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## MEASUREMENTS OF HEAT RELEASE OF DIESEL PM FOR ADVANCED THERMAL MANAGEMENT STRATEGIES FOR DPF REGENERATION

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*Diesel engines typically require diesel particulate filter (DPF) systems to reduce particulate matter (PM) emissions in order to meet increasingly stringent emission regulations. While there have been noticeable advances in DPF technology, significant efforts are still needed to develop optimum DPF regeneration strategies and achieve efficient removal of diesel PM. In particular, the development of an effective thermal management system is essential to prevent the potential failure of the DPF system by the thermal runaway during soot oxidation in DPF regeneration. In an effort to develop optimum thermal management strategies, this experimental investigation is concerned primarily 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 (model) soot. The diesel samples were collected from a cordierite particulate filter, where PM emissions bypassing the exhaust pipe of a light-duty diesel engine were deposited. Furthermore, a thermogravimetric analyzer (TGA) was used to obtain dry diesel soot samples with no volatile components present. 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. 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, significant differences were found on the results for dry diesel soot samples with respect to the oxidation temperatures of 550°C and below 550°C in air. The heat release rate profile for the 550°C case exhibited a continuous sharp decrease after the peak value, while those for the 535°C and 525°C cases indicated first a sharp decrease, followed by slow and then sharp decrease again. The present experimental data are expected to lead to better predictive tools for thermal energy distribution during DPF regeneration, and thus the development an optimum thermal management system for DPF systems.*

**Keywords:** Diesel particulate matter; DPF regeneration; Heat release rate measurements

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## INTRODUCTION

Diesel engines typically require after-treatment devices to control exhaust emissions. The increasingly strict emissions standards continue to motivate researchers and engineers to develop advanced diesel after-treatment systems that can significantly reduce tail-pipe exhaust emissions. In particular, diesel particulate filter (DPF) systems with both active and passive regeneration<sup>1</sup> have been developed to remove particulate matter (PM) emissions emitted from diesel vehicles. However, major efforts are still needed in order to attain high filtration efficiency and optimum regeneration strategies for DPF systems. In particular, an effective thermal management system is considered necessary to prevent the failure of a DPF system caused by the thermal runaway, which can occur during the oxidation of excess soot deposit in DPF regeneration. To this end, while a number of studies has been reported dealing with the oxidation kinetics of diesel PM (Collura et al., 2005; Kalogirou et al., 2007; Messerer et al., 2006; Neeft et al., 1997; Setiabudi et al., 2004; Stratakis et al., 2003; Yezerets et al., 2005), very few studies have focused on measuring the temporal variations of heat release rate during oxidation. Clearly, there is a need for detailed experimental information on heat release characteristics during the oxidation of diesel PM. Such information is important not only for devising an efficient thermal management system for DPF regeneration, but also for developing an accurate predictive tool.

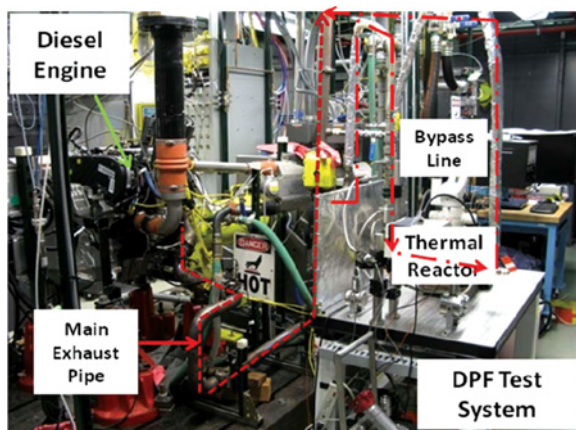
In general, diesel particulates contain various chemical components, such as elemental carbons, soluble organic fraction (SOF), sulfuric compounds, and metal oxides. The SOF is a major component often contained in diesel PM emissions. It mainly consists of heavy hydrocarbons (Forti et al., 2005) such as aliphatic hydrocarbons, poly-cyclic aromatic hydrocarbons (PAHs), nitride- or oxy PAH, and aldehydes, which are produced due to incomplete combustion of diesel fuels (Durán et al., 2002) or lubricating oils (Durán et al., 2002; Schramm et al., 2006). An important observation reported in previous studies (Lee et al., 2002, 2003) was that the amount of SOF in diesel PM strongly depends on engine speed and load conditions, and there are significant differences in morphology between the particulates sampled at different engine operating conditions. Particles sampled at low engine speed and loads appeared to be amorphous and nebulous, while those sampled at high engine speed/load conditions exhibited graphitic structures. The authors attributed the amorphous structures to a saturation of SOFs initially residing in exhaust gas emissions, where combustion temperatures were relatively low. In contrast, graphitic structures are formed under high temperature and pressure conditions. Although any direct linear relation has not been shown in the literature, the Raman spectroscopic analyses indicated that the degree of graphitic structures increased linearly with engine speed. Finally, while SOF containing PM emissions are known to be detrimental to human health (Bünger et al., 2000; Riedl and Diaz-Sanchez, 2005), one advantage in utilizing these particulates is the potentially low energy input required for DPF regeneration, because the SOF would enhance the ignition and oxidation of particulates. However, little attention has been given to the effects of SOF concentration on the thermal energy released during the oxidation of diesel PM, nor has there been any evaluation of the total heat release per unit mass of diesel PM with different SOF concentrations.

