IMPACT OF OXYGEN ENRICHMENT ON SOOT PROPERTIES AND
SOOT OXIDATIVE REACTIVITY

A Dissertation in
Energy and Geo-Environmental Engineering

by

Hee Je Seong

© 2010 Hee Je Seong

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2010
The dissertation of Hee Je Seong was reviewed and approved* by the following:

André L. Boehman  
Professor of Fuel Science and Materials Science and Engineering  
Dissertation Advisor  
Chair of Committee

Angela D. Lueking  
Associate Professor of Energy and Mineral Engineering

Randy L. Vander Wal  
Associate Professor of Energy and Mineral Engineering

Richard A. Yetter  
Professor of Mechanical Engineering

R. Larry Grayson  
Professor of Energy and Mineral Engineering  
Graduate Program Officer of Energy and Mineral Engineering

*Signatures are on file in the Graduate School
ABSTRACT

Heavy duty diesel engines have been key power generators in transportation and power plants around the world. However, the hazardous pollutants emitted from diesel engines have driven their emissions to be regulated in increasingly stringent ways. Among the pollutants, particulate matter (PM) has long been studied as to why it is generated during the combustion process and how it can be effectively reduced via fuel injection strategy, fuel modifications and after-treatment systems. In order to meet current and future standards, diesel particulate filter (DPF) systems have become the primary means to remove PM.

DPF systems involve particulate filtration from the exhaust and subsequent burn-off of the filtered particulates. Consequently, the effects of engine operation and fuel formulation on particulate oxidation have been of great interest because of the relevance to the application of DPF systems. Previous studies showed that physical and chemical properties of soot, which are represented by the volatile organic fraction of the particulate matter, and the crystalline structure, O and H content and surface oxygen functional groups of the primary soot particles, are significantly affected by engine operations and fuel formulations. Furthermore, the soot properties are observed to have a great impact on soot oxidative reactivity. In spite of the efforts to elucidate certain soot properties affecting soot oxidative reactivity, there are few investigations made on the influence of the combustion process on soot oxidative reactivity. Since oxygen enrichment has a great effect on the combustion process, various oxygen concentrations were examined in a diesel engine and a diffusion flame burner to determine the impact of oxygen enrichment on soot properties.

Oxygen addition to the engine was carried out by intake oxygen enrichment and by fuel oxygenation at low load and high load. The analyses of heat release rates and cylinder temperatures indicate that the effect of oxygen enrichment is more appreciable at high load than
at low load. Correspondingly, there are more noticeable changes in crystalline structure and oxidative reactivity of soot from high load than of soot from low load. However, surface O content and oxygen functional groups are shown to have mixed results without any consistency at low and high loads with oxygen enrichment. In addition, soot generated from high load with intake oxygen enrichment is observed to contain some metallic species, while soot from low load has little or no metallic species. Although the higher temperature induced by higher oxygen concentration was thought to be a main factor affecting the oxidation of lubricating oil, it is shown that there should be a synergistic effect of high oxygen concentration and high temperature in order to accelerate the oxidation of lubricating oil. There might be an effect of soot crystalline structure on soot oxidative reactivity, but the major influence on the reactivity is shown to be closely related to the amounts of metallic species present in soot due to the catalytic role of metallic species in soot oxidation.

In order to better understand the effect of soot properties on soot oxidative reactivity, a diffusion flame burner was employed at various oxygen concentrations. There is a clear inverse relation observed between adiabatic flame temperature and soot oxidative reactivity. However, detailed experiments suggest that the primary factors impacting soot oxidative reactivity are the soot inception time and the soot oxidation process. The earlier soot is formed, the less reactive soot becomes. Accordingly, ethylene-derived soot is shown to be less reactive than \( n \)-heptane-derived soot under the same carbon flow rate and the same adiabatic flame temperature, because soot is formed at an earlier stage with ethylene than with \( n \)-heptane. In addition, increasing oxygen concentration in the oxidizer stream made soot less reactive, because not only is the soot inception time shortened by the increase in the flame temperature, but also the soot oxidation process is enhanced by increased abundance of oxidizing gases during the combustion process.

From these results, it is concluded that the reason why soot derived from oxygenated fuel (a mixture of 70 vol. % \( n \)-heptane and 30 vol. % monoglyme) is more reactive than soot from \( n \)-
heptane fuel is related to the lengthened soot inception time caused by reduced soot precursor particles.

Raman spectroscopy, x-ray diffraction (XRD), electron energy loss spectroscopy (EELS) and near edge x-ray absorption structure spectroscopy (NEXAFS) showed that the crystalline order of soot is strongly related to soot oxidative reactivity. However, the trend in the crystalline order of soot is observed to be opposite for soot from the diffusion flame burner and soot from the diesel engine with increasing oxygen concentration. Interestingly, engine soot from high load becomes less ordered in its crystalline structure with increasing oxygen concentration in spite of increasing cylinder temperature, which is contradictory with others’ results. From the study with the diffusion flame burner, it is suggested that since soot precursor particles are oxidized by abundant amounts of oxidizing gases at high temperature, there is a limitation for soot precursor particles to transform to soot particles, which delays soot inception time, resulting in reducing the crystalline order of soot.

It is difficult to evaluate the effect of surface O content on soot oxidative reactivity in the case of diesel soot, but the study on flame soot clearly indicates that surface O content correlates with soot oxidative reactivity. A detailed XPS study suggests that C-O groups in alcohol, and carboxylic anhydride and/or ester groups are the most abundant on the soot surface, and upon oxidation C=O groups and COOH groups increase gradually in their relative ratios, whereas C-O groups, and carboxylic anhydride and/or ester groups decrease. Also, it is suggested that soot oxidative reactivity depends more on the active sites that remain in the soot structure than on surface oxygen functional groups.
# TABLE OF CONTENTS

LIST OF FIGURES .................................................................................................................. viii

LIST OF TABLES ..................................................................................................................... xiii

ACKNOWLEDGEMENTS ......................................................................................................... xv

Chapter 1 Introduction ........................................................................................................... 1

1.1 Background .................................................................................................................... 2
1.2 Scope of this Study ....................................................................................................... 3
1.3 Hypotheses and Objectives ......................................................................................... 6
1.3.1 Hypotheses ........................................................................................................... 6
1.3.2 Objectives ............................................................................................................ 6
1.4 Technical Approach .................................................................................................... 7

Chapter 2 Literature Review ............................................................................................... 10

2.1 Soot Oxidation in Diesel Particulate Filter (DPF) ..................................................... 10
2.2 Soot Formation and Soot Oxidation Processes during Combustion ....................... 14
   2.2.1 Overview of Soot Formation Process ................................................................ 14
   2.2.2 Effect of Temperature and Oxygen Enrichment on Soot Formation and
       Soot Oxidation ..................................................................................................... 15
2.3 Effect of Properties in Soot on Soot Oxidative Reactivity ........................................ 18
   2.3.1 Physical and Chemical Properties ................................................................. 18
   2.3.2 Instrumental Approaches for Soot Properties .............................................. 22

Chapter 3 Experimental ..................................................................................................... 30

3.1 Experimental Instruments .......................................................................................... 30
3.2 Characterization Tools ............................................................................................... 36

Chapter 4 Study on Crystalline Structure and Oxygen Content of Soot ......................... 42

4.1 Comparison of Crystallite Size by XRD and Raman Spectroscopy ......................... 42
   4.1.1 TGA Results ................................................................................................... 42
   4.1.2 XRD Results ................................................................................................... 43
   4.1.3 Raman Analysis .............................................................................................. 45
4.2 Soot Surface Modification Study ............................................................................... 51
   4.2.1 Soot Oxidative Reactivity ............................................................................... 51
   4.2.2 Surface O Content and Oxygen Functional Groups ...................................... 53
       4.2.2.1 TPM-MS ............................................................................................... 53
       4.2.2.2 XPS ....................................................................................................... 57

Chapter 5 Effect of Soot Properties on Soot Oxidative Reactivity Using a Diesel Engine .... 66

5.1 Apparent Heat Release Rate ....................................................................................... 66
5.2 Bulk Cylinder Gas Temperature ............................................................................... 69
5.3 TEM Analysis of Particle Aggregates................................................................. 71
5.4 Impact of Soot Properties on Soot Oxidative Reactivity ........................................ 73
  5.4.1 Soot Oxidative Reactivity by TGA ................................................................. 73
  5.4.2 Elemental Analysis and Oxygen Functional Groups.................................... 75
    5.4.2.1 Inorganic Species by XPS and SEM-EDS ........................................... 75
    5.4.2.2 Effect of Metallic Species on Soot Oxidation ...................................... 79
    5.4.2.3 Surface O Content by XPS ................................................................. 81
    5.4.2.4 Surface Oxygen Functional Groups by XPS .................................... 85
  5.4.3 Crystalline Structure of Diesel Soot.............................................................. 88
    5.4.3.1 XRD Analysis ...................................................................................... 88
    5.4.3.2 Raman Analysis .................................................................................... 90
  5.4.4 Soot Oxidation Process .................................................................................. 95

Chapter 6 Effect of Soot Properties on Soot Oxidative Reactivity Using a Diffusion Flame Burner..................................................................................................... 98

  6.1 Study on Oxidative Reactivity and Properties of Flame Soot.............................. 98
    6.1.1 Soot Inception Time .................................................................................... 98
    6.1.2 Soot Properties ........................................................................................... 107
      6.1.2.1 Oxygen Content and Oxygen Functional Groups ................................. 107
      6.1.2.2 Active Surface Area (ASA) ................................................................. 110
      6.1.2.3 Soot Crystalline Structure ................................................................. 111
      6.1.2.4 HR-TEM Images and \( \pi/\sigma \) investigation .................................... 115
      6.1.2.5 Difference in the Crystalline Structure between Diesel Soot and Flame Soot ................................................................. 119
  6.2 Changes in Soot Properties during Oxidation ....................................................... 121
    6.2.1 Soot Crystalline Structure ........................................................................ 121
    6.2.2 Surface O content and Oxygen Functional Groups ..................................... 125

Chapter 7 Conclusions and Recommendations for Future Work............................................. 130

  7.1 Conclusions ...................................................................................................... 130
  7.2 Recommendations for Future Work .................................................................. 132

References ................................................................................................................. 135

Appendix A Raman Analysis.......................................................................................... 150

Appendix B Supplemental Results for Engine Soot and Flame Soot ............................ 162
LIST OF FIGURES

Figure 1-1. TEM images of primary soot particles from different sources of flame: (a) soot from a diffusion flame burner, (b) soot from a light duty diesel engine, (c) soot from a heavy duty diesel engine, (d) soot from a single cylinder locomotive engine......4

Figure 2-1. Reaction mechanism of the noncatalytic oxidation of carbon [15].................................11

Figure 2-2. Illustration of NOx-aided CRT [15] ............................................................................13

Figure 2-3. Schematic diagram of the steps in the soot formation process [27].........................14

Figure 2-4. Schematic view: (a) perfect graphite lattice and schematic model of disordered carbon [62], (b) crystallite size in c- and a-direction...............................................19

Figure 2-5. Curve-fitted shape of SCE soot : (a) 2 lorentzian and 1 gaussian, (b) 3 lorentzian (c) 3 lorentzian and 1 gaussian, (d) 4 lorentzian, (e) 4 lorentzian and 1 gaussian, (f) 5 lorentzian ..................................................................................................23

Figure 2-6. Surface oxygen functional groups [20] .......................................................................27

Figure 3-1. Schematic of engine operation ..................................................................................33

Figure 3-2. Flame in a diffusion flame burner and soot collection ...........................................34

Figure 4-1. TGA results of soot samples at 550 °C isothermal condition.....................................43

Figure 4-2. XRD patterns of soot samples..................................................................................44

Figure 4-3. Crystallite sizes of soot samples against 1/t50% .......................................................45

Figure 4-4. Comparison of Raman spectra of soot samples: (a) first-order Raman spectra, (b) second-order Raman spectra.......................................................................................46

Figure 4-5. Comparison of crystallite width: I_D/I_G from raw spectra was used for Knight and White’s method, and A_D/A_G from 3L1G fitting method was used for Cançado et al.’s method........................................................................................................49

Figure 4-6. Comparison of crystallite width: Knight and White1 uses I_D/I_G and Knight and White 2 uses A_D/A_G from the 3L1G fitting method.................................................50

Figure 4-7. TGA results of surface modified soot samples at 500 °C isothermal condition....52

Figure 4-8. Deconvolution of CO and CO2 evolved in TPD-MS: (a) and (b) original flame soot, (c) and (d) soot acidified by HNO3 at room temperature, (e) and (f) soot acidified by HNO3 at 60 °C. (1) strongly acidic carboxylic groups, (2) weakly acidic carboxylic groups, (3) phenol and/or carboxylic anhydride groups, (4) carbonyl and/or quinone groups, (5) carboxylic anhydride, (6) lactones..............................................................................54
Figure 4-9. XPS results of acidified soot samples: (a) surface O content, (b) C1s, (c) O1s... 58

Figure 4-10. Comparison of curve-fitted C1s for high load soot samples: (a) original flame soot, (b) soot acidified with HNO3 at room temperature, (c) soot acidified with HNO3 at 60 °C. (1) C-O in alcohol and/or ether groups, (2) C=O in quinone and/or carbonyl groups, (3) O=C-O in carboxylic acid, ester and/or carboxylic anhydride groups...

Figure 4-11. Comparison of curve-fitted O1s at different oxidized stages: (a) original flame soot, (b) soot acidified with HNO3 at room temperature, (c) soot acidified with HNO3 at 60 °C.... 62

Figure 4-12. TGA results of thermally treated soot samples at 500 °C isothermal condition...

Figure 5-1. Apparent heat release rate for oxygen enrichment tests: (a) 30% load, (b) 75 and 90% loads...

Figure 5-2. Bulk cylinder gas temperature for oxygen enrichment tests: (a) 30% load, (b) 75 and 90% loads...

Figure 5-3. TEM images of soot aggregated particles collected by thermophoretic sampling: (a) 30% load at 21% O2, (b) 30% load at 24% O2, (c) 75% load at 21% O2, (d) 75% load at 27% O2...

Figure 5-4. TGA results of soot samples for oxygen enrichment tests: (a) 30% load, (b) 75 and 90% loads...

Figure 5-5. SEM image of the 27% O2 soot from 75% load...

Figure 5-6. TGA results of soot and carbon black in the presence of metals: (a) soot mixed with Ca at 500 °C isothermal oxidation, (b) carbon black mixed with Ca and Zn at nonisothermal oxidation...

Figure 5-7. O/C on soot measured by XPS as a function of oxygen content in the exhaust gas and bulk cylinder gas temperature: (a) 30% load, (b) 30% load, (c) 75 and 90% loads, (d) 75 and 90% loads...

Figure 5-8. XPS peak patterns of C1s and O1s: (a) C1s for 30% load, (b) O1s for 30% load, (c) C1s for 75% and 90% loads, (d) O1s for 75 and 90% loads...

Figure 5-9. Comparison of curve-fitted C1s for high load soot samples: (a) 21% O2 soot of 75% load, (b) 24% O2 soot of 75% load, (c) 90% load soot. (1) C-O in alcohol and/or ether groups, (2) C=O in quinone and/or carbonyl groups, (3) O=C-O in carboxylic acid, ester and/or carboxylic anhydride groups...

Figure 5-10. XRD patterns of soot samples for oxygen enrichment tests: (a) 30% load, (b) 75 and 90% loads...
Figure 5-11. Raman analyses of soot samples with standard deviation for 30% load: (a) D3 band area ($A_{D3}$), (b) $A_{D1}/A_{G}$ (Area ratio), (c) D1 FWHM .......................................... 91

Figure 5-12. Raman analyses of soot samples with standard deviation for 75 and 90% loads: (a) D3 band area ($A_{D3}$), (b) $A_{D1}/A_{G}$ (Area ratio), (c) D1 FWHM .......................................... 92

Figure 5-13. D1 FWHM magnitudes of soot samples with standard deviation as a function of maximum bulk cylinder gas temperature ...................................................... 92

Figure 5-14. Raman analyses of soot samples during soot oxidation: (a) $A_{D1}/A_{G}$ (area ratio), (b) D1 FWHM ....................................................................................................... 96

Figure 5-15. HR-TEM images during soot oxidation ............................................................................................. 97

Figure 6-1. TGA results of soot samples collected from different oxidizer flow rate under the same O$_2$ concentration in the oxidizer stream at 500 °C isothermal oxidation .......... 99

Figure 6-2. TGA results of soot samples at 500 °C isothermal oxidation: (a) O$_2$ variation in the oxidizer stream, (b) Ar variation in the balance of the oxidizer stream ................. 100

Figure 6-3. TGA results of soot samples showing similar adiabatic flame temperatures at 500 °C isothermal oxidation........................................................................................................... 101

Figure 6-4. TGA results of soot samples from the increased ratio of carrier gas to fuel in the fuel stream at 500 °C isothermal oxidation: flame temperature in (C) is increased by replacing a portion of N$_2$ with Ar in the oxidizer stream ............................................ 103

Figure 6-5. TGA results of $n$-heptane soot and ethylene soot at 500 °C isothermal oxidation: flame temperature in (B) is increased by replacing a portion of N$_2$ with Ar in the oxidizer stream ............................................ 104

Figure 6-6. Major reaction pathways for (a) $n$-heptane, (b) ethylene [170] ...................................................... 106

Figure 6-7. XPS results of flame soot samples: (a) surface O content, (b) C1s, (c) O1s............. 108

Figure 6-8. Active surface area against soot oxidative reactivity: A, B, C, D and E are soot samples as shown in Table 6-2........................................................................................................... 111

Figure 6-9. XRD results of flame soot samples: (a) XRD patterns, (b) crystallite size against soot oxidative reactivity........................................................................................................... 112

Figure 6-10. Comparison of Raman parameters: (a) D3 band area ($A_{D3}$), (b) area ratio of D1 to G ($A_{D1}/A_{G}$), (c) D1 FWHM........................................................................................................... 114

Figure 6-11. HR-TEM images of flame soot samples: (a) $n$-heptane, O$_2$ in oxidizer = 21%, ................................................................................................................................. 116

Figure 6-12. Comparison of STEM images, EELS analyses selected at their corresponding images and EXAFS analyses: (a) $n$-heptane, O$_2$ = 21%, (b) $n$-heptane, O$_2$ = 35%, (c) ethylene, O$_2$ = 21%, (d) EELS results, (e) NEXAFS results ............................................................................................. 118
Figure 6-13. Variation in crystallite size of flame soot during oxidation

Figure 6-14. Variations in Raman parameters of diffusion soot during oxidation: (a) height and area in D3 band (I_{D3} and A_{D3}) from 3L1G fitting, (b) height and area ratios of D3 to (G+D3) (I_{D3}/I_{G+D3} and A_{D3}/A_{G+D3}) from 3L1G fitting, (c) height and area in D3 band (I_{D3} and A_{D3}) from 4L1G fitting, (d) height and area ratios of D3 to (G+D2+D3) (I_{D3}/I_{G+D2+D3} and A_{D3}/A_{G+D2+D3}) from 4L1G fitting

Figure 6-15. Variations in Raman parameters of diffusion soot during oxidation: (a) area ratio of D1 to G (A_{D1}/A_{G}) from 3L1G fitting, (b) D1 FWHM from 3L1G fitting

Figure 6-16. Comparison of XPS peaks during soot oxidation: (a) C1s, (b) O1s

Figure 6-17. Comparison of curve-fitted C1s at different oxidized stages: (a) 0% oxidation, (b) 33% oxidation, (c) 67% oxidation, (d) 90% oxidation. (1) C-O in alcohol and/or ether groups, (2) C=O in quinone and/or carbonyl groups, (3) O=C-O in carboxylic acid, ester and/or carboxylic anhydride groups

Figure 6-18. Comparison of curve-fitted O1s at different oxidized stages: (a) 0% oxidation, (b) 33% oxidation, (c) 67% oxidation, (d) 90% oxidation. (4) 530~532 eV is C=O in quinone, carbonyl and/or carboxylic acid, (5) 531~534 eV is O=C in ester and anhydride and C=C in ether and/or alcohol, (6) 532~535 eV is O=C in ester, anhydride and carboxylic acid

Figure A-1. Comparison of Raman parameters from 2L1G fitting: (a) height ratio of D1 to G (I_{D1}/I_{G}), (b) area ratio of D1 to G (A_{D1}/A_{G}), (c) D1 FWHM

Figure A-2. Comparison of Raman parameters from 3L fitting: (a) height ratio of D1 to G (I_{D1}/I_{G}), (b) area ratio of D1 to G (A_{D1}/A_{G}), (c) D1 FWHM

Figure A-3. Comparison of Raman parameters from 3L1G fitting: (a) height ratio of D1 to G (I_{D1}/I_{G}), (b) area ratio of D1 to G (A_{D1}/A_{G}), (c) D1 FWHM

Figure A-4. Comparison of Raman parameters from 4L fitting: (a) height ratio of D1 to G (I_{D1}/I_{G}), (b) area ratio of D1 to G (A_{D1}/A_{G}), (c) D1 FWHM

Figure A-5. Comparison of Raman parameters from 4L1G fitting: (a) height ratio of D1 to G (I_{D1}/I_{G}), (b) area ratio of D1 to G (A_{D1}/A_{G}), (c) D1 FWHM

Figure A-6. Comparison of Raman parameters from 5L fitting: (a) height ratio of D1 to G (I_{D1}/I_{G}), (b) area ratio of D1 to G (A_{D1}/A_{G}), (c) D1 FWHM

Figure B-1. TGA results of flame soot collected from different burner tests at 500 °C isothermal condition

Figure B-2. Repeatability of TGA results for flames soot at 500 °C isothermal condition

Figure B-3. TGA results of soot samples pretreated at different temperatures: (a) engine soot at 550 °C isothermal condition, (b) flame soot at 500 °C isothermal condition
Figure B-4. TGA results of soot samples at different isothermal temperatures: (a) 500 °C, (b) 600 °C

Figure B-5. Chemisorption of O₂ at different temperatures

166
## LIST OF TABLES

Table 1-1. Locomotive emission standards (g/bhp-hr) [4] .............................................................. 1

Table 2-1. Assignment of oxygen functional groups in XPS ...................................................... 26

Table 2-2. Assignment of oxygen functional groups in TPD-MS .............................................. 28

Table 3-1. Engine specifications ................................................................................................. 31

Table 3-2. Properties of diesel fuel and diglyme ...................................................................... 32

Table 3-3. Experimental conditions and O/C in a diesel engine .............................................. 32

Table 3-4. Experimental conditions in a diffusion flame burner ............................................. 35

Table 4-1. 50% of soot burn-off time at different temperatures .............................................. 43

Table 4-2. Height and area ratios of D to G for raw spectra and the 3L1G fitting method ....... 47

Table 4-3. Total amounts of CO and CO$_2$ calculated from TPD-MS ...................................... 53

Table 4-4. Results of the CO and CO$_2$ amounts and their corresponding centered temperature: (1), (2), (3), (4) and (5) are oxygen functional groups from Figure 4-8, and A, B and C are soot samples as shown in Table 4-3 ................................................................. 56

Table 4-5. Results of total CO and CO$_2$ amounts for each functional group: (1), (2), (3), (4) and (5) are oxygen functional groups from Figure 4-8, and A, B and C are soot samples as shown in Table 4-3 ................................................................. 56

Table 4-6. Relative ratio of oxygen functional groups in curve-fitted C1s with surface modification: (1), (2) and (3) are oxygen functional groups from Figure 4-10, and A, B and C are soot samples as shown in Figure 4-9(a) .............................................................................. 61

Table 4-7. Relative ratio of oxygen functional groups in curve-fitted O1s with surface modification: (4), (5) and (6) are oxygen functional groups from Figure 4-11, and A, B, C are soot samples as shown in Figure 4-9(a) .............................................................................. 63

Table 4-8. Peak assignment of O1s in O=C-O groups ............................................................. 63

Table 5-1. Ignition characteristics in pilot and main injection with oxygen enrichment for 75% load ...................................................................................................................................... 68

Table 5-2. Elemental analyses of inorganic species in the soot samples by XPS and SEM-EDS: samples for XPS are thermally treated at 500 °C, and samples for SEM-EDS are as-received .................................................................................. 76
Table 5-3. Atomic percentages of elements in soot samples by XPS .........................................82

Table 5-4. Relative ratio of oxygen functional groups in curve-fitted C1s for high load soot samples: (1), (2) and (3) are oxygen functional groups from Figure 5-9 .........................87

Table 5-5. Crystallite sizes calculated from XRD patterns of soot samples .................................90

Table 6-1. Relative ratio of oxygen functional groups in curve-fitted C1s and O1s .......................109

Table 6-2. Active surface area according to adsorbed O2 amounts for several soot samples ....110

Table 6-3. Relative ratio of oxygen functional groups in curve-fitted C1s and O1s: (1), (2), (3), (4), (5) and (6) are oxygen functional groups as shown in Figures 6-17 and 6-18 ..................................................................................................................................128

Table A-1. Comparison of chi-square error at different curve-fitting methods .........................150

Table A-2. Height, area and FWHM of D3 band at different curve-fitting methods ..........151

Table B-1. Emissions and fuel consumption from the diesel engine with oxygen enrichment ..............................................................................................................................162

Table B-2. Volatile organic fraction (VOF) of engine soot calculated from TGA treated at 500 °C---------------------------------------------------------------------------------------------162

Table B-3. Volatile organic fraction (VOF) of flame soot calculated from TGA treated at 300 °C ......................................................................................................................................163

Table B-4. BET surface areas of flame soot samples ..................................................................167
There are many people to whom I am grateful for their guidance and support during my Ph.D. study at Penn State.

At first, I want to express my deep gratitude to my research advisor, Dr. André L. Boehman who has guided me up to this point with his excellent directions. Thanks to his generous and patient support, I could accomplish what was needed for this work. I will not be able to forget his warm smiles and kindness he has always given me.

I would also like to express my grateful mind to the committee members: Dr. Angela D. Lueking, Dr. Randy L. Vander Wal and Dr. Richard A. Yetter. Thanks to their invaluable suggestion and comments on my research, the quality of this thesis could be greatly improved.

And, I give my thanks to General Electric Global Research Center and General Electric Transportation for sponsoring this study. I also acknowledge that the support was given by the U.S. Department of Energy under No. 08NT002788.

There are more people in the school, whom I should appreciate for their works and support. I would like to thank Vince Bojan for XPS analysis, Dr. Joe Kulik for TEM analysis, Nichole Wonderling for XRD analysis, Joe Stitt for Raman analysis in the Materials Characterization Lab, and Dr. Yongsheng Chen and Kyungsoo Kim for NEXAFS analysis. I am also thankful to Vince Zello and Greg Lilik for many helps regarding engine operation, Dr. Yu Zhang for the study of diffusion flames and Kuen Yehliu for valuable discussions regarding soot study in our research group. And, I am very much thankful to Dr. Cigdem Shalaby, Na Li and Chung-Hsuan Huang for TPD-MS and soot acidification in the EMS Energy Institute.

I have had many unforgettable memories with people from St. Paul’s United Methodist Church. I truly appreciate Pastor Edwin Zeiders and Eric Shafer, and choir members for their
prayer and support while I was the member of Chancel choir in the church. In particular, I am sincerely thankful to Jack and Marsha Willenbrock for their taking me to fun and memorable places and for their important life advice to me, Larry and Micki Pharo for their warm holiday dinner invitations every year, Mike and Sue Rice for their wonderful friendship and Linda Schimmel for providing me her beautiful artwork and taking me to the place of her artwork, Spruce Creek, PA. I especially give my deepest gratitude to Gayl Lent and her sister Jean Rounds, and Lefty and Connie McIntyre who let me stay in their houses when I was finishing this thesis. They took care of me like their own son.

My gratitude is also extended to my parents who have always given their unconditional love for their last son. I am inexpressibly grateful to them for their guiding me to right directions. I also give my thanks to my two brothers, two sisters and their families for their loving encouragement. And, I am truly thankful to my parents-in-law who have been supporting me with their prayer everyday. Also, I thank my brother-in-law and his wife for their prayer.

