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ADVANCED DIESEL COMBUSTION OF HIGH CETANE NUMBER FUELS
AND THE IMPACTS ON THE COMBUSTION PROCESS

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by
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ABSTRACT

Advanced diesel combustion is of great interest due to the promise of simultaneously reducing emissions of nitrogen oxides (NO\(_x\)) and particulate matter (PM), while maintaining or improving efficiency. However, the extended ignition delay along with the combustion of a partially premixed charge results in excessive emissions of total hydrocarbons (THC) and carbon monoxide (CO) from incomplete combustion. In this study, a light-duty turbodiesel engine was operated in an advanced diesel combustion mode, specifically high efficiency clean combustion (HECC), using three different fuels including a conventional ultra-low sulfur diesel fuel (diesel), a synthetic fuel produced in a high temperature Fischer-Tropsch (HTFT) process, and a synthetic fuel produced in a low temperature Fischer-Tropsch (LTFT) process. Start of injection (SOI) timing was swept from -8° ATDC to 0° ATDC to find the optimized injection timing for each fuel. The HTFT fuel, which had a derived cetane number (DCN) of 51, was found to decrease THC and CO emission by 32% and 31%, respectively, compared to the diesel fuel, which had a DCN of 45. The higher ignition quality of the HTFT fuel was found to reduce emissions from incomplete combustion by presumably consuming more of the fuel charge before it reached a region of the cylinder where it was too lean to effectively burn. However, with the HTFT fuel, NO\(_x\) and PM emissions increased relative to the diesel baseline due to a higher peak heat release rate, presumably caused by 2% less EGR during the HTFT fuel’s operation. In contrast, the LTFT fuel with a DCN of 81 enabled an 80% reduction in THC emissions and a 74% reduction in CO emissions compared to the diesel fuel. The LTFT fuel, though having a very short ignition delay, did not
increase NO\textsubscript{x} and PM emissions apparently due to the fuel burning in a shorter, less intense premixed combustion phase followed by a prominent mixing-controlled combustion phase. This study revealed that a high ignition quality (DCN 81) fuel is well suited for operation under a high EGR advanced diesel combustion mode and led to reductions in all primary pollutant emissions.

Many factors were suggested which contribute to the lower THC and CO emissions produced by the combustion of a high cetane fuel. Among the factors was the theory that a high cetane number fuel will have a lower combustion lean limit than a lower cetane number fuel, thus resisting incomplete combustion. This theory was examined in a subsequent study where the critical equivalence ratio (\(\Phi\)), the minimum equivalence ratio at which a fuel can autoignite, was identified for the diesel, HTFT and LTFT. The fuels were vaporized and premixed with air heated to 260 °C then fed into a modified Cooperative Fuels Research (CFR) Octane Rating engine, at compression ratios of 4, 5, 6 and 8. Equivalence ratio (\(\Phi\)) was gradually increased until the critical \(\Phi\) was determined. At the lowest compression ratio of 4, the diesel fuel did not autoignite while the HTFT and the LTFT fuels did at critical \(\Phi\) of 0.76 and 0.35, respectively. At the highest compression ratio of 8, the critical \(\Phi\) of the fuels began to converge where diesel, HTFT, and LTFT had critical \(\Phi\) of 0.23, 0.20 and 0.17, respectively. However, in the presence of simulated EGR (\(\text{O}_2\) 10.7 vol. %, \(\text{CO}_2\) 8 vol. % and \(\text{N}_2\) 81.3 vol. %) at a compression ratio of 8, the critical \(\Phi\) diverged dramatically, where the diesel, HTFT and LTFT had critical \(\Phi\) of 1.00, 0.77 and 0.38, respectively. \(n\)-Hexane, \(n\)-heptane and \(n\)-dodecane were used as single-component surrogates of similar ignition quality as the
diesel, HTFT and LTFT, respectively. The single-component surrogates had leaner critical $\Phi$ than their multi-component counterparts did.

The higher ignition quality fuels were shown to have leaner critical $\Phi$, but a question remained regarding fuel compositional effects on critical $\Phi$. Blends of n-dodecane/toluene and n-dodecane/isooctane were prepared to have the same DCN as n-heptane. Critical $\Phi$ measurements of the two blends and n-heptane revealed that critical $\Phi$ could vary between fuels with the same DCN. The n-dodecane/toluene blend was found to have a leaner critical $\Phi$ than the n-dodecane/iso-octane blend under low compression ratios (CRs) or simulated EGR. It was concluded that the 11% greater n-paraffin content of the n-dodecane/toluene blend compared to the n-dodecane/isooctane, resulted in more LTHR and a leaner critical $\Phi$. The critical $\Phi$ of the low cetane number FACE fuels were also determined. A linear correlation with an $R^2$ coefficient of 0.949 was observed between critical $\Phi$ and n-paraffin mass content of the low CN FACE fuels. This result corroborated with the conclusion of the DCN parity blends, that the critical $\Phi$ of a fuel is governed by the fraction of reactive components (n-paraffins), which increases low temperature heat release (LTHR). The critical $\Phi$ measurements of the low cetane number FACE fuels were compared to CO and THC emissions from a light-duty turbodiesel engine operating in advanced combustion mode with the low cetane number (CN) FACE fuels. Low CO and THC emission produced from early SOI timings are suggestive of a correlation with lean critical $\Phi$ measurements. It was concluded that the relationship between low CO and THC emissions and a lean critical $\Phi$ is only present when early SOI timing produces an overly-lean fuel-air charge.
It was conjectured that the contribution of CO and THC emissions from overly-rich regions becomes larger, and a fuel with a leaner critical $\Phi$ would not reduce these emissions. These results suggest that a fuel can be blended to have a low ignition quality, which is desired for high efficiency advanced combustion operations and with high n-paraffin content to reduce CO and THC emission.
# TABLE OF CONTENTS

TABLE OF CONTENTS........................................................................................................... vii  
LIST OF FIGURES.................................................................................................................. x  
LIST OF TABLES................................................................................................................... xviii  
NOMENCLATURE ................................................................................................................... xx  
ACKNOWLEDGEMENTS......................................................................................................... xxiii  
DEDICATION.......................................................................................................................... xxiv  

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

Chapter 2 Literature Review .................................................................................................. 3  
2.1 Physical Ignition Delay..................................................................................................... 7  
2.2 Chemical Ignition Delay................................................................................................. 7  
2.3 Low Temperature Oxidation......................................................................................... 10  
2.4 Intermediate Temperature Oxidation............................................................................ 12  
2.5 High Temperature Oxidation......................................................................................... 12  
2.6 Direct Injection of a Diesel Fuel Jet .............................................................................. 13  
   2.6.1 Effects of Spreading Angle on Fuel Jet Penetration ............................................. 14  
   2.6.2 Effects of Vaporization on Fuel Jet Penetration .................................................. 15  
   2.6.3 Effects of Combustion on Fuel Jet Penetration .................................................... 15  
   2.6.4 Liquid-phase Fuel Penetration ............................................................................ 16  
   2.6.5 Flame Lift-Off ..................................................................................................... 18  
   2.6.6 Oxygen Entrainment .......................................................................................... 18  
   2.6.7 Physical ID and Chemical ID .............................................................................. 20  
2.7 NOx Formation ............................................................................................................. 21  
2.8 Particulate Matter.......................................................................................................... 23  
   2.8.1 Soot Formation Process ....................................................................................... 24  
   2.8.2 Soot Formation in a Contention Diesel Engine .................................................... 28  
   2.8.3 Contribution of Soluble Organics ..................................................................... 30  
   2.8.4 NOx-PM Trade Off ............................................................................................. 31  
2.9 Sources of Incomplete Combustion ............................................................................. 33  
   2.9.1 Total Hydrocarbon Formation ........................................................................... 34  
   2.9.2 Carbon Monoxide Formation ............................................................................. 35  
2.10 Conventional Diesel Fuels .......................................................................................... 36  
2.11 Fischer–Tropsch Synthesis .......................................................................................... 39  

Chapter 3 Hypotheses and Objectives .................................................................................. 43
3.1 Hypotheses ...................................................................................................... 43
3.2 Objectives ....................................................................................................... 43

Chapter 4 Advanced Diesel Combustion of a High Cetane Number Fuel with Low Hydrocarbon and Carbon Monoxide Emissions ........................................ 44
4.1 Introduction ..................................................................................................... 44
4.2 Experimental ................................................................................................... 49
  4.2.1 Engine and Test Facility ....................................................................... 49
  4.2.2 Fuel ....................................................................................................... 51
  4.2.3 Test Conditions ..................................................................................... 52
4.3 Results ............................................................................................................. 55
  4.3.1 Needle Lift ............................................................................................ 55
  4.3.2 Apparent Rate of Heat Release ............................................................. 56
  4.3.3 Brake Specific Fuel Consumption ........................................................ 61
  4.3.4 NOx Emissions ..................................................................................... 64
  4.3.5 Particulate Matter Emissions ................................................................. 69
  4.3.6 Soot Emissions ..................................................................................... 70
  4.3.7 Total Hydrocarbon Emissions .............................................................. 74
  4.3.8 Carbon Monoxide Emissions ............................................................... 76
  4.3.9 THC-NOX Trade-off ............................................................................. 77
4.4 Discussion ....................................................................................................... 78
  4.4.1 LTFT Fuel Effects ................................................................................ 80
  4.4.2 Optimized Injection Timing ................................................................. 85
4.5 Conclusion ...................................................................................................... 88

Chapter 5 Effects of Fuel Ignition Quality on Critical Equivalence Ratio .......... 89
5.1 Introduction ..................................................................................................... 89
5.2 Experimental ................................................................................................... 92
  5.2.1 Engine and Test Facility ....................................................................... 92
  5.2.2 Test Condition ...................................................................................... 94
  5.2.3 Exhaust Species Analysis ..................................................................... 95
  5.2.4 In-cylinder Pressure Data Analysis ...................................................... 95
  5.2.5 Test Fuels .............................................................................................. 96
  5.2.6 Residual Gas Fraction ........................................................................... 100
5.3 Results ............................................................................................................. 103
  5.3.1 Critical Φ Criterion ............................................................................... 103
  5.3.2 Heat Release Rate.................................................................................. 109
  5.3.3 Maximum Bulk Cylinder Temperature ............................................... 117
  5.3.4 CO and CO₂ Emissions ......................................................................... 121
  5.3.5 Low Temperature Fuel Reactivity ....................................................... 124
  5.3.6 Summary of Critical Φ under Ambient Air Composition .................... 126
  5.3.7 Effect of EGR on Critical Φ Ratio ......................................................... 130
5.4 Discussion ....................................................................................................... 131
5.5 Summary and Conclusions .................................................................................. 137

Chapter 6 Effects of Fuel Composition on Critical Equivalence Ratio .................. 139

6.1 Introduction....................................................................................................... 139
6.2 Experimental.................................................................................................... 140
  6.2.1 Engine and Test Facility ............................................................................ 140
  6.2.2 Exhaust Species Analysis and In-cylinder Pressure Data Analysis .......... 141
  6.2.3 DCN Parity Blends .................................................................................. 141
6.3 FACE Fuels .................................................................................................... 143
  6.3.1 Test Condition of the FACE Fuels ............................................................ 146
6.4 Results............................................................................................................. 148
  6.4.1 Critical $\Phi$ vs. Fuel Composition ....................................................... 148
  6.4.2 FACE Fuels Ignition Quality ................................................................. 159
  6.4.3 Effect of Ignition Quality on Critical $\Phi$ ............................................. 161
  6.4.4 Effect of n-Paraffins on Critical $\Phi$ ..................................................... 164
6.5 Comparison of Critical $\Phi$ to Emissions of Incomplete Combustion from a
  Multi-Cylinder Engine ..................................................................................... 168
6.6 Discussion....................................................................................................... 171
6.7 Summary and Conclusions ............................................................................ 174
6.8 Acknowledgements........................................................................................ 176

Chapter 7 Conclusions and Recommendations.................................................... 177

7.1 Summary of Dissertation............................................................................... 177
7.2 Conclusion from Chapter 4, Advanced Diesel Combustion of a High
  Cetane Number Fuel with Low Hydrocarbon and Carbon Monoxide
  Emissions ........................................................................................................... 178
7.3 Conclusion from Chapter 5, Fuel Ignition Quality Effects on Critical $\Phi$...... 179
7.4 Conclusion from Chapter 6, Fuel Compositional Effects on Critical
  Equivalence Ratios ......................................................................................... 180
7.5 Recommendations for Future Work ............................................................. 181

References............................................................................................................ 183

Appendix A Start of Combustion Algorithm ......................................................... 191
Appendix B Error Analysis of the Light-Duty Turbodiesel Engine Test Stand...... 194
Appendix C Repeatability of Critical $\Phi$ Measurement ..................................... 197
LIST OF FIGURES

Figure 2-1: A model of CI 3D-CFD model to map equivalence ratio vs. temperature. Developed by Akihama [3] and later modified by Assanis [4].

Figure 2-2: Conventional DI diesel rate of heat release vs. crank angle of the major phases of the diesel combustions process [5].

Figure 2-3: “Regimes of hydrocarbon oxidation chemistry as delineated by the main kinetic chain branching processes. The upper line connects points where overall H + O2 reaction is neutral: above the line is net branching; below the line is net terminating. The lower lines are where the peroxy chemistry is neutral: above these lines there is net termination and below net branching. The ‘low,’ ‘intermediate’ and ‘high’ temperature regions are broadly characterized by the types of chemistry indicated” [7]. Originally printed in Morley and Philling [8].

Figure 2-4: Heat release curve from constant volume combustion chamber with iso-octane fuel.

Figure 2-5: A general scheme of alkane oxidation, where R denotes an alkyl radical and Q denotes a CnH2n.

Figure 2-6: “Schematics showing how the relative spatial relationship between fuel vaporization and combustion zones and the percent of stoichiometric air entrained up to the lift-off length can change with conditions in a DI-type diesel fuel jet under quiescent conditions. The schematic at the left is for an ambient-gas temperature and density of 1100 K and 23 kg/m3, and an orifice pressure drop and orifice diameter of 40 MPa and 250 μm. The schematic at the right is for an ambient-gas temperature and density of 1000 K and 20 kg/m3, and an orifice pressure drop and orifice diameter of 200 MPa and 100 μm” [15].

Figure 2-7: “Schematic diagram of the steps in the soot formation process from gas phase to solid agglomerated particles” [19].

Figure 2-8: “The HACA mechanism for planar PAH growth (a), and extended to the surface growth of soot (b)” [26].