The present study is aimed at measuring the instantaneous rate of heat release during the oxidation of diesel PM collected directly from a DPF, as well as the total

amount of heat release per unit soot mass. The study is motivated from the consideration of developing optimum thermal management strategies for DPF regeneration. We performed the same analysis by using diesel PM and commercially available synthetic or surrogate soot to examine differences in heat release characteristics. It is important to note that in many previous investigations, oxidation experiments have been performed with PM samples collected from lab-scaled burners (Higgins et al., 2006) or commercially available soot artifacts such as Printex-U (Nejar et al., 2007). In contrast, the PM samples used in this work were collected directly from a filter membrane in a DPF system, which was connected to a diesel exhaust pipe. Thus, the PM samples analyzed in this work were approximately the same as the soot cake built in commercial DPFs in terms of their properties, and thereby our experiments are expected to provide more accurate results in subsequently predicting the temporal distributions of thermal energy during DPF regeneration. Experiments using the diesel PM and commercially available synthetic soot were performed using a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA), respectively. First, the heat release data were obtained and analyzed for the oxidation of surrogate soot. The experiments were then performed to evaluate heat release rates during the oxidation of diesel PM with different levels of SOF concentrations. In addition, the heat release rates were measured with SOF-containing diesel PM and dry diesel soot (with no volatile components) under identical conditions. Finally, the experimental results were analyzed to examine differences between the heat release characteristics during the oxidation of diesel PM, dry diesel soot, and surrogate soot.

## EXPERIMENTAL METHOD

Diesel PM samples used in this study were collected from a non-catalytic cordierite DPF membrane placed in a flow reactor of a laboratory scale DPF test system, where no regeneration was conducted. As illustrated in Figure 1, the DPF system



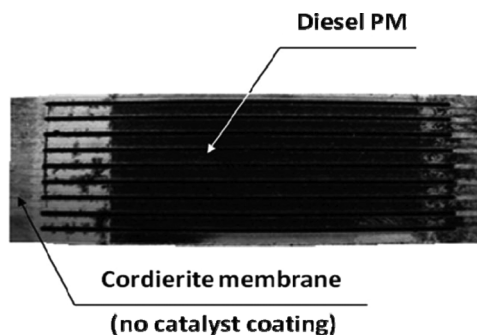
**Figure 1** DPF test system connected to the exhaust pipe of a 1.9 L four-cylinder light-duty diesel engine. (Figure is provided in color online.)

was connected to the exhaust pipe of a 1.9 L four-cylinder light duty diesel engine. This engine is equipped with a variable geometry turbocharger (VGT) to boost the intake air to the desired pressure and has a self-contained exhaust gas recirculation (EGR) system. The engine is capable of producing 150 hp with a maximum speed of 5000 rpm. It has multiple-injection capability, and both the EGR rate and VGT setting are electronically controlled. The common-rail injection system can be operated at a maximum injection pressure of 1600 bar.