Finally, I want to express my special thanks to my wife, HyeYoung who has been my very best friend and the most important part of my life for the last 16 years. Without her wisdom, I could not become the person who I am now. Also, I cannot skip expressing my loves and gratitude to our 10 year-old Toy poodle, Roy who moved to Penn State all the way from Korea with me and has lived his entire life with me as well. He has been one of my greatest joys and has been brightening my everyday with his genuine happiness.

Last but not least, I am forever grateful to God who is the greatest stronghold of my life.
Chapter 1

INTRODUCTION

Heavy duty diesel engines have been widely used for trucks, ships, locomotives and power plants. Despite their substantial role in transportation, diesel particulate emissions have been mandated to be reduced continuously, since they are known to cause people’s health problems like respiratory and allergic diseases. Accordingly, various fuel injection strategies [1], fuel modifications [2] and after-treatment systems [3] have been developed to reduce diesel particulates by means of engine and fuel modifications as well as after-treatment systems. Recently the U.S. EPA proposed new regulations for locomotive engines as shown in Table 1-1. The present standard for diesel particulate matter (PM) emissions is achievable with engine calibration optimization and engine hardware design modification. However, high efficiency diesel particulate filters (DPFs) are required to meet the more stringent future standards such as Tier 4.

Table 1-1. Locomotive emission standards (g/bhp-hr) [4]

<table>
<thead>
<tr>
<th>Tier of standards</th>
<th>Year of original manufacture</th>
<th>Line-haul / Switch</th>
<th>NOx</th>
<th>PM</th>
<th>HC</th>
<th>CO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tier 0</td>
<td>1973-1992 / 1973-2001</td>
<td>8.0 / 11.8</td>
<td>0.22/0.26</td>
<td>1.00/2.10</td>
<td>5.0/8.0</td>
<td></td>
</tr>
<tr>
<td>Tier 1</td>
<td>1993-2004 / 2002-2004</td>
<td>7.4 / 11.0</td>
<td>0.22/0.26</td>
<td>0.55/1.20</td>
<td>2.2/2.5</td>
<td></td>
</tr>
<tr>
<td>Tier 2</td>
<td>2005-2011 / 2005-2010</td>
<td>5.5 / 8.1</td>
<td>0.10/0.13</td>
<td>0.30/0.60</td>
<td>1.5/2.4</td>
<td></td>
</tr>
<tr>
<td>Tier 3</td>
<td>2012-2014 / 2011-2014</td>
<td>5.5 / 5.0</td>
<td>0.10/0.10</td>
<td>0.30/0.60</td>
<td>1.5/2.4</td>
<td></td>
</tr>
<tr>
<td>Tier 4</td>
<td>2015 or later / 2015 or later</td>
<td>1.3 / 1.3</td>
<td>0.03/0.03</td>
<td>0.14/0.14</td>
<td>1.5/2.4</td>
<td></td>
</tr>
</tbody>
</table>
Since burn-off of the particulate matter, particularly diesel soot, is a critical process in DPF systems, the effect of the physical and chemical properties of diesel soot on reactivity has been of interest for many researchers. PM varies in compositions in terms of elemental carbon (EC), volatile hydrocarbons and ash with different engine loads, engine sizes and fuel formulations. And, the degree of order in the crystalline structure of diesel soot is also greatly influenced by these factors. Since these factors are closely linked to soot oxidative reactivity, it is more effective to use DPFs at engine operating conditions where engines produce more reactive soot particles to assist the regeneration of the DPF.

1.1 Background

According to Vander Wal and Tomasek, soot nanostructure is much affected by fuel and combustion conditions [5]. They demonstrated that soots derived under conditions of low flow rate of fuel and high temperature are more ordered regardless of fuel type. However, soot nanostructure might be amorphous or less ordered at the condition of low temperature and high flow rate of fuel, depending upon the fuel composition. They also indicated in a follow-up study that initial soot nanostructure would determine soot oxidative reactivity [6].

As soot nanostructure is affected by fuel formulation and engine operating conditions, so also is soot morphology in terms of soot particle size and its fractal dimension. Lee et al. observed that primary particle size decreased as the engine load increased, which was caused by particle oxidation due to the increased combustion temperature [7]. Lapuerta et al. also studied the effect on particle size of several engine parameters [8]. Their results showed that the primary particle size decreased with increased engine speed and with decreased engine load, which is contradictory to Lee et al.’s study. They assumed that combustion temperature was not enough to oxidize diesel particles because of the retarded injection timing. Zhu et al. analyzed primary
particle diameters, radii of gyration and fractal dimensions for a light-duty diesel engine and a heavy-duty diesel engine [9]. From their fractal dimension analyses, it is concluded that the light duty diesel engine produces more chain-like particles than the heavy duty diesel engine.

Due to the complex reactions involved in engines during the combustion process, flame burners have been widely used to study the soot formation process. Dobbins showed that there is a strong similarity of the nanoparticles from an inverse diffusion flame and from a diesel engine, in their morphology and polycyclic aromatic hydrocarbon (PAH) species [10]. As shown in Figure 1-1, primary soot particles appear to be spherical with similar apparent nanostructures regardless of flame type. The effort to understand the combustion processes in diesel engines using a diffusion flame study was also pursued by Al-Qurashi and Boehman [11]. They displayed that exhaust gas recirculation (EGR) soot is shown to be less ordered in its crystalline structure than non-EGR soot, from two different engines and a diffusion flame burner. After systematic tests using a flame burner they concluded that among the thermal, dilution and chemical effects of EGR, the thermal effect is the dominant factor determining soot nanostructure with EGR application. Since EGR lowers the combustion flame temperature, their result seems to support Vander Wal and Tomasek’s study [5], in spite of their differences in the reactor systems and operating conditions.

1.2 Scope of this Study

Müller et al. found that the physical and chemical properties of soot are closely related to soot oxidative reactivity, based on TEM, EELS, XPS and TGA [12,13]. Although they showed surface oxygen functional groups on the soot, their study was based on a qualitative analysis using only XPS.
Figure 1-1. TEM images of primary soot particles from different sources of flame: (a) soot from a diffusion flame burner, (b) soot from a light duty diesel engine, (c) soot from a heavy duty diesel engine, (d) soot from a single cylinder locomotive engine
In order to investigate these relationships, flame soot was modified forcefully by reacting with HNO₃ liquid acid. Surface oxygen content of soot was examined using XPS with respect to soot oxidative reactivity. And, the role of surface oxygen functional groups in soot oxidative reactivity was further studied by the quantification of each functional group using XPS and TPD-MS.

While there have been numerous studies on the effect of oxygenated fuel on physical and chemical properties of diesel soot, there has been no investigation about the effect of intake oxygen enrichment. Since intake oxygen enrichment affects the combustion process by increasing soot formation and soot oxidation, its impact on the physical and chemical properties of soot can provide valuable information about the relation between soot properties and soot oxidative reactivity. For this study, a light duty diesel engine was employed at low and high loads with different intake oxygen concentrations, in order to observe the effect of engine cylinder temperature on soot properties. Furthermore, a diffusion flame burner was also used to understand more clearly the relationship between soot oxidative reactivity and the combustion process in a diffusion flame. From this study, a primary factor in the combustion process affecting soot oxidative reactivity was examined.

Carbon crystalline structure is known to influence soot oxidative reactivity, so its evaluation has been made by Raman spectroscopy and XRD for various carbonaceous materials. Therefore, good Raman parameters are critical in evaluating soot crystalline structure, with respect to soot oxidative reactivity. For various peak curve-fitting methods regarding first-order Raman spectra, Raman parameters were compared with respect to soot oxidative reactivity. From these analyses, the best peak curve-fitting method was chosen to evaluate soot crystalline structure. Furthermore, this fitting method was investigated if it can be useful at calculating
crystallite size of soot in comparison to Knight and White’s formula [14] which has been used to calculate crystallite size of various carbonaceous materials.

1.3. Hypotheses and Objectives

1.3.1 Hypotheses

1) Soot inception time is a critical parameter determining soot oxidative reactivity, because there is more time for soot to mature, if soot inception occurs at an earlier stage during the soot formation process.

2) Initial surface oxygen functional groups in soot play an enhancing role in soot oxidation and there is a transforming step for functional groups during soot oxidation.

1.3.2 Objectives

1) Understanding of an impact of the soot formation and soot oxidation processes on soot oxidative reactivity

There have been many studies on the effects of fuel oxygenation and oxygen concentration in intake air, and thermal and dilution effects on the soot formation and soot oxidation processes. Also, soot oxidative reactivity has been studied for soot samples from oxygenated fuel and different oxygen concentration in intake air. However, there has been no effort carried out to correlate the soot formation and soot oxidation processes with soot oxidative reactivity. For this study, fuel oxygenation and various oxygen concentrations in intake air were applied to a diesel engine and a laminar diffusion flame burner in order to impact the soot formation and soot oxidation processes. And, the oxidative reactivities of soot samples from these conditions were investigated to evaluate if the soot formation and soot oxidation processes are a
predominant factor influencing soot oxidative reactivity. In addition, soot properties such as surface O content and soot crystalline structure were further examined in order to elucidate the differences in soot oxidative reactivity.

2) Study on the role of surface oxygen in soot during soot oxidation

Surface oxygen content in carbonaceous materials is known to be related with carbon oxidative reactivity. However, few studies about this relation have been performed with diesel soot. In addition, the role of surface oxygen functional groups in soot oxidation has rarely been studied. Accordingly, it is of great interest in this study to quantitatively examine the importance of surface oxygen content and surface oxygen functional groups in soot oxidation. Furthermore, surface oxygen functional groups are examined during oxidation in order to better understand the soot oxidation process.

3) Evaluation of experimental uncertainty in Raman spectroscopy and XPS analyses of soot

Raman spectroscopy and XPS have been widely used to measure the crystalline structure and oxygen functional groups of soot. However, since researchers have used their own methods to evaluate the properties of carbonaceous materials, their results may not be applicable for soot studies. Accordingly, Raman spectroscopy and XPS are further examined as analytical tools to evaluate the crystalline structure and oxygen functional groups of soot.

1.4 Technical Approach

To examine the hypotheses of this study and to achieve the objectives, the following tasks were employed.

1) Investigation of Raman parameters
As a way to interpret the Raman spectra, the spectral information is typically curve-fitted for first-order Raman spectra to analyze and quantify spectral features. Since Raman spectroscopy is sensitive to edge sites in crystallites, it is presumed that there should be a good correlation between Raman bands and oxidative reactivity when using the right fitting method. For this study, curve-fitting methods with different number of peaks were examined for four soot samples and one carbon black with different oxidative reactivity, and several Raman parameters were analyzed for each fitting method. Accordingly, the selected Raman parameters were used to evaluate the degree of crystalline structure in soot and its relation to oxidative reactivity.

2) Study on surface oxygen in soot

Since surface oxygen content and oxygen functional groups in soot are in general similar for soots from different sources and conditions, it is difficult to determine if there is any relation between surface oxygen and soot oxidative reactivity. Accordingly, soot surface was forcefully oxidized by HNO₃ treatment in order to increase surface oxygen. Although XPS has been popularly used to assign oxygen functional groups, some oxygen functional groups have been differently assigned by different researchers. TPD-MS was employed to determine which oxygen functional groups are abundant in each sample, and XPS was used to assign surface oxygen functional groups in the C1s and O1s spectra according to the TPD-MS results.

3) Application of oxygen enrichment to a diesel engine

Oxygen addition to the engine was studied for low and high loads in order to investigate its effect on soot oxidative reactivity and soot properties. Heat release rates at various oxygen concentrations were examined to evaluate the impact of oxygen enrichment on the combustion process. TGA was used to investigate soot oxidative reactivity, and Raman spectroscopy, XRD, XPS and TEM were further employed to evaluate soot properties. Consequently, the primary factors affecting soot oxidative reactivity were elucidated.
4) Application of oxygen enrichment to a diffusion flame burner

A diffusion flame burner was employed using \( n \)-heptane fuel as a primary fuel to simulate the combustion process for diesel engines under well-controlled conditions. Oxygen concentration in the oxidizer stream was varied in order to influence soot formation and soot oxidation processes. In addition, thermal and dilution effects on soot oxidative reactivity were further investigated along with fuel formulation, and soot oxidative reactivity was evaluated with respect to soot inception time and the soot oxidation process.
Chapter 2

LITERATURE REVIEW

2.1 Soot Oxidation in Diesel Particulate Filter (DPF)

Diesel PM is made up of soot particles, condensed hydrocarbons, H₂SO₄ droplets and some inorganics [15], and its adverse effects on environment and human body are known to be detrimental. Accordingly, the wall-flow monolith was developed in the 1980s to trap diesel particulates by means of surface filtration called deep-bed filtration and cake filtration, by forming a layer of filtered particulates [16]. During the process of particulate capture, this layer exhibits enhanced capture efficiency of particulates with increasing thickness of the filtered layer, which results in the flow restriction and finally increases the pressure drop in the filter. Accordingly, a filter regeneration strategy must be implemented to maintain filtration process over long period of engine operation [15].

Since soot oxidation during filter regeneration is a key process in DPF operation, its mechanism has long been of interest. The details of soot oxidation mechanism are different depending upon if the filter is catalyzed or uncatalyzed, and what the oxidizing gases are. For noncatalytic oxidation, a reaction mechanism for the carbon-oxygen reaction is summarized as shown in Figure 2-1 [15]. Graphitic surface containing a ketone surface-oxygen complex reacts with oxygen to form a surface semiquinone group at step (a). Since this semiquinone complex is a stable surface-oxygen complex, it does not decompose at this step. However, due to the electronegativity of the oxygen atoms in the semiquinone complex, a semiquinone complex with off-plane oxygen is formed at step (b), resulting in lowering of the C-C bond strength of the
neighboring C atoms. The complex decomposes as in step (c), forming a carbonyl group. And, the carbonyl complex further reacts by O\textsubscript{2} attack.

Figure 2-1. Reaction mechanism of the noncatalytic oxidation of carbon [15]

While soot oxidation by oxygen requires high temperature over 500 °C, NO\textsubscript{2} was found to lower the oxidation temperature to below 300 °C [17]. In order to understand the reason why NO\textsubscript{2}-soot oxidation is achieved at lower temperature, many studies have been carried out. From the reaction of carbon materials and NO\textsubscript{2}, Muckenhuber and Grothe proposed that NO\textsubscript{2} is bound via its nitrogen atom to graphitic surface areas in the carbon and forms carboxylic anhydrides which are due to the oxidation reaction between NO\textsubscript{2} and pre-existing functional groups [18].
Azambre et al. also showed that surface oxygenated species like carboxyles, anhydrides and lactones are found as intermediates in the process of NO$_2$-soot from the dissociative reduction of NO$_2$ [19], and they suggested the following reaction mechanism of NO$_2$ with diesel soot.

$$ R \xrightarrow{NO_2} R(NO_2)_{ADS} \quad (2.1) $$

$$ R(NO_2)_{ADS} \rightarrow R - NO_2 \quad (2.2) $$

$$ R(NO_2)_{ADS} \rightarrow R - ONO \quad \text{(isomerization)} \quad (2.2') $$

$$ R(NO_2)_{ADS} \rightarrow R - O' + NO \rightarrow RO_x + \text{carboxy-carbonates} \quad (2.3) $$

$$ R - O' + NO_2 \rightarrow R - ONO_2 \quad (2.4) $$

$$ R(NO_2)_{ADS} + NO_2 \rightarrow R - ONO_2 + NO \quad \text{(disproportionation)} \quad (2.5) $$

$$ R(NO_2)_{ADS} \xrightarrow{\Delta} R + NO_2 \quad (2.6) $$

$$ R - NO_2 \xrightarrow{\Delta} R + NO_2 \quad (2.7) $$

$$ R - ONO \xrightarrow{\Delta} R - O', R0_x + NO \xrightarrow{\Delta} R^* + CO_2, CO \quad (2.8) $$

$$ R - NO_2 \xrightarrow{\Delta} R^* + CO_2 + NO, NO_2 \quad (2.9) $$

$$ RO_x, \text{carbonates} \xrightarrow{\Delta} R^* + CO_2, CO \quad (2.10) $$

where R is a surface site and R* is a regenerated active site.

Although NO$_2$ is found to be more reactive than O$_2$ in soot oxidation, soot oxidation by NO$_2$ is enhanced in the presence of O$_2$. According to Setiabuti et al. [20], soot oxidation is initiated by NO$_2$ to create surface oxygen complexes (SOCs) and these intermediates are further reacted into CO and CO$_2$ by O$_2$. However, Jequirim et al. indicated that NO$_2$ interacts with the oxygen complexes formed during O$_2$-soot reaction, which releases the excess of CO$_2$ during TPD below 500 °C [21]. Accordingly, they concluded that there is a destabilization effect of the carbon-oxygen complexes by NO$_2$.

Uncatalyzed filters are effective for soot oxidation via the NO$_2$-O$_2$ reaction system, but catalytic filters are shown to provide better soot oxidation performance. There are two popular ways known for catalytic soot oxidation [22]; one is to mix catalytic fuel additives into fuels (i.e., fuel borne catalysts such as cerium oxide and iron-strontium complexes) to ensure that the active components are in intimate contact with diesel particulates during engine operation and the other
is to coat catalyst on filters for direct contact with diesel particulates. Much attention has been paid to the quality of contact between soot and the active sites of the catalyst [23-25]. If the active sites are not intimate with the carbon surface, their catalytic effect is diminished. Neeft et al. claimed that monolithic traps impregnated with catalyst show the loose contact condition, while a full tight contact condition can be achieved when catalyst is added in fuels [23]. Although tight contact is found to be more efficient in soot oxidation, some catalyst studies have shown that an intimate contact between catalyst and carbonaceous particles is not essential in soot oxidation. One example is NOx-aided gas-phase mechanism discovered by Cooper and Thoss [26]. In the absence of physical contact, NO₂ oxidized from NO in the exhaust gases using oxidizing catalyst is used as an activated mobile component to enhance soot oxidation. From this discovery, the NOx-aided CRT (continuous use of NO₂ in a continuously regenerating trap) was invented and is being sold in the market for trucks and buses, as shown in Figure 2-2.

Figure 2-2. Illustration of NOx-aided CRT [15]
2.2 Soot Formation and Soot Oxidation Processes during Combustion

2.2.1 Overview of Soot Formation Process

Figure 2-3. Schematic diagram of the steps in the soot formation process [27]

Figure 2-3 depicts a sequence in the soot formation process from liquid fuel to solid agglomerated particles. Liquid fuel is pyrolyzed into smaller chain molecules, and radical species like H, O and OH are also generated during the pyrolysis process, which accelerate the process [27,28]. With further pyrolysis and oxidation of hydrocarbons, unsaturated hydrocarbons are formed. Many researchers have proposed different detailed mechanisms in the first appearance of aromatic species, but the reaction of C2- and C4- species and/or the combination of two propargyl radicals, C3H3, are likely to form the first aromatic ring (i.e., ring condensation) [29-31]. The aromatic rings grow into polycyclic aromatic hydrocarbons (PAHs) by hydrogen abstraction acetylene addition reaction (HACA), where the aromatic radical is formed by hydrogen abstraction and acetylene reacts with this radical, and/or direct combination of aromatic compounds [29]. Further growth of PAHs is achieved by the previous reactions to a certain point, where there is a transition from molecules into a particle nucleus. The nucleated soot particles increase in mass by accepting gas phase hydrocarbons like acetylene, which is called surface growth, until the particles move away into less reactive regions. During the mass growth process, coalescence occurs when particles collide and 10-50 nm of spherical shaped primary particles are formed. Finally, primary particles stick together to form chain-like structures by agglomeration.
2.2.2 Effect of Temperature and Oxygen Enrichment on Soot Formation and Soot Oxidation

Since soot is a major pollutant in many combustion applications using hydrocarbon fuels, understanding the soot formation process at different operating conditions is critical in reducing soot emissions. Accordingly, flame temperature, oxygen concentration in the fuel stream and the oxidizer stream, and gas additives have been greatly studied.

Gülder examined soot volume fractions with increased flame temperature in diffusion flames [32]. He observed that maximum soot volume fractions and soot formation rates increase with increasing flame temperature, and olefins show a lower sensitivity to flame temperature than alkanes. Kumfer et al. also showed the same increasing trend in soot volume with increasing flame temperature [33].

The impact of oxygen concentration on soot formation has been of great interest. Oxygen enrichment, which is achieved with oxygenated fuels [34-36] and increased oxygen concentration in the intake air (intake oxygen enrichment) [36-39], has been investigated for diesel emission control. Likewise, low oxygen concentration in the oxidizer stream has been studied from a practical sense via exhaust gas recirculation (EGR) in engines [11]. Oxygenated fuels have been studied as a promising method to reduce soot production from engines [2,34-36]. It is observed that oxygenated fuels are effective in the reduction of soot because oxygen in fuels forms as CO and/or CO₂ during fuel pyrolysis, which limits the amount of carbon that develops into soot precursors [35,40]. Glaude et al. showed that dimethyl carbonate (DMC) is not an effective oxygenated fuel because the channel leading to CO₂ dominates over the one leading to CO [40]. Mueller et al. also showed that tri-propylene glycol methyl ether (TPGME) is more effective than di-butyl maleate (DBM) due to the fact that all of the oxygen in the former is available for soot precursor reduction [35]. According to Miyamoto, when fuel oxygen content reaches 27 – 35%, there is a complete or nearly complete elimination of soot [41].
As briefly summarized in the previous section, benzene formation is a critical step in the soot formation process. The chemical structure of the fuel appears to affect significantly the mechanisms of benzene formation [42], because it leads to different pathways to C₂H₂, C₄H₅ and C₃H₃, which are key reactants for benzene formation. Accordingly, the effect of intake oxygen enrichment on soot formation is observed to be different depending upon the fuel examined. Oh and Shin observed in coflow diffusion flames that the increase of oxygen concentration enhances soot nucleation, which increases the residence time of soot [43]. Comparing methane/50% oxygen and methane/air flames, Lee et al. found that the rate of soot inception becomes stronger and soot yields diminish with increasing oxygen concentration in the oxidizer stream [44]. Although the higher temperature in the oxygen-enriched flame enhances soot formation, an ample amount of oxygen is shown to promote soot oxidation. However, Leusden and Peters found in a counterflow laminar flame with acetylene that soot volume fraction increases with oxygen addition to the oxidizer stream, which is attributed to a thermal effect [45]. According to McLintock [46], the increasing sooting tendency with increasing oxygen concentration at low oxygen concentrations is because of the predominance of pyrolysis of fuel over oxidation in this temperature range, but at higher temperature and higher oxygen concentrations, oxidation is increasingly favored over pyrolysis and the sooting tendency decreases. The addition of oxygen to the fuel stream also has been of interest. As Gülder noted, this experiment involves complicated chemical effect as well as temperature effect and dilution effect, with different fuels [47]. Propane and n-butane flames showed enhanced soot formation, while methane flames suppressed soot formation. Engine tests also confirmed there is a reduced soot production with oxygen enrichment in the intake air [36,37,48]. Since oxygen enrichment lowers the peak premixed burn and increases heat release in the mixing-controlled combustion phase, which is more apparent at high load conditions, oxygen enrichment lowers soot precursor formation and increases soot oxidation. It is unclear whether intake oxygen enrichment leads to higher or lower
rates of soot formation in engine operations, but an increased oxygen concentration in the combustion process is always accompanied by increased flame temperature, which enhances soot oxidation.

Soot formation has been much studied in the addition of inert gases to the fuel stream and the oxidizer stream. With dilution, temperature is reduced, affecting soot formation rate. Gülder and Snelling attributed the reduction in soot formation to the reduced flame temperature and fuel concentration in dilution experiments [49]. Axelbaum and Law showed in coflow diffusion flames that when moderate amounts of inert are added to the fuel stream, the effect of dilution can be greater than that of temperature because the temperature decrease is relatively small [50]. At large amounts of inert, however, the thermal effect may be a predominant factor over the dilution effect. And, Du et al. found that He addition to the fuel stream is more effective in suppressing soot formation than Ar addition, in spite of their similar heat capacities, because He addition lowers the temperature more significantly due to the large diffusivity of He, which influences the Lewis number of the reactant mixture [51].

As summarized earlier, flame temperature, oxygen enrichment and dilution effect are shown to affect the soot formation process. In addition, these factors are found to influence soot inception time as well as soot volume. According to Du et al., with increasing flame temperature, soot inception time becomes shortened for C₂H₄ and C₃H₈ in diffusion flames [51]. And, Du and Axelbaum also showed that with increasing oxygen concentration in the oxidizer stream, soot inception time becomes shorter, and with dilution in the fuel stream, it becomes longer [52]. Lin and Faeth also measured soot inception time for C₂H₂, C₂H₄, C₂H₆ and C₃H₈ in opposed-jet diffusion flames using the same method as Du and coworkers did [53]. And, soot inception time is observed to be short in the order of C₂H₂, C₂H₄, C₃H₈ and C₂H₆, which is consistent with the time to form benzene which is a main soot precursor. Consequently, soot volume and soot
inception time are shown to be closely related to each other, when soot oxidation is not considered.

2.3 Effect of Properties in Soot on Soot Oxidative Reactivity

2.3.1 Physical and Chemical Properties

Diesel particulate matter emitted from diesel engines has different composition of volatile fraction, sulfur and elemental carbon, and different size distributions depending upon engine operation and fuel formulation. Accordingly, diesel particulate matter has different O and H content, volatile organic fraction (VOF) or soluble organic fraction (SOF) and crystalline structure. And, the effects of these compositional factors on soot oxidative reactivity have been of great interest among DPF researchers. In this section, these chemical and physical properties are summarized, with respect to operating condition, fuel formulation and soot oxidative reactivity.

Organic carbon (OC), which includes n-alkanes, PAH, isoprenoids, cycloalkanes, organic acids, hopanes and steranes [54], and elemental carbon (EC) concentrations from diesel engines have been examined [55,56]. It is hard to compare OC and EC concentrations quantitatively for different engines with different fuel sulfur content, but it is found that the fraction of EC increase with increasing load. Compared to diesel, EC/OC ratio is shown to be smaller with biodiesel [56]. Although SOF, which is contributed from lubricating oil and unburned fuel, is different from OC in its definition, SOF is shown to decrease with increasing load and increase with biodiesel [34], as does OC. Since SOF varies much with engine condition and fuel, the effect of SOF on PM oxidative reactivity has been of interest. Collura et al. showed that since SOF is desorbed at lower temperature than at the onset temperature of the soot oxidation, it is not involved in soot oxidation [57]. Stratakis et al. observed that different oxidation rates at the center and the periphery of a filter are caused by different SOF contents at those points, which makes the regeneration process inhomogeneous throughout the filter, although a nonuniform temperature
distribution is another factor [58,59]. The role of surface oxygen groups in soot oxidation is also of interest, although it is not clear whether they are directly adsorbed at the edges of aromatic planes [60]. There have not been many studies carried out for soot in order to investigate surface oxygen groups [12,13,61], but Müller et al. showed that there are some functional groups such as C=O, C-O-C and C-OH observed, and their intensities directly correlate with soot oxidative reactivity [12,13].

Figure 2-4. Schematic view: (a) perfect graphite lattice and schematic model of disordered carbon [62], (b) crystallite size in c- and a-direction
Graphite is composed of several graphene layers stacked in a hexagonal system (ABAB structure) in an idealized state as shown in Figure 2-4. However, with internal lattice defects such as vacancies, graphene layers are stacked in a disordered form and the number of stacked layers decreases until one layer is left, as the sample becomes less ordered [62]. Accordingly, the crystallite sizes in c- (height) and a-direction (width) are reduced.