Figure 2-9: Paths to soot formation on plot of species molecular weight M versus hydrogen mol fraction XH. Originally printed in Homann [27], reprinted in Haynes and Wagner [22].
Figure 2-10: Micrograph of diesel soot [28]............................................................... 27

Figure 2-11: A schematic of the conceptual model with fuel-rich premixed flame, soot formation, soot oxidation and NO formation zones [31]................................. 29

Figure 2-12 Typical composition and structure of engine exhaust particles [33]........ 30

Figure 2-13: Typical particle composition for a heavy-duty diesel engine tested in a heavy-duty transient cycle [33]................................................................. 31

Figure 2-14: General layout of the quasi-dimensional thermodynamic simulation showing [40]. Reprinted in Yao et al. [2]................................................................. 34

Figure 2-15: FT stepwise growth process [49] ......................................................... 41

Figure 4-1: Needle lift for advanced diesel combustion at -8°, -6°, -4°, -2° and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel, HTFT and LTFT fuels......................... 56

Figure 4-2: Apparent rate of heat release and needle lift for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel, HTFT and LTFT fuels. Needle Lift is from the injection of the LTFT fuel ....................................................................................................................... 60

Figure 4-3: Brake specific fuel consumption for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels................................................................. 63

Figure 4-4: Brake thermal efficiency for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels................................................................. 63

Figure 4-5: Combustion efficiency for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels................................................................. 64

Figure 4-6: Emissions index NOX for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels................................................................. 67
Figure 4-7: EGR% recirculated for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.................................................................68

Figure 4-8: Emissions index NOX vs. peak bulk cylinder gas temperature for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.................................................................68

Figure 4-9: Emissions index NOX vs. maximum ROHR for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.................................................................69

Figure 4-10: Emissions index particulate matter emissions for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.................................................................70

Figure 4-11: Emissions index soot emissions for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.................................................................72

Figure 4-12: Qualitative observations on filter containing PM (top) and post soxhlet extraction filters containing soot (bottom) for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel, HTFT and LTFT fuels.................................................................74

Figure 4-13: Emissions index THC emissions for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.................................................................76

Figure 4-14: Emissions index CO emissions for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.................................................................77

Figure 4-15: Emissions index THC vs. Emissions index NOX for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.................................................................78

Figure 4-16: Emissions index THC vs. ignition dwell for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.................................................................82
Figure 4-17: Comparison of optimized start of injection of advanced diesel combustion for brake thermal efficiency, NOx, PM, THC and CO of diesel (□), HTFT (■) and LTFT (■) fuels. .................................86

Figure 5-1: Modified Cooperative Fuels Research (CFR) engine. Originally printed in Szybist et al. [12] and reproduced in Zhang et al. [74]. ......................... 93

Figure 5-2: Simulated distillation curves of diesel (●), HTFT (▲) and LTFT (♦); using ASTM method D2887, with a 90% of mass cut point (▬▬). ..................... 97

Figure 5-3: Comparison of GCMS chromatograph for the diesel by full boiling range, 1 to 90% of mass removed after vacuum distillation and 90 to 100% of mass separated after vacuum distillation. Note that the response of the 90 to 100% chromatograph is high due to the increased concentration of the fraction after distillation. ........................................99

Figure 5-4: Example of critical Φ criterion for n-dodecane at a CR of 4, indicated by CO (●), CO2 (▲), maximum bulk in-cylinder temperature K (♦) and the critical Φ (——). .........................................................105

Figure 5-5: Example of heat release rate data for n-dodecane at a CR of 4 with gradual increase in Φ, with Φ of 0.1 (………), 0.2 (●●●●), 0.3 (———), 0.33 (——), 0.34 (——·) and 0.35 (——). .............................................. 106

Figure 5-6: Example of critical Φ criterion for n-dodecane at a CR of 5, indicated by CO (●), CO2 (▲), maximum bulk in-cylinder temperature K (♦) and the critical Φ (——). ........................................................................................................107

Figure 5-7: Example HRR profiles for n-dodecane at a CR of 5 and gradually increasing Φ of 0.1 (………), 0.2 (●●●●), 0.24 (———), 0.25 (——), 0.26 (——·) and 0.27 (——). ................................................................. 108

Figure 5-8: Example HRR profiles for n-dodecane at a CR of 4 and Φ 0.25 for six individual combustion cycles. The 10 cycles are cycle #1 (………), cycle #2 (●●●●), cycle #3 (———), cycle #4 (———), cycle #5 (——·) and cycle #6 (——). ................................................................. 108

Figure 5-9: Example HRR profiles for diesel at a CR of 6 and gradually increasing Φ of 0.1 (………), 0.2 (●●●●), 0.3 (———), 0.38 (———), 0.39 (——·) and 0.4 (——). ................................................................. 111

Figure 5-10: Example HRR profiles for HTFT at a CR of 6 and gradually increasing Φ of 0.1 (………), 0.2 (●●●●), 0.25 (———), 0.29 (———), 0.3 (——·) and 0.31 (——). ........................................................................ 111
Figure 5-11: Example HRR profiles for LTFT at a CR of 6 and gradually increasing $\Phi$ of 0.1 (-- ---), 0.17 (-----), 0.19 (-- --), 0.2 (--- ---), 0.21 (----- -), and 0.22 (---- ---). ................................................................................... 112

Figure 5-12: HRR profiles for n-hexane (-- ---), n-heptane (-----), n-dodecane (-- --), diesel (--- ---), HTFT (----- -) and LTFT (---- ---) fuels at an $\Phi$ 0.1 and CR of 6. .......................................................................................................... 114

Figure 5-13: Correlation of SOC LTHR and CA50 to DCN for diesel (●), HTFT (▲), LTHR (♦), n-hexane (×), n-heptane (+) and n-dodecane (■) fuels at a CR of 6 and $\Phi$ of 0.1. ............................................................................................ 115

Figure 5-14: Heat release rate of n-hexane (-- ---), n-heptane (-----), n-dodecane (-- --), diesel (--- ---), HTFT (----- -) and LTFT (---- ---) fuels at an $\Phi$ of 0.2 and CR of 6. ................................................................................................. 116

Figure 5-15: Maximum bulk cylinder temperature of diesel fuel with an increase $\Phi$ sweep at CR of 8 (●), CR of 6 (×), CR of 5 (+) and CR of 4 (■). .................... 119

Figure 5-16: Maximum bulk cylinder temperature of HTFT fuel with an increase $\Phi$ sweep at CR of 8 (●), CR of 6 (×), CR of 5 (+) and CR of 4 (■). .................... 120

Figure 5-17: Maximum bulk cylinder temperature of LTFT fuel with an increase $\Phi$ sweep at CR of 8 (●), CR of 6 (×), CR of 5 (+) and CR of 4 (■). .................... 121

Figure 5-18: Volumetric exhaust CO (ppm) emissions over an $\Phi$ sweep diesel (●), HTFT (▲), LTHR (♦) fuels. ................................................................................. 122

Figure 5-19: Volumetric exhaust CO2 (%) emissions over an $\Phi$ sweep diesel (●), HTFT (▲), LTHR (♦) fuels. ................................................................................. 124

Figure 5-20: Emission Index CO of n-dodecane (■), LTFT (●), n-heptane (+), n-hexane (×), HTFT (▲) and diesel (●), at a CR of 4, over an increasing $\Phi$ sweep. ................................................................. 125

Figure 5-21: Emission Index CO of n-dodecane (■), LTFT (●), n-heptane (+), n-hexane (×), HTFT (▲) and diesel (●), at a CR of 6, over an increasing $\Phi$ sweep. ................................................................. 126

Figure 5-22: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 4. Note that the blend-derived cetane number of n-hexane is shown for comparison. .................................................. 128
Figure 5-23: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 5. Note that the blend-derived cetane number of n-hexane is shown for comparison. ..................................................... 128

Figure 5-24: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 6. Note that the blend-derived cetane number of n-hexane is shown for comparison. ..................................................... 129

Figure 5-25: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 8. Note that the blend-derived cetane number of n-hexane is shown for comparison. ..................................................... 129

Figure 5-26: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, HTFT and diesel fuel at a CR of 8 and simulated EGR. Intake charge was composed of 10.7 vol. % O$_2$, 8 vol. % CO$_2$ and 81.3 vol. % N$_2$. Note that the motored cetane number of n-hexane is shown for comparison. ..................................................... 131

Figure 5-27: Summary of critical $\Phi$ of diesel (■), HTFT (■), LTFT (■), n-hexane (/), n-heptane (/) and n-dodecane (/) at CR 4, CR 5, CR 6 CR 8 and CR 8 with EGR. ..................................................................................................................... 132

Figure 5-28: Second order polynomial of critical $\Phi$ and DCN at a CR of 8 (●), CR of 6 (√), CR of 5 (+) and CR of 4 (■). ..................................................................................................................... 133

Figure 5-29: Critical $\Phi$ vs. DCN of n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 5. Note that the motored cetane number of n-hexane is shown for comparison. Lines shown to connect the multi-component fuels (— — —), single-component fuels with blend-derived CN value of n-hexane (—— ·) and single-component fuels with DCN value of n-hexane (———). ..................................................................................................................... 135

Figure 6-1: Modified Cooperative Fuels Research (CFR) engine. Originally printed in Szybist et al. [12] and reproduced in Zhang et al. [74]. ..................................................................................................................... 141

Figure 6-2: FACE Fuels Matrix of targeted properties ..................................................................................................................... 144

Figure 6-3: Critical $\Phi$ vs. DCN for n-heptane (+), D61/T39 blend (▲) and D50/I50 blend (●) at CR of 4, 5, 6 and 8. ..................................................................................................................... 149

Figure 6-4: Critical $\Phi$ vs. intake O$_2$ percentage for n-heptane (+), D61/T39 blend (▲) and D50/I50 blend (●) at CR of 8. ..................................................................................................................... 150

Figure 6-5: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (▲) and D50/I50 blend (●) over an $\Phi$ sweep at CR of 8 with 21 vol. % intake O$_2$. ..................................................................................................................... 151
Figure 6-6: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (∆) and D50/I50 blend (●) over an Φ sweep at CR of 8 with 17 vol. % intake O₂. ........................................................................ 152

Figure 6-7: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (∆) and D50/I50 blend (●) over an Φ sweep at CR of 8 with 15 vol. % intake O₂. ........................................................................ 153

Figure 6-8: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (∆) and D50/I50 blend (●) over an Φ sweep at CR of 8 with 12 vol. % intake O₂. ........................................................................ 154

Figure 6-9: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (∆) and D50/I50 blend (●) over an Φ sweep at CR of 8 with 10.7 vol. % intake O₂. ..................................................................... 154

Figure 6-10: Apparent heat release rate of n-heptane (-------) and iso-octane (———), calculated from pressure traces produced in the IQT constant volume combustion chamber. ............................................................................... 158

Figure 6-11: Comparisons of FACE fuels’ ignition quality, comparing CN measured with ASTM method D613 by CPChem (■) [85] and SwRI (■) [85], with DCN measured with ASTM method D6890 by NREL (□) [85] and PSU (■). ........................................................................................................................ 160

Figure 6-12: Average CN value (■) of CPChem and SwRI, as well as Average DCN value (□) of NREL and PSU. ........................................................................................................ 161

Figure 6-13: Critical Φ vs. CPChem CN for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4 (○) at CR of 7. .............................................................................. 163

Figure 6-14: Critical Φ vs. SwRI CN for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4 (○) at CR of 7. .............................................................................. 163

Figure 6-15: Critical Φ vs. NREL DCN for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4 (○) at CR of 7. .............................................................................. 163

Figure 6-16: Critical Φ vs. PSU DCN for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4 (○) at CR of 7. .............................................................................. 164

Figure 6-17: Critical Φ vs. peak area percent n-paraffins for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4 (○) at CR of 7. ............................................. 165

Figure 6-18: PIONA analysis by carbon number from C3 and C11 (components below 200 °C) and GC-FIMS analysis for carbon number from C11 and C21 (components above 200 °C) for FF1 (■), FF2 (■), FF3 (□) and FF4 (■). .......... 167
Figure 6-19 Critical $\Phi$ vs. mass percent n-paraffins for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4(○) at CR of 7. ........................................168

Figure 6-20: Emission Index CO vs. SOI timing sweep for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4(○) at CR of 7. .........................169

Figure 6-21: Emission Index THC vs. SOI timing sweep for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4(○) at CR of 7. .........................169

Figure 6-22: $R^2$ coefficient of the correlation between critical $\Phi$ and emissions index CO (■) as well as the correlation between critical $\Phi$ and emissions index THC (□) at SOI times -20, -18.5, -17, -15.5 and -14 °ATDC ..............................171

Figure C-1: Trial 1 of critical $\Phi$ repeatability study for n-heptane at a CR of 8, indicated by CO (●), CO$_2$ (▲), maximum bulk in-cylinder temperature (K) (■) and the critical $\Phi$ (▬▬). ........................................................................................198

Figure C-2: Trial 2 of critical $\Phi$ repeatability study for n-heptane at a CR of 8, indicated by CO (●), CO$_2$ (▲), maximum bulk in-cylinder temperature (K) (●) and the critical $\Phi$ (▬▬). ........................................................................................198

Figure C-3: Trial 3 of critical $\Phi$ repeatability study for n-heptane at a CR of 8, indicated by CO (●), CO$_2$ (▲), maximum bulk in-cylinder temperature (K) (●) and the critical $\Phi$ (▬▬). ........................................................................................199

Figure C-4 Trial 4 of critical $\Phi$ repeatability study for n-heptane at a CR of 8, indicated by CO (●), CO$_2$ (▲), maximum bulk in-cylinder temperature (K) (●) and the critical $\Phi$ (▬▬). ........................................................................................199
LIST OF TABLES

Table 2-1: Effect of injection parameters on liquid length based on Siebers [15]. ..... 17
Table 2-2: Effect of injection parameters on lift-off length based on Sibers [15]....... 18
Table 2-3: Injection parameter effect of stoichiometric oxygen entrained upstream of lift-off length based on Sibers [15]. .......................................................... 19
Table 4-1: DDC 2.5L Engine Specification............................................................... 50
Table 4-2: Properties of fuels examined. Test methods: a ASTM D-4052; b D-445; c ASTM D-240; d ASTM D-5453; e D-5291-02; f ASTM D-2887; g ASTM D-6890; h ASTM D-1319. ........................................ 52
Table 4-3: Key operation condition parameters. IMEP was calculated from the average of 200 cycles from all four cylinders. .................................................... 54
Table 4-4: Combustion phasing for start of combustion (SOC), ignition delay (ID), mass fraction burn of 5%, 50% and 90% of fuel. ........................................ 61
Table 5-1: Operational conditions. ....................................................................... 94
Table 5-2: Comparison of final boiling points and DCN of the full boiling fuels and the 1 to 90% mass of the diesel, HTFT and LTFT fuels. ......................... 98
Table 5-3: Experimental fuels.......................................................... 100
Table 5-4: Key phasing parameters of the HRR traces for diesel, HTFT, LTFT, n-hexane, n-heptane and n-dodecane at a CR of 6 and Φ of 0.1. ................. 114
Table 5-5: Key phasing parameters of the HRR traces for diesel, HTFT, LTFT, n-hexane, n-heptane and n-dodecane at a CR of 6 and Φ of 0.2. ................. 117
Table 6-1: Composition and DCN of n-heptane, D61/T39 and D50/I50 fuels. ....... 142
Table 6-2: Operational conditions for DCN parity blends. Value for simulated EGR based on Kook et al. [78]. ............................................................... 143
Table 6-3: Comparisons between target and actual values of cetane number, T90 distillation point, and percent aromatics composition for the Face Fuels matrix. Target values are those reported from ChevronPhillips Chemical Company in the CRC Report No. FACE-1 [85]. ............................................................... 145
Table 6-4: Derived cetane number (DCN) of FACE Fuels measured with ASTM method D6890. ................................................................................................................................. 145

