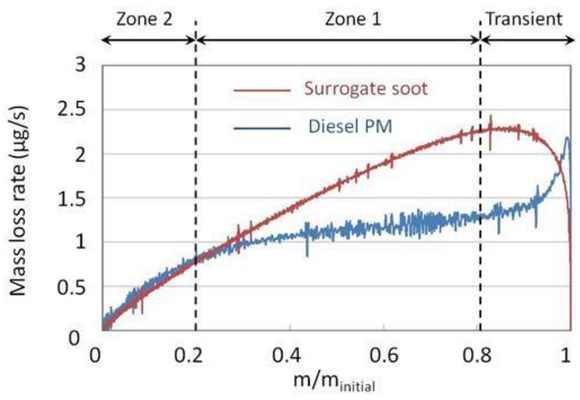
SOF-Containing diesel PM



Surrogate soot



The temporal variation of mass loss rate during the oxidation with respect to a function of sample mass normalized by the mass at the start of oxidation in the isothermal condition



- The initial mass reduction of diesel PM and surrogate soot was due to the evaporation of volatile components of SOFs in the helium environment. Approximately 19.6% and 2.5% of the initial mass was lost for diesel PM and surrogate soot, respectively. The subsequent reduction in mass is due to the reaction of dry soot samples with air. After complete oxidation, the amounts of residues were measured to be 0.612 mg and zero mg, respectively, for the two samples.
- The oxidation rate of surrogate soot initially increases, as helium is being replaced by air, and then decreases as the sample is oxidized. The oxidation of diesel soot also exhibits an initial transient period during which the oxidation rate increases rapidly, as helium is being replaced by air. Following this short transient period, the oxidation rate of diesel soot becomes nearly constant until about 80% of the mass is oxidized, and then decreases as the sample is completely oxidized.

Global kinetic parameters determined by differential method

Rate equation of oxidation

$$\frac{dm_c}{dt} = -A \cdot \exp\left(-\frac{E_a}{R_u \cdot T}\right) \cdot [m_c]^{n_c} \cdot [P_{O_2}]^{n_{O_2}}$$

A: Pre-exponential factor [1/s]
E_a: Activation energy [J/mol]
R_u: Universal gas constant (8.31447 J/mol·K)
T: Temperature [K]
m_c: Sample mass [mg]
n_c: Reaction order of sample
Po_2: Partial pressure of oxygen
no_2: Reaction order of oxygen

Reaction order with respect to soot

$$\ln\left[-\frac{dm}{dt}\right] = n_c \cdot \ln[m] - \left(\frac{E_a}{R_u}\right)\frac{1}{T} + n_{O_2}\ln[P_{O_2}] + \ln A$$

Isothermal Temperature (° C)	Diesel PM		Surrogate soot
	Zone 1	Zone 2	
600	0.16	0.67	0.79
550	0.28	0.83	0.81
500	0.25	0.71	0.77

Activation energy (kJ/mol)

$$\ln\left[-\frac{dm}{dt}\right] - n_c \cdot \ln[m] = -\left(\frac{E_a}{R_u}\right)\frac{1}{T} + n_{O_2}\ln[P_{O2}] + \ln A$$