Like carbon black and activated carbon, soot is shown to be disordered in its carbon crystalline structure. Its detailed TEM image indicates that graphene layers are oriented concentrically in the outer shell of a soot particle, while the inner core is composed of a spherical nucleus with an amorphous structure [22,63]. Due to the similarity in primary particles between soot and carbon black, carbon black has been a popular surrogate for soot [20,21,25,64]. However, carbon black is known to have larger diameter, lower O and H content with less surface functional groups, and more ordered in the crystalline structure than soot [12,65]. And, carbon black is found to be less oxidatively reactive than soot [13,20]. As shown in these studies, the conditions of nucleation and growth in soot formation determine the different soot properties. It is shown that soot from an idling condition in an engine is less ordered in the crystalline structure, due to the low cylinder temperature, than from a high load condition [7,66]. Al-Qurashi and Boehman also showed that EGR soot is less ordered than non-EGR soot, primarily because of the lowered cylinder temperature in the engine [11]. Likewise, temperature is found to be a key parameter influencing carbon crystalline structure, because thermal annealing is associated with structural ordering of the carbon on a molecular level [67]. From the pyrolysis of acetylene in a quartz reactor, Ruiz showed that with increasing reaction temperature, soot has higher C/H ratio and aromaticity, resulting in more ordered soot [68]. More systematic study about temperature effect is found in the work of Vander Wal and Tomasek [5], in which soot formed at 1250°C in a furnace appears to be amorphous nanostructure, while soot formed at 1650°C shows graphite-like nanostructure. And, benzene-derived soot, exhibiting short individual graphene segments with no
orientation relative to each other, oxidizes five times faster than acetylene-derived soot with extended carbon lamellae [5]. Their following paper clearly showed that fuel identity determines soot nanostructure under combination of temperature and fuel flow rate, such as curved nanostructure or graphitic nanostructure, because soot nanostructure results from the pyrolysis kinetics of the fuel [6].

As with soot crystalline structure, HR-TEM (high resolution transmission electron microscopy) images enables evaluation of the degree of disorder in soot nanostructure, thanks to the computational analysis. Su’s group observed that the soot from a fast spark-discharge process has short and strongly bent graphene structures, as fullerene-like soot, due to the short time of formation for graphene planes [12,69,70]. Vander Wal and Mueller examined soot nanostructure from a diesel engine [71]. They concluded that with increasing the degree of fuel oxygenation, there is an increasing degree of amorphous nanostructure with narrow fringe length distributions, and broader and larger tortuosity. Likewise, Song et al. investigated the nanostructures of biodiesel soot and Fischer-Tropsch diesel soot (FT soot) during oxidation [60]. Although the initial nanostructures of these samples obtained from an engine were similar, biodiesel soot contained more oxygen functional groups and underwent an internal burning process, and was observed to be more oxidatively reactive than FT soot, whereas FT soot oxidizes through a shrinking core process.

Since diesel fuels and lubricating oils contain many kinds of metals as additives, their impact on PM emissions and consequently on the human body has been a major concern [72]. From electron probe micro analysis (EPMA), scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) and inductively coupled plasma mass spectroscopy (ICP), there are Ca, Mg, Fe, P, Zn and other elements present in diesel particulates [72,73]. Also, Lim et al. [73] showed that the concentrations of these elements increase with increasing load. And, Jung et al.
examined the effect of the amount of lubricating oil consumed on the oxidative reactivity of diesel particles [74]. From this work, it is evident that metallic species from lubricating oil play a catalytic role in soot oxidation. As mentioned earlier, soot oxidative reactivity is much influenced by the physical and chemical properties of soot. When it comes to soot from diesel combustion, however, metallic species need to be taken into account in elucidating the impact of soot properties on soot oxidative reactivity.

2.3.2 Instrumental Approaches for Soot Properties

Raman spectroscopy has been employed widely to study carbonaceous materials, because it is non-destructive and sensitive to intrinsic defects of the graphitic lattice, as well as, chemical doping. Many carbonaceous materials show two characteristic peaks appearing at \( \sim 1360 \text{ cm}^{-1} \) (D peak) and \( \sim 1590 \text{ cm}^{-1} \) (G peak) for first-order Raman spectra. The G peak is a stretching mode of \( E_{2g} \) symmetry at sp\(^2\) sites [75,76], but the origin of the D peak has been debated [77,78]. It is traditionally known as a breathing mode of \( A_{1g} \) symmetry at the edges of graphite planes in sp\(^2\) carbon materials [76-79]. As symbolized by its name, the D peak has been used misleadingly to represent the presence of disorder in the crystalline structure, but it has been proven that it is due to the breakdown in the k=0 selection rule of large crystals from the existence of edge sites and the relative position of the laser spot with respect to the edge [80-83]. Some carbonaceous materials like polycrystalline graphite show only sharp D and G peaks [84,85], but many disordered and amorphous carbons also indicate additional peaks appearing at \( \sim 1180 \text{ cm}^{-1} \) (D4), \( \sim 1500 \text{ cm}^{-1} \) (D3) and \( \sim 1620 \text{ cm}^{-1} \) (D2), which are related to sp\(^3\) carbon or impurities [84-86], amorphous carbon [87,88] and disordered carbon [84,89,90], respectively. Thereafter, many analytical studies have proposed a relationship between these peaks and particular carbon structural information [84-86,91-93]. Although the D peak, in principle, has nothing to do with disorder, it
becomes larger when there are more defects in a disordered carbon like soot, which contains more edge sites [77]. Since edge sites are closely related with active sites on carbon surfaces, where oxygen is adsorbed in the oxidation process [94,95], Raman spectroscopy can provide valuable information with respect to carbon oxidation if the Raman parameter is carefully selected. In many examples, height and area ratios of the D to the G band, widths and positions in the D and G bands have been often used to describe the carbon structural information [11,60,76-79,83-86,91-93]. To interpret the Raman spectra, the spectral information is typically curve-fitted to analyze and quantitative spectral features. Different methods of analysis employ from two to as many as five peaks that comprise the features in the spectral results, as shown in Figure 2-5.

Figure 2-5. Curve-fitted shape of SCE soot : (a) 2 lorentzian and 1 gaussian, (b) 3 lorentzian (c) 3 lorentzian and 1 gaussian, (d) 4 lorentzian, (e) 4 lorentzian and 1 gaussian, (f) 5 lorentzian
Since disordered carbon structures are convoluted under the D and G bands, three [60,96,97], four [91,98], and five curve [11,85,92,93] fitting methods by the peak deconvolution of the D and G bands have been proposed to analyze the crystalline structure of disordered carbons. In spite of these attempts, there has been no effort made to compare these parameters extensively for the different curve-fitting methods.

XRD is popularly used in the characterization of the crystalline structure of carbonaceous materials. In addition to their diffraction patterns, interlayer spacing ($d_{002}$) and crystallite size, represented by crystallite height ($L_c$) and width ($L_a$), are used as indices of crystallite shape and disorder [99-101]. Therefore, much study has been focused on the relationship between these structural parameters and carbon oxidative reactivity [11,60,102,103]. Carbonaceous materials with smaller crystallite size are observed to be more reactive due to the increased number of active sites that result from increased disorder. Tuinstra and Koenig’s pioneering work showed that there exists an inverse correlation between crystallite size from XRD and $I_D/I_G$ from Raman spectra for graphite fibers [79]. Furthermore, Knight and White expanded Tuinstra and Koenig’s work, covering various carbonaceous materials such as diamond films, glassy carbons and graphites [14]. In spite of a good agreement for several carbonaceous materials between XRD and Raman spectroscopy, however, there is a significant deviation observed between the two characterization methods in the case of some disordered carbons, because smaller domain size in carbon is not correctly measured by XRD [76,104,105].

Since diamond-like carbons (DLC) were discovered, the measurement of their $sp^3$ content has been greatly developed using electron energy loss spectroscopy (EELS) [11,12,60,106], near edge X-ray absorption fine structure (NEXAFS) [66,107] and X-ray photoelectron spectroscopy (XPS) [108,109]. Since soot and other disordered carbonaceous materials also contain $sp^3$ carbon in their crystalline structures, the relative ratio of $sp^2$ to $sp^3$ carbon has been widely used to evaluate carbon crystalline structure. Since the near-edge structure of carbon-K-ionization edge
can be deduced from EELS, the unoccupied antibonding ($\pi^*$)/the antibonding ($\sigma^*$) has been investigated to measure $\text{sp}^2/\text{sp}^3$ [11,12,60]. Zhu et al. showed that the characteristic peak appearing between 291 - 310 eV, associated with $\sigma^*$, is missing or muted for carbon black, showing an absence of triple bonds [110]. Müller et al. found that with increasing content of $\text{sp}^2$, soot became more ordered with larger graphene size and less curvature [12]. The same result is also observed for Knauer et al.’s study [111]. Although Boehman and co-workers didn’t calibrate $\text{sp}^2/\text{sp}^3$ using highly ordered pyrolytic graphite (HOPG), they confirmed that the intensity ratio of $\pi^*$ to $\sigma^*$ is closely related to the degree of soot crystalline order [11,60]. In spite of great capability for measuring $\text{sp}^2/\text{sp}^3$, NEXAFS has not been popular for soot studies. It is shown to detect not only $\pi^*$ and $\sigma^*$, but also surface oxygen functional groups. Therefore, Braun et al. attributed the deficiency in the detection of those functional groups using EELS to the sample alteration from the high energy of the electron beam [112].

The positive effect of O and H content on carbon oxidation reactivity is evidenced using char, soot and other carbonaceous materials [13,20,113]. However, the relationship between surface oxygen functional groups and carbon oxidation is still unclear, although Müller et al. reported some results. Since oxygen functional groups play various roles in many applications such as absorbents and catalysts, the assignment of oxygen functional groups has been greatly studied for activated carbon [114,115], carbon fibers [116,117] and carbon black [118] using XPS, FT-IR, TPD-MS, titration [119] and NEXAFS [66,112]. Although XPS is capable of measuring $\text{sp}^2/\text{sp}^3$ for DLC films, many studies have been focused on surface oxygen functional groups in carbon materials. In order to quantify each functional group, a deconvolution of overlapping peaks is often used. Although the detailed function (e.g. the ratio of Gaussian to Lorentzian) and width in each curve-fitting can be influenced by the surface characteristics of each material, the centered peak for each functional group is assigned differently among researchers as summarized in Table 2-1, referring to Figure 2-6.
<table>
<thead>
<tr>
<th>Functionality</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><strong>C1s (eV)</strong></td>
</tr>
<tr>
<td><strong>Graphite or aromatic</strong></td>
<td>284.6-285.1 [114], 284.6 [117], 284.5 [118,120]</td>
</tr>
<tr>
<td><strong>Aliphatic</strong></td>
<td>285.1 [117]</td>
</tr>
<tr>
<td><strong>C=O in ketone</strong></td>
<td>286.4 [118]</td>
</tr>
<tr>
<td><strong>C=O in carbonyl</strong></td>
<td>287.5-288.1 [114], 286.4 [118], 287.3-287.6 [124,125]</td>
</tr>
<tr>
<td><strong>C-O in ether</strong></td>
<td>286.3-287.0 [114]</td>
</tr>
<tr>
<td><strong>C-OH in alcohol</strong></td>
<td>286.3-287.0 [114], 286.1 [117], 285.4 [118], 286.1-286.3 [124,125]</td>
</tr>
<tr>
<td><strong>O=C-O in ester</strong></td>
<td>289.3-290.0 [114], 288.4-288.9 [124], 288.8-289.1 [125]</td>
</tr>
<tr>
<td><strong>O=C-O-C=O in anhydride</strong></td>
<td></td>
</tr>
<tr>
<td><strong>COOH in carboxylic</strong></td>
<td>289.3-290.0 [114], 289.1 [117], 288.7 [118], 288.4-288.9 [124], 288.8-289.1 [125]</td>
</tr>
<tr>
<td><strong>Adsorbed water</strong></td>
<td></td>
</tr>
</tbody>
</table>
Since XPS is a surface-sensitive technique probing the top 10 nm of samples, its results can be misleading when characterizing porous samples, when their exterior surface is more oxidized than the bulk [126]. Infrared spectroscopy (IR) is known to provide qualitative analysis of oxygen functionality, but carbons make the analysis difficult due to the absorption of the radiation in the visible spectrum [119]. Therefore, TPD-MS is often used to support XPS by measuring CO and CO$_2$ emitted, with respect to temperature [115,116]. The assignment of each oxygen functional group by TPD is also summarized in Table 2-2. As seen in Table 2-2, the temperatures of TPD spectra differ in details, because the pore structure and the heating rate have a significant impact on CO and CO$_2$ evolved [119].

Figure 2-6. Surface oxygen functional groups [20]
Table 2-2. Assignment of oxygen functional groups in TPD-MS

<table>
<thead>
<tr>
<th>Functionality</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CO</td>
</tr>
<tr>
<td>Carboxylic</td>
<td>530-600(Strong) [127], 700-750(Weak) [127]</td>
</tr>
<tr>
<td>Carboxylic anhydride</td>
<td>623-900 [115], 673-723 [116], 884-955 [126], 800-900 [127]</td>
</tr>
<tr>
<td>Phenols</td>
<td>873-973 [115], 873-973 [116], 933-998 [126], 940-990 [127]</td>
</tr>
<tr>
<td>Carbonyls</td>
<td>973-1253 [115], 1073-1173 [116], 1091-1158 [126], 1090-1150 [127]</td>
</tr>
<tr>
<td>Quinones</td>
<td>973-1253 [115], 1073-1173 [116], 1091-1158 [126], 1090-1150 [127]</td>
</tr>
<tr>
<td>Hydro quinones</td>
<td>873-973 [116]</td>
</tr>
<tr>
<td>Lactones</td>
<td>623-923 [115], 623-673 [116], 917-1095 [126], 950-1050 [127]</td>
</tr>
<tr>
<td>Lactols</td>
<td>973 [115]</td>
</tr>
<tr>
<td>Ethers</td>
<td>973 [115]</td>
</tr>
<tr>
<td>Peroxides</td>
<td>823-873 [116]</td>
</tr>
</tbody>
</table>

Müller et al. examined the impact of surface oxygen functional groups in soot using XPS [12], but their result was based on a qualitative analysis without any supplemental characterization. Song et al. also carried out a qualitative analysis using FT-IR in order to find why biodiesel soot is more reactive than FT soot [60]. Although there is no quantitative analysis for functional groups in soot using XPS and/or TPD-MS, Braun et al. showed the first quantitative result for soots from engine idling and load conditions with NEXAFS using a curve-fitting method, in which idling soot had more C=O, COOH and C-OH [112]. NEXAFS was
presented to analyze functional groups for other carbons [128], but there is no supplemental evidence about how the various oxygen functional groups were assigned. Since NEXAFS provides valuable information such as surface functional groups and sp²/sp³, there should be more stress on its quantitative application, supported by other techniques. Then, the role of surface oxygen functional groups in soot oxidative reactivity will be more clearly understood.

Although the total surface area (TSA) of carbons is thought to be a direct indicator of the reactivity in heterogeneous reactions between oxidizing gases and carbons, active surface area (ASA) representing active sites is found to be more relevant to the reaction rate [129]. Since oxidizing gases are chemically adsorbed on active sites or edge sites during oxidation, their measurement is critical in evaluating carbon oxidative reactivity. Although Raman spectroscopy is known to measure the density of edge sites indirectly, the oxygen chemisorption method is more straightforward. Good agreement between ASA and carbon oxidative reactivity was observed for chars [113,129,130], activated carbons [131-133] and soot [11]. However, in past work the temperatures employed during chemisorption were different among different researchers. Radovic et al. tested chars at 375 K [130], and Cheng and Harriott did chars between 573 and 673 K [131]. Arenillas et al. [132] chose 523 K as an optimized temperature showing equilibrium was reached in a reasonable period of time without gasification. Accordingly, ASA can be regarded as a relative index influenced by the chemisorption temperature. Consequently, its values from different temperatures should be carefully compared in concluding the relationship between ASA and soot oxidative reactivity.
Chapter 3

EXPERIMENTAL

3.1 Experimental Instruments

3.1.1 Engine Operation

Two different diesel engines were employed in this study. A light duty diesel engine used is a four cylinder turbo-charged common rail diesel engine. It was operated at 30, 75 and 90% of full load at 1800 rpm. An ETAS hardware and an INCA software interface was used to access an electronic control unit (ECU) on the engine, which permits adjustment of fuel injection parameters. Injection timing was fixed and used a dual injection strategy as oxygen concentration and fuel composition were varied. The other engine is a single cylinder locomotive engine. It was operated at full load at 1050 rpm with varying exhaust gas recirculation (EGR) ratio. The soot used in this study was sampled at full load at 1050 rpm with 10% EGR ratio. The detailed specifications of the two engines are shown in Table 3-1.

Oxygen addition to the combustion was studied by intake oxygen enrichment and by fuel oxygenation. Intake oxygen enrichment was carried out by increasing O₂ concentration in the intake of the engine, which was achieved by supplying additional gaseous O₂ from compressed cylinders to a surge tank where O₂ was mixed with air, and the O₂ concentrations in the intake air and exhaust gases were monitored using an AVL Combustion Emissions Bench II. The oxygenated fuel was a mixed fuel of 30% diethylene glycol dimethyl ether (diglyme, C₆H₁₄O₃) and 70% ultra low sulfur diesel fuel, whose properties are shown in Table 3-2. Diesel particulates were collected on 47 mm Teflon filters (Teflo membrane, Pall Corp.) from the exhaust gases of the engine using a vacuum pump, and the PM was subsequently scraped from the filters. The
detailed engine operating conditions and the ratio of oxygen to carbon (O/C) in the engine for each condition are given in Table 3-3, and an overall schematic of the engine system is in Figure 3-1.

Table 3-1. Engine specifications

<table>
<thead>
<tr>
<th>Engine</th>
<th>Light duty diesel engine (DDC/VM Motori 2.5L)</th>
<th>Single cylinder locomotive diesel engine</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Configuration</td>
<td>In-line 4</td>
</tr>
<tr>
<td></td>
<td>Displacement</td>
<td>2499 cc</td>
</tr>
<tr>
<td></td>
<td>Combustion system</td>
<td>Direct injection</td>
</tr>
<tr>
<td></td>
<td>Compression ratio</td>
<td>7.5:1</td>
</tr>
<tr>
<td></td>
<td>Air induction</td>
<td>Turbocharged intercooled</td>
</tr>
<tr>
<td></td>
<td>Rated power</td>
<td>103 kW@4000 RPM</td>
</tr>
<tr>
<td></td>
<td>Peak torque</td>
<td>340 N·m@1800 RPM</td>
</tr>
<tr>
<td></td>
<td>Injection system</td>
<td>Electronically controlled common rail</td>
</tr>
<tr>
<td></td>
<td>Valve train</td>
<td>DOHC, 4 valves/cylinder</td>
</tr>
</tbody>
</table>

3.1.2 Laminar Diffusion Flame Burner

In order to simulate the sooting process in diesel engines, a co-flow laminar diffusion flame burner was chosen, because soot is produced mainly from the diffusion phase of diesel combustion. Since the soot formation process in a co-annular laminar diffusion flame has been extensively studied by Santoro and coworkers, the burner with a similar configuration to theirs was employed for the present study [134].
Table 3-2. Properties of diesel fuel and diglyme

<table>
<thead>
<tr>
<th>Properties</th>
<th>Diesel</th>
<th>Diglyme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane number</td>
<td>45</td>
<td>112</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>184/347</td>
<td>162</td>
</tr>
<tr>
<td>Oxygen content (wt %)</td>
<td>0</td>
<td>35.8</td>
</tr>
<tr>
<td>Specific density (g/cm³)</td>
<td>0.8466</td>
<td>0.943</td>
</tr>
<tr>
<td>Heating value (MJ/kg)</td>
<td>42.8</td>
<td>30.3</td>
</tr>
<tr>
<td>Sulfur content (ppm)</td>
<td>9.7</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3-3. Experimental conditions and O/C in a diesel engine

<table>
<thead>
<tr>
<th>Engine load</th>
<th>Fuel injection timing</th>
<th>Experimental condition</th>
<th>O/C in engine*</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>Pilot : 17.7BTDC</td>
<td>21% O₂ in intake, 100% diesel</td>
<td>7.45</td>
</tr>
<tr>
<td></td>
<td>Main : 2.7ATDC</td>
<td>24% O₂ in intake, 100% diesel</td>
<td>8.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27% O₂ in intake, 100% diesel</td>
<td>9.64</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21% O₂ in intake, 30% diglyme + 70% diesel</td>
<td>7.85</td>
</tr>
<tr>
<td>75%</td>
<td>Pilot : 39.0BTDC</td>
<td>21% O₂ in intake, 100% diesel</td>
<td>4.48</td>
</tr>
<tr>
<td></td>
<td>Main : 6.6BTDC</td>
<td>22.5% O₂ in intake, 100% diesel</td>
<td>4.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24% O₂ in intake, 100% diesel</td>
<td>4.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27% O₂ in intake, 100% diesel</td>
<td>5.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21% O₂ in intake, 30% diglyme + 70% diesel</td>
<td>4.57</td>
</tr>
<tr>
<td>90%</td>
<td>Pilot : 42.9BTDC</td>
<td>21% O₂ in intake, 100% diesel</td>
<td>3.71</td>
</tr>
<tr>
<td></td>
<td>Main : 6.3BTDC</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*: C_{15}H_{27.66} is used to calculate [36]
In this study, a high performance liquid chromatography (HPLC) pump from Waters (model 590) was used to deliver liquid fuels at constant volumetric flow rates, which were vaporized in the stainless steel tubing controlled by heating bands at over 200 °C. In order to get sufficient fuel vaporization and to eliminate flame fluctuation, a piece of 1” OD stainless steel tubing (10 cm length) filled with quartz beads was placed in the middle of the vaporized tubing line and vaporized fuels were carried by N\textsubscript{2} gas in the fuel stream. For the delivery of a gaseous fuel, the same configuration was used without heating the fuel delivery line. The coannular diffusion flame burner includes a brass fuel delivery tube (1.11 cm ID) within an oxidizer flow annulus (10.2 cm ID), where the fuel delivery tube extends 0.4 cm above the oxidizer flow annulus. The oxidizer flow annulus is composed of a perforated brass plate, a series of wire mesh, a bed of glass beads and a honeycomb layer in order to obtain a uniform gas flow at the exit of the annulus. Flame soot samples were collected from the top of flames with a quartz plate as shown in Figure 3-2.
The fuel flow rate was held constant at 0.39 carbon g/min (C g/min) and the flow rate of carrier gas in the fuel stream was varied to influence the soot formation process. In order to study the effect of oxygen to carbon ratio (O/C) on soot oxidative reactivity, two sets of experiments were employed. One is to increase O/C by increasing the flow rate of the oxidizer stream at the same 21% O₂ concentration in the oxidizer stream. The other is to increase O/C by increasing O₂ concentration in the oxidizer stream while keeping the same flow rate of the oxidizer stream. In addition, N₂ gas in the oxidizer stream was partly or fully replaced by Ar in order to increase flame temperature. The detailed experimental conditions are given in Tables 3-4.
Table 3-4. Experimental conditions in a diffusion flame burner

<table>
<thead>
<tr>
<th>Carbon Flow Rate (g/min)</th>
<th>Fuel</th>
<th>O2 in Oxidizer (%)</th>
<th>Oxidizer Flow Rate (l/min)</th>
<th>Balance Gas in Oxidizer</th>
<th>Oxygen to Carbon ratio (O/C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>21</td>
<td>6.33</td>
<td>100% N₂</td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21</td>
<td>9.50</td>
<td>100% N₂</td>
<td>5.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21</td>
<td>12.66</td>
<td>100% N₂</td>
<td>7.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>21</td>
<td>9.50</td>
<td>50% N₂, 50% Ar</td>
<td>5.50</td>
</tr>
<tr>
<td>0.39</td>
<td>n-heptane</td>
<td>21</td>
<td>9.50</td>
<td>100% Ar</td>
<td>5.50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>24</td>
<td>6.33</td>
<td>100% N₂</td>
<td>4.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27</td>
<td>6.33</td>
<td>100% N₂</td>
<td>4.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>6.33</td>
<td>100% N₂</td>
<td>5.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>35</td>
<td>6.33</td>
<td>100% N₂</td>
<td>6.11</td>
</tr>
<tr>
<td></td>
<td>ethylene</td>
<td>21</td>
<td>6.33</td>
<td>100% N₂</td>
<td>3.66</td>
</tr>
<tr>
<td></td>
<td>monoglyme mixture*</td>
<td>21</td>
<td>6.33</td>
<td>100% N₂</td>
<td>3.66</td>
</tr>
</tbody>
</table>

*: 70 vol. % n-heptane + 30 vol. % monoglyme (dimethoxyethane, C₄H₁₀O₂)

3.1.3 Soot Surface Chemistry Modification

As-received flame soot samples were modified as follows in order to study the effect of oxygen functional groups on soot oxidative reactivity.

Firstly, 0.1 g of flame soot was transferred into a flask and 10 g of HNO₃ (70%, Sigma-Aldrich) was added. The mixed slurries with HNO₃ were stirred at 160 rpm with an electromagnetic bar at room temperature and 60 °C for 24 hours. These slurries were filtered and washed thoroughly with distilled water until the filtrates became neutral. The filtered samples were placed in an oven at 110 °C overnight for drying. In order to examine newly-generated oxygen functional groups, XPS and TGA-MS were employed.
3.2 Characterization Tools

3.2.1 Removal of Volatile Compounds

Sampled diesel particulates from the diesel engine were thermally treated at 500 °C for 60 minutes in a Perkin Elmer TGA 7 thermogravimetric analyzer under nitrogen in order to drive off volatile compounds. And, soot samples from the diffusion flame burner were thermally treated at 300 °C in the Perkin Elmer TGA 7 under nitrogen. As indicated in Appendix B, flame soot samples contain much less volatile organic fraction (VOF) than diesel soot samples. After thermal treatment, soot samples were characterized using HR-TEM, EELS, Raman spectroscopy, XRD, XPS and NEXAFS.

3.2.2 Thermogravimetric Analysis (TGA)

An SDT Q600 from TA Instruments thermogravimetric analyzer was employed to evaluate soot oxidative reactivity. Each diesel PM sample was placed in 90 μL of an alumina sample cup and was heated to 500 °C and kept for 60 minutes to drive off volatile compounds under N2 gas with 100 cc/min. After thermal treatment, the sample was kept at 500 °C or heated to 550 and 600 °C, and N2 gas was replaced by ultra zero air (99.0% purity) with 100 cc/min for isothermal experiments. The mass loss of each sample during isothermal oxidation was normalized with respect to the weight after thermal treatment, and the normalized mass loss was compared for each sample to evaluate soot oxidative reactivity. Soot oxidative patterns of the soot samples from the diffusion flame burner were also investigated using the same method as described in the above procedure. However, thermal treatment of these soot samples was carried out at 300 °C to drive off volatile compounds. As shown in Appendix B, there is no appreciable difference in soot oxidative reactivity between 300 and 500 °C treatments.

Oxygen chemisorption was carried out for soot samples collected from the diffusion flame burner to evaluate active surface area (ASA). The thermally treated sample was cooled to
275 °C and ultra zero air was introduced into the instrument with 100 cc/min. After oxygen adsorption was carried out for 20 hours, gaseous N₂ displaced air for 60 minutes. The amount of chemisorbed O₂ is converted into the area occupied by O₂ according to Equation 3.1 [133]. The converted area, which is called ASA, is used as an index to represent edge sites or active sites on the soot surface.

\[
ASA = \frac{N_0 \sigma_o N_A}{w}
\]

Equation 3.1

where \( N_0 \) is the number of moles of chemisorbed oxygen,
\( \sigma_o \) is the area occupied by each oxygen atom (0.083 nm²),
\( N_A \) is Avogadro’s number,
\( w \) is the initial mass of soot.

