Investigation of loose contact oxidation kinetic analysis on diesel particulate filter’s wall surface using non-isothermal TGA technique

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Abstract
Carbonaceous soot particles emitted from diesel engines are dangerous to human health because of its carcinogenic activity and can penetrate into lungs. In order to control soot emissions, diesel particulate filters (DPFs) are widely used to meet progressively stringent regulations of vehicle emissions limits. In this article, the characterization of conventional DPF microstructure was briefly investigated by scanning electron microscopy (SEM) addition with energy dispersive X-ray analysis (EDX) and X-ray fluorescence analysis (XRF). Non-isothermal oxidation mechanism of soot on conventional DPF was carried out from thermogravimetric analysis (TGA) under air atmosphere with the flow rate of 40ml/min at the heating rates of 5, 10, and 15 °C/min. The kinetic parameters were calculated by three non-isothermal model-free methods. The average value of apparent activation energy obtained by Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Kissinger (K) were 77.02, 65.29 and 70.48 kJ/mol, respectively at different heating rates. The average results got from this work indicate that non-isothermal experiments were quite low compared to kinetics parameters estimated by the isothermal method from previous research.

Keywords: Particulate matter, Diesel particulate filter, Soot oxidation, Thermogravimetric analysis, Non-isothermal method

1. Introduction
Compression ignition (diesel) engines are the entire power source in heavy-duty trucks and off-road vehicles as well as their usage is rapidly increasing in passenger cars owing to offering high fuel efficiency. Anyway, the tremendous amount of particulate matter (PM) or soot emissions from diesel exhaust system cause serious health issues and environmental consequences, resulting in the increment of strict emission regulations [1]. The compositions of diesel particulate matter include mainly of soot (solid carbon), agglomerated carbonaceous compounds, ash and volatile components. However, each of PM composition from diesel engine mainly depends on the engine operating conditions and properties...
of fuel [2]. Since the substantial knowledge of PM formation and oxidation processes have been improved from previous research, it can support a dramatic development of controlling diesel exhaust emissions in aftertreatment technologies [3, 4].

Currently, installing the diesel particulate filter (DPF) in exhaust pipe system is one of the trending technologies of reducing PM from diesel engines. The working principle of DPF filtration system is carried out through a physical trapping mechanism of PMs in the honey-comb shaped structure with alternating channels which the particles are trapped and accumulated on the wall surface. Hence, the cleaned exhaust gas is released into the atmosphere [5]. The trapped PMs are needed to be thermally regenerated in order to burn off the soot cake layer from the filter. The removal of particles in active (periodical) regeneration, along with the increasing of the temperature inside a DPF, or passive (continuous) regeneration, through the normal activity of DPF filtration mechanism. During the active regeneration, the temperature rise is occurred by post-injection of a certain amount of fuel to burn out the DPF upstream itself and heat the gas temperature inside the filter. This type of regeneration is compulsory, when the temperature inside DPF stream is not adequate to make sure a passive regeneration [6].

Some of the materials applied in fabricating of porous ceramics DPFs involve cordierite, silicon carbide (SiC), silicon nitride, mullite and aluminium titanite [7]. Currently, cordierite and SiC are popular and generally used in the market. Cordierite materials are normally made up of using the sources from talc, alumina and clay to fabricate cordierite all round many steps of reaction [8]. Cordierite DPF is popular by its ceramic structure and not only has a low coefficient of thermal expansion but also has a good thermal shock resistance [8].

Besides the influence of mechanical properties, the PM trapping and soot burning (oxidation) of diesel particles emission is also the important role of DPFs. Previous research has been reported that the methods for calculating the reaction kinetics of soot oxidation by isothermal thermogravimetric analysis (TGA) and temperature program oxidation (TPO) with conventional cordierite DPF powers [9]. It can be seen that the microstructure and oxidation properties of carbon black (CB) are the acceptable sample to simulate instead of real diesel soot particles [10]. In this work, soot burning (oxidation) mechanism of CB on DPF powders was studied by thermogravimetric analysis using the non-isothermal technique. The complete kinetics estimation was carried out by three different model-free methods. The morphology characteristics and chemical and elemental composition of conventional DPF structure were also briefly determined by SEM-EDX and XRF analysis.