The engine was operated at various randomly selected engine speeds and loads in order to simulate conditions that practical DPF systems undergo in vehicle operation. At each engine operating condition, the engine was stabilized (by maintaining coolant and lubricating oil temperatures constant) while the target speed/load condition was maintained constant for several minutes. Engine exhaust emissions were bypassed from the main exhaust pipe, of which soot particles were filtered in the DPF filter membrane, while gaseous emissions were ventilated back to the engine exhaust stream. In order to collect enough PM emissions, each experiment was run for several hours, and then soot samples were taken from the filter one at a time. Figure 2 shows a cordierite DPF membrane loaded with PM emissions in the DPF test bench. The PM samples were carefully collected from the filter membrane and transferred to an environmentally controlled glove box in a clean laboratory. The DPF inlet temperatures were measured in a range of about 80–200°C. Soot oxidation reactions are not expected to occur at these temperatures, which are fairly low compared to those in the main exhaust pipe, because the exhaust is cooled down through the fairly long sampling line. The uncoated filter membrane was not preconditioned for the soot loading.

An ultra-low sulfur diesel (ULSD) fuel and conventional SAE15 W-40 lubricating oil were used for this work. The diesel fuel had an ash content of about 0.002 wt.%, sulfur content of about 15 ppm, carbon content of about 86.9 wt.%, hydrogen content of about 13.1 wt.%, and a cetane number of 46. The lubricating oil has an ash content of 1.3 wt.%, Zn of 2.5 wt.%, and sulfur content less than 0.005 wt.%.

DSC experiments were conducted to measure heat release from the commercially available model soot first. Note that a DSC measures the amount of heat generated or consumed by a given sample undergoing oxidation in flowing gas. In



**Figure 2** Diesel PM loaded in the cordierite DPF membrane taken out from the thermal reactor in the DPF test system.

our study, a sample was placed in the reaction chamber of DSC, and subjected to a specific temperature profile in flowing air to measure the total amount of heat and the temporal variation of heat flow rate during the sample oxidation. Because the chemical composition of model or surrogate soot is less complex than that of diesel PM emission, the analysis for the surrogate soot was carried out in order to optimize the temperature profile used for the sample oxidation and to clarify differences in the temporal variation of heat release rates during the oxidation of real diesel PM and surrogate soot. A DSC was used to measure the instantaneous heat release during soot oxidation under specified temperature profiles in air, while a TGA was used to measure the amount of volatile components of SOF in PM samples and also to provide the dry diesel soot samples.

In principle, the DSC measures the amount of heat either supplied to a sample or abstracted from it. The generation or consumption of heat in the present case occurs mainly due to chemical reactions, and affects a temperature change in a DSC component that measures the amount of heat exchanged. A control system equipped with the DSC adjusts the temperature difference between these two components, caused by chemical reactions, to zero. Thus, the DSC measures the total power needed for adjusting the temperature difference to zero, and the data are recorded in terms of heat flow rate (mW).

In DSC experiments, the melting temperature and standard enthalpy of fusion of a reference sample were used as calibration parameters for temperature and heat flow measurements. High purity indium and tin were prepared as the references, and then calibration samples of each substance were weighed and loaded into the aluminum pans. The indium sample was first heated up to 300°C at a temperature gradient of 10°C/min in nitrogen to measure the melting temperature and the standard enthalpy of fusion. The values measured for those two parameters were corrected with respect to the melting temperature, 156.6°C, and enthalpy of fusion, 28.45 J/g of standard indium, respectively. In addition, the same calibration was carried out to assure the accuracy in temperature measurement. The melting temperature measured for tin was corrected with respect to the melting temperature, 231.95°C, of standard tin and then temperature calibration was completed by two-point temperature calibration.

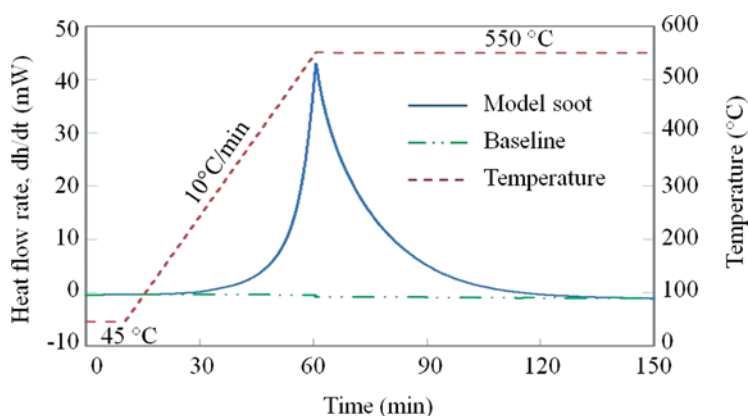
After calibration, samples were accurately weighed and loaded into the aluminum sample pans. A baseline of experimental data needs to be determined to attain high accuracy in measuring heat release during the sample oxidation. An experiment for determining the baseline was conducted in nitrogen under a specified temperature profile with an empty reference pan and a pan loaded with a sample. For measuring instantaneous heat release rate, the sample was heated to 550°C and then maintained at this temperature (i.e., isothermal condition) until the oxidation was completed. Prior to the temperature increase, the DSC was stabilized at 45°C for 10 min to eliminate small data fluctuations detected. For both determination of the baseline and measurement of heat release, the sample and reference pans were open to nitrogen gas, of which the flow rate was set at 60 mL/min.