### 3.2.3 Raman Analysis

A soot sample was pressed with a spatula onto a glass microscope slide to keep particles in place. A WITec Confocal Raman Microscope CRM 200 was focused on each sample with the white light source using a 100X objective lens, and the light was switched to the laser beam with an Ar ion laser source (514.5 nm), where wavelength was calibrated with a silicon wafer at 520 cm⁻¹. Raman spectra were recorded at 10 – 15 different positions for each sample, where integration time is 10s with 10 hardware accumulation. Among many curve-fitting methods, three, four and five peak curve-fitting methods were employed for first-order Raman spectra via an IGOR Pro 6.10 software (Wavemetrics Inc.) as summarized by Sadezky et al. [85], where 2 Lorentzian (L) (D1:1360cm⁻¹ and G:1590cm⁻¹) and 1 Gaussian (G) (D3:1500cm⁻¹), 3L (D1, D3 and G), 3L (D1, D4:1180cm⁻¹and G) and 1G (D3), 4G (D1, D3, D4 and G), 4L (D1, D2:1620cm⁻¹, D4 and G) and 1G (D3), and 5L (D1, D2, D3, D4 and G) were fitted to the Raman spectra as indicated in Figure 2-5. From each fitted curve, the height ratio of D1 to G (I_D1/I_G), the area ratio
of D1 to G (A_D1/A_G), and the D1 full width at half maximum (D1 FWHM) were investigated as Raman parameters. In addition, the D3 band was further studied as a way to evaluate amorphous carbon in the soot samples. Each Raman parameter was averaged for all the examined positions to compute standard deviations in order to compare the results statistically. As shown in Appendix A, the 3L1G fitting method indicates that all the Raman parameters examined in this work correlate well with soot oxidative reactivity. Accordingly, the 3L1G fitting method was used to investigate the crystalline structure of all the soot samples.

3.2.4 X-ray Diffraction (XRD) Analysis

XRD patterns of soot samples were collected using a PANalytical X’Pert Pro MPDθ/θ goniometer with Cu-Kα radiation, and fixed slit incidence (0.5° divergence, 1.0° anti-scatter, specimen length 10 mm) and diffracted (0.5° anti-scatter, 0.02 mm nickel filter) optics. Samples were prepared by the back-loading method in which a powder sample is pressed into the cavity of a quartz low-background support. Data was collected at 45 kV and 40 mA from 5-110° 2θ using a PIXcel detector in scanning mode with a PSD length of 3.35° 2θ, and 255 active channels for a duration time of ~1 hour. Resulting patterns were corrected for both 2θ position and instrumental peak broadening using NIST 640c silicon and analyzed with Jade+9 software by MDI of Livermore, CA. Using Jade+9 software, the full width at half maximum (FWHM) was manually post-processed for (002) and (10) peaks with a linear background for 5 times, and they were averaged. The crystallite height (Lc) and crystallite width (La) were calculated from (002) and (10) peaks, respectively, from their FWHMs using Scherrer’s equations as follows.

\[
L_a = \frac{K_a \lambda}{B_a \cos \theta}
\]  
Equation 3.2

\[
L_c = \frac{K_c \lambda}{B_c \cos \theta}
\]  
Equation 3.3
where $K_a = 1.84$, $K_c = 0.9$, $\theta = $ the Bragg’s angle (the angle between the atomic planes and the incident X-ray beam), $B_a = \text{FWHM from (10)}$ and $B_c = \text{FWHM from (002)}$.

### 3.2.5 Transmission Electron Microscope (TEM)

TEM was employed in order to observe the morphology and nanostructure of soot particles directly. First, 0.5 ~ 1.0 mg of each sample was dispersed in 10 ml of ethanol or acetone using an ultrasonic cleaner until the solution became homogeneous, and a drop of the solution was transferred to a lacey C/Cu TEM grid. The grid was loaded onto a single-tilt holder and analyzed in the TEM mode using a JEOL EM-2010F with field emission source at 200 kV accelerating voltage. All images were taken in a Gatan DigitalMicrograph with a slow scan CCD camera using 150 $\mu$m of condenser aperture size. And, the element content of primary soot particles was investigated using TEM equipped with an energy-dispersive x-ray spectrometer (EDXS).

### 3.2.6 Electron Energy Loss Spectroscopy (EELS)

To examine soot structure, EELS spectra were obtained with an Enfina 2000 coupled with the JEOL EM-2010F using scanning TEM mode (STEM). The STEM images were acquired with 0.5 nm spot size and 7.0 cm camera length with 40 $\mu$m condenser aperture size. The energy resolution which is the full width at half maximum of zero loss peak is 1.2 eV and the spectra were acquired at a dispersion of 0.2 eV per channel with 1 second of integration using 3 mm of aperture. A beam shower treatment was carried out before STEM mode in order to avoid hydrocarbon contamination on the carbon, which was examined with STEM images and EELS spectra during the test. The EELS spectrum of each sample was obtained for 5~6 different primary particles using an area scanning in order to get a representative result with a standard deviation. The spectra were background subtracted by fitting the pre-edge backgrounds with a
power-law function provided by Gatan DigitalMicrograph and the intensity ratio of 285 eV to 292 eV was used to measure the relative degree of crystalline order of soot.

### 3.2.7 X-ray Photoelectron Spectroscopy (XPS)

To examine the soot surface composition, XPS spectra were recorded in an Axis Ultra from Kratos Analytical using a monochromatic Al-Kα X-ray source operated at $10^{-8}$ mbar. The analysis area is roughly $1 \text{ mm} \times 1.5 \text{ mm}$, and the sample surface was oriented normal to the analyzer entrance. The pass energies were 80 and 20 eV for surveys and high resolution scans, respectively. Samples were mounted on double-sided conductive carbon tape which was fastened to a Cu substrate. The influence of the charge-neutralizer was checked on each sample. If no peak shifts were observed when the charge neutralizer was turned on, then the neutralizer was left off for that sample. If the charge neutralizer did cause an observable peak shift, neutralizer settings were chosen to eliminate peak distortion. CasaXPS software was employed to measure surface O, C and other elements in the soot, where atomic composition was calculated based upon the spectra with Shirley background from survey scans, and high resolution C1s and O1s were examined to identify surface oxygen functional groups.

### 3.2.8 Temperature Programmed Desorption-Mass Spectroscopy (TPD-MS)

An AutoChem 2910 from Micromeritics was employed to analyze oxygen functional groups in soot by TPD coupled with a mass spectroscopy. About 50 mg of each sample was placed in a quartz tube, and a thermocouple was inserted into the sample to measure the bed temperature during the process. The samples were initially dried at 120 °C for 1 hr under 50 ml/min of a He flow. After cooling down to room temperature, they were heated to 1000 °C at a rate of 5 °C/min under 50 ml/min of a He flow. The evolved gases were continuously measured
by a quadrupole mass spectrometer using Dycor model 2000. The spectrometric response of CO and CO$_2$ was calibrated using a weighed amount of calcium oxalate (CaC$_2$O$_4$·H$_2$O) as a standard sample. The CO and CO$_2$ evolved profiles were deconvoluted by multiple Gaussian functions using IGOR Pro 6.10 to identify various functional groups referring to Figueiredo and coworkers [115,126,127].

3.2.9 Scanning Electron Microscope (SEM)

Hitachi S-3500 SEM was employed to observe the morphologies of soot particles. Samples were mounted on double-sided conductive copper tape and the operation was conducted at low vacuum status to keep soot particles from scattering. And, energy dispersive spectroscopy (EDS) was coupled with the SEM instrument to quantify elemental composition in and on soot samples.

3.2.10 Near Edge X-ray Absorption Fine Structure Spectroscopy (NEXAFS)

NEXAFS spectra at the carbon K-shell absorption edge were recorded at beamline U4B at the national synchrotron light source in Brookhaven national laboratory. The pressed samples were mounted on double-sided copper tape, and the target current signals were obtained using Auger electrons.
Chapter 4

STUDY ON CRYSTALLINE STRUCTURE AND OXYGEN CONTENT OF SOOT

4.1 Comparison of Crystallite Size by XRD and Raman Spectroscopy

As a way to evaluate soot crystalline structure, the 3 Lorentzian 1 Gaussian (3L1G) curve-fitting method was chosen based on the empirical study shown in Appendix A. Knight and White’s empirical formula [14] is discussed to estimate crystallite size of soot in comparison to crystallite size calculated by XRD.

4.1.1 TGA Analysis

In order to compare soot oxidative reactivity with the crystalline structure of soot, soot oxidation was carried out in TGA. Four soot samples used in this study are SCE soot, which is soot sampled from the single cylinder locomotive engine, DDC 30 and DDC 75 soots, which were obtained from the light duty diesel engine at 30% and 75% of full load, respectively, and flame soot collected from the diffusion flame burner. And, the fifth sample is a carbon black. The oxidative trends for the 5 samples were compared at 550 °C as shown in Figure 4-1. Flame soot is the most reactive among the samples, and carbon black is the least reactive. The time to be completely oxidized for SCE soot and DDC 30 soot is almost the same, but DDC 30 soot is shown to be more reactive in the earlier stages of oxidation. The oxidative trend in this study is well represented by the 50% burn-off time as indicated as t_{50%} in Table 4-1, which was also used by Dong et al. [135]. Greater 1/t_{50%} indicates more reactive soot. Since the difference is not significant at 600 °C, 1/t_{50%} at 550 °C was introduced in this study as a parameter representing soot oxidative rate. It should be noted that mass diffusion must be considered in TGA experiments, because oxidant gas flows across the mouth of a crucible in order to react with soot.
As reviewed by Stanmore et al. [22], however, the Thiele modulus in the soot bed in a TGA is high due to the significant diffusion constraints, leading to the surface layer burning. Therefore, although each soot sample may have different mass transfer of oxidant gas in a crucible, soot oxidative reactivity is thought to be kinetically controlled in this study.

![TGA results of soot samples at 550 °C isothermal condition](image)

Figure 4-1. TGA results of soot samples at 550 °C isothermal condition

Table 4-1. 50% of soot burn-off time at different temperatures

<table>
<thead>
<tr>
<th>Operating temperature (°C)</th>
<th>Flame soot</th>
<th>SCE soot</th>
<th>DDC 30 soot</th>
<th>DDC 75 soot</th>
<th>Carbon black</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>7.31e-3</td>
<td>5.11e-3</td>
<td>5.94e-3</td>
<td>4.49e-3</td>
<td>0*</td>
</tr>
<tr>
<td>550</td>
<td>3.72e-2</td>
<td>2.11e-2</td>
<td>2.30e-3</td>
<td>1.92e-2</td>
<td>1.93e-3</td>
</tr>
<tr>
<td>600</td>
<td>1.02e-1</td>
<td>6.61e-2</td>
<td>7.11e-2</td>
<td>5.94e-2</td>
<td>8.10e-3</td>
</tr>
<tr>
<td>650</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.80e-2</td>
</tr>
</tbody>
</table>

* : $1/\infty$ because there was no reaction at this temperature

### 4.1.2 XRD Results

Before the crystalline structures of the soot samples were investigated by Raman spectroscopy, the x-ray diffraction patterns of these samples were also examined as shown in
Figure 4-2. All the samples show broad peak patterns at 27, 42 and 77°, which arise from (002), (10) and (110), respectively. However, carbon black has sharper (002), (10) and (110) peaks. In order to find the relationship between soot oxidative reactivity and crystallite size, crystallite sizes of the samples were further investigated and plotted against t_{50%} in Figure 4-3. Overall, both Lc and La show similar trends against the soot oxidative rate: flame soot has the smallest crystallite size, and carbon black has the largest. However, the crystallite sizes of SCE soot, DDC 30 soot and DDC 75 soot are not much different despite their reactivity differences. Although crystallite size has been used to indicate disorder of carbonaceous materials, it is not sensitive enough to indicate oxidative reactivity differences when the reactivity differences are not large as shown in this study. As confirmed for the present XRD and TGA results, crystallite size from XRD seems to be limited to represent soot oxidative reactivity. Therefore, in spite of the popularity of XRD to characterize the crystalline structure of carbonaceous materials, care should be taken especially for highly disordered carbon, such as soot, in the evaluation of soot oxidative reactivity via XRD analysis.

Figure 4-2. XRD patterns of soot samples
4.1.3 Raman Analysis

First- and second-order Raman spectra of the samples are compared in order to find if there are any unique characteristics in the Raman spectra of the samples. The first-order Raman spectra of the samples are shown in Figure 4-4(a). As observed for many disordered carbonaceous materials, all the samples show two broad peaks at 1360 and 1590 cm\(^{-1}\). Although there is no appreciable variation in the positions of the D and G bands among the samples, there are two trends observed in the patterns with respect to oxidative reactivity. With the decreasing oxidative reactivity, one is the decrease in the height of the valley between the D and G bands, and the other is the decreasing width in the D band. Since the valley and the D band width account for the D3 band and D1 width, respectively, in the assignment, their variation may have a significant effect on Raman parameters depending upon curve-fitting methods. Indeed, the D3 band doesn’t appear for ordered crystallites like graphite [84,85].
Figure 4-4. Comparison of Raman spectra of soot samples: (a) first-order Raman spectra, (b) second-order Raman spectra
Table 4-2. Height and area ratios of D to G for raw spectra and the 3L1G fitting method

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Raman parameter</th>
<th>Raman parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$I_D/I_G$ (with no fitting)</td>
<td>$I_D/I_G$ (with 3L1G)</td>
</tr>
<tr>
<td>Flame soot</td>
<td>0.960±0.009</td>
<td>1.381±0.035</td>
</tr>
<tr>
<td>SCE soot</td>
<td>1.032±0.038</td>
<td>1.283±0.030</td>
</tr>
<tr>
<td>DDC 30 soot</td>
<td>0.965±0.035</td>
<td>1.294±0.040</td>
</tr>
<tr>
<td>DDC 75 soot</td>
<td>1.028±0.022</td>
<td>1.174±0.031</td>
</tr>
<tr>
<td>Carbon black</td>
<td>1.047±0.075</td>
<td>0.959±0.093</td>
</tr>
</tbody>
</table>

I indicates height intensity, and A does area intensity.

In addition, the second-order Raman spectra of the samples are also compared in Figure 4-4(b). The four soot samples show similarly broad patterns in the range of 2000 to 4000 cm$^{-1}$, but carbon black shows 4 distinct peaks appearing at 2450, 2700, 2900 and 3200 cm$^{-1}$, which are assigned as 2*D4, 2*D1 overtones, G+D1 combination and 2*D2 overtone, respectively [85]. The peaks at 2700, 2900 and 3200 cm$^{-1}$ are shown to become more distinct with increasing crystalline order [84], so the broad peaks for the four soot samples indicate that the soot samples are less ordered in their structure than carbon black, which is consistent with the first-order Raman spectra and XRD patterns.

As noted in Table 4-2, the present result shows that $I_D/I_G$ is not well correlated to the oxidative reactivity for the examined samples. Although there is no clear order in the ratio, flame soot and DDC 30 soot, which have lower intensities in Table 4-2, have a wider D band than the other samples, and carbon black has the narrowest width in Figure 4-4(a). According to Ferrari and Robertson [76], the broadening of the D band is correlated to a distribution of clusters with different orders and dimensions. Thus, less distorted aromatic rings show higher D intensity, and the D width depends on the disorder. Accordingly, rings other than six-membered rings have the tendency to decrease the peak height and increase its width. In this light, the height ratios in Table 4-2 and the D band shapes in Figure 4-4(a) may indicate that flame soot and DDC 30 soot have more distorted aromatic rings and disordered crystallites than the other samples, and carbon black...
has the least disordered crystallites. In comparison to $I_D/I_G$ from raw spectra, Table 4-2 also indicates that $I_{D1}/I_G$ and $A_{D1}/A_G$ from the 3L1G fitting method are in good agreement with soot oxidative reactivity. As shown in Appendix A, all the Raman parameters from the 3L1G fitting method are observed to correlate well with soot oxidative reactivity.

According to Tuinstra and Koenig [79], $I_D/I_G$ is inversely correlated to crystallite width ($L_a$), and Knight and White proposed the following equation covering from amorphous carbon to graphite [14].

$$ L_a = 4.4\left(\frac{I_D}{I_G}\right)^{-1} \quad \text{Equation 4.1} $$

However, Cançado et al. proved that Equation 4.1 is only valid for 514.5 nm, because $A_{D}/A_G$ is dependent upon the laser energy [136]. Accordingly, they provided a universal equation considering all the laser energies as given in Equation 4.2 from the studies of XRD and scanning tunneling microscopy (STM).

$$ L_a = \frac{560}{E_l} \left(\frac{A_D}{A_G}\right)^{-1} \quad \text{Equation 4.2} $$

where $E_l$ is a laser energy (eV), $A_{D}/A_G$ is area ratio of D to G and $E_l$ is 2.41 eV for 514.5 nm.

Using Equations 4.1 and 4.2, crystallite width was calculated for soot samples and it is compared to the values calculated by XRD as shown in Figure 4-5. As evidenced in Figure 4-5, $L_a$ is shown to be similar regardless of soot sample, when it is calculated using Equation 4.1. So, this result suggests that $I_D/I_G$ from raw Raman spectra is not a good parameter in evaluating crystallite size of soot samples. In comparison, the $L_a$ values calculated from Equation 4.2 are significantly larger than those from XRD. Indeed, the material performed in Cançado et al.’s study is diamondlike carbon (DLC) films with $L_a$ from 20 to 490 nm, and the D and G bands are discrete
with narrow D bands, unlike soot samples. Therefore, Cançado et al.’s empirical formula also
doesn’t seem to be applied to disordered carbon like soot and carbon black with wide D bands.

Figure 4-5. Comparison of crystallite width: $I_{D1}/I_G$ from raw spectra was used for Knight and
White’s method, and $A_{D1}/A_G$ from 3L1G fitting method was used for Cançado et al.’s method

Instead of using $I_D/I_G$ from raw Raman spectra, Knight and White’s formula was further
investigated for the 3L1G fitting method. The calculated LA values from Equation 4.3 and
Equation 4.4 are also compared to those from XRD as shown in Figure 4.6.

$$L_a = 4.4\left(\frac{I_{D1}}{I_G}\right)^{-1}$$  \hspace{1cm} \text{Equation 4.3}

$$L_a = 4.4\left(\frac{A_{D1}}{A_G}\right)^{-1}$$  \hspace{1cm} \text{Equation 4.4}

where $I_{D1}/I_G$ and $A_{D1}/A_G$ are obtained from 3L1G fitting method.
Figure 4-6 indicates that the crystallite width is overestimated with $I_{D1}/I_G$ for soot samples compared to the XRD result except carbon black, and it is underestimated with $A_{D1}/A_G$ for all the examined samples. However, Equations 4.3 and 4.4 seem to provide more reasonable results than Equation 4.1, when XRD result is considered. However, it is still difficult to judge if $L_a$ determined by Raman spectroscopy should be similar to that by XRD in the case of soot with small crystallites, because XRD is known to be more sensitive to larger crystallites.

Figure 4-6. Comparison of crystallite width: Knight and White1 uses $I_{D1}/I_G$ and Knight and White 2 uses $A_{D1}/A_G$ from the 3L1G fitting method

In comparison, TEM image analysis provides direct information about the distribution of crystallite width in carbon crystallites. According to Vander Wal et al. [137], the crystallite width of soot treated at 1350 °C, which is called fringe length, distributes from 0.5 to 3.5nm and its median value is ~1 nm. Although there is no way to compare the present soot samples with theirs, the examined four soot samples are ranged from 1 to 2 nm of crystallite width using Equation 4.4. In this sense, the present result from Equation 4.4 seems to be consistent with Vander Wal et al.'s
fringe analysis. Since Equation 4.1 is an empirical formula covering many different carbonaceous materials from small to large crystallite size, it is arguable that Equation 4.4 can substitute Equation 4.1 for soot samples. Therefore, Equation 4.4 should be further probed for various soot samples if it can predict a similar result to a fringe analysis by TEM.

4.2 Soot Surface Modification Study

Flame soot samples modified by HNO₃ were examined for soot oxidative reactivity in order to study the effect of surface O content and oxygen functional groups. The results from TPD-MS and XPS for the soot samples were quantitatively compared for O content and oxygen functional groups.

4.2.1 Soot Oxidative Reactivity

Weight loss curves from TGA of acid treated soot samples are compared in Figure 4-7. It is observed that soot becomes significantly more reactive with the acidification, in which the acidification at 60 °C enhances the reactivity more than that at room temperature. This result suggests that HNO₃ treatment increases the oxidative reactivity of soot. Many researchers have shown that HNO₃ treatment can influence surface chemistry of carbonaceous materials and pore structures. The effect of HNO₃ treatment on the pore structure is observed to differ depending upon carbon type. With HNO₃ treatment, surface area is found to decrease for carbon black [138,139], to be similar for carbon nanotubes [140] and to increase for carbon xerogels [127] and activated carbons [141]. In addition, HNO₃ treatment is known to create more defects and/or active sites in carbon crystallites [142,143], or increase the stability of carbon crystalline structures by removing weak structures [138]. Whether HNO₃ treatment induces the disorder in the crystalline structure of carbon depends on carbon type, but it is consistently observed that HNO₃ treatment increases surface oxygen functional groups in and on carbonaceous materials.
The role of pore structure in soot oxidation is of interest with HNO$_3$ treatment. Rios et al. observed that the surface area of an activated carbon increases from 1183 to 1393 m$^2$/g by HNO$_3$ treatment, and it increases further from 1393 to 1428 m$^2$/g by thermal treatment at 700 °C with He [141]. However, it is still questionable whether HNO$_3$ treatment increases the surface area of soot. Borah et al. showed that HNO$_3$ treatment reduces the surface area of carbon black from 59.4 to 31.8 m$^2$/g [138], and Carmo et al. also observed a decrease in the surface area of carbon black [139]. Since soot has 80 – 100 m$^2$/g surface area as shown in Table B-4 of Appendix B, its pore structure may be similar to that of carbon black, rather than that of activated carbon. Then, the surface area of soot would be reduced with HNO$_3$ treatment due to the blocking effect by increased surface oxygen functional groups. In this light, if the surface area is decreased by HNO$_3$ treatment, the increased soot oxidative reactivity by HNO$_3$ treatment cannot be explained by the decreased surface area. Consequently, the increase in soot oxidative reactivity with HNO$_3$
treatment seems to be more related to the increase in active sites and surface oxygen functional groups.

4.2.2 Surface O Content and Oxygen Functional Groups

4.2.2.1 TPD-MS

TPD-MS can provide quantitative information about oxygen functional groups. Since oxygen functional groups have different sensitivities toward temperature (i.e., different stability and therefore response to temperature), CO and CO₂ evolved at certain temperatures have been widely used to assign oxygen functional groups [115,116,126,127]. Table 4-3 shows the total amounts of CO and CO₂ evolved from 100 to 1000 °C in TPD-MS for acidified soot samples. The amounts of CO and CO₂ increase with HNO₃ at room temperature and they increase more significantly with HNO₃ at 60 °C, which indicates that HNO₃ treatment at 60 °C generates more oxygen functional groups on the soot. Also, the ratio of CO to CO₂ (CO/CO₂) is shown to be larger than 1 and to decrease with acidification, which is consistent with Silva et al. [127]. According to Silva and coworkers, HNO₃ treatment introduces more oxygen functional groups with increasing temperature, when carbon xerogels and single-walled carbon nanotubes (SWCNTs) were examined [127,140]. The assignment of functional groups [115,126,127,144] via the deconvolution of CO and CO₂ peaks followed the work of Figueiredo and co-workers [127,144].

Table 4-3. Total amounts of CO and CO₂ calculated from TPD-MS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total amount (μmol/g soot)</th>
<th>CO/CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Original soot</td>
<td>871</td>
<td>162</td>
</tr>
<tr>
<td>(B) Soot acidified with HNO₃ at room</td>
<td>1659</td>
<td>492</td>
</tr>
<tr>
<td>(C) Soot acidified with HNO₃ at 60 °C</td>
<td>3452</td>
<td>1888</td>
</tr>
</tbody>
</table>
Silva et al. used 5 peaks for CO and CO\textsubscript{2} profiles [126], respectively, but 4 peaks were used for each profile in the present work because all the samples show 4 characteristic peaks for CO and CO\textsubscript{2} as indicated in Figure 4-8.

Figure 4-8. Deconvolution of CO and CO\textsubscript{2} evolved in TPD-MS: (a) and (b) original flame soot, (c) and (d) soot acidified by HNO\textsubscript{3} at room temperature, (e) and (f) soot acidified by HNO\textsubscript{3} at 60 °C. (1) strongly acidic carboxylic groups, (2) weakly acidic carboxylic groups, (3) phenol and/or carboxylic anhydride groups, (4) carbonyl and/or quinone groups, (5) carboxylic anhydride, (6) lactones
The detailed CO and CO₂ profiles are shown to be much different for the original flame soot and the acidified soot samples. The peaks at (1) and (2) for CO and CO₂ correspond to strongly acidic carboxylic acid and weakly acidic carboxylic acid, respectively. The temperature zone between 400 and 800 °C, where the peak at (3) for CO appears, is further deconvoluted into phenol groups and carboxylic anhydride groups [127,144], so the peak at (3) is attributed to these groups. The peak at (4) for CO is known to be related to carbonyl and/or quinone groups, and that at (5) for CO₂ also corresponds to carboxylic anhydride. Finally, the peak at (6) is ascribed to lactone groups. The peaks at (1) and (2) for CO, which are missing in the original soot, are newly generated with mild acidification, which is consistent with the CO₂ profiles by showing an increase in (1) and (2). With the increase in the degree of acidification, the peak at (3) increases gradually, but the increase in the peak at (4) is relatively small. In order to better understand the impact of acidification, the CO and CO₂ amounts evolved at each peak are quantitatively compared in Table 4-4, and the total CO and CO₂ amounts corresponding to each oxygen functional group are also compared in Table 4-5. As evident in Table 4-5, the initial amounts of carboxylic acid groups in the original sample are much less than C-O and C=O groups, but they are observed to be greatly increased by HNO₃ treatment. The C-O groups, which are carboxylic anhydride and phenol groups, are also increased significantly by HNO₃ treatment, but the C=O groups, which are associated with quinone and/or carbonyl groups, are mildly increased by strong acidification. Therefore, this result suggests that HNO₃ treatment increases carboxylic acid favorably in soot and it enhances mildly the amounts of phenol, carboxylic anhydride, carbonyl and/or quinone groups. HNO₃ treatment has been commonly observed to increase carboxylic acid groups for various carbon materials [124,127,142,145,146]. According to previous studies, aromatic carbons are known to oxidize as follows [124,147,148].

\[ C=\text{C} \rightarrow -\text{C-OH} \rightarrow -\text{C}=\text{O} \rightarrow -\text{COOH} \]
Table 4-4. Results of the CO and CO$_2$ amounts and their corresponding centered temperature: (1), (2), (3), (4) and (5) are oxygen functional groups from Figure 4-8, and A, B and C are soot samples as shown in Table 4-3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO evolved</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1) µmol/g</td>
<td>T$_m$ (°C)</td>
<td>(2) µmol/g</td>
<td>T$_m$ (°C)</td>
<td>(3) µmol/g</td>
<td>T$_m$ (°C)</td>
<td>(4) µmol/g</td>
</tr>
<tr>
<td>A</td>
<td>-</td>
<td>232</td>
<td>-</td>
<td>378</td>
<td>689</td>
<td>871</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>50</td>
<td>236</td>
<td>183</td>
<td>440</td>
<td>621</td>
<td>876</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>232</td>
<td>-</td>
<td>378</td>
<td>689</td>
<td>871</td>
<td>-</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO$_2$ evolved</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1) µmol/g</td>
<td>T$_m$ (°C)</td>
<td>(2) µmol/g</td>
<td>T$_m$ (°C)</td>
<td>(3) µmol/g</td>
<td>T$_m$ (°C)</td>
<td>(4) µmol/g</td>
</tr>
<tr>
<td>A</td>
<td>20</td>
<td>236</td>
<td>414</td>
<td>59</td>
<td>643</td>
<td>864</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>72</td>
<td>230</td>
<td>340</td>
<td>211</td>
<td>575</td>
<td>891</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>410</td>
<td>245</td>
<td>369</td>
<td>1018</td>
<td>592</td>
<td>824</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4-5. Results of total CO and CO$_2$ amounts for each functional group: (1), (2), (3), (4) and (5) are oxygen functional groups from Figure 4-8, and A, B and C are soot samples as shown in Table 4-3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total CO and CO$_2$ amounts (µmol/g soot)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1) + (2)</td>
<td>(3)</td>
<td>(4)</td>
<td>(5)</td>
<td>(6)</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>79</td>
<td>387</td>
<td>484</td>
<td>50</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>550</td>
<td>934</td>
<td>458</td>
<td>190</td>
<td>19</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2215</td>
<td>1730</td>
<td>935</td>
<td>438</td>
<td>23</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total CO and CO$_2$ amounts (µmol/g soot)</th>
<th>C-O and anhydride</th>
<th>C=O groups</th>
<th>Carboxylic acid groups</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>((3) + (5))</td>
<td>(1) + (2)</td>
<td>((1) + (2))</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>437</td>
<td>484</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>1124</td>
<td>458</td>
<td>550</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>2168</td>
<td>935</td>
<td>2215</td>
<td></td>
</tr>
</tbody>
</table>

Zhang et al. noted from the oxidation of SWCNTs that the generation of C-OH groups and C=O groups is the step to create active sites, and transforming C-OH into C=O groups depends on the oxidant [147]. Although the amounts of C=O groups in the sample B (HNO$_3$ at room temperature) are observed to be less than those in the sample A (original soot), it seems that C=O
groups in the sample A were consumed and those in the sample B were newly generated during the oxidation process by HNO₃ treatment. The results also suggest that although HNO₃ treatment at room temperature could create new active sites, it was not enough to transform C-O → C=O → COOH. However, HNO₃ treatment at 60 °C enabled C-O to further oxidize into COOH, which became the dominant oxygen functional group on the soot sample.