2. Experimental Setup and Methodology
2.1. Physicochemical characterization of conventional diesel particulate filter (DPF)
A conventional diesel particulate filter (DPF) sample was investigated in this study as displayed in Figure 1. The morphological information of DPF sample was determined by SEM micrographs. A HITACHI SU5000 model of FESEM in the resolution of 30kV providing 10 to 600,000x magnification with BSE detector was carried out to focus on the sample’s microstructure surface. The identification of the elemental composition of a DPF sample was investigated by using EDX detector together with SEM which can observe the periodic elements from the range between Be to Pu. X-Ray fluorescence analysis

![Figure 1. The microstructure of (a) Cross-sectional surface, (b) wall surface, and (c) wall surface in micro-scale of investigated conventional diesel particulate filter.](image-url)
was also applied to make sure the detail chemical composition of a sample which can detect elements in wider ranges than EDS analysis.

The investigation of soot (CB) oxidation mechanism on DPF’s surface was carried out with thermogravimetric analyzer (NETZSCH) by mixing of DPF sample in powder condition and CB N330 as in a ratio of 1:1 referring to the loose contact method for the laboratory-scale study described in the literature [11]. For non-isothermal technique, the sample weight of approximately 2-5 mg with 0.1% accuracy in mass balance was placed into the aluminum dioxide (Al₂O₃) crucible pan and heated at a temperature from 30 to 900 °C accompanied by three various rates of heating in 5, 10 and 15 °C/min undergoing air atmosphere with a flow rate of 40ml/min. Thermal kinetics of soot (CB) oxidation on DPF’s surface was studied by characterization of mass conversion patterns from experimental TGA data.

2.2. Kinetic estimations of non-isothermal analysis

Equation (1) represents the soot (CB) combustion reaction which can be observed during the thermogravimetric experiment. Based on the basic principle of chemical kinetics reaction [12], the oxidation behavior with non-isothermal technique is described by Equation (2).

\[ C + O_2 \rightarrow CO_2 \]  \hspace{1cm} (1)
\[ \frac{d[C]}{dt} = k \ [C]^n [O_2]^m \]  \hspace{1cm} (2)

where \( C \) is mass of carbon black, \( t \) is reaction time, \( k \) is the constant of chemical reaction rate, \( m \) and \( n \) are the orders of reaction in regards to \( C \) and \( O_2 \), respectively. The reaction order \( n \) is presumed to be 1 when the whole internal \( C \) surface is fully diffused by oxygen molecules and the rate of reaction is approximately proportional to the concentration of \( C \) [13, 14]. Hence, the oxygen limitation of CB particles diffusion in the internal surface can be negligible and thus the order of \( m \) becomes zero.

Referred to the Arrhenius Equation [12], the rate of a chemical reaction can be illustrated as:

\[ k = A e^{-\frac{E_a}{RT}} \]  \hspace{1cm} (3)

where \( A \) is the pre-exponential factor, \( E_a \) is the apparent activation energy in kJ/mol, \( R \) is the value of an ideal gas constant in 8.314 J/mol K, \( T \) is the kelvin temperature. The kinetics equation can be obtained by substitution of Equation (2) into Equation (3):

\[ \frac{d[C]}{dt} = Aexp \left[ -\frac{E_a}{RT}\right][C] \]  \hspace{1cm} (4)

For non-isothermal experimental condition, the sample is heated at a linear rate, \( \beta = \frac{dT}{dt} \). Equation (4) can be rewritten as:

\[ \frac{d[C]}{dT} = A \beta \exp \left[ -\frac{E_a}{RT}\right][C] \]  \hspace{1cm} (5)

For estimating solid-state kinetics parameters form thermogravimetric analysis, both model-fitting and model-free (isocconversional) methods can be used [15]. For non-isothermal studies, the model-fitting approach requires to extract the specified value of kinetic parameters for the overall process while in fitting different models to conversion and temperature curves. However, this method may lead to obtaining unpredictable values of Arrhenius parameters [16]. On the other hand, model-free methods allow the estimation of activation energy for an independent model at specific degrees of conversion with a sequence of evaluation data using various linear heating rates [16]. In this paper, the kinetics parameters such as apparent activation energy and pre-exponential factor were estimated by model free methods of Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Kissinger (K).