Dry soot samples were prepared by using a TGA. In general, a TGA measures the temporal variation of a given sample mass under a specified temperature profile. The change in sample mass may occur due to either oxidation with reactants, or evaporation in an inert gas environment. The procedure for yielding dry soot

samples is the same as reported in our previous study (Chong et al., 2010). In TGA experiments, two standard weights were used to calibrate the microbalance, while the temperature calibration was performed with alumel and nickel in the heating mode. Calibration samples were accurately weighed and loaded into the TGA pan, and then exposed to an elevated temperature profile of  $10^{\circ}\text{C}/\text{min}$  in a nitrogen atmosphere to measure Curie point temperatures of the calibration samples. The measured temperatures were corrected to  $157.0^{\circ}\text{C}$  and  $368.8^{\circ}\text{C}$ , respectively. After calibrations, the model soot<sup>2</sup> or diesel PM sample taken in a pan of the TGA was heated in a nitrogen atmosphere from  $45^{\circ}\text{C}$  up to  $550^{\circ}\text{C}$  with a temperature gradient  $10^{\circ}\text{C}/\text{min}$ , and then maintained at this temperature for 1 h. During the isothermal condition, the volatile components of SOFs dissolved in the diesel PM sample were completely removed in nitrogen. From this thermal treatment by TGA, dry diesel soot can be obtained. The mass of sample residues was then accurately measured by a microbalance.

## RESULTS AND DISCUSSION

As noted earlier, the DSC experiments were first conducted to measure heat release from the commercially available model soot first. Figure 3 presents the temporal variation of heat release rate during the oxidation of a model (surrogate) soot sample in air subjected to a given temperature profile, and the baseline determined for the data. As described earlier, the temperature profile consists of a progressive temperature mode with temperature increasing from  $45^{\circ}\text{C}$  to  $550^{\circ}\text{C}$  at a constant rate of  $10^{\circ}\text{C}/\text{min}$ , followed by an isothermal mode. Note that the maximum temperature for the DSC experiments is  $550^{\circ}\text{C}$  in the isothermal mode. The model soot sample was weighed (3.719 mg) and loaded into an aluminum sample pan of the DSC. For establishing the baseline, high purity nitrogen gas was used to provide an inert environment to suppress chemical reactions under this temperature profile. The heat flow rate profile for this case clearly indicates the endothermic process associated with the heating of the sample during the temperature ramp-up period.



**Figure 3** Temporal variation of heat release rate during the oxidation of a synthetic (model) soot sample in air under a specified temperature profile for the baseline case. (Figure is provided in color online.)

After the baseline was determined, the model soot sample was reacted in an oxidizing environment with an airflow rate of 60 mL/min under the same temperature profile as described above. As shown in the figure, the reaction was stabilized in the initial heating period from 45°C to about 200°C for about 20 min, and then increased rapidly with time until the ambient temperature reached the isothermal condition. Subsequently the heat flow rate decreased exponentially with further oxidation of sample soot during the isothermal condition maintained at 550°C until it eventually became zero, indicating the termination of oxidation reaction.

For a given soot sample, the total amount of heat release per unit sample mass can be evaluated by integrating the heat release rate data with respect to time as

$$q = \left[ \int_{t_1}^{t_2} \frac{dH}{dt} dt \right] \cdot \left( \frac{1}{M_o - M_r} \right) \quad (1)$$

where  $dH/dt$  denotes the heat flow rate measured by the DSC,  $t_1$  and  $t_2$  correspond to times at the start and termination of oxidation, respectively, and  $M_o$  and  $M_r$  are initial sample<sup>3</sup> mass and residue mass, respectively. Note that the integral in Equation (1) represents the area under the heat flow rate curve. This net amount of heat release, associated with the soot oxidation, was obtained by subtracting the area defined by the baseline from the total heat release computed by Equation (1).