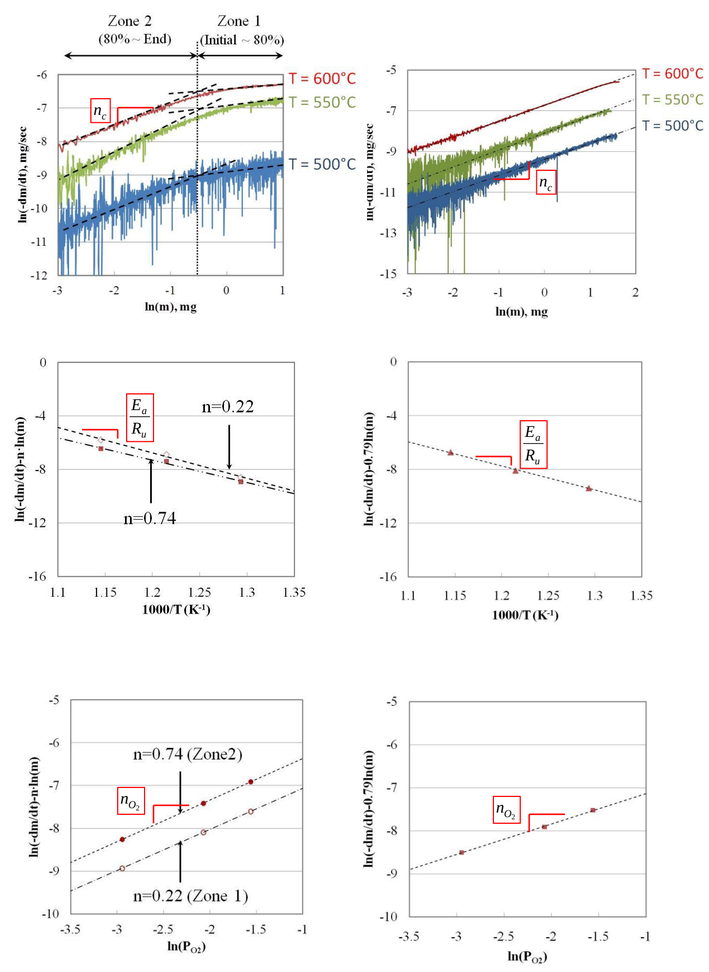
Diesel PM (kJ/mol)		Surrogate soot (kJ/mol)
Zone 1	Zone 2	
139.6	136.3	148.2

Reaction order with respect to oxygen

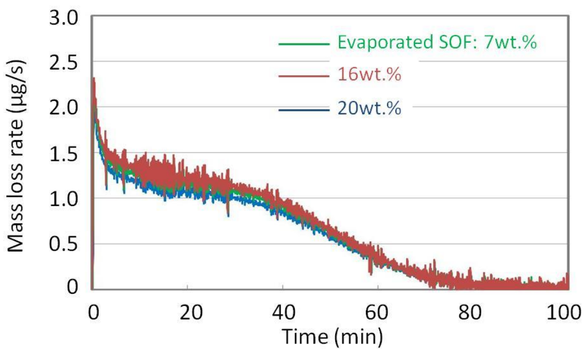
$$\ln\left[-\frac{dm}{dt}\right] - n_c \cdot \ln[m] = n_{O_2}\ln[P_{O2}] + \ln A - \left(\frac{E_a}{R_u}\right)\frac{1}{T}$$

Parameter	Diesel PM		Surrogate soot
	Zone 1	Zone 2	
n_{O_2}	0.96	0.97	0.93
A	0.31x 10^7	0.05 x 10^7	4.34 x 10^6

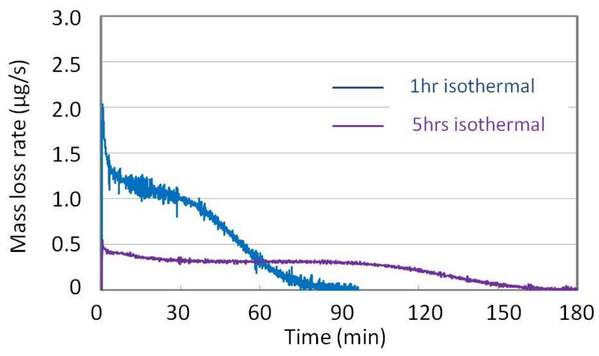
Dry diesel PM **Dry surrogate soot**



The effect of volatile components of SOF on the oxidation of diesel PM



The effect of thermal aging on the oxidation of diesel PM



- Using different heat treatment schemes allowed us to vary the amount of volatile components of SOF evaporated from PM samples. The first one involved heating the PM sample in helium at a rate of 100° C/min to 550° C, and then subjecting to oxidation at the indicated temperature. For the second scheme, the heating rate was reduced to 10° C/min, while for the third case, the sample was heated in helium at a rate of 10° C/min to 550° C and then maintained at that temperature for 1 hour, prior to oxidation.
- Approximate 7%, 16%, and 20% of initial sample mass was lost during these processes.
- The result from this oxidation experiment reveals that the amount of SOFs in diesel PM does not have a significant effect on the oxidation behavior of diesel PM.
- Two heat treatments prior to oxidation consisted of heating the samples to a temperature of 550° C at a rate of 10° C/min and maintaining this temperature in helium for 1 hour and 5 hours respectively.
- The diesel soot reactivity or the oxidation rate is significantly reduced due to thermal aging, which is expected to make the soot structure more graphitic.