Table 6-5: Quantitative hydrocarbon speciation by peak area percent of the FACE fuels measured with a 2-D GC-FID, reported in the CRC Report No. FACE-1 [85]. ........................................................................................................................................ 146

Table 6-6: Operational conditions for FACE Fuels tests......................................................... 147

Table 6-7: Specifications of the GM 1.9 L Engine................................................................. 147

Table 6-8: Specification of the engine operational conditions. ............................................. 148

Table B-1: Major sources of instrument errors, which affect gaseous emissions. ...... 195

Table B-2: Major sources of instruments errors, which affect PM emissions. ............ 195

Table B-3: Major sources of systematic errors, which affect gaseous and PM emissions. ............................................................................................................................... 195
<table>
<thead>
<tr>
<th>NOMENCLATURE</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>After Top Dead Center</td>
<td>ATDC</td>
</tr>
<tr>
<td>Apparent Heat Release Rate</td>
<td>AHRR</td>
</tr>
<tr>
<td>Apparent Rate of Heat Release</td>
<td>ROHR</td>
</tr>
<tr>
<td>Before Top Dead Center</td>
<td>BTDC</td>
</tr>
<tr>
<td>Brake Mean Effective Pressure</td>
<td>BMEP</td>
</tr>
<tr>
<td>Brake Specific</td>
<td>BS</td>
</tr>
<tr>
<td>Brake Specific Fuel Consumption</td>
<td>BSFC</td>
</tr>
<tr>
<td>Brake Thermal Efficiency</td>
<td>BTE</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>CN</td>
</tr>
<tr>
<td>ChevronPhillips Chemical Company</td>
<td>CPChem</td>
</tr>
<tr>
<td>Compression Ratio</td>
<td>CR</td>
</tr>
<tr>
<td>Cooperative Fuel Research</td>
<td>CFR</td>
</tr>
<tr>
<td>Crank Angle where 50% of cumulative heat release occurs</td>
<td>CA50</td>
</tr>
<tr>
<td>Derived Cetane Number</td>
<td>DCN</td>
</tr>
<tr>
<td>Direct Injection</td>
<td>DI</td>
</tr>
<tr>
<td>Electronic Control Unit</td>
<td>ECU</td>
</tr>
<tr>
<td>Emissions Index</td>
<td>EI</td>
</tr>
<tr>
<td>End of Combustion</td>
<td>EOC</td>
</tr>
<tr>
<td>End of Injection</td>
<td>EOI</td>
</tr>
<tr>
<td>Environmental Protection Agency</td>
<td>EPA</td>
</tr>
<tr>
<td>Equivalence Ratio</td>
<td>Φ</td>
</tr>
<tr>
<td>Term</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>--------------</td>
</tr>
<tr>
<td>Exhaust Gas Recirculation</td>
<td>EGR</td>
</tr>
<tr>
<td>Final Boiling Point</td>
<td>FBP</td>
</tr>
<tr>
<td>Fischer–Tropsch</td>
<td>FT</td>
</tr>
<tr>
<td>Flame Ionization Detector</td>
<td>FID</td>
</tr>
<tr>
<td>Fuels for Advanced Combustion Engines</td>
<td>FACE</td>
</tr>
<tr>
<td>Gas Chromatographic</td>
<td>GC</td>
</tr>
<tr>
<td>Gasoline Direct Injection</td>
<td>GDI</td>
</tr>
<tr>
<td>Gas-to-liquids</td>
<td>GTL</td>
</tr>
<tr>
<td>H-Abstraction-C$_2$H$_2$-Addition</td>
<td>HACA</td>
</tr>
<tr>
<td>Heat Release Rate</td>
<td>HRR</td>
</tr>
<tr>
<td>Heptamethylnonane</td>
<td>HMN</td>
</tr>
<tr>
<td>High Efficiency Clean Combustion</td>
<td>HECC</td>
</tr>
<tr>
<td>High Resolution Transmission Electron Microscopy</td>
<td>HRTEM</td>
</tr>
<tr>
<td>High Temperature Fischer–Tropsch</td>
<td>HTFT</td>
</tr>
<tr>
<td>High Temperature Heat Release</td>
<td>HTHR</td>
</tr>
<tr>
<td>Homogeneous Charge Compression Ignition</td>
<td>HCCI</td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>HC</td>
</tr>
<tr>
<td>Ignition Delay</td>
<td>ID</td>
</tr>
<tr>
<td>Intermediate Temperature Heat Release</td>
<td>ITHR</td>
</tr>
<tr>
<td>Low Temperature Combustion</td>
<td>LTC</td>
</tr>
<tr>
<td>Low Temperature Fischer–Tropsch</td>
<td>LTFT</td>
</tr>
<tr>
<td>Low Temperature Heat Release</td>
<td>LTHR</td>
</tr>
<tr>
<td>Term</td>
<td>Abbreviation</td>
</tr>
<tr>
<td>------</td>
<td>--------------</td>
</tr>
<tr>
<td>Mass Air Flow</td>
<td>MAF</td>
</tr>
<tr>
<td>Modulated Kinetics</td>
<td>MK</td>
</tr>
<tr>
<td>Negative Temperature Coefficient</td>
<td>NTC</td>
</tr>
<tr>
<td>Non-Methane Hydrocarbon</td>
<td>NMHC</td>
</tr>
<tr>
<td>Oak Ridge National Laboratory</td>
<td>ORNL</td>
</tr>
<tr>
<td>Paraffin Enhanced Clean Combustion</td>
<td>PECC</td>
</tr>
<tr>
<td>Paraffins, Iso-paraffins, Olefins, Naphthenes, and Aromatics</td>
<td>PIONA</td>
</tr>
<tr>
<td>Partially Premixed Charge Compression Ignition</td>
<td>PCCI</td>
</tr>
<tr>
<td>Particulate Matter</td>
<td>PM</td>
</tr>
<tr>
<td>Polycyclic Aromatic Hydrocarbon</td>
<td>PAH</td>
</tr>
<tr>
<td>Rate of Heat Release</td>
<td>ROHR</td>
</tr>
<tr>
<td>Soluble Organic Fraction</td>
<td>SOF</td>
</tr>
<tr>
<td>Southwest Research Institute</td>
<td>NREL</td>
</tr>
<tr>
<td>Spark Ignited</td>
<td>SI</td>
</tr>
<tr>
<td>Start of Combustion</td>
<td>SOC</td>
</tr>
<tr>
<td>Start of Injection</td>
<td>SOI</td>
</tr>
<tr>
<td>Temperature at 90 volume % distilled (mass when specified)</td>
<td>T90</td>
</tr>
<tr>
<td>The Pennsylvania State University</td>
<td>PSU</td>
</tr>
<tr>
<td>Top Dead Center</td>
<td>TDC</td>
</tr>
<tr>
<td>Total Hydrocarbon</td>
<td>THC</td>
</tr>
<tr>
<td>Unburned Hydrocarbon</td>
<td>UHC</td>
</tr>
</tbody>
</table>
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DEDICATION

To my favorite brother, Chris.
Chapter 1

Introduction

The goal of this work is to eliminate incomplete combustion in advanced diesel combustion processes. Chapter 2 presents a general literature review, which covers key combustion concepts. A brief literature review on specific topics is presented in each of the subsequent results sections. Chapter 3 provides hypotheses and objectives, which are the focus of this work.

In Chapter 4, a combination of advanced diesel combustion and high ignition quality fuel is demonstrated to simultaneously produce low NO\textsubscript{X}, PM, THC and CO emissions, in a light-duty diesel engine, while maintaining brake thermal efficiency, in comparison to a conventional diesel fuel, which produced low NO\textsubscript{X} and emission with elevated THC and CO emissions. This is a novel achievement since increased incomplete combustion, which manifests as THC and CO emissions, is an undesirable consequence of advanced combustion operations. Chapter 4 was published in 2011, under the title of “Advanced Diesel Combustion of a High Cetane Number Fuel with Low Hydrocarbon and Carbon Monoxide Emissions” in the journal *Energy and Fuels*.

In Chapter 5, a pseudo-fundamental experiment is conducted in a motored engine, which demonstrates that the leaner critical $\Phi$ of a high ignition quality fuel is a factor, which results in the reduction of incomplete combustion during advanced diesel combustion. Furthermore, critical $\Phi$ is presented as a novel measurement to compare the ignition behavior among different fuels.
Finally, in Chapter 6 it is shown that the critical $\Phi$ of a fuel is governed by the fraction of reactive components (n-paraffins), which increases LTHR. In a light duty engine, incomplete combustion is then demonstrated to be decreased due to the fraction of n-paraffins in a fuel, regardless of ignition quality. Ultimately, this result indicates that incomplete combustion can be decreased in advanced combustion modes that rely on both high and low ignition quality fuels by increasing the fraction of n-paraffins in the fuel.
Chapter 2

Literature Review

The pursuit of an idealized combustion process, which offers maximum efficiency and the lowest possible emissions from incomplete combustion, is the governing motivation behind this work. To achieve such a lofty goal, it is practically necessary to identify the possibility and limitations available to modify the internal combustion engine combustion process, through advanced combustion techniques, fuel effects or both.

Advanced combustion or low temperature combustion (LTC) is a relatively novel area of research compared to conventional combustion; however it is a heavily studied topic which is evident by two review articles recently published by Dec [1] and Yao et al. [2]. The aforementioned review papers also are evidence that a universally accepted nomenclature for advanced diesel combustion has yet to be identified. Unfortunately, the term homogeneous charge compression ignition (HCCI) is often used as a ‘blanket’ term that covers both gasoline and diesel advanced combustion regimes. For the purposes of this work, diesel advanced combustion is considered best associated with the term partially premixed charge compression ignition (PCCI). As indicated by its name, PCCI is a combustion method in which there is enhanced premixing of the air-fuel charge prior to ignition. Premixing of the charge can be promoted by injecting high-pressure jets of fuel significantly before or significantly after the high in-cylinder pressure that occurs when an engine piston is at top-dead-center (TDC). Furthermore, premixing of the air-fuel charge is further enhanced by the extension of ignition delay (ID) due to the
dilution of intake air with exhaust gas, via exhaust gas recirculation (EGR). The premixing of the air-fuel charge is ultimately desired to reduce local equivalence ratio (\(\Phi\)) and reduce localized temperature, compared to that achieved during conventional diesel combustion. The benefit of advanced combustion is that it occurs in a combustion regime which avoids the NO\(_X\)-soot tradeoff, commonly associated with conventional diesel combustion, as shown in Figure 2-1 [3]. The formation of NO\(_X\) and soot are discussed in detail in a later section of this literature review.

![Figure 2-1: A model of CI 3D-CFD model to map equivalence ratio vs. temperature. Developed by Akihama [3] and later modified by Assanis [4].](image)

Dec [1] and Yao et al. [2] discuss the challenges and voids of knowledge that still remain for advanced diesel combustion. Among the most predominant challenges are the high carbon monoxide (CO) and hydrocarbon (HC) emissions that are produced from advanced diesel combustion [1, 2]. Dec [2] also notes that “improved chemical-kinetic
models that more accurately predict low temperature heat release, pressure-boost effects, and the behavior of realistic fuels” would benefit advanced combustion. Yao et al. [2] stated that “optical diagnostics will provide foundations for the in-depth physical understanding and reliable predictive submodels for HCCI in-cylinder processes,” which will enhance the understanding of advanced combustion.

The obstacles mentioned above are directly related to the fuel autoignition process. Advanced diesel combustion and conventional diesel combustion may occur in different regimes of localized temperature and equivalence ratio, but they do share many of the same features or thermo-fluid phenomena. The phases of conventional diesel combustion according to Heywood [5] are given in Figure 2-2. The rate at which heat is released during the oxidation of hydrocarbon fuels is described chronologically by the crank angle at which the event occurs during a compression ignition combustion cycle.

![Figure 2-2: Conventional DI diesel rate of heat release vs. crank angle of the major phases of the diesel combustions process [5].](image-url)
Heywood [5] describes the conventional combustion process, shown in Figure 2-2, to occur as follows. The start of injection (SOI) is the point at which fuel first enters the combustion chamber, which occurs as the piston is traveling towards top-dead-center (TDC). As the fuel is injected into the chamber, heat is absorbed by the liquid fuel and the fuel is vaporized. Once a given droplet of fuel is vaporized, chemical kinetics govern the rate of oxidation. The ignition delay (ID) is the period required for a sufficient amount of fuel to be oxidized, such that a net positive rate of heat is released. Even as vaporized fuel begins to be oxidized, liquid can still be injected and penetrate throughout the cylinder, allowing fuel to mix with air. The fuel and air, which premix, eventually autoignite producing a high rate of heat release in what is known as the premixed combustion phase. As a side note, HCCI operations will ideally only have premixed combustion. After the premixed fuel-air charge is consumed and fuel is still being injected into the cylinder, there is a transition to a diffusion burn and a lower rate of heat release. This highly stratified condition is known as the mixing-controlled combustion burn. At 180 crank angle degrees, the piston hits TDC. Eventually the end of injection (EOI) occurs, but the highly stratified fuel-air charge continues to burn in the mixing-controlled burn. The piston has been traveling away from TDC, decreasing both pressure and temperature inside of the cylinder. Meanwhile, the little fuel, which remains is consumed in an ever-decreasing rate of heat release called the late combustion phase.

The ID period, shown in Figure 2-2, is of great interest since this initial event in the combustion process affects the course in which fuel oxidizes. For example, a long ID will allow for a greater degree of air-fuel premixing and thus a lower localized equivalence ratio, which subsequently affects gaseous exhaust emissions. As indicated
above, the ID is comprised of a physical ID and a chemical ID. Since a diesel injector produces a very stratified fuel jet, and injection of fuel can occur well after the ignition event, the physical ID and the chemical ID can overlap.