Table 1 summarizes results from the DSC experiments using various temperature ramp rates (ranging from 3°C/min to 100°C/min) for model soot samples. Results are shown in terms of the total heat released and the heat release per unit soot mass. For each ramp rate, the temperature profile consisted of increasing the temperature from 45°C to 550°C at a given ramp rate, and then maintaining an isothermal condition until the sample was completely oxidized. The results indicate that while the total heat release varies with the ramp rate, the heat per unit mass is essentially independent of the ramp rate, except for the fast ramp rates of 80°C/min and 100°C/min. For these ramp rates, temperature fluctuations were observed during transition from the progressive temperature profile to the isothermal mode. From these experiments, therefore, the amount of heat release per unit mass of model soot was evaluated to be 14.02 kJ/g. In addition, an optimum ramp rate of 10°C/min was

**Table 1** Total heat evolved and heat evolved per unit sample mass during the oxidation of surrogate (model) soot subjected to different temperature ramp rates in DSC experiments

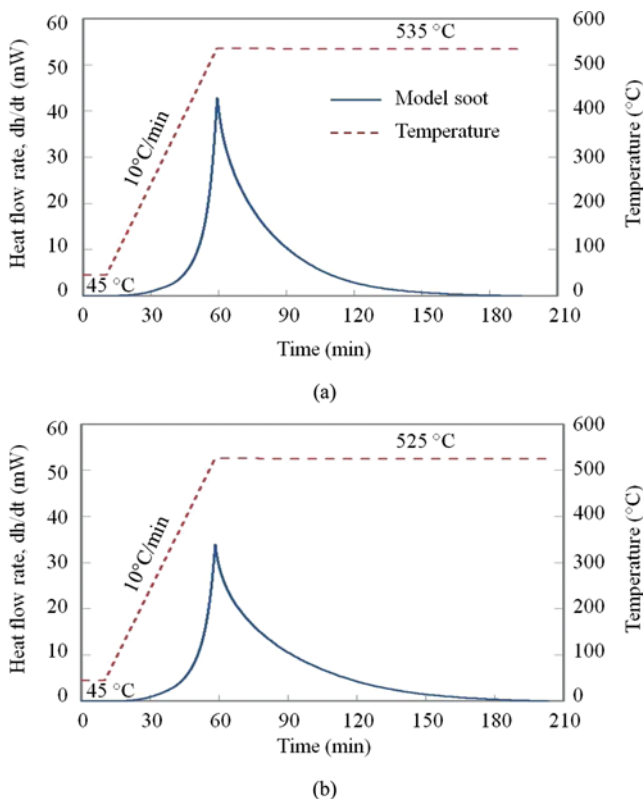
Ramp rate (°C/min)	$M_o$ (mg)	Total heat released (J)	Specific heat released (kJ/g)
3	5.299	74.35	14.03
5	4.329	60.7	14.02
10	3.719	52.15	14.02
20	4.307	60.4	14.02
40	4.474	62.73	14.02
60	4.741	66.47	14.02
80	4.791	67.93	14.18
100	5.613	81.56	14.53



determined, which offers both high accuracy in data acquisition and time saving in performing the experiments.

The next set of experiments focused on the effects of peak temperatures set for isothermal conditions. Two more model soot samples were individually heated up to 535°C and 525°C at a temperature gradient of 10°C/min in air, respectively, and then maintained at these temperatures until the oxidation was completed, the same as in the previous experiment for 550°C (cf. Figure 3). The results are shown in Figure 4, which presents the temporal variations of heat release rate for the two soot samples. Note that for each plot, the baseline heat flow rate has already been subtracted so that the data exhibit the heat flow rates generated solely by soot oxidation. The total heat release and heat release per unit soot mass for these three cases are listed in Table 2. The results indicate that although the peak heat release rate and the total heat release are different for the three different isothermal conditions, the heat release per unit mass remains the same (=14.02 kJ/g) for the three cases.