Kinetic analysis on the effects of volatile components and thermal aging on the oxidation of surrogate soot and diesel PM

Surrogate soot

Experimental Scheme		Oxidation temperature (° C)			Average reaction order (n_c)	Activation energy , E_a (kJ/mol)	Reaction order of oxygen (no_2)	Pre-exponential factor, A (1/s)
		500	550	600				
Heating rate	100° C/min	0.78	0.8	0.8	0.79 ± 0.02	147.8	0.94	3.24 ×10^6
	10° C/min	0.79	0.81	0.77	0.79 ± 0.01	145.2	0.95	2.49 ×10^6
Isothermal period	1 hr	0.77	0.81	0.79	0.79 ± 0.02	148.2	0.93	4.34 ×10^6
	5 hr	0.8	0.77	0.76	0.78 ± 0.02	149.1	0.95	4.54 ×10^6
Average		0.78 ± 0.02	0.8 ± 0.03	0.78 ± 0.02		147±2	0.94 ±0.01	3.68 ×10^6 ±0.81×10^6

Diesel PM

The effect of thermal aging on the oxidation

Heating & Flue gas condition		Heating rate (°C/min)	100			10			10			10		
	He	Isothermal period at 550°C (Hr)	-			-			1			5		
	Air	Oxidation temperature (°C)	500	550	600	500	550	600	500	550	600	500	550	600
Amount of evaporated volatile components			4.1	7.1	13.1	12.1	16.5	21.9	19.4	19.6	20.0	23	22.9	21.8
n_c		Zone 1	0.3	0.29	0.18	0.24	0.29	0.19	0.25	0.28	0.19	0.05	0.08	0.09
		Zone 2	0.72	0.87	0.68	0.72	0.87	0.64	0.71	0.83	0.67	0.77	0.75	0.78
n_{o2}		Zone 1	0.95			0.95			0.96			0.96		
		Zone 2	0.97			0.96			0.97			0.97		
E_a (kJ/mol)		Zone 1	139.1			136.8			139.6			153.1		
		Zone 2	133.1			129.5			136.3			155.1		
A (1/s)		Zone 1	0.68 x 10^7			0.21 x 10^7			0.31 x 10^7			0.27 x 10^7		
		Zone 2	0.18 x 10^7			0.1 x 10^7			0.05 x 10^7			0.28 x 10^7		

The effect of volatile components on the oxidation

- The oxidation behavior of surrogate soot is essentially independent of the various heat treatments and other conditions, while that of diesel soot is strongly influenced by them
- The variation in n_c and n_{O2} with respect to the heat treatment scheme are small. Similarly, the activation energy exhibits a relatively small variation with respect to the amount of volatile components in diesel PM. The pre-exponential factors, however, exhibit more noticeable variation, with values ranging from 0.21 × 10^7 to 0.68 × 10^7 (1/s) in zone 1, and from 0.05 × 10^7 to 0.18 × 10^7 (1/s) in zone 2, depending upon the heat treatment scheme.
- The reaction order of diesel soot in zone 1 decreases on an average from 0.26 to 0.08 in zone 1, while the activation energy is increased from 139.6 to 153.1k*J/mol*, as the isothermal period is increased from 1 hour to 5 hours.

The oxidation characteristics of diesel PM are only weakly influenced by the presence of the volatile components of SOFs. However, the heavier SOF components and thermal aging seem to have a strong influence on diesel soot oxidation. The diesel soot reactivity is observed to decrease with thermal aging.

Department of Mechanical & Industrial Engineering
University of Illinois at Chicago

Center for Transportation Research, Argonne National Laboratory

Hwan Soo Chong | hchong@uic.edu