4.2.2.2 XPS

To support the observations from TPD-MS analyses of the soot samples, XPS also was employed to characterize the acidified soot samples. As evidenced in Figure 4-9(a), O content greatly increases with the surface modification, and it displays a linear relationship with soot oxidative reactivity, which is consistent with other studies [12,13,129]. The peak intensity in C1s and O1s is not a direct quantitative indicator representing increased oxygen functional groups. So, the comparison of their peaks should be qualitatively considered. As indicated in Figures 4-9(b) and (c), with HNO₃ treatment the broadening of the C1s is observed and the O1s peak increases. In particular, HNO₃ treatment at 60 °C is observed to create a significant peak at 289 eV. Although the difference in the C1s peak between sample A (original soot) and ample B (soot acidified by HNO₃ at room temperature) is not appreciable, it is noted that the peak appearing at 285.5 - 286 eV, which is assigned to be C-OH in alcohol groups and/or C-O in ether groups, increases for the sample B. The O1s peaks show more clearly that all the functional groups increase with acidification, and their increase is more noticeable with the acidification at 60 °C.
Figure 4-9. XPS results of acidified soot samples: (a) surface O content, (b) C1s, (c) O1s
Although the O1s peak has been assigned differently by different researchers as shown in Table 2-1, the assignment of oxygen functional groups in C1s is commonly observed as follows: (1) ~286 eV is C-O groups in alcohol and/or ether groups, (2) ~287 eV is C=O groups in quinone and/or carbonyl groups, and (3) ~289 eV is O=C-O in carboxylic acid, ester and/or carboxylic anhydride groups. Although Vander Wal showed that the C1s peak of carbonaceous materials may have sp$^2$ carbon, sp$^3$ hybridized carbon and oxygen functional groups [149], many researchers haven’t considered sp$^3$ hybridized carbon in the deconvolution of the C1s peak. Accordingly, the deconvolution of the C1s peak was made without considering sp$^3$ hybridized carbon in the present work using mixed Gaussian and Lorentzian functions (G/L=0.3) according to the peak shape, and the result is shown in Figure 4-10.

As indicated in Table 4-6, all the functional groups increased with mild acidification, and with the increase in the amounts of COO- groups, those of C-O and C=O groups decrease with strong oxidation. This result is not quantitatively consistent with the TPD result, especially for the original soot. The C=O groups are observed to be much less than the C-O groups in the C1s spectra, whereas C=O and C-O are observed at similar abundance as in the TPD analysis. Moreover, COO- groups are shown to be as prevalent as C=O groups. Since some of COO- groups can be contributed by carboxylic anhydride groups, carboxylic acid groups existing in the soot could be much smaller than this value. In addition, some C=O groups in soot may not be correctly detected by XPS. Interestingly, the amounts of C=O and COO- groups are found to be more abundant in XPS than in TPD for oxidized soot samples, unlike the original soot. Since HNO$_3$ treatment can create oxygen functional groups on the outermost surface of soot, the XPS analyses indicate that there are more C=O and COO- groups observed on the outermost surface by the oxidation process such as C-O $\rightarrow$ C=O $\rightarrow$ COOH.
Figure 4-10. Comparison of curve-fitted C1s for high load soot samples: (a) original flame soot, (b) soot acidified with HNO₃ at room temperature, (c) soot acidified with HNO₃ at 60 °C. (1) C-O in alcohol and/or ether groups, (2) C=O in quinone and/or carbonyl groups, (3) O=C-O in carboxylic acid, ester and/or carboxylic anhydride groups
Table 4-6. Relative ratio of oxygen functional groups in curve-fitted C1s with surface modification: (1), (2) and (3) are oxygen functional groups from Figure 4-10, and A, B and C are soot samples as shown in Figure 4-9(a)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
</tr>
<tr>
<td>A</td>
<td>15.91</td>
</tr>
<tr>
<td>B</td>
<td>18.14</td>
</tr>
<tr>
<td>C</td>
<td>13.36</td>
</tr>
</tbody>
</table>

In the same way, the O1s peak was also deconvoluted for a quantitative comparison in Figure 4-11. Some researchers curve-fitted the O1s peak with a two peak curve-fitting method [118,123,150,151], where the peak corresponding water is not considered, but the two peak curve-fitting method doesn’t fit the O1s peak of soot in the present work. Accordingly, a three peak curve-fitting method was employed, as shown in other studies [143,145]. Temporarily, three peaks can be assigned as follows, referring to several papers [114-116,120-123]: (4) 530 - 532 is C=O in quinone and/or carbonyl, (5) 531 - 534 is C-O in ether, C-OH in alcohol, O=C-O in ester and/or O=C-O-C=O in anhydride, and (6) 532 - 535 is COOH. According to the area under each peak, the relative ratio is also displayed in Table 4-7. As observed in Table 4-7, the ratios in (4), (5) and (6) are not much influenced by mild acidification. And, the sample acidified at 60 °C indicates that the amounts of quinone and/or carbonyl groups increase greatly, while ether, alcohol, ester and/or anhydride groups decrease. However, this result contradicts the results of TPD in Table 4-5 and C1s in Table 4-6 showing that C-O groups are more abundant in all the samples than C=O groups. Moreover, the O1s peak analysis cannot explain the increasing trend in carboxylic acid groups with acidification. As assigned in this study, some researchers used only one peak to assign the O1s in O=C-O for carboxylic acid [115,116,122,125,143,144]. But, other researchers assigned two different peaks for two different O atoms bonded to carbon atom. For a clear comparison, the peak assignment is shown in Table 4-8.
Figure 4-11. Comparison of curve-fitted O1s at different oxidized stages: (a) original flame soot, (b) soot acidified with HNO₃ at room temperature, (c) soot acidified with HNO₃ at 60 °C
Table 4-7. Relative ratio of oxygen functional groups in curve-fitted O1s with surface modification: (4), (5) and (6) are oxygen functional groups from Figure 4-11, and A, B, C are soot samples as shown in Figure 4-9(a)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(4)</td>
</tr>
<tr>
<td>A</td>
<td>16.43</td>
</tr>
<tr>
<td>B</td>
<td>17.06</td>
</tr>
<tr>
<td>C</td>
<td>40.53</td>
</tr>
</tbody>
</table>

Table 4-8. Peak assignment of O1s in O=C-O groups

<table>
<thead>
<tr>
<th>Groups</th>
<th>Reference</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O=C (eV)</td>
</tr>
<tr>
<td>O=C-O in ester</td>
<td>115, 116</td>
<td>532.3</td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>532.3 - 532.8</td>
</tr>
<tr>
<td></td>
<td>123</td>
<td>-</td>
</tr>
<tr>
<td>O=C-O-C=O in anhydride</td>
<td>115, 116</td>
<td>532.3</td>
</tr>
<tr>
<td></td>
<td>122</td>
<td>532.3 - 532.8</td>
</tr>
<tr>
<td></td>
<td>123</td>
<td>-</td>
</tr>
<tr>
<td>O=C-OH in carboxylic acid</td>
<td>117</td>
<td>531.1 - 531.8</td>
</tr>
<tr>
<td></td>
<td>121</td>
<td>532</td>
</tr>
</tbody>
</table>

As seen in the table, O=C and C-O in ester and anhydride are assigned at 532.3 - 532.8 and 533.1 - 533.8 eV, respectively, and those in carboxylic acid are assigned at 531.1 - 532 and 532.3 - 533.5 eV. Although Table 4-8 shows that Desimoni et al. [117] assigned C-O in carboxylic acid at the same range of O=C in ester and anhydride assigned by others, it is generally observed that carboxylic acid groups appear at ~533.5 eV [115,116,125,144,145]. When the above discrete assignments of O=C-O in ester, anhydride and carboxylic acid is applied to the current O1s result, the following assignments can be made: the peak at (4) is C=O in quinone, carbonyl and/or carboxylic acid, the peak at (5) is O=C in ester and anhydride and C-O in ether and/or alcohol, and the peak at (6) is O-C in ester, anhydride and carboxylic acid. Then, the peak pattern in Figure 4-11(c) can be explained as follows. The reason the peak at (6) is high can be due to the
contribution of ester and carboxylic anhydride as well as carboxylic acid. The peak at (4) greatly increases with a significant increase in quinone, carbonyl and carboxylic acid, whereas that at (5) decrease with the reduction of ester, carboxylic anhydride, alcohol and ether, resulting in decreasing the peak at (6). Although this presumption is based upon the trend in the C1s, there is no clear proof possible because peak curve-fitting and peak assignment are highly dependent on the materials used. Consequently, the present result may show only a qualitative trend in the peak patterns of O1s, in which there is a great increase in the peak at (4) due to the oxidation process in HNO3, by transforming C-O into C=O and carboxylic acid groups.

The effect of oxygen functional groups on soot oxidative reactivity is also of interest in this study. Overall, the abundance of oxygen functional groups is closely related to soot oxidative reactivity, such as surface O content. For this study, the original soot and acidified soot were thermally treated at 800 °C for 30 min to drive off oxygen functional groups, because TPD-MS showed that most of oxygen functional groups exist below this temperature. Then, the oxidative reactivities of the soots were compared in Figure 4-12. Both soot samples experience the decrease in the reactivity after thermal treatment. The reason soot oxidative reactivity decreases can be ascribed to the structural realignment after exposure to high temperature. However, it is shown that acidified soot is still obviously more reactive than the original soot. Accordingly, although surface O content and the corresponding abundance of functional groups can be good indicators of soot oxidative reactivity, there seems to be no correlation between specific oxygen functional groups and soot oxidative reactivity. As studied by others, HNO3 treatment generates defects and/or active sites in carbonaceous materials [152,153]. When Larciprete et al. annealed an oxidized double walled carbon nanotubes (DWCNTs) at 950 °C, the O1s signal in XPS disappeared completely, but the C1s signal in XPS still reflected the presence of lattice defects [143]. Therefore, the defects that remain after thermal treatment seem to resume serving as active sites, when oxidizing gases are available.
The present result indicates that HNO$_3$ treatment increases significantly surface O content and surface functional groups of soot. Surface O content is shown to be in good agreement with soot oxidative reactivity, as other studies observed [12,13,129]. However, it is not noticeable whether surface oxygen functional groups influence soot oxidation. Consequently, it is concluded that one of the hypotheses in this study that initial surface oxygen functional groups of soot enhances soot oxidation is not correct.
Oxygen enrichment was applied to a diesel engine at low and high loads to study the effect of soot properties on soot oxidative reactivity. From the analyses of the soot properties, the main factors affecting soot oxidative reactivity were investigated.

5.1 Apparent Heat Release Rate

Figure 5-1 displays apparent heat release rates computed from cylinder pressure traces at low and high loads. For 30% load, the start of pilot combustion is advanced with intake oxygen enrichment, and it is the most advanced with the 30% diglyme fuel mixture. Since injection timing is held constant in this study, the physical ignition delay is considered to be the same. Accordingly, the chemical ignition delay, which begins after the air-fuel mixing process, is more responsible for the advanced start of pilot combustion. Since oxygen in oxygenated fuels is directly incorporated in the fuel, the ignition delay with oxygenated fuels is generally shorter than that with intake oxygen enrichment, despite the greater availability of oxygen with intake oxygen enrichment. However, the advanced start of pilot combustion for the 30% diglyme fuel mixture is due to a cetane number effect, by shifting explosion limits for the reactant mixture to lower temperature and lower pressure [36]. As a consequence of shorter ignition delay, the peak heat release rate for the pilot combustion was lower, because less fuel is available for combustion.
Figure 5-1. Apparent heat release rate for oxygen enrichment tests: (a) 30% load, (b) 75 and 90% loads
Table 5-1. Ignition characteristics in pilot and main injection with oxygen enrichment for 75% load

<table>
<thead>
<tr>
<th>Condition</th>
<th>Start of combustion in pilot (CAD)</th>
<th>Start of combustion in main (CAD)</th>
<th>Duration of premixed burn in main (CAD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21% O₂</td>
<td>333.6</td>
<td>358.8</td>
<td>2.4</td>
</tr>
<tr>
<td>22.5% O₂</td>
<td>335.9</td>
<td>358.7</td>
<td>2.2</td>
</tr>
<tr>
<td>24% O₂</td>
<td>335.1</td>
<td>358.4</td>
<td>2.2</td>
</tr>
<tr>
<td>27% O₂</td>
<td>335.1</td>
<td>358.1</td>
<td>2.0</td>
</tr>
<tr>
<td>30% diglyme</td>
<td>333.3</td>
<td>358.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

However, the effect of oxygen enrichment on the mixing-controlled burn is not noticeable in this study. Accordingly, oxygen enrichment seems to be limited in its effect on the mixing-controlled burn at low load. Heat release patterns at high load indicate much different trends from those at 30% load in the premixed burn and the mixing-controlled burn with oxygen enrichment. An advanced start of pilot combustion is also observed at 75% load with oxygen enrichment. The peak heat release in the pilot combustion is increased and earlier start of main combustion is also observed with oxygen enrichment. Since cylinder temperatures are higher at high load than at low load, the peak heat release patterns in the pilot combustion appear increased with oxygen enrichment despite the shorter ignition delay.

Figure 5-1(b) also indicates that intake oxygen enrichment increased the heat release rate in the mixing-controlled burn compared to that of the 21% O₂ condition. Since there is more oxygen available in the mixing-controlled burn phase with intake oxygen enrichment, a more rapid reaction occurred at higher O₂ concentration in the intake air. On the other hand, there is no appreciable increase in the heat release rate of the mixing-controlled burn for the 30% diglyme fuel, because available oxygen at this condition, where O/C ratio is 4.57, is not much higher than at the 21% O₂ condition, where O/C ratio is 4.48. At 90% load there is a similar peak heat release during pilot combustion to that for 75% load, but the former shows a greater rate of heat release.
during main combustion phase due to the increased fuel supply, resulting in a more vigorous mixing-controlled burn.

According to Dec’s conceptual model [154], soot particles are generated just after the fuel-rich premixed combustion takes place. Soot volume increases in the diffusion flame along the centerline of the fuel spray, and these soot particles are oxidized in the near-stoichiometric diffusion flame around the periphery of the spray flame. Although there has been no detailed investigation about the soot formation and soot oxidation processes with intake oxygen enrichment using spatially integrated natural luminosity (SINL) data in engines, the processes at oxygen enriched conditions can be understood as an extension of EGR studies. With decreasing oxygen concentration, combustion temperature is reduced, which tends initially to increase soot emissions and then at sufficiently high EGR, soot emissions will decrease. The decreased rate of oxygen entrainment prolongs the combustion duration and increases the time for soot formation [155,156]. Correspondingly, with increased oxygen concentration soot volume is expected to be increased with higher combustion temperature, and the soot formation process is shortened with reduced combustion duration. Since engine-out soot emissions decrease with increasing oxygen concentration in spite of increased soot volume, the rate of soot oxidation is higher in the diffusion flame at oxygen enriched conditions [155].

5.2 Bulk Cylinder Gas Temperature

In order to examine the effect of oxygen enrichment on cylinder gas temperature, the measured cylinder pressures were used to calculate bulk gas temperature for low and high loads at each condition. At 30% load, Figure 5-2(a) shows that the 24% O₂ condition reached the lowest bulk temperature at 1380 K, while the 27% O₂ condition reached the highest bulk temperature at 1405 K, which is similar to that of the 21% O₂ condition and the 30% diglyme condition.
Figure 5-2. Bulk cylinder gas temperature for oxygen enrichment tests: (a) 30% load, (b) 75 and 90% loads
These minor temperature changes with oxygen enrichment are consistent with the small changes in the heat release of the mixing-controlled burn at 30% load. For high load, Figure 5-2(b) displays that the 27% O₂ condition achieved the highest bulk temperature of 1930 K, and the 21% O₂ condition had the lowest bulk temperature of 1830 K. And, the temperatures of the 24% O₂ and the 30% diglyme conditions are similar in spite of the different operating conditions. As expected from the heat release rate, the 90% load condition shows the highest bulk temperature of 2100 K. Accordingly, a strong impact of intake oxygen enrichment on cylinder temperature is clearly observed at the high load condition as many researchers have observed [157,158]. The temperature increase caused by increased oxygen at 75% load is not surprising as observed in the increased heat release rate of the diffusion burn phase, because more abundant oxidizing gases are involved in the combustion process.

5.3 TEM Analysis of Particle Aggregates

TEM images at 30 and 75% loads are compared in Figure 5-3. As shown in other studies, soot aggregates are distributed from small size to larger size [9,44]. In general, there are many larger aggregates observed for 75% load than for 30% load, which is attributed to the particle agglomeration due to the increased temperature [9]. At 30% load, Figures 5-3(a) and (b) show similar size distributions from small aggregates to large aggregates at 21% O₂ and 24% O₃. As shown in Figure 5-2(a), since there is no appreciable temperature effect at 30% load with increased oxygen concentration, intake oxygen enrichment seems to have a minor effect on the size distribution of soot aggregates. The wide size distribution of soot aggregates is also observed for 75% load with 21% O₂, but there are larger aggregates with scarce small aggregates for 75% load with 24% O₂, as indicated in Figures 5-3(c) and (d). According to Zhu et al. [9], the number of primary particles and the size of soot aggregates increases to some extent with engine load due to increased temperature.
Figure 5-3. TEM images of soot aggregated particles collected by thermophoretic sampling: (a) 30% load at 21% O₂, (b) 30% load at 24% O₂, (c) 75% load at 21% O₂, (d) 75% load at 27% O₂
As the temperature increases further, the size decreases because soot oxidation becomes a dominant factor over the particle growth through agglomeration. Although there is an enhanced soot oxidation with increased oxygen concentration, it doesn’t seem to be enough to oxidize large aggregates to smaller size during the short oxidation process. Consequently, it is speculated that most of small soot aggregates are oxidized and the remaining large aggregates are emitted from the cylinder without much oxidation during the soot oxidation process. Since hydrocarbon emissions decrease dramatically by oxidation with increasing oxygen concentration [39], soot precursors as well as small aggregates are expected to be oxidized at higher oxygen concentration.

5.4 Impact of Soot Properties on Soot Oxidative Reactivity

5.4.1 Soot Oxidative Reactivity by TGA

Isothermal oxidation was performed at 550 °C in order to examine soot oxidative reactivity. Figure 5-4(a) shows that the soot samples from 30% load have similar weight loss patterns, except for the 27% O₂ soot. The three soot samples were completely oxidized in 110 min at this temperature, and the complete oxidation of the 27% O₂ soot was observed after 90 min. In comparison to the TGA result from Figure 5-4(a), the soot samples from the high load appear more diverse in their oxidation behavior as shown in Figure 5-4(b). The 21% O₂ soot from 75% load is the least reactive, which takes 150 min for complete oxidation, and the 24% O₂ soot from 75% load was shown to be the most reactive among the examined samples. In particular, the two most reactive soot samples, the 22.5% O₂ soot and the 24% O₂ soot, show that ash remained after the completion of TGA test. Accordingly, this may indicate that there are inorganic compounds present in these soot samples, as observed in others’ investigations of diesel particulate matter [72,73].
Figure 5-4. TGA results of soot samples for oxygen enrichment tests: (a) 30% load, (b) 75 and 90% loads
In addition, the 30% diglyme soot from 75% load is found to be slightly more reactive than the 21% O₂ soot from 75% load. Song et al. observed that biodiesel soot is significantly more reactive than Fischer-Tropsch soot (FT soot), and the former oxidizes through a unique capsule-type oxidation process [60]. Also, Vander Wal and Mueller noted that increasing the level of fuel oxygenation generates soot with less ordered structure [71]. Correspondingly, the 30% diglyme soot from 75% load also seems to reflect more reactive soot, although the increase in soot oxidative reactivity is not significant.

As observed for the combustion analyses from heat release rates and the corresponding bulk cylinder gas temperatures, there is a consistent trend in soot reactivity that oxygen enrichment has a greater effect on soot samples from the high load than on soot samples from the low load. Therefore, the physical and chemical properties of the soot samples were extensively investigated to find the main factors affecting soot oxidative behavior with oxygen enrichment.

5.4.2 Elemental Analysis and Oxygen Functional Groups

5.4.2.1 Inorganic species by XPS and SEM-EDS

At first inorganic species were investigated using XPS, because ash remained after the completion of TGA. As evident in Table 5-2, some metallic species are present only on soot samples from particular conditions, 27% O₂ at 30% load, and 22.5% O₂ and 24% O₂ at 75% load. Although the 27% O₂ soot from 30% load and the 22.5% O₂ soot from 75% load contain very small amounts of Zn and P, the 24% O₂ soot contains N, Ca and Si as well as more abundant Zn and P. Although ash contents after TGA tests are not matched with the total amounts of metals using XPS for these soot samples, the presence of ash during TGA is due to the metallic species present in soot samples. It is known that these metals are components of friction reduction additives in lubricating oil. High cylinder temperatures contribute to volatilization and subsequent
oxidation of lubricating oil [159], but the soot from the 90% load condition, which has the highest bulk cylinder gas temperature, doesn’t contain any metals.

Table 5-2. Elemental analyses of inorganic species in the soot samples by XPS and SEM-EDS: samples for XPS are thermally treated at 500 °C, and samples for SEM-EDS are as-received

<table>
<thead>
<tr>
<th>Load</th>
<th>Condition</th>
<th>XPS (atomic %)</th>
<th>SEM-EDS (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Zn  P  Ca  Si</td>
<td>Zn  P  Ca  Si  Fe  S</td>
</tr>
<tr>
<td>30%</td>
<td>21% O₂</td>
<td>0    0   0   0</td>
<td>Not measured</td>
</tr>
<tr>
<td></td>
<td>24% O₂</td>
<td>0    0   0   0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>27% O₂</td>
<td>0.07 0   0   0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30% diglyme</td>
<td>0    0   0   0</td>
<td></td>
</tr>
<tr>
<td>75%</td>
<td>21% O₂</td>
<td>0    0   0   0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>22.5% O₂</td>
<td>0.06 0.1 0   0</td>
<td>Not measured</td>
</tr>
<tr>
<td></td>
<td>24% O₂</td>
<td>0.3  0.37 0.2 0.23</td>
<td>2.79 2.46 3.77 1.01 1.45 2.11</td>
</tr>
<tr>
<td></td>
<td>27% O₂</td>
<td>Not measured</td>
<td>2.05 1.64 3.51* 1.88*</td>
</tr>
<tr>
<td></td>
<td>30% diglyme</td>
<td>0    0   0   0</td>
<td></td>
</tr>
<tr>
<td>90%</td>
<td>21% O₂</td>
<td>0    0   0   0</td>
<td>Not measured</td>
</tr>
</tbody>
</table>

*: analysis at spot #2 in Figure 5-5

Since XPS can probe the outer 0 – 10nm of the surface of a sample with ~0.1 atomic % detection limits, XPS may not detect all the species in the soot samples. Also, the samples may lose some additional inorganic species during the thermal treatment under N₂ flow. Accordingly, SEM-EDS was applied to as-received soot samples in order to detect all the available species present in the soot. Table 5-2 reveals that sulfur is observed in all the samples with SEM-EDS, while there is no sulfur observed with XPS. Although XPS was not employed for the 27% O₂ soot from 75% load due to the small quantity of the sample, abundant Zn, Si, P and Ca were also
observed for the 27% O₂ soot with the SEM-EDS, as with the 24% O₂ soot from the 75% load. In addition, there are Si, S and Ca observed for the 90% load soot, which were not detected with XPS. Accordingly, SEM-EDS seems to detect more abundant inorganic species in and on soot samples. Also, the SEM image also shows that metallic species are in-homogeneously present in the samples. As shown in Figure 5-5, there are bright particles scattered on the 27% O₂ soot. The analysis on a small spot in Table 5-2, which is spot #2 in Figure 5-5, shows much different compositional results from the analyses on larger areas. Accordingly, elemental analysis by SEM-EDS in this work seems to be area-dependent. Although SEM-EDS indicates that metallic species are inhomogeneously scattered in and on the soot samples, it is still difficult to determine if the reason why SEM-EDS provides more abundant amounts of inorganic species than XPS is because SEM-EDS can survey deeper sites within the soot, or because the as-received soot samples contain more inorganic species. In the case of sulfur present in the soot samples, N₂ may drive off sulfur with thermal treatment. However, it is questionable if N₂ can also remove other metallic species in and on the soot samples, since thermal treatment was performed in TGA, where N₂ gas diffuses into the soot particles. Accordingly, the different amounts of metallic species between the two instruments can be ascribed to the difference in detection areas employed by these instruments. Therefore, the results of XPS and SEM-EDS should be accepted as qualitative tools in this work. Despite the different amounts of metallic species observed using the two instruments, they both provide valuable information that ash content is from the metallic species, resulting from the vaporized lubricating oil during the combustion process.

In order to investigate whether soot contains metallic species inside the primary soot particles, as-received 27% O₂ soot and 21% O₂ soot from 75% load were examined using TEM-EDS. The results show that there are 0.096 and 0.022 atomic % of Si and Ca, respectively, for the 8 primary particles of the 27% O₂ soot, and the 21% O₂ doesn’t have any metals inside. Not only
are the amounts of Si and Ca from TEM-EDS significantly smaller than those from SEM-EDS, but also other metallic species such as Zn and P are not detected using TEM-EDS.

![SEM image of the 27% O2 soot from 75% load](image)

Figure 5-5. SEM image of the 27% O₂ soot from 75% load

Therefore, it is presumed that most of the metallic species are not incorporated within the soot particles during the soot formation process but are deposited on the outermost surface of soot. If these particles are representative of primary soot particles, this TEM-EDS result indicates that the soot formation process occurs before the vaporization of lubricating oil, although there is a chance that a small amount of metallic species are incorporated within the soot particles. When Song et al. investigated primary soot particles after burning diesel fuel containing 200 wt ppm of a metal additive containing Fe and Sr, the existence of Fe and Sr was clearly observed inside the primary particles from HR-TEM [160]. Therefore, although it is unknown how much metal additives in the lubricating oil were consumed during engine operation, the process of incorporation of metals present in lubricating oil into soot particles seems to be different from
that of the metal additive in fuel during soot formation. From the elemental analyses, it is plausible that higher oxygen concentration in the cylinder, which was not involved in the combustion process, serves to raise peripheral temperatures in the cylinder, which vaporizes lubricating oil on the cylinder walls, and enhances the oxidation of the vaporized oil, from which metals deposited on the soot particles which were formed earlier than the vaporization of lubricating oil. This may be due to increased flame radiation to the cylinder walls, or greater rates of convection due to thinning of the quench layer with higher oxygen availability, although there has been no research known on this effect. And, this hypothesis applies only for high temperature, but not for lower temperature conditions, because there is no metal observed on the 24% O₂ soot from 30% load, in spite of the high oxygen concentration in the intake air.