Further oxidation experiments were performed to illustrate differences in the temporal variation of heat release rate associated with the oxidation of two diesel



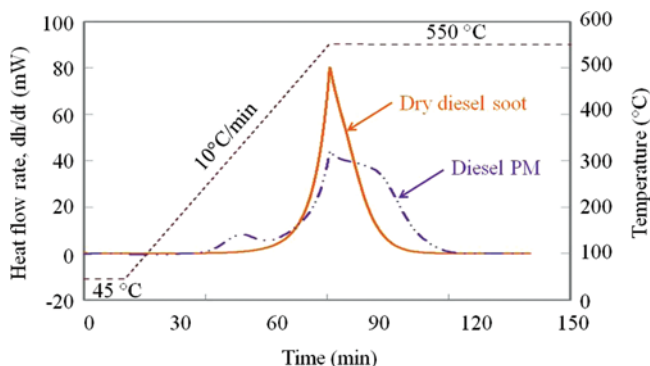
**Figure 4** Temporal variation of the net heat flow rate associated with the oxidation of model soot samples in air subjected to two different temperature profiles with ramp rate of 10°C/min. The peak temperatures at isothermal conditions are 535°C and 525°C in Figures 4a and 4b, respectively. (Figure is provided in color online.)

**Table 2** Peak heat release rate, total heat release, and heat release per unit mass in the oxidation of surrogate (model) soot sample subjected to different isothermal conditions in DSC experiments

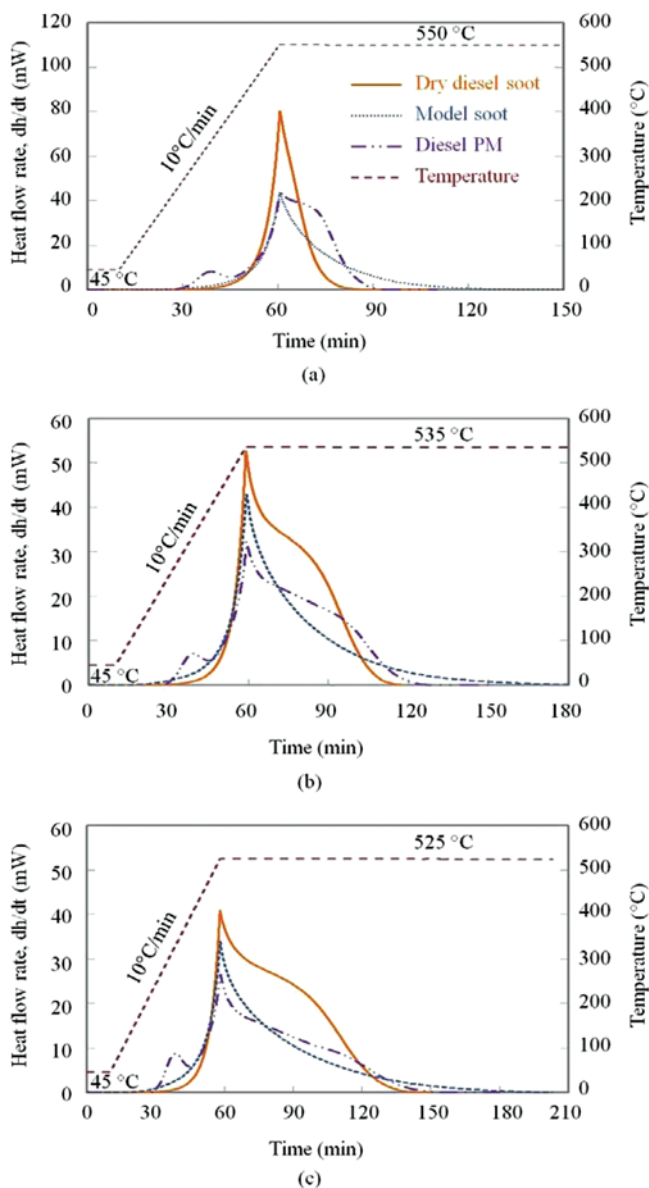
Isothermal temperature (°C)	Ramp rate (°C/min)	M <sub>o</sub> (mg)	Peak heat release rate (mJ/s)	Total heat release (J)	Specific heat release (kJ/g)
550	10	3.719	43.01	52.15	14.02
535	10	4.893	41.96	68.62	14.02
525	10	4.767	33.10	66.85	14.02