2.1 Physical Ignition Delay

Combustion systems, which utilize high-pressure liquid fuel injection systems, such as diesel engines are subject to a fuel vaporization event referred to as the physical ignition delay. In contrast, HCCI engines, rapid compression machines and shock tubes combust fuel, which has been vaporized before entering the combustion system. In combustion systems where fuel has been pre-vaporized, negative heat release from vaporization is not present in the apparent rate of heat release traces. The physical ignition delay is the period of time which elapses between the introductions of liquid fuel into the cylinder to the moment the fuel changes phase to vapor. An extended discussion of an igniting liquid fuel jet is given later. It is first necessary to discuss the chemical ignition process.

2.2 Chemical Ignition Delay

According the Westbrook [6], “the key to understanding ignition kinetics is to identify the chain branching steps under the condition being studied.” The energy contained in a hydrocarbon fuel is released as heat as the fuel oxidation process undergoes chain branching reactions. In general, oxidation of heavy hydrocarbon fuels,
in an internal combustion engine during autoignition, initiates in the “low” temperature regime and passes onto the “intermediate” temperature (850 K to 1200 K) and “high” temperature (T ≥ 1200 K) regimes as temperature increases. However, if initial temperature is high enough and pressure is low enough, it is possible for oxidation to initiate in the intermediate temperature regime. Figure 2-3 provides a general indication of hydrocarbon oxidation chemistry, where the temperature of a given temperature regime is relative to pressure.

![Figure 2-3](image)

**Figure 2-3:** “Regimes of hydrocarbon oxidation chemistry as delineated by the main kinetic chain branching processes. The upper line connects points where overall H + O₂ reaction is neutral: above the line is net branching; below the line is net terminating. The lower lines are where the peroxy chemistry is neutral: above these lines there is net termination and below net branching. The ‘low,’ ‘intermediate’ and ‘high’ temperature regions are broadly characterized by the types of chemistry indicated” [7]. Originally printed in Morley and Philling [8].

As seen in Figure 2-4, the oxidation of a hydrocarbon fuel can release heat in two stages. The initial heat release, which occurs due to low temperature chemistry, is often
referred to as cool flame or first stage heat release. The onset of the first stage heat release is referred to as the first stage ignition. The onset of the second heat release event, or second stage ignition, occurs due to intermediate temperature chemistry. However, the majority of fuel consumption and heat release is due to high temperature chemistry during the second stage heat release. The second stage ignition identifies the temporal location of the overall ignition delay, while the majority of heat is released during the second stage heat release. However, first stage heat release is important since it hastens the onset of the second stage heat release [9].

Figure 2-4: Heat release curve from constant volume combustion chamber with iso-octane fuel.
Alkane oxidation mechanisms are used to describe the general oxidation chemistry of a hydrocarbon, due to the simplicity of alkane chemistry. Furthermore, long chain alkanes have the highest propensity for autoignition, compared to other hydrocarbon chemical structures. A general scheme for the oxidation of an alkane is given in Figure 2-5. Westbrook [6], Curran et al. [10], Battin-Leclerc [11] and Zhang [7] give more detailed descriptions of kinetic routes of hydrocarbon oxidation.

Figure 2-5: A general scheme of alkane oxidation, where \( \cdot \) denotes an alkyl radical and \( Q \) denotes a \( \text{C}_n\text{H}_{2n}\).

2.3 Low Temperature Oxidation

The initiation step of oxidation under low temperature conditions is due to H-atom abstraction to form alkyl radicals, where the tertiary then secondary hydrogens are more likely to be abstracted (such that, \( \cdot \text{RH} + \text{O}_2 \rightarrow \cdot \text{R} + \text{HO}_2 \)). The alkyl radical then proceeds to chain branching through a series of two oxygen additions. The initial oxygen
addition produces peroxy alkyl radical (ROÔ) followed by internal isomerization to form a hydroperoxy alkyl radical species (QOOH). At this point, depending on temperature, the hydroperoxy alkyl radical can continue to chain branching by the addition of a second O₂ and isomerize into transition state rings via the intermolecular H-atom transfer. A detailed description of heptyl radical formation into a transition state ring is given by Zhang [7]. The result of the isomerization is the formation of a ketohyperoxide (HOOQ′=O), which then decomposes to form two radicals. This low temperature chain branching is indicated by low temperature heat release also referred to as cool flame behavior, as seen in Figure 2-4.

The route to low temperature chain branching is highly temperature dependent. As temperature increases, reactivity decreases in what is known as negative temperature coefficient (NTC) behavior [10]. The NTC region is observed in Figure 2-4 as the area of low heat release between the first and second stage ignition. Sufficiently low initial temperature and a sufficiently high initial pressure will cause low temperature oxidation chain branching to occur, releasing heat. However, if initial temperatures are high enough and initial pressures low enough, low temperature chemistry will be bypassed and the lack of cool flame heat release will delay the occurrence of second stage heat release. NTC behavior can be attributed to a shift into three non-branching reaction pathways, due to temperature. First, at increased temperatures the peroxy alkyl radical dissociates back into an alkyl radical and oxygen becomes preferable over the forward reaction (R + O₂ → ROÔ), which has a zero activation energy [10]. Secondly, with increased temperatures, the chain propagation to aldehyde, olefin and cyclic ether pathways, shown in Figure
2-5, gains importance over the chain branching pathway. Lastly, as temperature increases, the combustion regime transitions to that of intermediate temperature oxidation chemistry where fuel consumption is lower.

### 2.4 Intermediate Temperature Oxidation

Intermediate temperature oxidation chemistry is comparatively simple compared to that of low temperature. The intermediate temperature oxidation chemistry initially involves low reactivity, slightly exothermic reactions, which are considered by some to be part of the NTC regime [12, 13]. During this reaction regime, a pool of hydrogen peroxide (H₂O₂) builds-up until it decomposes at temperatures between 950 K and 1000 K [6]. The decomposition of hydrogen peroxide is a chain branching reaction which forms two hydroxide radicals (OH), ushering in the onset of the high temperature oxidation chemistry. Westbrook [6] describes the intermediate oxidation chemistry as the following three reactions.

\[
\begin{align*}
\hat{H} + O_2 + M & \rightarrow H\hat{O}_2 + M \quad \text{(R 2-1)} \\
\hat{R} + H\hat{O}_2 & \rightarrow \hat{R} + H_2O_2 \quad \text{(R 2-2)} \\
H_2O_2 + M & \rightarrow \hat{O}H + \hat{O}H + M \quad \text{(R 2-3)}
\end{align*}
\]

### 2.5 High Temperature Oxidation

The hydroxyl radicals formed by the intermediate temperature chemistry now begin consuming fuel and the second stage heat release produces large quantities of heat.
The hydroxide radicals along with O and H radicals attack the remaining fuel molecules, breaking the hydrocarbon chains into smaller olefins by H-atom abstraction, and carbon-carbon cleavage, following the β-scission rule [14]. Meanwhile the radical pool is increased by the high temperature chain branching reaction:

\[
\text{H} + \text{O}_2 \rightarrow \text{O} + \text{OH}
\]  

(R 2-4)

The chain branching reactions of the low and high temperature regimes are responsible for the majority of heat released during combustion, as shown in Figure 2-4.

2.6 Direct Injection of a Diesel Fuel Jet

The direct injection (DI) of diesel fuel into a combustion chamber is a process that contains many competing phenomena that are difficult to decouple. Many factors or injection parameters are intimately intertwined with ignition delay and ultimately production of pollutants. Siebers [15] is among the leading authorities on DI of diesel fuel and the accompanying physical processes, which lead to ignition. A recent book chapter by Siebers [15] chronicles the current understanding of diesel jet injection process. Much of the work noted in the following section was produced under quiescent engine conditions, using a common-rail DI constant volume chamber. Nevertheless, the fundamental concepts discussed below extend to more complex diesel engine systems.

Siebers [15] identifies key parameters that affect the diesel fuel jet by comparing empirical results, that include an injection of a non-vaporizing fuel jet, injection of a non-combusting vaporizing fuel jet and injection of a combusting fuel jet, to a penetration scaling law model developed by Naber and Siebers [16]. The penetration scaling law
describes a non-vaporizing, or isothermal, fuel jet that is dependent on fuel jet spread angle, effective orifice diameter, fuel velocity, fuel density, ambient gas density, orifice diameter, fuel injection pressure and ambient gas pressure. The comparison between the experimental results and the scaling law model allowed for decoupling of injection parameters. The law assumes radially uniform velocity, a constant fuel concentration profile, an instantaneous start of injection and no velocity slip between the injected fuel and the entrained air. In general, the law correlates non-dimensional penetration time to non-dimensional penetration distance. As such, the penetration of a fuel jet was simply reported as a velocity.

### 2.6.1 Effects of Spreading Angle on Fuel Jet Penetration

Among the many parameters that will affect fuel jet penetration is spreading angle. Spreading angle of a fuel jet is the angle at which a single fuel jet widens. Spread angle is dependent on orifice geometry, orifice shape, orifice orientation, injector needle interaction and ambient gas density [15]. The penetration scaling law indicates that an increased spreading angle results in slower penetration of fuel jet. Reduced penetration velocity occurs as a wide-spreading angle fuel jet entrains more air. The mass increase of the fuel jet due to the entrained air will result in a lower overall jet velocity due to the conservation of jet momentum. Furthermore, large differences in fuel and ambient gas densities have an effect on turbulent mixing and air entrainment of the jet.
2.6.2 Effects of Vaporization on Fuel Jet Penetration

Experimental testing of a vaporizing fuel jet in a constant volume chamber, under non-combusting conditions, was compared to the non-vaporizing fuel jet of the penetrating scaling law [15, 16]. The non-vaporizing experimental condition was achieved by the use of an ambient gas, which did not contain oxygen. The comparison indicates that the vaporization process of a fuel jet slows penetration (decreases penetration) relative to a non-vaporizing fuel jet. The magnitude of the reduction was found to be as much as 20% under lower ambient gas density conditions. The comparison further indicated that as the fuel jet enters the region where evaporation was complete, the vaporized fuel jet had a decreased impact on the fuel jet tip penetration. This effect was attributed to vaporization that produces a cooling effect, which results in a higher density fuel jet and thus slower penetration velocity. A less prominent competing effect is the reduction of air entrainment through vaporization.

2.6.3 Effects of Combustion on Fuel Jet Penetration

The comparison of a non-combusting fuel jet to the combusting fuel jet indicated similar penetration by the two jets until the point of combustion [15, 16]. Compared to a non-combusting jet, the combusting fuel jet decreased speed less rapidly in the combusting region of the jet. Two reasons were hypothesized for the faster penetration rate of a combusting jet. The heat release caused the average density of the fuel jet to decrease, resulting in faster penetration by the conservation of jet momentum. In
addition, the heat release decreased air entrainment, reducing mass in the fuel jet, and again increased penetration rate based on the conservation of jet momentum.

### 2.6.4 Liquid-phase Fuel Penetration

In the previous sections, experimental data was compared to the penetration scaling law by Siebers [15]. The mass of the fuel jet was indicated to govern the velocity of the fuel jet based on the conservation of jet momentum. In this section, the empirical effect of fuel jet penetration will be examined under parametric variation of key parameters. The maximum penetration length of a fuel jet, from orifice to jet top, is referred to as “liquid length.” The end of the liquid length is defined by the point in which fuel is vaporized. Increased liquid fuel jet penetration enhances air-fuel mixing through entrainment and turbulent mixing. Air-fuel mixing is required to reduce localized equivalence ratios to reduce NO\textsubscript{X} and PM emissions during advanced combustion. However, over-penetration of liquid fuel can result in liquid fuel impingement on the cylinder and/or the piston bowl. As such, liquid fuel impingement can be a source of emissions of incomplete combustion such as HC and CO. Results of many experimental studies were compiled, which indicate the effect of injector orifice diameter, pressure drop across the injector, ambient gas density, ambient gas temperature and fuel volatility on liquid length [15]. Table 2-1 examines the effect of injector orifice diameter, pressure drop across the orifice, ambient gas density, ambient gas temperature and fuel boiling point on liquid length.
**Table 2-1: Effect of injection parameters on liquid length based on Siebers [15].**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effect on liquid length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector orifice diameter</td>
<td>Strong linear dependent decrease with decrease in diameter.</td>
</tr>
<tr>
<td>Pressure drop across injector orifice</td>
<td>Independent of pressure drop.</td>
</tr>
<tr>
<td>Ambient gas density</td>
<td>Decreases with increased ambient gas density due to increased air entrainment (based on jet conservation of momentum).</td>
</tr>
<tr>
<td>Ambient gas temperature</td>
<td>Decreases with increased ambient gas temperature due to the temperature effect on fuel volatility.</td>
</tr>
<tr>
<td>Fuel boiling point</td>
<td>Linear decrease with decreasing boiling point for both single and multi-component fuels. Most pronounced at lower temperature conditions.</td>
</tr>
</tbody>
</table>
2.6.5 Flame Lift-Off

According to Siebers [15], the lift-off length is defined as the distance from the fuel injector to nearest the region in which the injected fuel jet is combusting. The lifted flame is believed to combust as a turbulent diffusion flame that surrounds the periphery of the fuel jet and as a rich partially premixed flame that occurs due to air entrainment by the liquid fuel jet. Lift-off length is most readily measured using chemiluminescence of the excited-state OH. Table 2-2 examines the effect of injector orifice diameter, pressure drop across the orifice, ambient gas density, ambient gas temperature and ambient gas oxygen concentration on lift-off length.

Table 2-2: Effect of injection parameters on lift-off length based on Sibers [15].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effect on lift-off length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector orifice diameter</td>
<td>Increases as the orifice diameter increases.</td>
</tr>
<tr>
<td>Pressure drop across orifice</td>
<td>Increases linearly with respect to the square-root of pressure drop (i.e. injection velocity).</td>
</tr>
<tr>
<td>Ambient gas temperature</td>
<td>Strong non-linear decrease with increase of ambient gas temperature.</td>
</tr>
<tr>
<td>Ambient gas density</td>
<td>Strong non-linear decrease with increase of ambient gas density.</td>
</tr>
<tr>
<td>Ambient gas oxygen concentration</td>
<td>Increase approximately proportional to the decrease of oxygen concentration.</td>
</tr>
</tbody>
</table>

2.6.6 Oxygen Entrainment

Another key distinguishing feature of the diesel fuel jet, noted by Siebers [15], is oxygen entrainment. Above, oxygen entrainment was mentioned to be a major factor in
diesel jet penetration. Furthermore, an increase of oxygen entrainment decreases localized equivalence ratio, which enhances soot oxidation. Siebers defines percentage of stoichiometric air ($\zeta_{st}$), entrained prior to the lift-off length, as the reciprocal of the average equivalence ratio multiplied by 100. Stoichiometric oxygen entrained upstream of the lift-off was noted by Siebers to have the following effects, noted in Table 2-3.