The Flynn-Wall-Ozawa, obtained from the integral isoconversional method [17] is derived applying Doyle’s approximation [18] for the integral to transform into new equation.

\[ \ln \beta_i = \ln \left( \frac{A_iE_a}{Rg(\alpha)} \right) - 5.331 - 1.052 \frac{E_a}{RT \alpha_i} \]  \hspace{1cm} (6)

In this Equation, \( g(\alpha) \) is used as the integral conversion form of reaction model which is equal to \(-\ln(1 - \alpha)\) for first order reaction [19]. FWO method enables the estimation of apparent activation energy (\( E_a \)) from a graph of heating rates (\( \ln \beta_i \)) versus the inverse temperature (\( 1/T_{\alpha i} \)) which represents
the linear reaction with an associated value of conversion at several heating rates. The slope and intercept values of linear straight lines from the plot can be calculated the activation energies and pre-exponential factors, respectively.

The Kissinger-Akahira-Sunose (KAS) method [20] applying with Coats-Redfern temperature integral approximation [21] can be improved to transform into iso-conversional approaches.

\[ \ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{A R}{E_\alpha G(\alpha)} \right) - \frac{E_\alpha}{RT_\alpha} \]  \hspace{1cm} (7)

The apparent activation energy \((E_\alpha)\) can be evaluated from the value of slope by a graph of \(\ln (\beta/\alpha T^2)\) versus \(1/T_\alpha\) for the variable fractional conversion values which make up the linear lines to the plot. The value of the pre-exponential factor \((A_\alpha)\) can be derived from the intercept of those straight lines.

The Kissinger (K), also called maximum rate method provides the kinetic parameters of a solid-state reaction which does not need to know the reaction mechanism. Kissinger method is invented for the model-free approach of non-isothermal technique but does not estimate apparent activation energy for each conversion [22].

\[ \ln \left( \frac{\beta}{T^2} \right) = \ln \left( \frac{A R}{E} \right) - \frac{E}{RT_m} \]  \hspace{1cm} (8)

The constant value of \(E_\alpha\) and \(A\) were calculated depending on equation (8) by the plotting of \(\ln (\beta/\alpha T^2)\) versus \(1/T_m\), where \(T_m\) means the temperature of the maximum weight loss peaks from DTG curves.

3. Results and Discussion

3.1. Surface Topography and characterization of DPF structure

Figure 2 presents the characterization of surface topography of DPF sample using SEM. The left image indicates SEM image with 300x magnification while the right image indicates 1000x magnification. It can be observed that the widely distributed pores are different in size and non-uniform in shape. As the microstructure of pore surfaces are strongly connected to the efficiency of surface filtration and soot burning mechanism [23], the result of opening in porosity was one of the advantageous properties of cordierite DPF. It was also found that some of the micro-cracks can be developed on DPF’s wall surface during the high-temperature fabrication processes because the material of cordierite has low heat capacity [8].

![Figure 2. Surface topograph of cordierite DPF sample using SEM.](image)

The elemental characterization of a DPF sample was described by applying EDX detector together with SEM in a small area of interest on the sample as presented in Figure 3. The energy of the emitted X-ray during the process can be detected the specific element which has a unique atomic structure. As reported by EDX analysis, the sample involves mainly of oxygen (O), silicon (S), aluminium (Al) and another trace element in impurity. Another elemental analysis results from XRF technique were expressed in figure 4. Form these results, we have found that both experiments observed
the same elements expect the highly reactive non-metal in XRF analysis. On the other hands, XRF technique can even detect very low weight percent of elements like Ti, Fe, Ni and Pt. These elements data assure that DPF sample has the ongoing ceramics form to be cordierite structure which is generally produced from low-cost natural clay materials such as talc and kaolin [8].

Figure 3. Elemental composition of cordierite DPF sample using EDX analysis.

Figure 4. Elemental composition of cordierite DPF sample using XRF analysis.