soot samples with different concentrations of the volatile components of SOF. Oxidation conditions in terms of the temperature profile (10°C/min) and air flow rate (60 mL/min) were the same as before with an isothermal condition at 550°C. The dry diesel soot sample was obtained by separating volatile components in SOF from the PM sample using the same procedure as reported in our previous study (Chong et al., 2010). For preparation of dry soot sample, a PM sample of initial mass of 4.274 mg was placed in the TGA unit and heated up to 550°C with a ramp rate of 10°C/min in nitrogen (inert) environment, and then maintained at this temperature for 60 min. During the isothermal condition at 550°C, volatile components of SOFs contained in the diesel PM sample were removed, which was confirmed by no more change in the sample mass. The amount of volatile component in SOF evaporated was found to be 0.855 mg or 20% by mass. This dry diesel soot sample of 3.419 mg then underwent oxidation in air under the same temperature profile as in the DSC experiment. After the complete oxidation of both diesel soot samples, the amount of residue was measured to be 0.266 mg for the PM sample and 0.393 mg for the dry soot sample, respectively.

Results from the DSC experiments for the diesel PM sample and dry soot sample are presented in Figure 5. An important difference in the data is that SOF-containing diesel PM sample shows two peak values of heat flow rate, while the dry diesel soot exhibited one peak. The first peak near  $t = 40$  min appears due to the exothermic reaction associated with the oxidation of SOFs, while the second peak near  $t = 60$  min is due to the oxidation of soot. The total amounts of heat release

**Figure 5** Temporal variation of the net heat flow rate measured during the oxidation of SOF-containing diesel PM sample and dry diesel soot sample in DSC experiments. (Figure is provided in color online.)

per unit mass calculated by using Equation (1) are 14.67 kJ/g and 17.3 kJ/g for the SOF-containing PM sample and dry diesel soot sample, respectively. These values are in good agreement with those reported previously (Yang et al., 2010). It is also important to that the above values are lower than those associated with the pure



**Figure 6** Temporal variation of the heat release rate during the oxidation of dry diesel soot, diesel PM, and model soot samples in air subjected to three different temperature profiles with ramp rate of  $10^{\circ}\text{C}/\text{min}$ . The peak temperatures at isothermal conditions are  $550^{\circ}\text{C}$ ,  $535^{\circ}\text{C}$ , and  $525^{\circ}\text{C}$  in Figures 6a, 6b, and 6c, respectively. (Figure is provided in color online.)

carbon burning to CO<sub>2</sub>, the latter being 32.8 kJ/g. While we did not measure the product species, the lower values of heat release may be attributed to the formation of CO. Evidence of this is provided by Reichert et al. (2008), who observed that the amount of CO formed was higher than that of CO<sub>2</sub>, when solid carbon was oxidized at temperatures over 400°C.

Additional oxidation experiments with diesel PM samples were conducted under two more isothermal conditions, corresponding to maximum (isothermal) temperatures of 535°C and 525°C, respectively. Figure 6 presents the temporal variations of heat release rates from the oxidation of diesel PM in air, in comparison with those from dry diesel soot and model soot samples (see Figure 4). Results for the 550°C case are also included in the figure. The comparison of data for diesel PM and dry diesel soot at three isothermal temperatures of 550°C/535°C/525°C indicate that the fractions of the energy, representing the integrated heat release rate as percentages of the total heat release of the sample, were 8.18%/7.35%/7.94% in the first peak and 91.82%/92.65%/92.06% in the second peak. Using the measured amounts of volatile components of SOF as 0.904 mg, 1.004 mg, and 0.982 mg, the amounts of heat released during the oxidation SOFs in diesel PM samples were evaluated to be 5.66 kJ/g, 5.24 kJ/g, and 5.5 kJ/g, respectively. Thus the average specific heat release from the oxidation of SOFs can be approximated as 5.47 kJ/g, which is small compared to that from the oxidation of dry diesel soot.

As indicated in Figure 6, the maximum value of heat release rate decreases for all the samples, as the isothermal temperature is reduced. However, the total heat release per unit mass of sample is the same for the three temperature cases. Another important observation is that for these cases, there are noticeable differences in the heat release rate curves for the dry diesel soot and model soot samples. These differences can be attributed to the chemical contents in the two soot samples. It is also

**Table 3** Sample mass ( $M_o$ ), residue mass ( $M_r$ ), net mass oxidized ( $M_o - M_r$ ), mass of volatile component of SOF ( $M_v$ ), total amount of heat release, and specific heat release in the oxidation of diesel PM, dry diesel soot, and model soot with respect to different temperature profiles in DSC experiments