Table 2-3: Injection parameter effect of stoichiometric oxygen entrained upstream of lift-off length based on Sibers [15].

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Effect on stoichiometric oxygen entrained upstream of lift-off length</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector orifice diameter</td>
<td>Decrease in injector orifice diameter strongly increases stoichiometric oxygen, which only partially counters the decrease in lift-off length.</td>
</tr>
<tr>
<td>Pressure drop across injector orifice</td>
<td>Linear increase with an increase of pressure drop. Due to coinciding increase in lift-off length.</td>
</tr>
<tr>
<td>Ambient gas temperature</td>
<td>Strong non-linear decrease with increase of ambient gas temperature. Due to the decrease in lift-off length.</td>
</tr>
<tr>
<td>Ambient gas density</td>
<td>No significant change due to ambient gas density, under constant temperature.</td>
</tr>
<tr>
<td>Ambient gas oxygen concentration</td>
<td>Increase approximately proportional to the decrease of oxygen concentration.</td>
</tr>
</tbody>
</table>
Siebers notes key implications of the comparisons of the liquid length scaling law to empirical data. One such implication is that the role of injector orifice diameter on vaporization is to increase the jet mixing process rather than increase atomization of droplets.

2.6.7 Physical ID and Chemical ID

Liquid length and lift-off length are measured based on time-averaged images of diesel fuel jets. If velocity of the diesel jet is known, then a discrete time can be applied to the location of the liquid length and the lift-off length. As such, the physical ID and the chemical ID can be deduced from a time-average image of a diesel jet.

Siebers makes note of two distinct cases of simplified and exaggerated diesel fuel jets. In the first case, the liquid length is longer, and in the second case, the lift-off length is longer, shown in Figure 2-6. Because the jet on the left has a longer liquid length than lift-off length, the physical ID overlaps into the chemical ID. However, the jet on the right, where the lift-off length is longer than the liquid length, has a distinct physical ID and chemical ID.
Figure 2-6: “Schematics showing how the relative spatial relationship between fuel vaporization and combustion zones and the percent of stoichiometric air entrained up to the lift-off length can change with conditions in a DI-type diesel fuel jet under quiescent conditions. The schematic at the left is for an ambient-gas temperature and density of 1100 K and 23 kg/m³, and an orifice pressure drop and orifice diameter of 40 MPa and 250 μm. The schematic at the right is for an ambient-gas temperature and density of 1000 K and 20 kg/m³, and an orifice pressure drop and orifice diameter of 200 MPa and 100 μm” [15].

2.7 NOₓ Formation

Oxides of nitrogen, known as NOₓ, are of concern due to their health and environmental effects. NO oxidizes to form NO₂ in the atmosphere, which is key in the production of photochemical smog and acid rain [14]. NOₓ is a term referring to nitric oxide (NO) and nitrogen dioxide (NO₂), collectively. Typically 95% of engine-emitted
NO\textsubscript{X} is NO\textsuperscript{[5]}. The majority of NO\textsubscript{X} formation is attributed to the thermal or Zeldovich mechanism given in (R 2-1) and (R 2-2) extended with (R 2-3)\textsuperscript{[14]}.  

\begin{align*}
\text{O} \leftrightarrow \text{NO} + \text{N} & \quad \text{(R 2-1)} \\
\text{N} + \text{O}_2 \leftrightarrow \text{NO} + \text{O} & \quad \text{(R 2-2)} \\
\text{N} + \text{OH} \leftrightarrow \text{NO} + \text{H} & \quad \text{(R 2-3)}
\end{align*}

The Zeldovich mechanism is thermally dependent and is active at \(\Phi\) nearing unity where temperatures upward of 2200 K lead to high rates of formation of NO\textsubscript{X}\textsuperscript{[2]}. Under advanced combustion or LTC conditions, other NO\textsubscript{X} formation mechanisms produce a more significant contribution to total NO\textsubscript{X} emissions. The Fennimore mechanism, or prompt NO, has been shown to rapidly form NO\textsubscript{X} due to hydrocarbon radicals before the Zeldovich mechanism has the time to produce NO\textsubscript{X}\textsuperscript{[14]}. The prompt NO\textsubscript{X} mechanism is given from (R 2-4) and (R 2-9), where the rate limiting reaction is (R 2-4)\textsuperscript{[14]}.  

\begin{align*}
\text{CH} + \text{N}_2 \leftrightarrow \text{HCN} + \text{N} & \quad \text{(R 2-4)} \\
\text{C} + \text{N}_2 \leftrightarrow \text{CN} + \text{N} & \quad \text{(R 2-5)} \\
\text{HCN} + \text{O} \leftrightarrow \text{NCO} + \text{H} & \quad \text{(R 2-6)} \\
\text{NCO} + \text{H} \leftrightarrow \text{NH} + \text{CO} & \quad \text{(R 2-7)} \\
\text{NH} + \text{H} \leftrightarrow \text{N} + \text{H}_2 & \quad \text{(R 2-8)} \\
\text{N} + \text{OH} \leftrightarrow \text{NO} + \text{H} & \quad \text{(R 2-9)}
\end{align*}

The prompt NO mechanism has also been shown to couple with the Zeldovich mechanism to destroy NO\textsuperscript{[14]}. HCN, produced early in the combustion event due to the prompt NO\textsubscript{X} mechanism, can convert NO formed by the Zeldovich mechanism back into \text{N}_2 and \text{O}.  

\
The N$_2$O-intermediate mechanism is a second minor NO$_X$ mechanism, which is important under fuel-lean conditions (Φ < 0.8) and low temperatures. N$_2$O emissions have been shown to significantly increase under HCCI conditions with incomplete combustion [17]. This would imply that NO$_X$ formed through the N$_2$O-intermediate mechanism is more significant during advanced combustion modes with incomplete combustion. The N$_2$O-intermediate mechanism is shown in (R 2-10), (R 2-11) and (R 2-12).

$$O + N_2 + M \leftrightarrow N_2O + M \quad \text{(R 2-10)}$$

$$H + N_2O \leftrightarrow NO + NH \quad \text{(R 2-11)}$$

$$O + N_2O \leftrightarrow NO + NO \quad \text{(R 2-12)}$$

2.8 Particulate Matter

The formation of soot in a diesel engine is a more complex and less understood process than that of NO$_X$. The term diesel soot is often used interchangeably with particulate matter (PM). This is because PM is composed of a solid carbon fraction or soot and a condensed fraction referred to as the soluble organic fraction (SOF) [5]. PM / soot emissions are of concern because particulates can cause multiple health disorders when inhaled. PM of 10 μm or less can penetrate deep into the lungs and can result in cancer, autoimmune disorders, alteration in blood coagulability and increased cardiovascular disorders [18]. Diesel combustion engines have historically produced large amounts of PM emissions over gasoline engines, due to the diesel combustion process [5].
2.8.1 Soot Formation Process

Diesel soot is formed under fuel-rich high temperature conditions via pyrolysis. At the heart of the soot formation process is the conversion of a hydrocarbon fuel with a typical H/C ratio of 2, to particles having a H/C ratio of 0.1 [5]. In a recent review, Tree [19] describes the soot formation process as seen in Figure 2-7, in the order: pyrolysis, nucleation, coalescence and agglomeration.

![Figure 2-7: “Schematic diagram of the steps in the soot formation process from gas phase to solid agglomerated particles” [19].](image)

Soot formation starts with fuel pyrolysis, which is an endothermic process that is temperature dependent. Pyrolysis is responsible for forming soot precursors in the presence of little to no oxygen. Polycyclic aromatic hydrocarbons (PAH) and acetylene (C2H2) have long been accepted as being the main soot precursors [20]. Experimental results show that the presence of PAHs corresponds with soot formation [21]. The precursors condense in the gas phase to form the nuclei of the soot particles [22]. The nuclei contain very little mass of the total soot particle. This is necessary for surface growth to occur.

Nucleation is the process of PAH growth. Aromatic rings are the necessary building material to form PAHs. The rings will either be available from pre-existing aromatics in the fuel or will be produced by the cyclization of chain hydrocarbons with
acetylene to form benzene rings [23]. According to Frenklach [24], the PAHs will form directly from aromatic fuels under the high temperature pyrolysis of benzene as the dominant PAH growth step. Frenklach [25] also describes the HACA (H-Abstraction-C$_2$H$_2$-Addition) mechanism, which has been accepted to be the main mechanism for PAH growth. In the HACA mechanism, hydrogen is first abstracted from an aromatic molecule followed by the addition of acetylene to promote the growth of PAH molecules. A summary of the HACA mechanism is given in Figure 2-8.

![Figure 2-8: The HACA mechanism for planar PAH growth (a), and extended to the surface growth of soot (b)" [26].](image)

The next stage involves the growth of the particle by a process of surface growth, which is the main source of particle mass. Smith defines the surface growth step as the addition of mass after nucleation [20]. According to a recent review by Tree [19], the
process of surface growth is not fully understood. It has been conjectured that surface growth follows a variation of Freenklach’s HACA [24, 25] mechanism [26]. It is, however, known that polyacetylenes are the main hydrocarbons added in surface growth. Haynes and Wagner [22] point out that high hydrogen content molecules are necessary for particle growth to occur via surface growth and coagulation. Figure 2-9 depicts the process in which dehydrogenation of the hydrocarbon species occurs only after the hydrocarbons condense on the soot particle, causing an increase of mass. In addition, the rate of surface growth is increased for smaller particles which have more reactive radical sites as compared to larger particles [19].

Figure 2-9: Paths to soot formation on plot of species molecular weight M versus hydrogen mol fraction XH. Originally printed in Homann [27], reprinted in Haynes and Wagner [22].

Coagulation occurs in parallel with surface growth. In this process, small soot particles of spherical shape collide to form larger soot particles that still retain the
spherical shape, which is referred to as coagulation [20]. Aggregation of particles also occurs by collision. In this process, soot particles collide to form long chains and clusters [19], which can be clearly seen in a micrograph of diesel soot shown in Figure 2-10.

![Figure 2-10: Micrograph of diesel soot [28].](image)

Oxidation of the soot being formed can occur any time throughout the soot formation process. In some very early work, Fenimore and Jones [29] showed soot formation to be a competition between agglomeration and oxidation. According to
Fenimore and Jones [29], soot oxidation mainly occurs by the OH radical in fuel-rich conditions. However, CO molecules are competing with soot for OH radicals as shown in (R 2-13) [30].

\[
\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H} \quad \text{(R 2-13)}
\]

### 2.8.2 Soot Formation in a Contention Diesel Engine

As mentioned by Smith, much of the early fundamental work done to understand diesel soot had not been done on diesel engines, but on simple systems such as premixed flame burners and diffusion burners, flame burners, and perfectly stirred reactors [20]. As such, the results from these fundamental experiments were assumed to apply to the more complex diesel combustion process. Early reviews, such as those by Heywood [5], Smith [20], Heynes and Wagner [22], discuss theoretical models and attempted to explain how soot was generated by the diesel jet in a diesel engine. However, based on extensive studies using optically accessible engines, Dec [31] has presented a conceptual model of soot formation in a diesel jet as shown in Figure 2-11.
It should be noted that the use of the term “premixed” in Figure 2-11 refers to air entrainment, where Heywood’s usage of “premixed” refers to the initial combustion event that occurs at the start of combustion. The model indicates a lift-off distance from the injector until the fuel ignites at an equivalence ratio of about 4. As the diesel jet progresses from left to right, the entrained air is replaced with gases formed from combustion, and pyrolysis occurs. Soot is formed along the length of the jet where it is finally re-circulated through the vortex at the head of the jet, when the soot particles grow in size. This corresponds to Glassman’s [32] conclusion that the average soot inception temperature in a diffusion flame is ~1600 K, based on the soot inception temperature of various simple alkane and alkene fuels. Temperature increases as the soot eventually reaches the outside of the diesel jet, where it is oxidized by the diffusion flame.
2.8.3 Contribution of Soluble Organics

When diesel particulate matter is collected on a filter for measurement, it is not diesel soot alone. Soluble organics in the form of liquid phase hydrocarbon, sulfur and metal are absorbed onto the surface of the soot [33]. The combination of soot and the soluble organic fraction (SOF) are commonly referred to as particulate, which is illustrated in Figure 2-12.

![Figure 2-12 Typical composition and structure of engine exhaust particles [33].](image)

Mass based-measurements of soot do not distinguish between SOF and soot. Figure 2-13 provides a mass fraction of a typical diesel particulate. The carbon portion of the particle is soot, formed in the process mentioned earlier. Unburned fuel is found in the exhaust, often when it is quenched on the cylinder walls, unable to find its way to a combustible zone. Lubricant oil can easily be vaporized and blown out the cylinder along with the exhaust. Heywood [5] reported sulfur content of diesel to be 0.5% in 1988, which is very high compared to current ultra-low sulfur diesel (ULSD) fuel, which
is required by the Environmental Protection Agency (EPA) to contain 15 ppm of sulfur [34]. Water is a product of complete combustion. Ash and other inorganics come from metal additives, put into lube oils and produced from engine wear.

![Pie chart showing typical particle composition for a heavy-duty diesel engine tested in a heavy-duty transient cycle [33].]

The typical method for removing SOF from soot is to use solvents such as methylene chloride [5]. However, after solvent extraction, it should not be assumed that only soot remains. Vander Wal et al. [35] reports the existence of hollows throughout soot particles. These soot particles hollows could contain SOF, which may not be removed from solvent extraction.

### 2.8.4 NOₓ-PM Trade Off

A diesel engine is conventionally operated with the majority of the combustion occurring in the mixing-controlled combustion phase at high loads. The premixed
combustion phase is the dominant combustion phase, under low load conditions and depending on the injection strategy. Throughout a vehicle’s drive cycle, combustion will shift from a rich mixing-controlled combustion phase to a high temperature premixed combustion phase. NO\textsubscript{X} and soot emissions will likewise transition, owing to the change in combustion phase. This is the basis of the NO\textsubscript{X}-soot trade off in conventional diesel combustion operations. A recent trend of shifting the diesel combustion operation to a premixed combustion phase operation and low combustion temperatures has been seen in literature [3, 4, 36, 37]. Due to the lean premixed nature of these new combustion modes, the combustion occurs at lower temperatures, and the regime of combustion is referred to as low temperature combustion (LTC). In terms of compression ignition engines, LTC combustion occurs as partially premixed charge compression ignition (PCCI). PCCI is often associated with homogeneous charge compression ignition (HCCI), though they are distinctly different combustion techniques [19]. The main drive to LTC combustion strategies is due to the mixing-controlled burning phase generates large amounts of temperature dependent NO\textsubscript{X} and particulate due to locally fuel-rich diffusion burning. This occurs during the globally fuel-lean combustion process, as shown in Figure 2-11 of the conventionally combusting diesel jet developed by Dec [31].