Figure 5. (a) TG and (b) DTG curves for soot oxidation process of DPF sample with the non-isothermal method at three different heating rates.
3.2. Non-isothermal soot oxidation reactions
Figures 5 (a) and (b) show the thermo gravimetric (TG) and derivative thermo gravimetry (DTG) curves of loose contact in soot burning (oxidation) process of CB with DPF powder under pure air atmosphere which were estimated at various heating rates of 5, 10, and 15°C/min, respectively. All of the TG curves were asymmetric as observed in figure 5 and the individual conversions were obtained at higher temperatures. This means that the maximum degradation points of TG and DTG are slightly moved towards the increasing of heating rate. The maximum soot mass reaction rate at 5 and 10°C/min occurred around the temperature between 600-700°C with well-defined peak while the value at 15°C/min was occurred nearby the temperature about 600-900°C with mildly shoulder peak. It can also be observed that the peaks on DTG curve become more widen with higher heating rate. Due to heat transfer limitations, the higher the heating rate, the larger the reaction time becomes.

3.3. Evaluation of kinetics parameter
The results got from TGA non-isothermal analysis were analysed by three model-free methods using Flynn-Wall-Ozawa (FWO), Kissinger-Akahira-Sunose (KAS) and Kissinger (K) methods to calculate the kinetics parameters such as the apparent activation energy (E_a) and pre-exponential factor (A) as shown in Figure 6,7 and 8. For all the soot oxidation value of 20-80%, the liner plots obtained by FWO, KAS, and K methods get in the coefficient of regression (r^2) higher than 0.9. Figure 9 shows the variation of apparent activation energy (E_a) depends on the soot oxidation value of 20-80% for the non-isothermal process of CB oxidation on DPF derived by model-free methods. It can be found that the data

**Figure 6.** FWO plot for different values of soot oxidation at three heating rates.

**Figure 7.** KAS plot for different values of soot oxidation at three heating rates.

**Figure 8.** Kissinger plot at three heating rates.

**Figure 9.** Dependence of activation energy of soot oxidation (%) derived by FWO, KAS and K methods.
of activation energy have a rising trend with increasing of soot oxidation value. The average values of activation energy and pre-exponential factor resulted from each method are described in table 1. The average activation energy value obtained from FWO and K methods were 77.02 and 70.48 kJ/mol, respectively as these values are greater than the value calculated by KAS method which was 65.29 kJ/mol. Previous research reported that the activation energy for isothermal soot oxidation on DPF powders was covered in the range from 109 to 131 kJ/mol [9]. While comparing with calculated $E_a$ value under isothermal technique, the result got under the non-isothermal condition in this work is quite low. However, the $E_a$ calculated from non-isothermal condition takes the mean value over the unpredictable range of rising temperature while the value estimated from isothermal condition takes the average value over the range of temperature chose for the analysis. One of the researcher groups has been suggested that the result of the analysis data generated from kinetics model under isothermal and non-isothermal experiments cannot be relevantly compared [24].

| Model-free (isoconversional) methods | Apparent Activation Energy, $E_a$ (kJ/mol) | Pre-exponential Factor, $A$ (min$^{-1}$) |
|-------------------------------------|-------------------------------------------|------------------------------------------|
| Flynn-Wall-Ozawa (average)          | 77.02                                     | 1.69E + 04                               |
| Kissinger-Akahira-Sunose (average)  | 65.29                                     | 1.76E + 03                               |
| Kissinger                           | 70.48                                     | 4.85E + 02                               |

4. Conclusion
The physicochemical analysis of pure DPF sample and soot oxidation mechanisms of loose contact on the surface of DPF were investigated in this work. The morphology of DPF structure was observed that the various pores are different in size and irregular in shape. The morphology and microstructure of the cordierite DPF sample were successfully observed by the elemental analysis using SEM-EDX and XRF technique. Non-isothermal thermogravimetric analysis was implemented at three different heating rates of 5, 10, and 15 °C/min undergoing pure air gas flow rate of 40 ml/min to study the estimation of kinetic parameters. From thermogravimetric soot oxidation graph, it has been observed that heating rate could affect TG curve locations, maximum soot mass conversion rate and position of the maximum temperature peak. The activation energy values derived from FWO and KAS methods were significantly increased as the soot oxidation was risen to 80 %. In Kissinger method, the activation energy value was constant at the various conversions. This work can be summarized that the average values of apparent activation energy of loose contact soot oxidation on DPF using three model-free methods were in the range between 65.29 – 77.02 kJ/mol.

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