Temperature profile			$M_o$ (mg)	$M_r$ (mg)	$M_o - M_r$ (mg)	$M_v$ (mg)	Total heat release (J)	Specific heat release (kJ/g)
Isothermal temperature (°C)	Ramp rate (°C/min)	Sample						
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
		Model soot	3.719	0	3.719	–	52.12	14.02
535	10	Diesel PM	5.021	0.158	4.863	1.004	71.32	14.67
		Dry diesel soot	6.233	1.095	5.138	–	88.62	17.3
		Model soot	4.893	0	4.893	–	68.62	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
		Model soot	4.767	0	4.767	–	66.85	14.02

important to note the difference in the heat release rate profile for the 550°C case and those for the 535°C or 525°C cases for the oxidation of dry diesel soot samples. The profile for the 550°C case exhibits a continuous sharp decrease after the peak value, while those for the 535°C and 525°C cases indicate first a sharp decrease, followed by slow decrease and then sharp decrease again. This indicates sensitivity of the oxidation process to reaction temperature, implying that dry diesel soot contains some chemical species that affect the temporal rate of heat release during oxidation at a given temperature.

The total amounts of heat release during the oxidation of SOF-containing diesel PM, dry diesel soot, and model soot samples were computed using Equation (1), and the results are summarized in Table 3. For these results, the samples were subjected to heating mode at the constant rate of 10°C/min and three different isothermal temperatures at 550°C, 535°C, and 525°C in an air environment. As shown in the table, the amount of heat release per unit mass of each sample is the same for the three different temperature profiles, although the instantaneous heat release rates during the oxidation are quite different (cf. Figures 5 and 6).

## CONCLUSIONS

In order to control the thermal runaway during the oxidation of excess soot deposit in DPF, it is necessary to have detailed experimental information on the total heat release and the temporal variation of heat release rate from the diesel PM oxidation under realistic conditions. Previous studies have often used commercial soot artifacts (model soot) or PM samples collected from lab-scaled burners for oxidation experiments, although there are inherent compositional and structural differences between the diesel PM and model soot. The effect of SOF concentration in the diesel PM on the heat release rate characteristics has also not been considered. Moreover, most previous investigations have focused on the oxidation characteristics of diesel PM. In the present study, we report detailed experimental information on the total heat release and the temporal variation of heat release rate during the oxidation of diesel PM, and elucidate differences in the heat release characteristics of surrogate (model) soot and diesel soot. The diesel soot samples were collected from a cordierite particulate filter, where PM emissions bypassing the exhaust pipe of a light-duty diesel engine were deposited. Measurements employed a differential scanning calorimeter (DSC) and a thermogravimetric analyzer (TGA). Important observations are as follows.

Measurements taken at various ramp rates indicated an optimum ramp rate of 10°C/min, which provide high accuracy and efficiency in measuring the temporal variation of heat release rate during soot oxidation. Furthermore, 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.

The DSC experiments revealed that the amounts of heat released from the oxidation of SOF-containing diesel PM sample, dry diesel soot, and commercially

available (surrogate) model 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.<sup>4</sup> 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 model soot. In particular, remarkable differences were found on the results for dry diesel soot samples with respect to the oxidation temperatures of 550°C and below 550°C in air. The heat release rate of dry diesel soot at the isothermal temperature of 550°C decreases monotonically as the complete mass is oxidized. In contrast, the rates of heat release at the isothermal temperatures of 535°C and 525°C first decrease rapidly, and then slowly. As the complete mass is oxidized, the rapid zone appears again.

The experimental data reported here is expected to provide better predictive tools for thermal energy distribution during DPF regeneration, and thus develop an optimum thermal management system for DPF systems.

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### NOTES

1. A passive regeneration is a catalytic regeneration technique in which either the fuel doped with catalytic additives or the DPF coated with a catalyst is used to lower the soot oxidation temperature. In active regeneration, additional device such as fuel burner, resistive heating coils, or microwave energy is used to provide heat to the diesel exhaust system.
2. In the present study, the terms surrogate soot and model soot refer to the same thing.
3. In experiments with model soot, the residual mass is zero (i.e.,  $M_r = 0$ ), since the soot sample undergoes complete oxidation with no ash remaining.
4. This is consistent with the results of previous studies which indicate that the specific heat release increases if the internal structures of carbon material becomes more ordered and contains less SOFs.

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