The concept of LTC combustion, or advanced combustion, is to operate the engine at temperatures and at equivalence ratios where soot and NO\textsubscript{X} do not form. In premixed combustion, soot is still formed; however, the rate of oxidation of the soot greatly increases over the rate of formation as the temperature increases [19]. The process of LTC in a compression ignition engine has been the focus of much work since the early 1980’s when Smith [20] wrote, “We therefore conclude, as others have done,
that soot formation is inherent in the operation of compression ignition engines.”

Through a series of experiments and models, Akihama [3] developed CI 3D-CFD numerical simulation that clearly shows the desirable region to avoid soot formation, given in Figure 2-1.

2.9 Sources of Incomplete Combustion

Products of incomplete combustion by definition are fuel products which do not oxidize to H₂O and CO₂ as final products [32]. HC, CO and PM emissions are all products of incomplete combustion. However, in this work the products of incomplete combustion will generally be referring to only HC and CO, since HC and CO are formed in the same location within the engine cylinder [38]. Although, the complete oxidation of HC and CO is inhibited by an insufficient radical pool. In contrast, soot is formed by pyrolysis, before the fuel even begins to oxidize.

The sources of incomplete combustion differ slightly under premixed conditions, compared to mixing-controlled conditions where stratified mixtures of fuel and air are predominate. Under premixed conditions, incomplete combustion will occur in regions of the combustion chamber where overly rich, overly-lean, or thermodynamically unfavorable conditions produce meager radical pools. Figure 2-14 shows key regions of the combustion chamber where thermal and chemical conditions vary. In an ideal premixed combustion environment, complete combustion will occur in the core gas region [2]. Incomplete combustion will occur in localized regions of the chamber where
combustion is quenched such, as the walls of the combustion chamber and the crevice volume [39].

![Diagram of crevice volume](image)

**Figure 2-14: General layout of the quasi-dimensional thermodynamic simulation showing** [40]. Reprinted in Yao et al. [2].

### 2.9.1 Total Hydrocarbon Formation

HC emissions are typically reported as total hydrocarbons (THC), unburned hydrocarbons (UHC) or non-methane hydrocarbons (NMHC). THC is a convenient method to report HC emissions when no attempt is made to distinguish the source of HC detected, or the composition of the hydrocarbon species such as in this work. Cheng et al. indicates some of the main sources of THC emissions are from premixed combustion. THC can manifest as fuel, which avoided any oxidation, such as when fuel leaks from exhaust valves. THC also manifests as partially oxidized stable intermediate species. The oxidation of fuel can be halted due to quenching in regions of the cylinder such as the cylinder walls, crevices volume or piston crown [39]. Fuel can absorb into the oil layer on the cylinder wall or deposits on the cylinder wall, then desorb during the exhaust
stroke [39]. In situations where $\Phi$ is stratified, partial oxidation of HC can occur in regions of the combustion chamber which are overly-lean or overly rich [5].

2.9.2 Carbon Monoxide Formation

In contrast to HC emissions, a detailed reaction mechanism can be identified for CO. CO is formed from aldehydes in both low temperature and high temperature hydrocarbon oxidation regimes [32]. Heywood [5] gives the generic CO formation mechanism in (R 2-14), where an aldehyde is shown to be the source of CO.

$$\text{RH} \rightarrow \text{R} \rightarrow \text{RO}_2 \rightarrow \text{RCHO} \rightarrow \text{CO} \quad \text{(R 2-14)}$$

Glassman [32] describes the CO formation mechanism in more detail. Under high temperature conditions, the thermolysis reaction (R 2-15) initially converts an aldehyde to an acetyl radical. After a sizeable H radical pool forms, the acetyl radical is produced through (R 2-16), where X can represent OH, O, H or CH$_3$. In contrast, under low temperature conditions, an acetyl radical is produced by abstracting hydrogen from an aldehyde, followed by oxidation, shown in (R 2-17).

$$\text{RCHO} + \text{M} \rightarrow \text{RCO} + \text{H} + \text{M} \quad \text{(R 2-15)}$$

$$\text{RCHO} + \text{X} \rightarrow \text{RCO} + \text{XH} \quad \text{(R 2-16)}$$

$$\text{RCHO} + \text{O}_2 \rightarrow \text{RCO} + \text{HO}_2 \quad \text{(R 2-17)}$$

The decomposition of an acetyl radical then leads to CO, as shown in (R 2-18).

$$\text{RCO} + \text{M} \rightarrow \text{R} + \text{CO} + \text{M} \quad \text{(R 2-18)}$$

A specific example of CO formation starts with formaldehyde (CH$_2$O). Formaldehyde produced during low temperature reaction will undergo a hydrogen
abstraction to form a formyl radical (H\(^{\cdot}\)CO), which then undergoes another hydrogen abstraction to form CO, shown in (R 2-19). The formyl radical can also be directly oxidized as shown in (R 2-20).

\[
\text{H\(^{\cdot}\)CO + M \rightarrow \text{H} + \text{CO} + M} \quad \text{(R 2-19)}
\]

\[
\text{H\(^{\cdot}\)CO + O}_2 \rightarrow \text{CO} + \text{HO}_2 \quad \text{(R 2-20)}
\]

Regardless of under which regime CO forms, CO is oxidized to CO\(_2\) through reaction in (R 2-21), during the end of the high temperature chemistry.

\[
\text{\(\cdot\)OH + CO \rightarrow \text{H} + \text{CO}_2} \quad \text{(R 2-21)}
\]

2.10 Conventional Diesel Fuels

Fuel properties are directly dictated by the molecular structure of the hydrocarbons in the fuel. Normal alkanes, branched alkanes, cyloalkanes, alkenes and aromatics account for the major species that comprise liquid hydrocarbon fuels. Hydrocarbon compounds containing nitrogen, sulfur or oxygen are known as NSO’s and contribute to the production of emissions such as oxides of sulfur and oxides of nitrogen [41].

Normal alkanes or paraffins have the general formula of C\(_n\)H\(_{2n+2}\). The straight chain structure of normal alkanes is saturated and thus composed of single bonds. Synthetically produced Fischer-Tropsch diesel is considered high quality conventional diesel fuel, as it contains mainly paraffins. Branched alkanes or iso-paraffins have the general formula C\(_n\)H\(_{2n+2}\), and can have many branches. Cyloalkanes or napthenes have the general formula of C\(_n\)H\(_{2n}\) and have at least one ring of 5 or 6 carbons. Alkenes or
olefins have the general formula of $C_nH_{2n}$ and are unsaturated hydrocarbon chains with at least one double bond. Aromatics have the general formula of $C_nH_{2n-6}$ and are characterized by having at least one benzene ring. As a general rule, the calorific value of a hydrocarbon fuel compared to another fuel of similar carbon number will reduce as the H/C ratio decreases [41].

The ignition quality of a fuel is the delay from the start of fuel injection to the first significant in-cylinder pressure increase due to ignition, which is defined as the cetane number of the fuel [41]. The molecular structure of a fuel directly affects the ignition quality and thus cetane number. In general, the cetane number of compounds with similar number of carbon atoms decreases to lower ignition quality in this order: n-alkane > alkene > cycloalkane > alkyl aromatic [41]. Furthermore, as chain length increases with the addition of carbons, cetane number increases. The cetane number of a fuel can be adjusted by altering the chemical composition and molecular structure. For example, the high cetane number of a highly paraffinic gas-to-liquids (GTL) fuels can be reduced with the addition of iso-paraffins [42]. Cetane number is a scale referring to the pure compounds n-hexadecane ($C_{16}H_{34}$), commonly called cetane, with a high ignition quality and a cetane number of 100 and heptamethylnonane (HMN) with a cetane number of 15. The cetane number of a given fuel can be quantified in comparison to a blend of cetane and HMN as in Eq. (2-1) [5].

$$CN = \text{percent cetane} + 0.15 \times \text{percent HMN} \quad (2-1)$$

There is an abundance of work, which examines the effects of fuel properties in fundamental experiments under conventional diesel combustion conditions and advanced combustion conditions. It is difficult to modify only a single fuel property without
altering other related fuel properties, thus making it tenuous to attribute causality to a single fuel property. To identify direct causality from an individual property change, it is necessary to perform well designed experimentation. In both conventional diesel studies and PCCI operation, HC and CO emissions have been shown to decrease with an increase of cetane number [43-45]. This trend is logical, given that highly ignitable fuels would be more likely to completely burn. NO\textsubscript{X} and PM, however, were shown to increase with an increasing cetane number [44, 45]. The cetane numbers of the fuels used in any of the studies were often as high as 60 [43] and even up to 90 [45], far beyond the range that a refinery would output as diesel fuel.

The aromatic content of a fuel is directly related to the ignition quality of a fuel. As such, NO, CO, HC and PM are reported to be sensitive to changes in aromatics [46, 47]. The ignition quality change due to alteration of aromatics would account for HC, CO and NO\textsubscript{X}, but not for changes in PM. The increase in PM is because the aromatic benzene ring is a precursor to the formation of soot and PAHs. Thus, any reduction in aromatics content of a fuel will reduce PM emissions.

Hydrocarbon size and length is also related to volatility of the fuel as well as with cetane number. For a liquid fuel to burn, it must vaporize into the gas phase. The rate at which the fuel vaporizes will affect ignition delay. Volatility is commonly quantified by the distillation curve given by the ASTM D86 test method [48]. In the D86 test method, fuel is evaporated at atmospheric pressure. The fuel temperature is increased to achieve a constant rate of evaporation, between 4 to 5 ml/min. The start of vaporization is defined as the temperature at which 10% of the fuel volume has evaporated, given as T\textsubscript{10}. The end of vaporization is defined as the point at which 90% of the fuel volume is evaporated.
and is given as $T_{90}$ [48]. $T_{90}$ is commonly used to specify volatility of fuels for comparison.

Volutility of a fuel is dictated by the size and structure of the hydrocarbon compounds that the fuel is composed of, with heavier compounds having a higher $T_{90}$ temperature. In general, for hydrocarbons of similar carbon number, volatility decreases from higher to lower volatility in the order: branched alkanes $>$ normal alkanes $>$ cycloalkanes $\geq$ aromatics [41]. The lower surface area of branched alkane isomers, as opposed to straight chain alkane structures, reduces the London forces interactions between the molecules, resulting in reduced volatility. The cyclic structure of cycloalkanes results in lower volatility due to the increased surface area of the cycloalkanes, as opposed to n-alkanes. It is difficult to generalize the volatility of aromatics as there are examples of aromatics having equal and lower volatility than cycloalkanes [41].

2.11 Fischer–Tropsch Synthesis

High quality diesel fuel can be produced from synthesis gas (CO and H$_2$) using Fischer–Tropsch synthesis. Feed stocks for synthesis gas can be methane, the reaction shown in (R 2-22), or coal, the reactions shown from (R 2-23) through (R 2-27), as well as biomass [41]. The ratio of CO to H$_2$ can be modified through the water gas shift reaction, shown in (R 2-28).

\[
CH_4 \text{ reforming} \quad CH_4 + H_2O \rightarrow CO + 3H_2 \quad (R \ 2-22)
\]
**Gasification**

\[ \text{C} + \text{O}_2 \rightarrow \text{CO}_2 \]  \hspace{1cm} (R 2-23)

\[ \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \]  \hspace{1cm} (R 2-24)

\[ \text{C} + \text{H}_2\text{O} \rightarrow \text{CO} + \text{H}_2 \]  \hspace{1cm} (R 2-25)

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (R 2-26)

\[ \text{C} + 2\text{H}_2 \rightarrow \text{CH}_4 \]  \hspace{1cm} (R 2-27)

**Water gas shift**

\[ \text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \]  \hspace{1cm} (R 2-28)

Synthesis gas is introduced to a reactor with catalysts to produce hydrocarbons. The hydrocarbons produced will depend on selection of catalysts, reactor temperature, reactor pressure and synthesis gas composition. An illustration of the chain growth process is shown in Figure 2-15, in which (R 2-29), (R 2-30) and (R 2-31) are represented [49].

\[ (2n + 1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{(2n+2)} + n\text{H}_2\text{O} \]  \hspace{1cm} (R 2-29)

\[ (n + 1)\text{H}_2 + 2n\text{CO} \rightarrow \text{C}_n\text{H}_{(2n+2)} + n\text{CO}_2 \]  \hspace{1cm} (R 2-30)

\[ 2n\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n} + n\text{CO}_2 \]  \hspace{1cm} (R 2-31)

**Figure 2-15** shows chain growth to initiate on the surface of the catalyst with (R 2-29). Then at each stage of growth the hydrocarbon can desorb as an alkene (R 2-30), desorb as an alkane with the addition of \( \text{H}_2 \), or simply continue to grow (R 2-31). The probability of chain growth \( (\alpha) \) depends on operating temperature, catalyst and operating pressures [49].
Initiation:

\[
\text{CO} \rightarrow \text{CO} + \text{H}_2 \rightarrow \text{CH}_2 + \text{H}_2\text{O}
\]

Chain growth and termination:

\[
\begin{align*}
\text{CH}_2 + \text{H}_2 & \rightarrow \text{CH}_4 \\
\alpha + \text{CH}_2 & \rightarrow \text{C}_2\text{H}_4 \\
\text{C}_2\text{H}_4 & \rightarrow \alpha + \text{CH}_2 \\
\text{C}_2\text{H}_6 & \rightarrow \text{C}_2\text{H}_4 + \alpha + \text{CH}_2 \\
\text{C}_3\text{H}_8 & \rightarrow \text{C}_2\text{H}_6 + \alpha + \text{CH}_2 \\
\text{C}_3\text{H}_6 & \rightarrow \text{C}_3\text{H}_8 + \alpha + \text{CH}_2 \\
etc. & \rightarrow \text{C}_3\text{H}_8 + \alpha + \text{CH}_2
\end{align*}
\]

Figure 2-15: FT stepwise growth process [49].
The two major Fischer–Tropsch processes are the high temperature Fischer–Tropsch (HTFT) process and low temperature Fischer–Tropsch (LTFT) process. The HTFT process is typically operated between 310 and 340 °C, with an iron catalyst and produces short hydrocarbons including paraffins and olefins and aromatics [49]. Hydrotreating of the straight run HTFT products is often needed to shift the fuel properties to that of a target fuel [50]. The LTFT process, typically operated between 210 and 260°C, can use either an iron or a cobalt catalyst, and produces long chain paraffins or wax [49]. The high boiling point of the wax produced from the LTFT process can be reduced by hydrocracking the wax into shorter hydrocarbons [50].
Chapter 3

Hypotheses and Objectives

3.1 Hypotheses

The following hypotheses have been formulated based on the gaps in the understanding found in the literature:

1. A fuel of high ignition quality will avoid incomplete combustion, which commonly occurs during advanced diesel combustion.