5.4.2.2 Effect of metallic species on soot oxidation

Figure 5-4 and Table 5-2 indicate that soot samples containing metallic species are more oxidatively reactive than those without metallic species. Although the 22.5% O₂ soot was not analyzed in the SEM-EDS, there should be an appreciable amount of metals present in it from the fact that Zn and P were observed with the XPS. The SEM-EDS result reveals that there is only Ca present in the 90% load soot, but the 24% O₂ soot from 75% load contains various metallic species such as Zn, Si, P, Fe and Ca. Zn, Si, Ca and Fe appear to be good catalysts in soot oxidation [160-162], but P is observed to inhibit carbon oxidation [163]. Therefore, the differences in soot oxidative reactivity seem to be related to the amounts of metallic species present in the soot samples in this study, although it is not clear how much a small amount of P present in soot suppresses soot oxidative reactivity. In order to examine the effect of Ca on soot oxidative reactivity, Ca was mingled with flame soot in two different ways; one is that 1 wt % of Ca was impregnated onto flame soot using calcium nitrate tetrahydrate (Ca(NO₃)₂·(H₂O)₄), and
the other is that 2 wt % of Ca was mixed with flame soot using calcium oxide. As shown in Figure 5-6(a), the oxidative reactivity of the Ca-impregnated soot is greatly increased, but that of the CaO2-mixed soot is not apparently different from that of the original soot.

Figure 5-6. TGA results of soot and carbon black in the present of metals: (a) soot mixed with Ca at 500 °C isothermal oxidation, (b) carbon black mixed with Ca and Zn at nonisothermal oxidation
According to Neeft et al. [162], the first method (impregnation) is a tight contact mode, and the other (physical mixing) is a loose contact mode. So, it seems that Ca plays a catalytic role in soot oxidation, when it is in the tight contact mode with soot. In this light, metallic species may deposit onto soot by tight contact at high temperatures during the combustion process. In addition, carbon black impregnated with Ca and Zn nitrates was further investigated using nonisothermal oxidation. As shown in Figure 5-6(b), 50% burn-off temperatures (T_{50\%}) of original carbon black, Ca-impregnated carbon black and Zn-impregnated carbon black are 733, 560 and 629 °C, respectively. Accordingly, the effect of Ca on soot oxidation is more significant than that of Zn as a single component, which is consistent with Neeft et al. [162]. Although the elemental content of these metallic species in and on the 22.5 % O$_2$ soot, the 24% O$_2$ soot and the 90% load soot is much smaller than 1 wt%, as a single component, the same enhancing effect by metallic species is expected. Consequently, the amounts of metallic species seem to be a predominant factor influencing soot oxidative reactivity, although other physical and chemical properties of soot should also be considered. Therefore, surface oxygen content and crystalline structure were investigated in the following sections.

### 5.4.2.3 Surface O content by XPS

As shown in Table 5-3, the surface O contents of the 27% O$_2$ soot and the 30% DG soot from low load are 8.43 and 8.46%, respectively, which is slightly larger than 7.87% for the 21% O$_2$ soot. And, the surface O content of the 24% O$_2$ soot, which is 10.76%, is shown to be much larger than those of the other soot samples. However, there is no noticeable trend in the surface oxygen concentration with increased intake oxygen concentration. In contrast, an increasing trend in the oxygen content is more pronounced for the soot samples from the high load with oxygen enrichment.
Table 5-3. Atomic percentages of elements in soot samples by XPS

| Engine load | Condition       | Element (atomic %) |
|            |                | O      | C      | Others  |
| 30%         | 21% O₂         | 7.87   | 92.13  |         |
|             | 24% O₂         | 10.76  | 89.24  |         |
|             | 27% O₂         | 8.43   | 91.50  |         |
|             | 30% diglyme    | 8.46   | 91.54  |         |
| 75%         | 21% O₂         | 5.75   | 94.25  |         |
|             | 22.5% O₂       | 8.43   | 91.41  |         |
|             | 24% O₂         | 9.12   | 90.21  |         |
|             | 30% diglyme    | 8.43   | 91.57  |         |
| 90%         | 21% O₂         | 11.49  | 88.51  |         |

Refer to Table 5-2

Figure 5-7. O/C on soot measured by XPS as a function of oxygen content in the exhaust gas and bulk cylinder gas temperature: (a) 30% load, (b) 30% load, (c) 75 and 90% loads, (d) 75 and 90% loads
Although the O/C in the engine is not high for the 30% diglyme conditions, the surface O content of the 30% diglyme soot is much higher than that of the 21% O₂ soot. Also, the 24% O₂ soot from 75% load contains a high amount of surface O compared to the 21% O₂ soot. However, since the 24% O₂ soot from 75% load includes more than 1% of metals, as evidenced in Table 5-2, it is difficult to determine how much O content of the 25% O₂ soot comes from surface oxygen functional groups. In order to investigate the effect of available oxygen in the exhaust on surface O content, the oxygen concentration in the exhaust was plotted against the surface O/C of soot for low and high loads as shown in Figures 5-7(a) and (c). As noted in the figures, there is no noticeable correlation between the exhaust oxygen concentration and the surface O/C for both the low and high loads. Even though it has the lowest oxygen concentration in the exhaust, the 90% load soot shows the highest O/C among the examined samples. The surface O/C of the soot samples is compared as a function of gas temperature in Figures 5-7(b) and (d). Figure 5-7(b) for 30% load shows that there is no indication that the temperature influences the surface O/C, which might not be observable at this narrow temperature range. However, Figure 5-7(d) shows a good correlation between soot surface O/C and gas temperature for high load. The 21% O₂ soot generated from the lowest bulk cylinder temperature contains the least O/C, and the 90% load soot shows the opposite result. From this result, the temperature in the engine seems to be the main factor affecting surface oxygen content of the soot from high load. However, there is an apparent contradiction in the soot characteristics that prevents generalizing this for the low and high loads, because the 21% O₂ soot at 30% load includes higher O/C than for 75% load. As discussed in the presentation of the heat release results, soot formation might be more dominant at 30% load, while soot oxidation might be more important at 75% load. Since the soot formation and soot oxidation processes from low and high loads are expected to produce different amounts of soot precursors, oxygen-related species, and soot oxidation environments, there should be
more factors taken into consideration for the comparison of the surface oxygen contents of soot from low and high loads.

Although surface O content of soot is shown to be a good indicator determining soot oxidative reactivity, it is difficult to judge its effectiveness for some soot samples in this work due to the metallic species present in and on samples. For the samples from 30% load, the 21% O₂ soot, the 24% O₂ soot and the 30% diglyme soot, which show similar soot oxidative reactivity, contain 7.87, 10.76 and 8.46 atomic % O content, respectively. If it is true that there are no metallic species present in and on these soot samples, the result of surface O content indicates that surface O content is not a proper indicator evaluating soot oxidative reactivity for these samples. However, the 21% O₂ soot and the 30% diglyme soot from 75% load, which contain 5.75 and 8.43 atomic % O content, respectively, display a reactivity difference. So, soot samples from low load and high load have contradictory results regarding the effect of surface O content on soot oxidative reactivity. Indeed, there is a possibility that the 30% diglyme soot from 75% load is also more oxidatively reactive due to the metallic species present, which were not detected by XPS. Song et al. also acknowledged that the residual impurity of potassium in biodiesel soot might act like an oxidation catalyst during soot oxidation, because biodiesel soot is significantly more reactive through a capsule-oxidation process than FT soot [60]. However, since its existence was not proved by EELS, they thought that more abundant surface oxygen functional groups in biodiesel soot is the primary factor leading to faster soot oxidation of biodiesel soot. Although the 30% diglyme soot from 75% load also shows similar aspects to those of biodiesel soot, it is still difficult to determine if surface O content is a key indicator influencing soot oxidative reactivity because of the contradictory results from low load and high load. As mentioned earlier, the combustion process in engines is too complicated to understand where oxygen functional groups are incorporated into soot for different loads. Accordingly, the role of surface O content in soot oxidation is an open question for diesel soot samples.
5.4.2.4 Surface oxygen functional groups by XPS

Carbonaceous materials have been widely used as catalysts and supports by surface modification through gas or liquid oxidation, where surface oxygen functional groups are increased \([115,116,125]\). As surface oxygen content of soot appears to increase with oxygen enrichment, especially for soot samples from high load, the impact of oxygen enrichment on surface oxygen functional groups on the soot was also investigated. Figure 5-8 shows the trends observed in the C1s and O1s peaks, irrespective of engine load. As summarized in Chapter 4, the assignment of surface oxygen groups is as follows: (1) ~286 eV is C-O groups in alcohol groups, (2) ~287 eV is C=O groups in quinone and/or carbonyl groups, (3) ~289 eV is O=C-O in carboxylic acid and ester groups, (4) 530 - 532 eV is C=O in quinone, carbonyl and/or carboxylic acid, (5) 531 - 534 eV is O=C in ester and anhydride and C-O in ether and/or alcohol, and (6) 532 - 535 eV is O-C in ester, anhydride and carboxylic acid. Figures 5-8(a) and (c) indicate that the peak (3) increases with the increase in the surface oxygen content. Figures 5-8(b) and (d) also show that the peak width becomes narrower as the surface oxygen content increases. Since the O1s peak becomes wider at the lower surface oxygen content, the ratio of the peak (6) to the peak (4) becomes larger with the increase in the surface O content. Since the C1s and O1s peaks of soot samples for high load are more obvious in their variation, the C1s peaks of the 75% load 21% O\(_2\) soot, the 75% load 24% O\(_2\) soot, the 30% diglyme soot and the 90% load soot were deconvoluted as shown in Figure 5-9, and the results is also indicated in Table 5-4. In comparison to the C1s peak of the 75% load 21% O\(_2\) soot, it is shown that the C1s peak of the 75% load 24% O\(_2\) soot shows slightly increases in (2) and (3), and a decrease in (1). And, the C1s peak of the 90% load soot displays a noticeable increase in all the peaks.
Figure 5-8. XPS peak patterns of C1s and O1s: (a) C1s for 30% load, (b) O1s for 30% load, (c) C1s for 75% and 90% loads, (d) O1s for 75 and 90% loads

Figure 5-9. Comparison of curve-fitted C1s for high load soot samples: (a) 21% O2 soot of 75% load, (b) 24% O2 soot of 75% load, (c) 90% load soot. (1) C-O in alcohol and/or ether groups, (2) C=O in quinone and/or carbonyl groups, (3) O=C-O in carboxylic acid, ester and/or carboxylic anhydride groups.
Table 5-4. Relative ratio of oxygen functional groups in curve-fitted C1s for high load soot samples: (1), (2) and (3) are oxygen functional groups from Figure 5-9

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(1)</td>
<td>(2)</td>
<td>(3)</td>
</tr>
<tr>
<td>75% load 21% O₂</td>
<td>18.25</td>
<td>8.10</td>
<td>5.92</td>
</tr>
<tr>
<td>75% load 24% O₂</td>
<td>17.72</td>
<td>8.34</td>
<td>6.30</td>
</tr>
<tr>
<td>90% load 21% O₂</td>
<td>28.41</td>
<td>11.12</td>
<td>7.86</td>
</tr>
</tbody>
</table>

Among those functional groups, the increase in alcohol groups is observed to be the most significant. In addition, the O1s peaks were qualitatively compared for the 21% O₂ soot and the 24% O₂ soot from 75% load, and the 90% load soot. As mentioned earlier, the 90% load soot which has more O content has a narrower O1s peak than that of the 75% load soot. According to the previous analogy used in Chapter 4, the decreasing trend in (4) may indicate that the contribution in (4) is mainly because of ester and carboxylic anhydride, not because of carboxylic acid, although some researchers assigned (4) to carboxylic acid. Since its increase is relatively small compared to (1) in the C1s peak, however, it seems to be more reasonable to identify (4) as carboxylic anhydride, ester and carboxylic acid. This presumption can be also supported by the present sample pretreatment method. Since soot samples were thermally pretreated at 500 °C, most of the carboxylic acid groups should be driven off. Since carboxylic anhydride groups will remain even at 600 °C, they could remain on the soot samples after thermal treatment.

In comparison to the O1s peaks of the other samples, the 24% O₂ soot from 75% load has a different peak pattern in the O1s peak as indicated in Figure 5-8(d), in which it has a wider peak. According to the C1s analyses, the 24% O₂ soot may have a similar peak pattern in O1s to that of the 21% O₂ soot. The reason may be found in the fact that this soot includes more than 1% of metals as indicated in Table 5-2. According to Dimitrov and Komatsu, P₂O₅, SiO₂, CaO, and ZnO have O1s binding energies in the range of 529.8 to 533.5 eV [164]. Since surface oxygen can exist as metal oxides and independent oxygen atoms adsorbed on metal surfaces as well as
oxygen in surface functional groups, a portion of the O1s may be associated with metal-related surface oxygen.

5.4.3 Crystalline Structure of Diesel Soot

5.4.3.1 XRD analysis

As evidenced by the bulk cylinder gas temperatures, intake oxygen enrichment significantly increases gas temperature at high load, although its effect is minor at low load. In general, the high temperature resulting from high load conditions is a major factor in producing more ordered soot particles [7,66]. In order to investigate the impact of oxygen enrichment on the crystalline structure of diesel soot, XRD patterns of soot samples were compared, as shown in 5-10(a). All the samples show a (002) peak at 27°, a (10) peak at 42° and a (110) peak at 77°, which are broad, as has been reported for disordered carbonaceous materials like soot and carbon blacks [11,165]. The soot samples from the 30% load conditions show no noticeable change in the XRD patterns with oxygen enrichment. However, there is a clear difference observed in the patterns of the samples from the high load condition. The (002) peak for the 24% O2 soot became sharp, but the 22.5% O2 soot has a similar pattern to that for the 21% O2. And, the 30% diglyme soot shows much reduced magnitudes in the (002) and (10) peaks compared to the other samples. The 90% load soot also has a similar pattern to that of the 21% O2 soot, despite much higher bulk cylinder gas temperature.
Figure 5-10. XRD patterns of soot samples for oxygen enrichment tests: (a) 30% load, (b) 75 and 90% loads.
Table 5-5. Crystallite sizes calculated from XRD patterns of soot samples

<table>
<thead>
<tr>
<th>Engine load</th>
<th>Condition</th>
<th>d_{002} (nm)</th>
<th>Lc (nm)</th>
<th>La (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>21% O₂</td>
<td>0.358</td>
<td>1.73</td>
<td>3.12</td>
</tr>
<tr>
<td></td>
<td>24% O₂</td>
<td>0.356</td>
<td>1.67</td>
<td>2.76</td>
</tr>
<tr>
<td></td>
<td>27% O₂</td>
<td>0.356</td>
<td>1.78</td>
<td>3.06</td>
</tr>
<tr>
<td></td>
<td>30% diglyme</td>
<td>0.358</td>
<td>1.63</td>
<td>2.93</td>
</tr>
<tr>
<td>75%</td>
<td>21% O₂</td>
<td>0.356</td>
<td>1.59</td>
<td>3.00</td>
</tr>
<tr>
<td></td>
<td>22.5% O₂</td>
<td>0.356</td>
<td>1.77</td>
<td>3.12</td>
</tr>
<tr>
<td></td>
<td>24% O₂</td>
<td>0.354</td>
<td>1.76</td>
<td>1.68</td>
</tr>
<tr>
<td></td>
<td>30% diglyme</td>
<td>0.355</td>
<td>1.67</td>
<td>1.87</td>
</tr>
<tr>
<td>90%</td>
<td>21% O₂</td>
<td>0.355</td>
<td>1.78</td>
<td>3.34</td>
</tr>
</tbody>
</table>

In order to better understand the crystalline structure of the soot samples, Lc and La were calculated as shown in Table 5-5. The interlayer spacing, d_{002}, and Lc show no obvious trends with engine load and oxygen enrichment. However, the 30% diglyme soot and the 24% O₂ soot from the high load have significantly reduced La. Since oxygen enrichment induces higher temperature than the 21% O₂ condition, higher temperature would be attributed to causing the reduced La. However, the 21% O₂ soot at 30% load has a similar crystallite size to the 21% O₂ soot at 75% load despite the large bulk cylinder gas temperature difference. According to Belenkov, high temperature favors an increased crystallite width due to the layer translation by higher activation energy [166]. Consequently, the temperature effect cannot explain the reduced crystallite width with oxygen enrichment at high load.

5.4.3.2 Raman analysis

Raman spectroscopy has been widely used to evaluate the soot crystalline structure. Using the parameters developed in this study, soot crystalline structure was evaluated. Figure 5-11 shows that D3 area (A_{D3}), A_{D1}/A_G and D1 FWHM for 30% load are similarly distributed for the samples. The A_{D1}/A_G varies in the range of 2.8 and 3.0, and the D1 FWHM varies in the range
of 175 and 180 cm⁻¹ with oxygen enrichment. In the case of soot for 75 and 90% loads, the $A_{D3}$ doesn’t vary significantly with oxygen enrichment, but the $A_{D1}/A_G$ and the D1 FWHM vary between 2.3 and 3.0 and between 145 and 180 cm⁻¹, respectively, with oxygen enrichment. Consistent with the other soot characterization results discussed in the previous sections, the variations of $A_{D1}/A_G$ and D1 FWHM also appear to be more significant for the soot samples from high load with oxygen enrichment. Figures 5-12(b) and (c) indicate that $A_{D1}/A_G$ increases with the increasing O/C, and D1 FWHM also shows a similar trend except for the 22.5% O₂ soot and the 30% diglyme soot. The Raman results are not completely consistent with the XRD results, because the 30% diglyme soot from 75% load shows a similar crystalline structure to the 21% O₂ soot from 75% load in terms of Raman parameters, in spite of smaller crystallite width of the 30% diglyme soot using XRD.

Figure 5-11. Raman analyses of soot samples with standard deviation for 30% load: (a) D3 band area ($A_{D3}$), (b) $A_{D1}/A_G$ (Area ratio), (c) D1 FWHM
Figure 5-12. Raman analyses of soot samples with standard deviation for 75 and 90% loads: (a) D3 band area ($A_{D3}$), (b) $A_{D1}/A_{G}$ (Area ratio), (c) D1 FWHM

Figure 5-13. D1 FWHM magnitudes of soot samples with standard deviation as a function of maximum bulk cylinder gas temperature
However, overall soot seems to become less ordered in the crystalline structure for 75% load with an increase in the O₂ concentration, whereas there is no noticeable effect on the order of the soot structure from 30% load with an increase in O₂ concentration. In general, there is a consensus that soot crystallites develop into more ordered structures as engine load increases because of increasing bulk cylinder gas temperature. In order to investigate the relationship between engine load and the order of the crystalline structure, D1 FWHM was plotted as a function of maximum bulk cylinder gas temperature in Figure 5-13. With the increase in the cylinder temperature, D1 FWHM tends to decrease for the soot samples from different loads at the same 21% O₂, although there is no clear correlation observed in the crystallite size by XRD. Therefore, the temperature effect on soot crystalline structure seems to be more apparent with the Raman analysis. In the same manner, Figure 5-13 also indicates that soot becomes less ordered with an increase in the temperature with increasing O₂ concentration for the same 75% load. Although higher bulk cylinder gas temperature contributes to increasing crystallite size, resulting in increasing the order of the crystalline structure, Figure 5-13 shows that high oxygen concentration at high engine load has an opposite effect on the crystalline structure. Therefore, although it was presumed that the increased heat release rate during the diffusion burn reflects the enhanced soot oxidation process with increasing O₂ concentration in the intake, the present result may indicate that the increased heat release rate is not relevant to the oxidation process, because the increased soot oxidation could induce soot to becoming more ordered.

It is also of interest whether soot particles are structurally influenced by the presence of metallic species. If most of metallic species are surface-bound as observed in the TEM-EDS of the 27% O₂ soot from 75% load, the effect of metallic species might be more important during the soot oxidation process than during the soot formation process. Although the amounts of metallic species and type of metallic species have different impacts on soot oxidation, Kim et al. observed that soot emissions decrease due to the enhanced soot oxidation, when iron pentacarbonyl was
added into isooctane diffusion flames [167]. If the oxidation process is also predominant in this work, primary soot particles experience shrinking in the size, which increases soot crystalline order. Accordingly, the reason soot became less ordered with increasing bulk cylinder gas temperature cannot be explained by the presence of metallic species deposited on soot particles. Consequently, the impact of metallic species on soot crystalline order was not considered in this aspect, and the role of oxygen concentration in the soot formation and soot oxidation processes will be discussed more in Chapter 6, with respect to soot crystalline order.

The difference in soot oxidative reactivity can be partly explained using the order of the crystalline structure. The 21% O\textsubscript{2} soot from 30% load, which is less ordered in the crystalline structure, is more oxidatively reactive than that from 75% load. Likewise, the small reactivity difference between the 21% O\textsubscript{2} soot and the 30% diglyme soot from 75% load would be attributed to the difference in crystallite width of the 21% O\textsubscript{2} soot. However, since this difference is not reflected in the Raman parameters, it is not obvious if the difference in crystallite width between two soots induces the reactivity difference, as observed in surface O content. According to Song et al., initial soot structure may not indicate oxidative reactivity differences [60]. If this is the same case for the 21% O\textsubscript{2} soot and the 30% diglyme soot as they observed, the investigation of soot crystalline structure during oxidation would show different patterns in soot crystalline structure. However, still there is a possibility that the 30% diglyme soot is more reactive than the 21% O\textsubscript{2} soot due to the presence of metallic species at concentrations below the detection limit.

### 5.4.4 Soot Oxidation Process

The soot samples containing metals were shown to be appreciably more reactive than the soot samples without metals. In order to investigate the effect of metals on the soot oxidation process, the 24% O\textsubscript{2} soot and the 30% diglyme soot for 75% load which showed similar
crystallite sizes and surface O content were examined. For this study, both soot samples were oxidized to 33 and 67 wt% oxidation and were studied using Raman spectroscopy and HR-TEM. Figure 5-14 displays the changes in the $A_{D_1}/A_G$ and D1 FWHM with the increase in the degree of oxidation. The $A_{D_1}/A_G$ values in both soot samples are shown to be invariant upon oxidation. Also, the D1 FWHM of the 24% $O_2$ soot decreases at the first stage of oxidation and it is observed to be constant at the later stage of oxidation. However, the 30% diglyme soot shows similar D1 FWHM during oxidation. Accordingly, soot oxidation may not affect significantly the crystalline structure of these soot samples. More ordered structure upon oxidation has been reported for many soot samples [11,60,92,111], because of the thermal annealing effect. Therefore, these soot samples from high load condition may have different crystalline characteristics during soot oxidation from other known soots. In addition, the HR-TEM images of the two soot samples were directly compared in Figure 5-15. Graphene layers in the centers of primary particles are observed to be less oriented, whereas outer graphene layers are more oriented and much longer in their length. Although it is not easy to find the differences in graphene layers during soot oxidation, Figure 5-15(c) clearly shows that the 24% $O_2$ soot has hollows inside the particles, while there is no hollowing for the 30% diglyme soot. Although the 24% $O_2$ soot was not investigated using TEM-EDS, it would be expected that most metallic species deposit on the outermost surface, such as for the 27% $O_2$ soot. If there is a small amount of metallic species inside primary soot particles, this raises a question of whether the metallic species can lead to capsule oxidation. These internal hollows are found in biodiesel soot [60], EGR soot [11] and soot oxidized in DPFs [168]. Since the inner structure in particles is less ordered than the outer structure, capsule oxidation is observed when inner pores are open to oxidizing gases during oxidation. Therefore, it is plausible that a small amount of metals inside particles induces the hollowing-out oxidation process, but also it is a possible scenario that the 24% $O_2$ soot, which is structurally disordered compared to the 30% diglyme soot, oxidizes
through an internal burning process, as Vander Wal et al. couldn’t find any internal hollows for printex U during oxidation [168].

Figure 5-14. Raman analyses of soot samples during soot oxidation: (a) $A_D/A_G$ (area ratio), (b) $D_1$ FWHM

Figure 5-14. Raman analyses of soot samples during soot oxidation: (a) $A_D/A_G$ (area ratio), (b) $D_1$ FWHM
Figure 5-15. HR-TEM images during soot oxidation
Chapter 6

EFFECT OF SOOT PROPERTIES ON SOOT OXIDATIVE REACTIVITY USING A DIFFUSION FLAME BURNER

The engine study showed that metallic species present in soot make it difficult to understand the effect of soot properties on soot oxidative reactivity. Also, the oxygen concentration in the intake air has a different impact on low load and high load, resulting in the different combustion processes. Accordingly, in order to reduce the complexity of the combustion process, a diffusion flame burner was employed to simulate a diesel engine. With various oxygen concentrations in the oxidizer stream and with dilution effect in the fuel stream, the combustion process was varied. And, its impact on soot maturity was evaluated with respect to soot oxidative reactivity.

6.1 Study on Oxidative Reactivity and Properties of Flame Soot

6.1.1 Soot Inception Time

Since the carbon flow rate affects the soot formation process [50], carbon flow rate was held constant throughout this study. The ratio of oxygen to carbon (O/C ratio) can be studied in two ways. One is to increase the oxidizer flow rate at constant O₂ concentration in the oxidizer stream, and the other is to increase O₂ concentration in the oxidizer stream at the same oxidizer flow rate. Figure 6-1 shows soot oxidative behavior with varying the oxidizer flow rate. When the O/C varies from 3.66 to 7.33 under the same O₂ concentration in the oxidizer stream, soot oxidative patterns are observed to be the same. The properties of these soot samples are not presented here, but this figure strongly indicates that oxidative characteristics are not influenced by the oxidizer flow rate under the same carbon flow rate. As generally accepted, adiabatic flame
temperature ($T_{ad}$) is constant at these conditions for the diffusion flame, where the ideal temperature is reached at the stoichiometric condition as indicated in Equation 6.1 for 21% O$_2$ in the oxidizer stream.

$$C_7H_{16} + eN_2 + 11O_2 + 41.38N_2 \rightarrow \text{products}$$  
\text{Equation 6.1}

where $eN_2$ represents premixed N$_2$ in the fuel stream as a carrier gas.

![Figure 6-1. TGA results of soot samples collected from different oxidizer flow rate under the same O$_2$ concentration in the oxidizer stream at 500 °C isothermal oxidation](image)

Although $T_{ad}$ is the same in diffusion flames regardless of gas flow rate under the same O$_2$ concentration, actual flame temperatures would be different with different N$_2$ absorption of thermal energy in the vicinity of the flame. Therefore, Figure 6-1 may reflect that soot properties generated at the present conditions are not sensitive enough to indicate soot oxidative differences.
The O/C ratio was also varied by increasing O\textsubscript{2} concentration in the oxidizer stream from 21 to 35\%, and its effect on soot oxidative reactivity was investigated in Figure 6-2(a).

![Graph showing TGA results of soot samples at 500 °C isothermal oxidation: (a) O\textsubscript{2} variation in the oxidizer stream, (b) Ar variation in the balance of the oxidizer stream.]

Figure 6-2. TGA results of soot samples at 500 °C isothermal oxidation: (a) O\textsubscript{2} variation in the oxidizer stream, (b) Ar variation in the balance of the oxidizer stream.
Although the variation in the oxidizer flow rate doesn’t affect soot oxidative reactivity, it is shown that soot becomes less reactive gradually with increasing the O/C ratio in the oxidizer stream. As indicated in Figure 6-2(a), adiabatic flame temperature also increases with the increase in the oxygen concentration. Therefore, soot oxidative reactivity seems to be inversely correlated with $T_{ad}$. Since $T_{ad}$ is also influenced by gas species involved in the reaction, $T_{ad}$ increases progressively by replacing N$_2$ in the oxidizer stream with Ar. As seen in Figure 6-2(b), soot becomes less reactive with Ar addition, which increases adiabatic flame temperature.