2. A high cetane number fuel will have a lower combustion lean limit than a lower cetane number fuel, thus avoiding incomplete combustion.

3.2 Objectives

The following objectives have been envisioned to test the aforementioned hypotheses:

1. The primary objective of this study is to demonstrate that a diesel engine can operate with reduced NO$_x$, PM, THC and CO emissions by synergistically combining advanced diesel combustion and a high ignition quality fuel.

2. The secondary objective of this study is to investigate the effects on the combustion process due to a high ignition quality fuel, which led to a reduction in incomplete combustion.
4.1 Introduction

Emissions from internal combustion engines can be reduced by three general methods: alteration of fuel, alteration of the combustion process, and exhaust aftertreatment. In this study, alteration of fuel and modifications of the combustion process were examined jointly to amplify the beneficial effects of both techniques. Low temperature combustion (LTC) is the concept at the heart of diesel advanced combustion, which is a general term for homogenous charge compression ignition (HCCI) combustion, and premixed charge compression ignition (PCCI) combustion. The theory behind LTC is explained by Akihama et al. [3], who simulated combustion with a compression ignition (CI) 3D-CFD KIVA2 model and plotted local equivalence ratio vs. local flame temperature for the stratified CI combustion process. This well-known figure depicts the NO\textsubscript{X}-PM trade-off associated with conventional diesel combustion, wherein the fuel-lean zones at the periphery of the spray flame produce abundant NO\textsubscript{X} and the fuel-rich zones within the spray flame produce abundant soot. Akihama et al. [3] showed with their model and Φ-T map that LTC occurs at low combustion temperatures below the formation regime of NO\textsubscript{X} and at local fuel equivalence ratios below the formation regime of diesel soot.

In its application in compression ignition engines, LTC can be practically achieved as PCCI. Diesel-LTC is also another general term used to describe the
application of advanced diesel combustion in a compression ignition engine [2]. PCCI is often associated with HCCI, though they are distinctly different combustion strategies. In classic HCCI, a near homogenous mixture of premixed fuel and air is combusted. However, diesel fuels with low volatilities and high cetane numbers inhibit the formation of uniform mixture [2]. In contrast, PCCI produces varying degrees of partial premixing depending on start of injection (SOI) timing, vary from early injection, near TDC injection and late injection [2]. Subsequently, PCCI can be regarded as a diesel combustion process, which shifts more of the combustion to the premixed combustion phase, and reduces the fraction of fuel conversion in the mixing-controlled combustion phase. The mixing-controlled combustion phase generates thermal NOX in the periphery of the spray flame where stoichiometric conditions produce high temperatures, while PM forms in the locally fuel-rich regions in the interior of the spray flame, as shown in a model developed by Dec [31] of the diesel spray flame under conventional combustion.

The particular PCCI process of interest in this study is High Efficiency Clean Combustion (HECC) [51-55]. The HECC condition is achievable in current production diesel engines by modifying several engine operation parameters via the electronic control unit (ECU). The rate at which exhaust gas recirculation (EGR) is introduced into the intake air is increased to enhance premixing before the onset of combustion by retarding the start of combustion and reducing the intensity of the ignition process. The injection strategy is set to a single advanced injection near TDC which, along with EGR, provides an increased ignition delay in which the fuel and air partially premix beyond that of conventional combustion. Fuel injection pressure is increased to enhance the penetration depth of the fuel jet. The HECC mode produces a decrease in both NOX and
PM emissions while maintaining, or even increasing, fuel efficiency. However, operation in the HECC mode, or any other PCCI mode, typically results in increased total hydrocarbons (THC) and carbon monoxide (CO) emissions and is limited to low and medium load operation [51-55]. Detailed discussions of elevated THC and CO emissions from PCCI can be found in recent review articles by Dec [1] and Yao et al. [2], both on advanced combustion modes.

Conventional diesel fuels are optimized for conventional diesel operation. Modifications of fuel composition and, thus, fuel properties have the potential to optimize PCCI operation processes, such as HECC, and eliminate undesirable effects arising from increasing the fraction of premixed combustion. Fuel properties are directly dictated by the molecular structure of the hydrocarbons in the fuel. Normal alkanes, branched alkanes, cycloalkanes, alkenes and aromatics account for the major species that comprise conventional liquid hydrocarbon fuels.

The ignition delay for a fuel is the time between SOI of the fuel and a significant in-cylinder pressure increase due to ignition, which is characterized by the fuel property cetane number [41]. Ignition delay is composed of a physical ignition delay, in which fuel and air mix, liquid fuel is atomized and fuel droplets evaporate, and a chemical ignition delay, which is kinetically controlled. The molecular structure of a fuel directly affects the ignition quality and thus the cetane number. In general, the cetane number of compounds with a similar number of carbon atoms follows this order: n-alkane > alkene > cycloalkane > alkyl aromatic [41]. Furthermore, as chain length increases with the addition of carbons, cetane number increases. The standard for diesel fuel oil is a
minimum cetane number of 40 [56]; however, Heywood [5] indicates that a normal diesel fuel has a cetane number range of 40 to 55.

There is an abundance of work that examines the effects of fuel composition in fundamental experiments and under conventional diesel combustion conditions. However, relatively little work has been conducted to examine fuel effects on diesel advanced combustion conditions. In conventional diesel studies with fuels up to a cetane number (CN) of 63 [43], and under PCCI operation with fuels up to 53 CN [44], THC and CO emissions have been shown to modestly decrease with an increase of CN. Modulated Kinetics (MK) combustion was shown to lower THC under cold start conditions with fuels of CN up to 85 [42]. This trend is logical, given that highly ignitable fuel would be more likely to completely burn. NO\textsubscript{X} and PM, however, were shown to increase with an increasing CN in both advanced [44] and conventional diesel [45] combustion. The ignition quality of a fuel is inversely related to the aromatic content of a fuel. As such, NO, CO, THC and PM are reported to be sensitive to changes in aromatics [46, 47].

Fujimoto et al. [57] have shown in both a light duty diesel engine and a rapid compression and expansion machine that increasing the molar fraction of high volatility fuel will increase emissions of HC and decrease soot. This same observation was made in work by Nishiumi et al. [45] in which aromatic free fuel was shown to further reduce PM emissions. Zannis et al. [47] reported that a decrease in soot, NO and CO emissions could be achieved in conventional diesel combustion with a reduction of distillation temperature and an increase of paraffin/naphthene ratio. Distinguishing the effects of volatility and CN is difficult, as the distillation range of the fuel will influence the value
of both properties such that a high temperature distillation will have low volatility and high cetane.

In a recent study, fuel samples from the Fuels for Advanced Combustion Engines (FACE) working group were combusted in a diesel engine operating in HECC [58]. The FACE fuels are a set of nine laboratory test fuels designed to vary in CN, volatility and aromatic content. CN was shown to be the fuel property having the largest effect on emissions. Specifically, it was shown that the set of fuels having a target CN of 30 produced nearly twice as much THC and CO emissions than the fuels having a target CN of 55.

In this study, a common rail turbodiesel engine was operated in the HECC advanced diesel combustion mode. The effect of cetane number (45 DCN, 51 DCN and 81 DCN) on advanced diesel combustion was examined. The engine was operated at steady-state conditions with a constant speed and load. The SOI timing command was swept from -8° ATDC to 0° ATDC to find an optimized injection condition for each specific fuel. In particular, this study demonstrates low NOx, PM, THC and CO emissions while preserving thermal efficiency by combining an advanced combustion process with a high ignition quality fuel. The combination of fuel and PCCI proposed and tested in this study is in stark contrast to recently presented PCCI concepts in which low cetane fuel and gasoline/diesel dual fueling are presented [59-61].
4.2 Experimental

4.2.1 Engine and Test Facility

Steady-state testing was conducted on a DDC/VM Motori 2.5L, 4-cylinder, turbocharged, common rail, direct injection, Euro 3 compliant light-duty diesel engine with an unlocked electronic control unit (ECU) (Table 4-1). The engine was coupled to a 250 HP Eaton eddy current water-cooled dynamometer. The engine and dynamometer were controlled by a Digalog Testmate control unit.

Particulate matter (PM) was sampled through a Sierra Instruments BG-3 micro-dilution tunnel using a dilution ratio of 10:1 with a sampling duration of 5 minutes for each of the three filters acquired per test mode. The BG-3 micro-dilution tunnel sampling parameters were chosen to collect particulate sample over the wide range of test points examined in this study. Soxhlet extraction was performed on the PM filters using dichloromethane as a solvent for 24 hours with approximately 300 wash cycles.

An AVL Combustion Emissions Bench II was used to measure gaseous emissions. \( \text{NO}_X \) and \( \text{NO} \) were measured using an EcoPhysics chemiluminescence analyzer. \( \text{NO}_2 \) was assumed to be the difference between \( \text{NO}_X \) and \( \text{NO} \). Total hydrocarbons and methane were measured by using two separate ABB flame ionization detectors. Total hydrocarbons were reported on the basis of \( \text{C}_3 \), by using a propane-N\(_2\) mixture as the calibration gas. \( \text{CO} \) and \( \text{CO}_2 \) were measured by two separate Rosemount infrared analyzers, and \( \text{O}_2 \) was measured by using a Rosemount paramagnetic analyzer. The hot exhaust sample going to the \( \text{CO}, \text{CO}_2 \) and \( \text{O}_2 \) analyzers was first chilled to reduce moisture; these emissions were reported on the basis of dry moles. Temperature,
pressure and emissions data were sampled every 10 seconds under steady-state operating conditions.

Pressure traces were measured using AVL GU12P pressure transducers, which replaced the glow plug in each of the four cylinders. The voltages from the pressure transducers were amplified by a set of Kistler type 5010 dual mode amplifiers. The amplified voltages were read by an AVL IndiModul 621 data acquisition system. Needle lift data were collected from a Wolff Controls Inc. Hall-effect needle lift sensor, which was placed on the injector of cylinder 1. The needle lift signal was also collected by the IndiModul, which was triggered by a crank angle signal from an AVL 365C angle encoder placed on the crankshaft. The pressure traces and needle lift data were recorded at a resolution of 0.1 crank angle degrees, and were averaged over 200 cycles. The real-time IndiModul data was transferred to a PC, which ran AVL IndiCom 1.3 and Concerto 3.90 software to calculate the apparent heat release rate [62].

<table>
<thead>
<tr>
<th>Table 4-1: DDC 2.5L Engine Specification.</th>
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<tbody>
<tr>
<td>Engine</td>
</tr>
<tr>
<td>Displacement</td>
</tr>
<tr>
<td>Bore</td>
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<tr>
<td>Stroke</td>
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<tr>
<td>Compression ratio</td>
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<td>Connecting rod length</td>
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<tr>
<td>Rated power</td>
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<td>Peak torque</td>
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<tr>
<td>Injection system</td>
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<tr>
<td>Valve / Cylinders</td>
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</tbody>
</table>
4.2.2 Fuel

Testing was conducted using three fuels: a conventional ultra-low sulfur diesel fuel (diesel), a synthetic fuel produced in a high temperature Fischer–Tropsch (HTFT) process, and a synthetic fuel produced in a low temperature Fischer–Tropsch (LTFT) process.

Table 4-2 indicates that the composition of the HTFT fuel is similar to that of the diesel fuel, as it contains some aromatics and olefins along with saturates. In contrast, the LTFT is composed singularly of saturates, providing for a derived cetane number (DCN) of 81. The DCN of the HTFT and diesel fuel are 51 and 45, respectively. DCN is a measure of fuel ignition quality, per ASTM D-6890, which is approximately equivalent to the measurement of CN. The consequence of the difference in cetane numbers of the three fuels is the primary focus of this study.
Table 4-2: Properties of fuels examined. Test methods: a ASTM D-4052; b D-445; c ASTM D-240; d ASTM D-5453; e D-5291-02; f ASTM D-2887; g ASTM D-6890; h ASTM D-1319.

<table>
<thead>
<tr>
<th></th>
<th>diesel</th>
<th>HTFT</th>
<th>LTFT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>0.84</td>
<td>0.82</td>
<td>0.76</td>
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<tr>
<td>Kinematic viscosity (cSt)</td>
<td>2.5</td>
<td>2.3</td>
<td>1.9</td>
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<tr>
<td>Heat of Combustion (MJ/kg)</td>
<td>45.7</td>
<td>45.9</td>
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<td>ppm S (wt)</td>
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<td>&lt;2</td>
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<tr>
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<td>84.6</td>
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<tr>
<td>Hydrogen (mass%)</td>
<td>12.8</td>
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<td>15.2</td>
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<tr>
<td>Nitrogen (mass%)</td>
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<td>0.02</td>
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<td>Distillation f</td>
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<tr>
<td>IBP (°C)</td>
<td>133</td>
<td>137</td>
<td>125</td>
</tr>
<tr>
<td>T50 (°C)</td>
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<td>246</td>
<td>236</td>
</tr>
<tr>
<td>T90 (°C)</td>
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<td>308</td>
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<tr>
<td>Derived Cetane Number g</td>
<td>45</td>
<td>51</td>
<td>81</td>
</tr>
<tr>
<td>Aromatics (vol%)</td>
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</tr>
<tr>
<td>Olefins (vol%)</td>
<td>1.7</td>
<td>1.2</td>
<td>0.6</td>
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<tr>
<td>Saturates (vol%)</td>
<td>66.8</td>
<td>68.4</td>
<td>99.4</td>
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4.2.3 Test Conditions

The three fuels were tested using advanced light duty diesel combustion conditions, under steady-state operation at 1500 RPM and ~2.7 bar BMEP. The advanced diesel combustion process was based on the HECC mode, using a single early fuel injection event, increased injection pressure, and a target of 40% EGR, though the actual EGR% was condition dependent. Injection timing was swept from -8° ATDC to top-dead-center (TDC) by increments of 2°. For a base of comparison, the fuels were also tested at 1500 RPM and ~2.7 bar BMEP using a conventional injection strategy defined by the ECU’s default parameters with a pilot and main injection event. The EGR
valve was fully opened to provide the maximum possible external EGR at all conditions. Because of the increased EGR rate, the EGR was cooled with an external coolant loop to offset the insufficient heat exchange capacity of the engine’s stock EGR cooler, which allowed the intake manifold temperature to remain between 41 to 59\degree\,C, depending on injection timing. Cooling the EGR is necessary to reduce NO\textsubscript{X} and PM emissions and to maintain the volumetric efficiency. The use of the external coolant loop to cool the EGR gas was justified by the assumption that a production engine intended to operate with large percentages of EGR would have an EGR cooler capable of providing appropriate cooling. As shown in Table 4-3 the operational modes were designated based on SOI timing. SOI timing and injection pressure were held constant. The dynamometer controls held the engine at a constant speed and injection duration was varied to maintain a constant load. Table 4-3 shows that key operating parameters such as intake manifold temperature, EGR \%, intake oxygen content and fuel flow rate were consistent for each of the three fuels tested at early injection timing. However, as the SOI timing approached TDC, the HTFT and more so the diesel fuel, experienced degraded combustion, and consequently less EGR was forced into the intake manifold. The EGR\% during the combustion of the HTFT fuel was 1-2\% lower than for the other fuels for injection timings from -8\degree to -4\degree ATDC, which affected NO\textsubscript{X} and PM emissions.
Table 4-3: Key operation condition parameters. IMEP was calculated from the average of 200 cycles from all four cylinders.