![Figure 6-3. TGA results of soot samples showing similar adiabatic flame temperatures at 500 °C isothermal oxidation](image)

Since 30% O$_2$ in the oxidizer in Figure 6-2(a) shows a similar adiabatic flame temperature to that of 100% Ar in the balance of the oxidizer in Figure 6-2(b), both oxidative patterns were compared to that of 21% O$_2$ in Figure 6-3. In spite of the similar flame temperatures, the 30% O$_2$ soot and the 100% Ar soot display a large difference in oxidative reactivity. This large difference
can be found in the physical and chemical properties of two soot samples formed during the different combustion processes. Although this diffusion burner was well controlled to obtain stable laminar flames, it is still challenging to understand the detailed soot formation and soot oxidation processes for the different test conditions. However, previous studies provide information that soot inception time becomes shorter and soot volume increases with increasing flame temperature due to the enhanced soot formation [32,33,51]. In addition, in coflow diffusion flames it is observed that the soot particle inception and subsequent coagulation, and growth are followed by oxidation [169]. Accordingly, it is shown that soot volume decreases with increasing O\textsubscript{2} concentration in the oxidizer beyond a certain level due to the enhanced soot oxidation [44,46]. Although soot volume was not measured during each test, apparent soot production was observed to reduce with increasing O\textsubscript{2} concentration in this work. Consequently, the decrease in soot oxidative reactivity with Ar replacement can be attributed to the increased soot formation process by thermal effect, and that with increasing O\textsubscript{2} concentration seems to be related to the soot formation and oxidation processes by thermal and chemical effects. However, two things should be noted in this presumption. Ar induces higher adiabatic flame temperature than N\textsubscript{2}, due to the smaller heat capacity of Ar, and subsequently soot oxidation can also be enhanced at higher flame temperature. In addition, the increased O\textsubscript{2} concentration may induce different soot formation pathways with more abundant radical species like O and OH, which also triggers a faster soot oxidation process. Therefore, the chemical effect in Figure 6-3 emphasizes the importance of the soot oxidation process, when comparing soot formation and soot oxidation.

As a way to influence soot formation, the carrier gas flow rate in the fuel stream was varied under the same oxidizer flow rate and O\textsubscript{2} concentration. As indicated in Figure 6-4, the adiabatic flame temperature is lowered by just 77 K with 10 times more carrier gas, since the portion of carrier gas in the fuel stream is still small in the overall reaction. Although the differences are shown to be not significant, the 80\% burn-off times are 213, 187 and 195 min for
A, B and C in Figure 6-4, respectively. As expected, sample B is more reactive than sample A due to the lowered adiabatic flame temperature.

![Graph showing TGA results](image)

Figure 6-4. TGA results of soot samples from the increased ratio of carrier gas to fuel in the fuel stream at 500 °C isothermal oxidation: flame temperature in (C) is increased by replacing a portion of N2 with Ar in the oxidizer stream

Subsequently, the reaction was adjusted to have a similar adiabatic flame temperature by replacing N2 with Ar in the oxidizer stream under the same ratio of the carrier gas to fuel. As evidenced in Figure 6-4, sample C is slightly less reactive than sample B with the increased adiabatic flame temperature, but still there exists a difference in soot oxidative reactivity between sample A and sample C. With the increase in the ratio of the carrier gas to fuel, there is a dilution effect as well as a thermal effect, both of which increase soot inception time and decrease the soot formation rate [51,52]. When the thermal effect is adjusted, it is still expected that the soot formation rate is reduced due to the dilution effect, because the flame location is slightly shifted to fuel side, where available fuel is reduced, resulting in the inhibition of fuel pyrolysis [52].
Consequently, Figure 6-4 also indicates that the soot formation process is a primary factor in controlling the soot oxidative reactivity.

In order to confirm this observation, ethylene soot from the same O/C ratio was further investigated. Since the carrier gas in the fuel stream affects the soot formation process, the same flow rate of N\textsubscript{2} was premixed with ethylene in the fuel stream as in the experiments with \textit{n}-heptane. As seen in Figure 6-5, ethylene soot is shown to be by far less reactive than \textit{n}-heptane soot. The adiabatic flame temperature of ethylene flame is higher by 97 K than that of \textit{n}-heptane flame, which may explain the reactivity difference observed. However, the \textit{n}-heptane soot whose flame temperature was corrected also shows that it is still more reactive than the ethylene soot.

Babushok and Tsang analyzed PAH production for \textit{n}-heptane using a kinetic model, and concluded that the main reactions determining the burning velocity of \textit{n}-heptane are similar to...
those determining the burning velocity of C1-C4 hydrocarbons [170]. Accordingly, they identified the major reaction routes of \( n \)-heptane and ethylene to form benzene which is a main precursor for soot inception, as shown in Figure 6-6. Although equivalence ratio, residence time and reaction temperature may lead to different reaction pathways, ethylene is a main product from \( n \)-heptane combustion. McEnally et al. also showed that \( n \)-heptane produces less soot than other heptane isomers, because \( n \)-heptane generates ethylene as a main product during combustion [171]. Likewise, it is often observed that soot production is higher with ethylene than with \( n \)-alkanes [172,173], because ethylene generates acetylene more easily, which is an important reactant in the HACA mechanism, without passing the pyrolysis step into ethylene from \( n \)-alkanes. Accordingly, these studies strongly support that soot inception time is closely related with benzene formation. Consequently, soot oxidative reactivity is well correlated with soot inception time in this study, because the earlier onset of soot formation can lead to maturing soot particles as Dobbins et al. showed [10]. There have been several papers discussing a thermal effect on soot oxidative reactivity. Al-Qurashi and Boehman showed that non-EGR soot is more reactive than EGR soot, where flame temperature is lowered with EGR condition due to the reduced oxygen concentration in the intake [11]. Since EGR condition is opposite to intake oxygen enrichment in terms of \( O_2 \) concentration in the oxidizer stream, soot inception time is expected to get longer with EGR condition. Also, Ruiz et al. observed that soot collected from lower reaction temperature is more reactive than from higher reaction temperature [68]. Likewise, lower reaction temperature induces lower flame temperature, resulting in longer soot inception time.
Figure 6-6. Major reaction pathways for (a) n-heptane, (b) ethylene [170]
Figure 6-5 also shows that soot obtained from a mixture of \( n \)-heptane and monoglyme (30% monoglyme fuel) is more reactive than \( n \)-heptane soot, although they have similar adiabatic flame temperatures. As observed, this result may reflect that the soot from 30% monoglyme fuel is more reactive because its inception time is longer than that of \( n \)-heptane soot. Indeed, when a mixture of 50 vol. % \( n \)-heptane and 50 vol. % monoglyme (50% monoglyme fuel) was burned in the diffusion flame burner, there was no soot observed. Although 50% monoglyme fuel contains ~15 wt % of oxygen in the fuel, oxygen in monoglyme would form CO during fuel pyrolysis, and CO would not decompose during further pyrolysis, which means that actual carbon numbers which can develop into soot precursors reduces. Therefore, fewer soot precursors are expected to form through fuel pyrolysis and benzene formation, as indicated in Figure 6-6. According to Hurt et al. [174], there is a threshold molecular weight for soot precursors to develop into soot particles at certain temperatures. Consequently, soot inception time can be delayed and those soot precursors which are late to develop into soot particles would be completely oxidized.

### 6.1.2 Soot Properties

Since soot oxidative reactivity is shown to be influenced by soot maturity, several soot samples were analyzed to correlate soot oxidative reactivity and soot properties.

#### 6.1.2.1 Oxygen content and oxygen functional groups

The effect of O content on soot oxidative reactivity is given in Figure 6-7. Sample A and sample C showing no reactivity difference have almost the same O content, and O content shows a decreasing trend as soot becomes less reactive. This is consistent with the previous result in Chapter 4 and other studies indicating a good agreement between carbon oxidative reactivity and O content [12,13,129]. However, it should be noted that there is ~10% error in the instrument measurement. Then, the O content of sample D is in the same range of those of A and C.
Figure 6-7. XPS results of flame soot samples: (a) surface O content, (b) C1s, (c) O1s
However, these results still reflect that more ordered soot has less O content, due to the reduced availability of active sites [175]. In the case of engine soot, O content was not in good agreement with soot oxidative reactivity, but it seems that O content can be used as an indirect index in determining active sites for the soot samples from the diffusion flames.

C1s and O1s are also shown in Figures 6-7(b) and (c) to examine surface oxygen functional groups. For a clear comparison, the C1s and O1s peaks were deconvoluted for three selected samples and the results are shown in Table 6-1. The assignment of C1s and O1s peaks was referred to Chapters 4 and 5 as follows; (1) ~286 eV is C-O groups in alcohol groups, (2) ~287 eV is C=O groups in quinone and/or carbonyl groups, (3) ~289 eV is O=C-O in carboxylic acid and ester groups, (4) 530 - 532 eV is C=O in quinone, carbonyl and/or carboxylic acid, (5) 531 - 534 eV is O=C in ester and anhydride and C=O in ether and/or alcohol, and (6) 532 - 535 eV is O-C in ester, anhydride and carboxylic acid.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Percentage (%)</th>
<th>C1s</th>
<th>O1s</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(1)</td>
<td>(2)</td>
</tr>
<tr>
<td>n-heptane 21% O2 soot</td>
<td>18.54</td>
<td>8.82</td>
<td>7.97</td>
</tr>
<tr>
<td>n-heptane 35% O2 soot</td>
<td>15.68</td>
<td>7.22</td>
<td>6.26</td>
</tr>
<tr>
<td>ethylene soot</td>
<td>16.26</td>
<td>6.16</td>
<td>6.04</td>
</tr>
</tbody>
</table>

As presumed in Figures 6-7(b) and (c), Table 6-1 indicates that the differences in oxygen functional groups are not appreciable among these soot samples. The n-heptane 21% O2 soot contains obviously more oxygen functional groups for (1), (2) and (3), and the n-heptane 35% O2 soot and the ethylene soot have similar amounts of oxygen functional groups. Although the difference between n-heptane 35% O2 soot and ethylene soot is not clear, there is a similarity observed for the trends between engine soot and flame soot; with increasing percentage in (1), (2)
and (3), there is a decrease in (4). Since (4) is related to (2) due to C=O groups, it may indicate that the small value in (4) is due to the limited contribution of carboxylic acid groups to (4). Accordingly, it is speculated that these soot samples have small amounts of carboxylic acid as indicated in the diesel soot samples.

6.1.2.2 Active surface area (ASA)

Oxygen content can be an indirect index in determining available active sites in soot, but the direct measurement of active sites is achieved with measurement of the active surface area (ASA). For this study, ASA converted from the amount of oxygen adsorbed on soot is used to measure active sites [133]. According to the result of some soot samples shown in Table 6-2, sample A has almost 5 times more active sites available than sample B. Again, these values are plotted against 1/t_{50\%} in Figure 6-8.

<table>
<thead>
<tr>
<th>Table 6-2. Active surface area according to adsorbed O(_2) amounts for several soot samples</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel</strong></td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>n-heptane</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>ethylene</td>
</tr>
</tbody>
</table>

ASA shows a good agreement with soot oxidative reactivity, although they are not in a linear relationship. In particular, sample B containing the smallest O content among the examined samples has the smallest ASA, resulting in retarded oxidation. As discussed in the previous section, this soot might be more severely oxidized during the soot oxidation process in the flame.
than the other soot samples, so there would be enough heat treatment to realign soot crystalline structure, leading to reducing active sites. In order to examine this assumption, soot crystalline order was investigated as described in the next section.

Figure 6-8. Active surface area against soot oxidative reactivity: A, B, C, D and E are soot samples as shown in Table 6-2

6.1.2.3 Soot crystalline structure

First, XRD patterns were compared for some of the soot samples. As shown in Figure 6-9(a), all the samples show disordered carbon patterns with broad (002), (10) and (110) peaks. In comparison to the other samples, sample B has a unique XRD pattern with much smaller intensities for (002), (10) and (110) peaks. Since these low intensities can be regarded as characteristics of amorphous carbon, some readers may argue that this sample has less ordered structure than the other samples. However, the present TGA, XPS and ASA results indicate that it would be more ordered in its crystalline structure.
Figure 6-9. XRD results of flame soot samples: (a) XRD patterns, (b) crystallite size against soot oxidative reactivity.
According to Burket et al. [176], carbon can have a significantly broad pattern, since a closed pore structure exists in the carbon crystalline structure. Indeed, although this soot is not available for the measurement of density due to the limited amount of sample, its apparent volume is almost one quarter of those of the other soot samples. In order to better understand the crystalline structures of these samples, crystallite size was calculated and plotted against soot oxidative reactivity in Figure 6-9(b). Crystallite height shows a good agreement with the reactivity, but crystallite width is not well-correlated with the reactivity. Regarding the poor correlation between La and soot oxidative reactivity, the difficulty in obtaining La should be noted. In general, the background under the (10) peak is manually determined in order to calculate FWHM for the (10) peak. Due to the characteristic long tail of the (10) peak, it is highly susceptible to drawing the wrong background for each peak, which may lead to an incorrect evaluation of La. In particular, the (10) peak of sample B is not noticeable, so the computed FWHM for (10) peak can be misleading. As noted in Chapter 4, the poor correlation between crystalline structure and La has been already noted for disordered carbonaceous materials like activated carbon and carbon black by many researchers [75,104,105]. Since they also have similar broad peak patterns for (10) peak, a misleading result might occur during the calculation of La as observed in this study.

The crystalline structures of the three soot samples, which are obviously distinct in their soot oxidative reactivities, were further investigated using Raman spectroscopy, EELS and NEXAFS. As Raman parameters, D3 area ($A_{D3}$), area ratio of D1 to G ($A_{D1}/A_G$) and D1 FWHM are compared in Figure 6-10. For all three parameters, sample B is shown to have the lowest values, which indicates that sample B has the least amorphous carbon content, density of edge sites and distribution of crystallite sizes among the samples. Accordingly, these results support the measured Lc from XRD and the conclusion that sample B is the most ordered in its crystalline structure despite its unusual XRD pattern.
Figure 6-10. Comparison of Raman parameters: (a) D3 band area ($A_{D3}$), (b) area ratio of D1 to G ($A_{D1}/A_G$), (c) D1 FWHM.
However, sample A and sample C show unclear results for amorphous carbon and the density of edge sites. In the case of amorphous carbon, they have similar values, so it is difficult to evaluate if this portion of the soot influences soot oxidative reactivity for both samples. When it comes to the density of edge sites, these samples are in the same range, given the standard deviation in the results. With regard to ASA, which is equivalent to the density of edge sites, sample A is observed to have a higher number of active sites than sample C. Although the difference of $A_{D1}/A_G$ for both samples is not statistically significant, the ASA result seems to support that sample A has more abundant active sites than sample C, as indicated in the mean values of $A_{D1}/A_G$. This assumption can be also supported by the D1 FWHM result as shown in Figure 6-10(c), representing that the distribution of crystallite size in sample A is wider than that in sample C. It is plausible that the distribution becomes narrower with the realignment of crystallites, due to increased soot maturity. Correspondingly, sample B with the narrowest distribution would have more chances to be realigned structurally due to the increased soot maturity by early soot formation and significant soot oxidation. Consequently, these Raman analyses also confirm that the oxidative reactivity of flame soot is related to the crystalline order.

### 6.1.2.4 HR-TEM images and π/σ investigation

The three samples in Figure 6-10 were also investigated via HR-TEM. The nanostructures of these samples show that their primary soot particles are aggregated, and their diameters are observed to range from 10 to 30 nm. As noted by many researchers, mature soot has discernible long graphene layers that are parallel to each other and which surround a less ordered core, as seen in Figure 6-11 [5,21,62]. As Vander Wal and Tomasek observed, soot nanostructure is seen as a mixture of amorphous carbon, curved structures and graphitic structures depending upon soot production conditions [5].
Figure 6-11. HR-TEM images of flame soot samples: (a) \(n\)-heptane, \(O_2\) in oxidizer = 21%, (b) \(n\)-heptane, \(O_2\) in oxidizer = 35%, (c) ethylene, \(O_2\) in oxidizer = 21%
The nanostructures of these flame soot particles exist as the mixtures of curved and graphitic structures. Although these nanostructures were compared in terms of fringe length using TEM image analyses, they are shown to be similar. It is possibly because these soot particles may not be representative of the entire population of soot particles. Accordingly, EELS was employed for several primary particles in order to determine the relative ratio of $\pi/\sigma$, because $\pi/\sigma$ ratio in C=C provides relative ratio of sp$^3$/sp$^2$ in the soot crystalline structure. As noted in Figure 6-12(d), the average value is larger in the order of sample C, sample A and sample B. Especially, sample C is shown to have smaller $I_\pi/I_\sigma$ than that of sample A, which means that sample C is structurally less ordered than sample A, which is inconsistent with results from other instruments. However, the differences are not statistically significant. Since the EELS spectra were obtained for randomly chosen 5~6 particles without any pre-evaluation of the particles, they may not represent all the particles. To prove this presumption, sample (A) and sample (C) were further examined using NEXAFS in Figure 6-12(e), because NEXAFS also provides the same carbon K-edge structural information. As Braun observed [66], NEXAFS spectra have several characteristic peaks. There are two sharp peaks appearing at 285 and 288 eV and a broad peak showing a maximum value at 293 eV. The peak at 285 eV is associated with the $1s \rightarrow \pi^*$ transition of sp$^2$ bonded carbon, and the broad peak at 293 eV is attributed to the $1s \rightarrow \sigma^*$ transition [66,107]. To quantify the crystalline order of soot, the relative intensity of 285 eV peak to 293 eV peak was calculated in Figure 6-12(e), as done by di Stasio and Braun [107]. Unlike the EELS result, sample A is shown to have a smaller ratio than sample C, which reflects that n-heptane soot is less ordered in the crystalline structure than the ethylene soot. Despite their contradictory results, NEXAFS seems to be more representative than EELS in this study, because the NEXAFS result is based upon a larger population of soot particles.
Figure 6-12. Comparison of STEM images, EELS analyses selected at their corresponding images and EXAFS analyses: (a) n-heptane, O₂ = 21%, (b) n-heptane, O₂ = 35%, (c) ethylene, O₂ = 21%, (d) EELS results, (e) NEXAFS results.
In addition, the 288 eV peak is known to be related to carboxylic acid, but the whole peak from 286 to 289 eV is assigned to various oxygen functional groups such as alcohol, ketone, carbonyl and carboxylic acid. Moreover, there is a shoulder next to the peak at 285 eV, which corresponds to quinones. Although these peaks cannot be quantified, the \textit{n}-heptane soot and the ethylene soot have similar peak patterns with respect to oxygen functional groups, at which \textit{n}-heptane soot has slightly higher peak intensity. The similarity in peak patterns was also observed for XPS as evidenced by Figure 6-7. Although there has been no study to compare XPS and NEXAFS analyses for soot, NEXAFS seems to provide consistent results to those of XPS for oxygen functional groups.

6.1.2.5 Difference in the crystalline structure between diesel soot and flame soot

It is worthwhile to discuss the difference in the crystalline structure between diesel soot and flame soot with increased oxygen concentration. It is speculated that diesel soot, which experienced partially premixed combustion and diffusion combustion during the engine operation, may have different characteristics from those of flame soot obtained from diffusion combustion, for example, in the relation between O content and soot crystalline structure. In particular, the present study shows that they have opposite trends in the crystalline structure with the variation in the oxygen concentration. Since it is more difficult to understand why engine soot becomes less ordered in the crystalline structure with increasing \(O_2\) concentration at high load, the result of flame soot seems to provide important information to understand this trend. The study of flame soot clearly shows that soot crystalline structure is closely related to the soot maturity from the soot formation and soot oxidation processes. When \(O_2\) concentration in the oxidizer stream increases, not only does the soot inception time become shorter, but also the soot oxidation rate is enhanced. Therefore, if this is equally applied to diesel combustion, the same result is expected for diesel soot. In this light, intake oxygen enrichment may provide different
oxidizing environments for diesel soot during the combustion process from those for flame soot. As observed, transparent precursor particles develop into opaque soot particles by the carbonization process with the growth of polycyclic aromatic hydrocarbons (PAHs) [174,177]. As mentioned earlier, there is a threshold molecular weight influencing a spontaneous disorder/order transition in soot formation [174]. Furthermore, Dobbins et al. noted that since combustion time is too short in engines, precursors would be unlikely to convert into carbonaceous soot depending upon the combustion temperature during the typical time of the combustion process and soot can be oxidized within the cylinder or possibly within the exhaust system under lean conditions [177]. Accordingly, it is plausible that soot precursors produced from 75% load may be oxidized by the abundant amounts of oxidizing gases at higher temperature with increased oxygen, which seems to limit the mass growth of soot precursors, resulting in delaying soot inception time. If this is true, the increased heat release rate with increasing O₂ concentration at high load is not because of the enhanced soot oxidation, but because of the enhanced soot precursor oxidation, which explains why soot particles become less ordered with increasing bulk cylinder gas temperature. In the case of precursors from 30% load, however, there are plenty of soot precursors available to be carbonized without oxidation with increased oxygen, but the combustion temperature is not high enough for soot precursors to develop into soot particles, or to mature incepted soot particles during a short period of time. In the case of fuel oxygenation, the actual numbers of carbon which can participate in the soot formation process would be reduced during engine operation, if the fuel flow rate had been fixed as carried out in the diffusion flame burner. However, since the heating value of 30% diglyme fuel was smaller than that of diesel fuel, the consumption rate of 30% diglyme fuel was larger than that of diesel fuel to produce the same power during engine operation, as indicated in Table B-1 of Appendix B. Therefore, the effect of diglyme in the fuel mixture is relatively negligible as observed in Chapter 5. The reason why diffusion flame soot becomes less ordered with increasing
oxygen concentration, which is opposite to diesel soot, is found in the fact that the diffusion flame burner was operated without premixed combustion under sooting conditions with longer combustion time, where there are enough precursors generated beyond the mass threshold for the carbonization process. In conclusion, soot maturity, influenced by soot inception time and soot oxidation, is a key factor impacting soot crystalline structure, when precursor particles reach a certain point of mass in order to be carbonized.

6.2 Changes in Soot Properties during Oxidation

6.2.1 Soot Crystalline Structure

As shown in Figure 6-13, both crystallite height and width increase gradually during oxidation. The stack height of the initial sample is 1.37 nm and that of 90% oxidized soot is 1.85 nm, while the crystallite width of the initial sample is 2.15 nm and that of 90% oxidized soot is 3.45 nm.

Figure 6-13. Variation in crystallite size of flame soot during oxidation
Both crystallite height and crystallite width increase during oxidation, but the increase in crystallite width is more noticeable than that in crystallite height. This trend indicates that small crystallites grow progressively during oxidation, by re-linking of small units [178]. Hence, the oxidation process at 550 °C seems to provide equivalence to an annealing condition for soot, like heat treatment at higher temperature. Consequently, despite the limitation of XRD to represent soot oxidative reactivity in the present study, it appears to be useful to measure structural variation during oxidation of the flame soot.

In order to investigate Raman parameters for the oxidized soot samples, the height and area in the D3 band (I_{D3} and A_{D3}) using 3L1G and 4L1G fitting methods, the area ratio of D1 to G (A_{D1}/A_G) and D1 FWHM using the 3L1G fitting method were chosen. In addition, the height and area ratios of D3 to (G+D3) (I_{D3}/I_{G+D3} and A_{D3}/A_{G+D3}) from 3L1G and those of D3 to (G+D2+D3) (I_{D3}/I_{G+D2+D3} and A_{D3}/A_{G+D2+D3}) from 4L1G were extensively investigated. Ivleva and coworkers [91,92,111] found A_{D3}/A_{G+D2+D3} to be a good parameter to indicate the abundance of amorphous carbon. In Figure 6-14(a), the D3 height from 3L1G fitting decreases gradually from 0.30 to 0.21 during oxidation, as observed in XRD. This decreasing trend is also found for the D3 area from 49.8 to 31.9, with standard deviation of around 3-4%, showing that the reproducibility at different positions is quite good. In comparison, I_{D3}/I_{G+D3} and A_{D3}/A_{G+D3} from 3L1G also exhibit decreasing trends during oxidation (Figure 6-14(b)). The same trends are found for 4L1G fitting in Figures 6-14(c) and (d). As Knauer et al. found that GfG soot (spark discharged model soot) and EURO IV soot (heavy duty diesel engine soot) decrease in their amorphous carbon structure during oxidation [111], A_{D3}/A_{G+D2+D3} from 4L1G fitting seems to be pretty informative regarding the amount of amorphous carbon. As observed, however, this value is much influenced by the D3 band itself. Therefore, I_{D3}/I_{G+D3} and A_{D3}/A_{G+D3} from 3L1G fitting seem to be sufficient in characterizing amorphous carbon, instead of using A_{D3}/A_{G+D2+D3} from more complicated 4L1G fitting.
Figure 6-14. Variations in Raman parameters of diffusion soot during oxidation: (a) height and area in D3 band (I_{D3} and A_{D3}) from 3L1G fitting, (b) height and area ratios of D3 to (G+D3) (I_{D3}/I_{G+D3} and A_{D3}/A_{G+D3}) from 3L1G fitting, (c) height and area in D3 band (I_{D3} and A_{D3}) from 4L1G fitting, (d) height and area ratios of D3 to (G+D2+D3) (I_{D3}/I_{G+D2+D3} and A_{D3}/A_{G+D2+D3}) from 4L1G fitting.
Area ratio of D1 to G ($A_{D1}/A_G$) and D1 FWHM from 3L1G fitting are also plotted in Figure 6-15. $A_{D1}/A_G$ also shows a decreasing trend from 3.68 to 2.75 with standard deviations of 0.14 and 0.06, respectively, when the soot is oxidized from 0 to 90%. However, the difference between 33 and 67% oxidation is not clearly observed by this parameter. And, D1 FWHM decreases gradually from 198 to 171 cm$^{-1}$ with ~2.5 cm$^{-1}$ standard deviation. Accordingly, these results for $A_{D1}/A_G$ and D1 FWHM may indicate that during oxidation, the distribution of crystallite size becomes narrower at the expense of small crystallites, resulting in reducing the density of edge sites.

Figure 6-15. Variations in Raman parameters of diffusion soot during oxidation: (a) area ratio of D1 to G ($A_{D1}/A_G$) from 3L1G fitting, (b) D1 FWHM from 3L1G fitting
6.2.2 Surface O content and Oxygen Functional Groups

The soot oxidation process has been extensively studied in order to understand how carbon is oxidized by the reaction with oxidizing gas [11,60,93,111]. As mentioned earlier, Raman spectroscopy and XRD clearly display that soot becomes more ordered upon oxidation, by relinking small crystallites through heat treatment. Since the behavior of surface functional groups is not clearly understood during soot oxidation, surface O content and oxygen functional groups were further studied using XPS. As shown in Figure 6-16(a), O content is observed to increase during oxidation from 0 to 33%, and O content remains steady during the rest of the oxidation process. This result is different from the previous study by Song et al. using EELS, where O content decreases as the oxidation proceeds [60]. As they acknowledged, their initial soot is as-received engine soot directly sampled from an engine, so it is highly possible that it has a higher O content than the thermally pretreated soot due to volatile organic fraction (VOF) that remained in the soot. In addition, the measurement of O content by EELS might be subjective to the particle selected, because soot particles are inhomogeneously aggregated. Another reason can be found in the fact that the engine soot experiences a different oxidation process from the flame soot. However, it is still useful to study flame soot during oxidation, because it can provide valuable insights on the soot oxidation process.

C1s and O1s spectra by high resolution XPS scan show clear variations as soot oxidation proceeds in Figures 6-16(a) and (b). The peak appearing at 284.6 eV becomes wider upon oxidation, because the graphitic structure oxidizes gradually. Although the peak at 289 eV corresponding to ester, carboxylic anhydride and carboxylic acid doesn't vary noticeably during oxidation, other peaks at 285.5 and 287 eV seem to increase as other oxygen functional groups are generated. In order to have a better understanding, the C1s and O1s peaks were further deconvoluted to quantify each peak as shown in Figures 6-17 and 6-18.
Figure 6-16. Comparison of XPS peaks during soot oxidation: (a) C1s, (b) O1s
Figure 6-17. Comparison of curve-fitted C1s at different oxidized stages: (a) 0% oxidation, (b) 33% oxidation, (c) 67% oxidation, (d) 90% oxidation. (1) C-O in alcohol and/or ether groups, (2) C=O in quinone and/or carbonyl groups, (3) O=C-O in carboxylic acid, ester and/or carboxylic anhydride groups

Figure 6-18. Comparison of curve-fitted O1s at different oxidized stages: (a) 0% oxidation, (b) 33% oxidation, (c) 67% oxidation, (d) 90% oxidation. (4) 530~532 eV is C=O in quinone, carbonyl and/or carboxylic acid, (5) 531~534 eV is O=C in ester and anhydride and C-O in ether and/or alcohol, (6) 532~535 eV is O-C in ester, anhydride and carboxylic acid
Table 6-3. Relative ratio of oxygen functional groups in curve-fitted C1s and O1s: (1), (2), (3), (4), (5) and (6) are oxygen functional groups as shown in Figures 6-17 and 6-18

<table>
<thead>
<tr>
<th>Oxidation (%)</th>
<th>Percentage (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oxidation (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>O1s</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>18.54</td>
<td>8.82</td>
<td>7.97</td>
<td>5.92</td>
<td>40.83</td>
<td>53.25</td>
</tr>
<tr>
<td>33</td>
<td>13.53</td>
<td>11.56</td>
<td>9.53</td>
<td>20.97</td>
<td>27.02</td>
<td>52.01</td>
</tr>
<tr>
<td>67</td>
<td>13.75</td>
<td>12.53</td>
<td>9.53</td>
<td>22.58</td>
<td>25.86</td>
<td>51.56</td>
</tr>
<tr>
<td>90</td>
<td>10.53</td>
<td>13.37</td>
<td>9.65</td>
<td>31.06</td>
<td>19.64</td>
<td>49.30</td>
</tr>
</tbody>
</table>

Each peak is also assigned as follows: (1) ~286 eV is C-O groups in alcohol groups, (2) ~287 eV is C=O groups in quinone and/or carbonyl groups, (3) ~289 eV is O=C-O in carboxylic acid and ester groups, (4) 530–532 eV is C=O in quinone, carbonyl and/or carboxylic acid, (5) 531–534 eV is O=C in ester and anhydride and C-O in ether and/or alcohol, and (6) 532–535 eV is O-C in ester, anhydride and carboxylic acid. The difference between 33% oxidized soot and 67% oxidized soot is not noticeable, but Table 6-3 clearly shows that upon oxidation, (1) and (4) increase gradually, while (2), (3), (5) and (6) decrease. Accordingly, it seems to be obvious that during oxidation, the amounts of C=O groups increase and those of C-O groups decrease. Unlike other soot samples, it is also noticeable that with increasing surface O content, (4) increases. Interestingly, these trends in the amounts of oxygen functional groups are consistent with those observed for acidified soot samples in Chapter 4. In an analogous manner, this result indicates that the contribution of carboxylic acid in (3) and (4) becomes larger. Since C-O groups in (1), and ester and carboxylic anhydride in (3) reduce in soot during oxidation, it is speculated that (5) also reduces on a percentage basis. In conclusion, the final results can be extracted from the XPS analyses upon oxidation: carboxylic acid, quinone and/or carbonyl groups increase, while ether, alcohol, ester and/or anhydride groups decrease as soot oxidation proceeds. Although electrochemical oxidation by liquid solution is not equivalent to the oxidation by oxidizing gas, soot oxidation by oxidizing gas seems to be the same as that by acidification as noted in Chapter.
4, which is a series of reactions from C=C to −COOH via −C−O and −C=O. Although the present result shows the variation in surface oxygen functional groups during oxidation, it is not clear whether COOH groups are the final step to generate CO and CO$_2$, or CO and CO$_2$ are also produced from other functional groups. According to van Setten et al. [15], CO can be desorbed from semiquinone complex. Also, Radovic showed from density functional theory (DFT) that carbon-oxygen surface complexes such as epoxide type are crucial for desorption of CO$_2$ [95]. Accordingly, COOH groups don’t seem to be the last oxygen functional groups to form CO and CO$_2$. Since XPS may not show various unstable carbon-oxygen surface complexes before desorption of CO and CO$_2$, it is understood that the relative ratios of −C−O, −C=O and −COOH groups during oxidation show the abundance of stable oxygen functional groups observed at certain oxidation stages. In addition, as far as soot crystalline structure is concerned, this result may indicate that less ordered soot structure is preferentially oxidized into oxygen functional groups during oxidation, as observed in Figures 6-14 and 6-15. Since amorphous carbon is removed by oxidation and small crystallites re-link with other small crystallites during the oxidation process, it is plausible that soot crystalline structure becomes more ordered as oxidation proceeds.
Chapter 7

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

7.1 Conclusions

The present study deals with the effect of oxygen enrichment on the physical and chemical properties of soot and on soot oxidative reactivity. In particular, the crystalline structure, surface O content and oxygen functional groups of various soot samples were studied. In order to evaluate the crystalline structure of soot, Raman parameters were investigated and compared with soot oxidative reactivity. XRD, EELS and NEXAFS were also carried out to support the Raman results. XPS was used to provide compositional information of soot such as O and metallic species, which were also characterized by SEM-EDS. In addition, TPD-MS was employed to assign the specific types of surface oxygen functional groups on the soot samples and compared with XPS results. Accordingly, XPS was used to examine surface oxygen functional groups in soot at various oxygen concentrations and it was expanded to study the variation in functional groups during oxidation. Finally, these engine soot and flame soot studies lead to the following conclusions.

- Study on Engine Soot
  1. Intake oxygen enrichment induces higher heat release rate with the increase in the oxygen concentration in the engine, resulting in higher cylinder temperature at high load, although its effect on cylinder temperature is not appreciable at low load.
2. Increased oxygen concentration by intake oxygen enrichment leads to increased vaporization of lubricating oil at high cylinder temperature, resulting in incorporation of metals into soot particles. Correspondingly, a major contribution to soot oxidative reactivity is from metallic species present in and on soot samples, which are from lubricating oil, although the reduced soot crystalline order may also contribute to the reactivity.

3. XRD and Raman results show that soot becomes less ordered in its crystalline structure with intake oxygen enrichment only at high load. Accordingly, it is presumed that soot precursors are oxidized at high temperature with abundant oxidizing species, which limits the spontaneous carbonization process from soot precursors to ordered soot particles.

- Study on Flame Soot

1. Soot oxidative reactivity is inversely correlated with soot inception time. In addition, increasing oxygen concentration in the oxidizer stream enhances the soot oxidation process, which further reduces soot oxidative reactivity. Consequently, soot oxidative reactivity is found to decrease by increasing oxygen concentration in the oxidizer stream, reducing diluted inert gas in the fuel stream and increasing flame temperature.

2. Soot derived from an oxygenated fuel (a mixture of \( n \)-heptane and monoglyme) is more reactive than \( n \)-heptane soot, although adiabatic flame temperatures are similar for both fuels, which is attributed to the differences in soot inception time due to the decreased soot precursors. Consequently, this result experimentally proves that there is a threshold molecular weight for precursor particles to develop into soot particles suggested by Hurt et al. [176].

3. The degree of soot crystalline order is observed to be inversely related with soot oxidative reactivity due to the decreased active sites. In addition, surface oxygen content is proportional to soot oxidative reactivity. Therefore, it can be used as an indirect indicator representing the degree of soot crystalline order.
4. The main oxygen functional groups present on the initial soot samples are C-O groups corresponding to alcohol, ester and anhydride groups. Upon oxidation, the portion of C=O groups in quinone and carbonyl groups, and COOH groups increases.

5. Soot oxidative reactivity is shown to be not influenced by specific types of oxygen functional groups.

7.2 Recommendations for Future Work

From the present study, there are several tasks recommended to go beyond the limitations in this work.

1. Study on the effect of additive-free lubricating oil in engine operation on soot properties

   The present work showed that lubricating oil is highly vaporized at high temperature with high oxygen concentration in the intake of engines. Accordingly, it is recommended to run the engine with additive-free lubricating oil at high oxygen concentration in the intake air. This study will clearly show the effect of soot properties on soot oxidative reactivity with intake oxygen enrichment.

2. Study on surface oxygen functional groups and crystalline structure in soot using NEXAFS

   XPS has often been coupled with TPD to study oxygen functional groups. As observed in this study, however, XPS result is not consistent with TPD results because XPS is more sensitive to the outermost surface of sample. And, the assignment of surface oxygen functional groups is subject to fitting methods, so incorrect conclusions can be extracted from XPS analysis without supporting instruments. NEXAFS, which is also surface-sensitive, provides similar information about C and O K-edge structures as XPS does. Therefore, a coupled study using two instruments can give clear answers about surface oxygen functional groups in soot. Furthermore, since C and O K-edge structures can be studied using NEXAFS, it has the same capability as
EELS. Since EELS is subjective to particles, many particles should be analyzed to have representative data. When the time to master EELS and to analyze particles using the instrument is considered, NEXAFS is much more efficient than EELS and the former provides more distinct spectra than the latter. Consequently, the more emphasis should be focused on NEXAFS for the future work.

3. Instrumental analyses

In the present work, there were many instruments employed to characterize soot properties. In the case of diesel soot, metallic species present in soot samples are a predominant factor affecting soot oxidative reactivity. Therefore, when soot is shown to be significantly more reactive than other samples, SEM should be used to investigate whether the sample contains metallic species. For soot crystalline structure, Raman spectroscopy is observed to be informative as other studies have shown. In addition, XPS analysis provides surface O content and surface oxygen functional groups. As recommended in 2, NEXAFS is a promising instrument, because it can detect sp\(^2\), sp\(^3\) and oxygen functional groups. Accordingly, NEXAFS can be a supplemental technique to Raman spectroscopy and XPS.

4. Study on the retarded fuel injection timing

The control of fuel injection timing has been studied to reduce NOx and soot simultaneously. In particular, the retarded fuel injection timing is shown to reduce cylinder temperature, which delays the soot formation process. Accordingly, soot generated from this condition may become more reactive due to the less ordered structure. Although other factors such as fuel consumption rate, total NOx and soot emissions should be considered in such a study, the retarded fuel injection timing seems to be a promising strategy at reducing soot emissions, when DPF systems are applied.
5. Improvement of diffusion flame burner to combust high boiling point fuels

The current diffusion flame burner has a limited capability in burning fuels and is limited to fuels, whose boiling point is below 140 °C. Accordingly, some high boiling point fuels such as oxygenated fuels cannot be used in this study. If high boiling point fuels can be used in this study, fuels having various oxygen functional groups can be directly burned. Then, the study on functional groups in soot can provide valuable information as to whether specific oxygen functional groups in fuels survive during the combustion process and remain in the soot itself. From this study, the surviving oxygen functional groups in soot can be more clearly understood with respect to the fuel pyrolysis process.

6. H content measurement using pyrolysis GC/MS for a small amount of soot sample

When the amount of soot is more than 50 mg, a CHNO analyzer can be used to measure O and H content of soot. However, since soot collection from diesel engines is difficult, the CHNO analyzer couldn’t be used in this work. Although O content of soot can be measured using XPS and TPD-MS for a small amount of soot, there is no direct way to detect H content of soot. In this sense, pyrolysis GC/MS is a useful instrument for analyzing a small amount of soot. Accordingly, the H/C and O/C analyses can give more clear information regarding soot crystalline order with increasing O and H content.
REFERENCES


Appendix A

Raman Analysis

A.1 Raman Parameters Using Curve-Fitted Peaks

The chi-square error for the Raman parameters was calculated for each sample using various fitting methods in order to investigate how well each fitting method represents the original spectra. As examined by Sadezky et al. [85], 4L1G shows the least chi-square error among the given fitting methods for all the samples in Table A-1. Although the 5L fitting is the second best fitting method in terms of the chi-square value according to their study, the present work showed that 3L1G fits better than 5L. Overall, chi-square error is smaller for the same peak number, when the D3 band is a Gaussian pattern. Accordingly, the D3 band seems to be more appropriate with a Gaussian pattern in terms of fit to the original spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2L1G</th>
<th>3L</th>
<th>3L1G</th>
<th>4L</th>
<th>4L1G</th>
<th>5L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flame soot</td>
<td>0.092±0.005</td>
<td>0.123±0.005</td>
<td>0.043±0.005</td>
<td>0.064±0.006</td>
<td>0.035±0.005</td>
<td>0.050±0.005</td>
</tr>
<tr>
<td>SCE soot</td>
<td>0.147±0.007</td>
<td>0.182±0.009</td>
<td>0.049±0.006</td>
<td>0.074±0.009</td>
<td>0.034±0.004</td>
<td>0.051±0.004</td>
</tr>
<tr>
<td>DDC 30 soot</td>
<td>0.099±0.007</td>
<td>0.140±0.007</td>
<td>0.043±0.005</td>
<td>0.072±0.009</td>
<td>0.029±0.003</td>
<td>0.044±0.005</td>
</tr>
<tr>
<td>DDC 75 soot</td>
<td>0.135±0.005</td>
<td>0.171±0.006</td>
<td>0.044±0.004</td>
<td>0.071±0.006</td>
<td>0.026±0.002</td>
<td>0.040±0.004</td>
</tr>
<tr>
<td>Carbon black</td>
<td>0.142±0.024</td>
<td>0.136±0.037</td>
<td>0.050±0.005</td>
<td>0.059±0.009</td>
<td>0.022±0.003</td>
<td>0.030±0.005</td>
</tr>
</tbody>
</table>

The D3 band has been studied to evaluate amorphous carbon, it was given a significant emphasis here on the samples using the different peak fitting methods, before covering the height and area ratios of D1 to G and D1 FWHM.
As evident in Table A-2, none of the D3 parameters from 2L1G, 3L and 5L curve-fitting methods correlate well with the oxidative reactivity. In the case of 4L, the D3 height is in good agreement generally with the reactivity, but the differences in the D3 area are not significant. In addition, there is no trend observed for D3 FWHM from any fitting method. In contrast, the D3 height and area from 3L1G and 4L1G indicate clear trends consistent with those in the reactivity. In spite of the physical characteristic of the D3 band, Cuesta et al. found out that the contribution of $I_{D3}/I_{D1+G}$ is poorly related with the degree of disorder for various carbonaceous materials [84], although it
is not clear which curve-fitting method was applied in their study. And, Zaida et al. investigated the variation of $I_{D2}/I_G$ from 4L fitting with increasing temperature for chars [91]. Since they didn’t examine the relation of this parameter and char reactivity, however, it is not possible to determine whether $I_{D3}/I_G$ from 4L fitting is also informative in char activity. Although there are not many reports about the effect of the D3 band on carbon oxidative reactivity, Ivleva and coworkers found that $A_{D3}/A_G$ and $A_{D3}/A_{G+D2+D3}$ from 4L1G provide good structural information for soot and other carbonaceous materials [92,93,111]. So, depending upon the fitting method, the D3 band seems to be a useful Raman parameter in the study of crystalline structure.

The curve-fitting methods assuming three peaks in the deconvolution, which are 2L1G and 3L fitting methods, were investigated for several Raman parameters. As shown in Figure A-1, $I_{D1}/I_G$, $A_{D1}/A_G$, and $D1$ FWHM increase with the increase in the reactivity for 2L1G fitting, although diffusion flame soot and DDC 30 soot have similar values despite a significant reactivity difference. Similar trends in the Raman parameters are also observed for 3L fitting with a less consistent result with respect to the oxidative reactivity in Figure A-2. With both 3L and 2L1G fitting methods, $D1$ FWHM appears to be quite reproducible at different positions of each sample with smallest standard deviation among the examined Raman parameters. Jawhari et al. also investigated $A_{D1}/A_G$ and $D1$ width for carbon black and microcrystallite graphite using 2L1G fitting [96]. They observed that microcrystallite graphite has a wider D peak than XE printex, despite significantly reduced $I_{D1}/I_G$ for the microcrystalline graphite, because the microcrystallite graphite has a wider distribution of crystallite size than the XE printex does. Although $A_{D1}/A_G$ and $D1$ FWHM indicate different crystalline information such as the distribution of crystalline size and defects of the graphitic lattice [76,96,135], the structural variations in these two parameters seem to correlate well for the soot samples used in this study with respect to the oxidative reactivity.
Figure A-1. Comparison of Raman parameters from 2L1G fitting: (a) height ratio of D1 to G (ID1/IG), (b) area ratio of D1 to G (AD1/AG), (c) D1 FWHM
Figure A-2. Comparison of Raman parameters from 3L fitting: (a) height ratio of D1 to G ($I_{D1}/I_G$), (b) area ratio of D1 to G ($A_{D1}/A_G$), (c) D1 FWHM.
Three Raman parameters were also investigated using 3L1G and 4L fitting methods, which use four peaks in the deconvolution of the raw Raman spectra. As evident in Figure A-3, $I_{D1}/I_G$, $A_{D1}/A_G$ and $D1$ FWHM using 3L1G fitting show a better correlation with the oxidative reactivity than those from the 2L1G and 3L fitting methods. The $I_{D1}/I_G$ of SCE soot is similar to that of the DDC 30 soot, and the $A_{D1}/A_G$ shows an increasing trend with respect to the reactivity, although the standard deviation of the DDC 30 soot is much higher than those of the other samples. In comparison, SCE soot and DDC 75 soot have similar $D1$ FWHM values. The trends in $A_{D1}/A_G$ and $D1$ FWHM from the 4L fitting method are also similar to those from 3L1G fitting as shown in Figures A-4(b) and (c). However, there is a poor correlation observed for the $I_{D1}/I_G$ as shown in Figure A-4(a). Accordingly, $I_{D1}/I_G$ from 4L fitting is not a good parameter in describing structural information, but $A_{D1}/A_G$ and $D1$ FWHM from 4L fitting can be useful like those from 3L1G fitting. Zaida et al.’s study implies that when the effect of heat treatment was investigated using cellulose chars, there was a gradual increase in $I_{D1}/I_G$ from 600 to 1900 °C and a decrease in $D1$ FWHM from 4L fitting with increasing temperature [91]. They speculated that the small $I_{D1}/I_G$ at low temperatures reflects the small crystallite size, where the Raman mode is inactive. However, it is possibly because this parameter is not suitable for the study of crystalline structure in comparison to $A_{D1}/A_G$, as Dong et al. also observed a huge discrepancy between $I_{D1}/I_G$ and $A_{D1}/A_G$ [135]. Although they didn’t investigate the variation of $D1$ FWHM with respect to char oxidation, however, this parameter seems to be a promising parameter in the study of soot crystalline structure.
Figure A-3. Comparison of Raman parameters from 3L1G fitting: (a) height ratio of D1 to G ($I_{D1}/I_G$), (b) area ratio of D1 to G ($A_{D1}/A_G$), (c) D1 FWHM.
Figure A-4. Comparison of Raman parameters from 4L fitting: (a) height ratio of D1 to G ($I_{D1}/I_G$), (b) area ratio of D1 to G ($A_{D1}/A_G$), (c) D1 FWHM.
Figure A-5. Comparison of Raman parameters from 4L1G fitting: (a) height ratio of D1 to G ($I_{D1}/I_G$), (b) area ratio of D1 to G ($A_{D1}/A_G$), (c) D1 FWHM.
Figure A-6. Comparison of Raman parameters from 5L fitting: (a) height ratio of D1 to G ($I_{D1}/I_G$), (b) area ratio of D1 to G ($A_{D1}/A_G$), (c) D1 FWHM
The results using five peaks to deconvolute the raw Raman spectra, referred to here as five curve-fitting methods, are shown in Figure A-5 and A-6. $I_{D1}/I_G$ and $A_{D1}/A_G$ from 4L1G fitting correlate poorly with the oxidative reactivity, while $D1$ FWHM shows a good trend consistent with that in the reactivity. Specifically, DDC 30 soot and DDC 75 soot have large standard deviations for $I_{D1}/I_G$ and $A_{D1}/A_G$. Although their large standard deviations were speculated to be due to noise in the peak at ~1590 cm$^{-1}$ with 10s of integration time, subsequent investigation with 40s and 120s integration time showed no appreciable effect on the peak shape. Therefore, the large standard deviations of these parameters seem to be characteristics of these samples, as Sadezky et al. observed [85]. In contrast, $D1$ FWHM is shown to be more stable as observed in other fitting methods. Since the deconvolution approach with G and D2 bands has a minor effect on the D1 band, there is no appreciable change in $D1$ FWHM from 4L1G compared to that from the curve-fitting methods assuming four peaks. Poor trends in $I_{D1}/I_G$, $A_{D1}/A_G$ are also observed for 5L fitting in Figure A-6(a). Despite the poor trend in $A_{D1}/A_G$ in this study, Al-Qurashi and Boehman found that $A_{D1}/A_G$ indicated a significant structural difference between non-EGR and EGR soot samples [11]. Since the present samples were obtained from different combustion sources, there are significant differences among the samples in their physical and chemical properties such as crystalline structure, pore structure, volatile fraction and oxygen functional groups. Although it is presumed that soot oxidative reactivity is closely related to the degree of structural disorder, $I_{D1}/I_G$ and $A_{D1}/A_G$ from 4L1G and 5L fitting methods may not fully indicate these structural changes for some materials. Indeed, Sadezky et al. also observed that there is no appreciable agreement between $A_{D1}/A_G$ from 4L1G and the oxidative reactivity for GfG soot (spark discharged soot) and EURO IV diesel soot, which have different physical and chemical properties [85], although Sheng obtained a positive result for coal chars [179]. Although it is hard to determine which material is suitable for 4L1G and 5L fitting methods, some materials seem to not be appropriate in the Raman analyses using $I_{D1}/I_G$ and $A_{D1}/A_G$ from these fitting methods.
The above results show that D1 FWHM correlates well with the oxidative trend using the four and five curve-fitting methods, and A_D1/A_G shows an excellent trend for the four peak curve-fitting method. Accordingly, 3L1G and 4L fitting methods from the four peak curve-fitting approach seem to provide good Raman parameters for the soot samples from this study. Although D1 FWHM using the five peak curve-fitting method is a good parameter as Ivleva and coworkers have used [92,93,111], the same trend can be obtained from that for the four peak curve-fitting methods. Since the trends in both intensity and area of D3 band from 3L1G fitting are also shown to correlate with oxidative reactivity in this investigation, 3L1G is found to be the best choice among the examined fitting methods. Consequently, it is concluded that the relation between soot oxidative reactivity and crystalline structure can be interpreted more reliably and consistently when all these parameters are analyzed. In this case, 3L1G fitting provides a reasonable explanation about the effect of crystalline structure on soot oxidative reactivity. The soot oxidative reactivity is closely related to the abundance of edge sites and amorphous carbon. Correspondingly, more reactive soot shows a wider distribution of crystallite sizes with increasing disorder.
Appendix B

Supplemental Results for Engine Soot and Flame Soot

Table B-1. Emissions and fuel consumption of the diesel engine with oxygen enrichment

<table>
<thead>
<tr>
<th>Engine load</th>
<th>Sample</th>
<th>NOx</th>
<th>CO</th>
<th>CO₂</th>
<th>Fuel consumption (g/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>21% O₂ soot</td>
<td>2.8</td>
<td>1.7</td>
<td>829.7</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>24% O₂ soot</td>
<td>9.3</td>
<td>1.0</td>
<td>849.8</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>27% O₂ soot</td>
<td>16.8</td>
<td>0.8</td>
<td>835.5</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>30% DG soot</td>
<td>3.0</td>
<td>1.2</td>
<td>818.0</td>
<td>1.37</td>
</tr>
<tr>
<td>75%</td>
<td>21% O₂ soot</td>
<td>5.97</td>
<td>4.3</td>
<td>784.4</td>
<td>2.72</td>
</tr>
<tr>
<td></td>
<td>24% O₂ soot</td>
<td>16.8</td>
<td>1.2</td>
<td>812.0</td>
<td>2.74</td>
</tr>
<tr>
<td></td>
<td>27% O₂ soot</td>
<td>25.8</td>
<td>0.5</td>
<td>798.4</td>
<td>2.78</td>
</tr>
<tr>
<td></td>
<td>30% DG soot</td>
<td>7.62</td>
<td>4.5</td>
<td>784.3</td>
<td>3.06</td>
</tr>
</tbody>
</table>

Table B-2. Volatile organic fraction (VOF) of engine soot calculated from TGA treated at 500 °C

<table>
<thead>
<tr>
<th>Engine load</th>
<th>Sample</th>
<th>VOF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30%</td>
<td>21% O₂ soot</td>
<td>12.08</td>
</tr>
<tr>
<td></td>
<td>24% O₂ soot</td>
<td>12.61</td>
</tr>
<tr>
<td></td>
<td>27% O₂ soot</td>
<td>13.12</td>
</tr>
<tr>
<td></td>
<td>30% DG soot</td>
<td>12.37</td>
</tr>
<tr>
<td>75%</td>
<td>21% O₂ soot</td>
<td>12.38</td>
</tr>
<tr>
<td></td>
<td>24% O₂ soot</td>
<td>13.91</td>
</tr>
<tr>
<td></td>
<td>27% O₂ soot</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>30% DG soot</td>
<td>13.73</td>
</tr>
</tbody>
</table>
### Table B-3. Volatile organic fraction (VOF) of flame soot calculated from TGA treated at 300 °C

<table>
<thead>
<tr>
<th>Fuel</th>
<th>O₂ in Oxidizer (%)</th>
<th>Oxidizer flow rate (l/min)</th>
<th>Balance gas in oxidizer</th>
<th>VOF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-heptane</td>
<td>21</td>
<td>6.33</td>
<td>100% N₂</td>
<td>0.40</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>9.50</td>
<td>100% N₂</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>12.66</td>
<td>100% N₂</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>9.50</td>
<td>100% Ar</td>
<td>0.43</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>6.33</td>
<td>100% N₂</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>6.33</td>
<td>100% N₂</td>
<td>1.09</td>
</tr>
<tr>
<td>ethylene</td>
<td>21</td>
<td>6.33</td>
<td>100% N₂</td>
<td>1.42</td>
</tr>
<tr>
<td>70 vol. % n-heptane + 30% monoglyme</td>
<td>21</td>
<td>6.33</td>
<td>100% N₂</td>
<td>0.69</td>
</tr>
</tbody>
</table>

### Figure B-1. TGA results of flame soot collected from different burner tests at 500 °C isothermal condition
Figure B-2. Repeatability of TGA results for flame soot at 500 °C isothermal condition
Figure B-3. TGA results of soot samples pretreated at different temperatures: (a) engine soot at 550 °C isothermal condition, (b) flame soot at 500 °C isothermal condition.
Figure B-4. TGA results of soot samples at different isothermal temperatures: (a) 500 °C, (b) 600 °C

Figure B-5. Chemisorption of O₂ at different temperatures
Table B-4. BET surface areas of flame soot samples

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Soot generation condition</th>
<th>BET surface area (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O₂ in Oxidizer (%)</td>
<td>Oxidizer flow rate (l/min)</td>
</tr>
<tr>
<td>n-heptane</td>
<td>21</td>
<td>6.33</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>9.50</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>9.50</td>
</tr>
<tr>
<td></td>
<td>27</td>
<td>6.33</td>
</tr>
</tbody>
</table>
VITA
Hee Je Seong

EDUCATION

Sep. 2006 – Aug. 2010  Ph.D. in Energy and Geo-Environmental Engineering,
                        The Pennsylvania State University: (Thesis - Impact of Oxygen
                        Enrichment on Soot Properties and Soot Oxidative Reactivity)

Mar. 1996 – Feb. 1998  M.S. in Chemical Engineering, Pohang University of Science and
                        Technology (POSTECH), Korea: (Thesis - NO Removal Activity of
                        SCR Catalyst Treated by Acid)


WORK EXPERIENCES

Jan. 2004 - July 2006  Chief Researcher in Energy & Environment Research Department,
                        Hyundai Heavy Industries Co., Ltd. (HHI), Korea