<table>
<thead>
<tr>
<th></th>
<th>Fuel</th>
<th>8</th>
<th>6</th>
<th>4</th>
<th>2</th>
<th>0</th>
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<tr>
<td>Pilot Inj. (ATDC)</td>
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<td>diesel</td>
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<td>LTFT</td>
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<td>Main Inj. (ATDC)</td>
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<td>Inj. Pressure (bar)</td>
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<tr>
<td>diesel</td>
<td>490</td>
<td>490</td>
<td>490</td>
<td>490</td>
<td>490</td>
<td>370</td>
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<tr>
<td>HTFT</td>
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4.3 Results

4.3.1 Needle Lift

The physical opening and closing of the cylinder #1 injector are displayed as needle lift profiles in Figure 4-1. The SOI command is shown to correspond to the actual SOI timing. The needle lift profiles indicate that the SOI timings of the diesel, HTFT and LTFT fuels were the same for the three fuels for each of the injection conditions. However, the magnitude of the needle lift and duration of the opening varied for the three fuels to maintain a constant engine output at all combustion conditions, given the difference in fuel properties. The most significant difference in needle lift is shown to be at an SOI timing of 0° ATDC, where the difference in fuel demand and fuel heating value caused the maximum needle lift height of the LTFT fuel, HTFT fuel and diesel fuel to vary from 0.129 mm, 0.133 mm, and 0.145 mm, respectively.
Figure 4-1: Needle lift for advanced diesel combustion at -8°, -6°, -4°, -2° and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel, HTFT and LTFT fuels.

4.3.2 Apparent Rate of Heat Release

The apparent rate of heat release (ROHR) and the LTFT needle lift are shown in Figure 4-2 for the three fuels tested. The combustion phasing for the diesel, HTFT and LTFT fuels was very similar when using the conventional combustion strategy. The start of combustion of the main injection occurred at 11° ATDC for both the diesel and HTFT. Here the start of combustion is defined as the crank angle where combustion causes the
ROHR to become positive, crossing zero. The higher cetane number of the LTFT fuel caused the start of combustion to occur at 9.5° ATDC. The conventional combustion mode burned primarily in a premixed combustion phase with an ignition delay between 7° and 6.5° for the fuel in the main injection, which is a common occurrence for low load, conventional CI combustion. The definitions used for premixed combustion phase and mixing-controlled combustion phase, or diffusion combustion, are those described by Heywood [5].

The ROHR of diesel fuel when using the advanced combustion mode indicated an increased intensity of the combustion process with earlier SOI timing. Comparing the two extremes, at an injection -8° ATDC, there was a maximum heat release rate of 107 J/degree, which occurred in a sharp and intense premixed combustion phase with an ignition delay of 9.5°. However, when injection occurred at 0° ATDC there was a weak premixed combustion with a maximum heat release rate of 27 J/degree in a premixed combustion phase, which then transitioned directly into diffusion combustion in a late combustion phase, with an ignition delay of 12.5°. As the injection timing was retarded, the combustion phasing shifted to a crank angle where the expansion process cooled the charge, further extending the ignition delay. The long ignition delay caused over-mixing of the fuel and air resulting in the weak combustion. Table 4-4 lists combustion parameters including the location of 50% mass fraction burn, which can be used to indicate combustion phasing. The retarded combustion phasing of the diesel and HTFT, most dramatically at 0° ATDC, resulted in elevated exhaust temperatures, Table 4-3. The increased temperature of the exhaust, due to retarded combustion phasing, reduced the mass of exhaust recirculated into the engine through the fully open EGR valve. The
result was lower EGR when combustion phasing was retarded. The HTFT fuel has a DCN that is 6 units higher than the diesel fuel, which resulted in shorter ignition delays (0.5° to 1°). The maximum rate of heat release of the HTFT was higher than the diesel fuel at each SOI timing, ranging from 0.27 to 17.94 J/degree higher. The shorter ignition delay of the HTFT fuel reduced the degree of over-mixing, which increased the burn rate. Also, the shortened ignition delay of the HTFT fuel caused combustion phases to occur closer to TDC, resulting in higher brake thermal efficiency (*Figure 4-4*), in comparison to the diesel fuel. However, at 0° ATDC the higher cetane number of the HTFT fuel could not compensate for the over-mixing and retarded combustion phasing induced by late injection timing. It was observed that at an injection timing of -2° ATDC the HTFT has a maximum heat release 17.9 J/degree greater than the diesel fuel, but at the later injection timing of 0° ATDC, the higher cetane number resulted in only a 4.3 J/degree increase in maximum heat release rate.

The apparent rate of heat release for the five advanced combustion injection timings for the LTFT fuel greatly differed from the apparent rate of heat release of the HTFT and diesel fuels. The ignition delay of the LTFT was 1.8° to 3.4° shorter than that of the HTFT fuel as injection was timing delayed. The shortened ignition delay of the LTFT fuel was due to its DCN of 81. This significantly reduced the over-mixing problem seen with the other fuels and caused the premixed combustion phasing for both early and late injection timings to be relatively close to TDC. However, the maximum heat release rates of the LTFT fuel at the earlier injection timings -8° and -6° ATDC were ~ 30 J/degree less than either the HTFT or the diesel fuel. The shorter ignition delay of the LTFT fuel caused less fuel to be premixed with air, resulting in a larger contribution
of diffusion combustion. In Figure 4-2, the LTFT fuel at all injection timings for advanced combustion was observed to have more combustion occurring in a mixing-controlled combustion phase late in the combustion process. As SOI timing was retarded and the ignition delay became longer, more fuel was burned in the premixed combustion phase than in the diffusion burn. This phenomenon was also observed by Yongcheng et al. [63] during the combustion of FT fuel in conventional diesel combustion.
Figure 4-2: Apparent rate of heat release and needle lift for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel, HTFT and LTFT fuels. Needle Lift is from the injection of the LTFT fuel.
Table 4-4: Combustion phasing for start of combustion (SOC), ignition delay (ID), mass fraction burn of 5%, 50% and 90% of fuel.

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4.3.3 Brake Specific Fuel Consumption

Brake specific fuel consumption (BSFC), shown in Figure 4-3, indicates an increase in fuel consumption as the combustion of the diesel and HTFT fuels occurred at retarded combustion phasing. The fuel consumption of the diesel and HTFT fuels at -2° and 0° ATDC increased steeply, reflecting the late combustion phasing indicated by the ROHR. In comparison, during advanced combustion the BSFC of the LTFT fuel at -2° and 0° ATDC did not increase significantly. This was due to the combustion phasing of the LTFT fuel, which was maintained near TDC, as indicated by the ROHR.
Furthermore, the LTFT fuel maintained a constantly lower BSFC, which is in part due to its higher energy density. The difference in energy density was accounted for by examining the fuels on the basis of brake thermal efficiency (BTE) in Figure 4-4. All three fuels were observed to maintain between 28% and 30% BTE except at SOI timings of -2° and 0° ATDC, where the diesel and HTFT undergo late combustion phasing, causing efficiency to plummet.

Combustion efficiency was calculated from the emissions of incomplete combustion based on CO, THC and soot emissions. The combustion efficiency produced smoother trends than that of the BSFC or the BTE, which are directly subject to fluctuations in engine power output and fuel flow rate measurements. In general, the combustion efficiency for the LTFT fuel was ~99.5% in all the advanced combustion conditions as well as in the conventional combustion condition. The diesel fuel and HTFT fuel achieved ~99% combustion efficiency at SOI timings of -8°, -6° ATDC and at the conventional combustion condition. However, as SOI timing was retarded, the combustion phasing occurred too late, resulting in degraded combustion efficiency. The diesel fuel, which has a DCN of 45, combusted at an efficiency of 93.9% at an SOI timing of 0° ATDC, while the HTFT fuel, having a DCN 6 units higher, combusted at an efficiency of 96.1%.
Figure 4-3: Brake specific fuel consumption for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.

Figure 4-4: Brake thermal efficiency for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.
Figure 4-5: Combustion efficiency for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.

4.3.4 NOx Emissions

Figure 4-6 shows the emissions index NOX for the diesel, HTFT and LTFT fuels. The HTFT and LTFT fuels were observed to produce 10% and 18% less NOX emissions than the diesel fuel during conventional combustion. A reduction in NOX emissions under conventional combustion utilizing FT fuels has been reported in previous work, in which the reduction of NOX was attributed to a shorter ignition due to the higher cetane number which reduced the peak heat release during premixed combustion and thus lowered the maximum cylinder temperature [64]. Furthermore, retarded injection timing has also been shown to decrease NOX emission as there is less time for cylinder temperatures to build and less time for thermal NOX formation [65]. As such, the
reduction in NOX emissions observed for all three fuels during the advanced combustion injection timing sweep could be attributed to four key factors: SOI, ID, ROHR and EGR%.

In Figure 4-6, the HTFT fuel under the advanced combustion conditions with SOI timings from -8° to -2° ATDC increased NOX emissions from 8% to 13%, with respect to the diesel fuel. The increase in NOX emissions, during the early SOI timings, corresponds to the previously mentioned lower rate of EGR recirculated during the combustion of the HTFT fuel. According to the ROHR data, Figure 4-2, the HTFT fuel burned in a potent premixed combustion phase from SOI timings -8° to -4° ATDC. NOX emissions at SOI timings -8° to -4° ATDC decreased with respect to the EGR% (Figure 4-7) achieved for each of the three fuels. For example, as the HTFT fuel combusted in the presence of lower EGR, higher NOX emissions occur at a given SOI time, from -8° to -4° ATDC, compared to the diesel fuel. At SOI timings of -2° to 0° for the diesel and HTFT fuels, NOX emissions are observed to further decrease despite less EGR having been recirculated at these SOI timings. The decrease in NOX emissions at SOI timings of -2° to 0° is due to a decreased rate of premixed combustion for both the diesel and HTFT fuels.

The LTFT fuel produced 17% to 20% less NOX than the diesel fuel at SOI timings from -8° to -4° ATDC. At SOI -2° to 0° ATDC LTFT fuel increased NOX emissions 3% and 5% with respect to the diesel fuel. The increase of NOX by the LTFT fuel can be attributed to the higher ROHR for the LTFT fuel relative to the diesel fuel at SOI -2° to 0° ATDC, where the diesel fuel and HTFT fuel burned with less efficient phasing.
A 2% difference in EGR% may not be sufficient to account for the significantly lower NOX emissions of the LTFT fuel at the early SOI timings. Cheng et al. [66] reported under a similar but more controlled set of experiments using simulated EGR, a reduction of NOX when operating with a high cetane fuel in comparison to a conventional cetane fuel. It was suggested that measurement of the localized flame temperature would be necessary to definitively interpret the data, though bulk cylinder temperature calculations, based on ideal gas law and in-cylinder pressure data, did provide correlation with NOX emissions trends.

In Figure 4-8, NOX and bulk cylinder gas temperature show a strong correlation at lowered temperatures, which are due to retarded SOI timing, where combustion phasing occur well into the expansion stroke. The NOX emissions of the diesel and HTFT fuels both have strong correlations to bulk cylinder gas temperature, having R² values of 0.9314 and 0.9533, respectively. However, the NOX emissions of the LTFT fuel have an R² value of 0.4617, indicating a weaker correlation to bulk cylinder gas temperature.

The correlation between NOX and maximum ROHR for advanced combustion yielded a very strong correlation for the diesel and HTFT fuels, respectively having R² values of 0.9664 and 0.9753, as shown in Figure 4-9. However, LTFT fuel yielded comparatively no correlation between NOX and maximum ROHR, having an R² value of 0.0959. Based on the correlation in Figure 4-8 and Figure 4-9, NOX emissions are slightly more dependent on the maximum heat release during combustion than the bulk cylinder gas temperature for the diesel and HTFT fuel. However, the LTFT fuel had a
modest dependence on bulk cylinder gas temperature, but no dependence on ROHR, which indicates that the LTFT fuel induced a unique alteration of the combustion process.

Figure 4-6: Emissions index NOX for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.
Figure 4-7: EGR% recirculated for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.

Figure 4-8: Emissions index NOX vs. peak bulk cylinder gas temperature for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.
Figure 4-9: Emissions index NO$_X$ vs. maximum ROHR for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.

4.3.5 Particulate Matter Emissions

The particulate matter (PM) emissions index for the conventional combustion mode, shown in Figure 4-10, indicates that with respect to the diesel fuel, the HTFT fuel increased PM by 33% and the LTFT fuel decreased PM by 44%. The HTFT fuel’s shorter ID could have caused less oxygen entrainment, resulting in higher PM. However, the LTFT produced less PM, although it had the shortest ignition delay of the three fuels. The difference is likely due to the 30.4% aromatic content of the HTFT fuel compared to the zero aromatic content of the LTFT, in conjunction with the LTFT fuel’s inherently low hydrocarbon emissions.

The diesel and HTFT fuels exponentially increased PM emissions as the advanced combustion injection timing approached TDC. Both fuels modestly increased PM as
injection moved from -8° to -4° ATDC, after which there was an abrupt increase at -2° ATDC where both fuels were observed to produce two orders of magnitude more PM than the LTFT fuel, while the LTFT fuel did not increase PM at all. The increase of PM by the diesel and HTFT fuels at -2° and 0° ATDC corresponds to the THC emissions, as will be discussed below.

![Figure 4-10: Emissions index particulate matter emissions for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.](image)

4.3.6 Soot Emissions

Soot extraction was performed on the PM sample filters to remove the soluble organic fraction (SOF), leaving behind the insoluble fraction (ISF) or soot. The SOF is assumed to be composed of the hydrocarbon fraction of the PM, along with incidental soluble contaminants. The ISF is assumed to be composed of soot, though it will also
contain other species not soluble in dichloromethane, which was used as the solvent. **Figure 4-11** shows that the soxhlet extraction process reduced the mass on the PM filters between one and two orders of magnitude, increasing the relative significance of the uncertainty inherent to the measurement. It should be acknowledged that some fraction of the soot that was collected on the PM filters might have been washed away in the soxhlet extraction process due to the high organic content of the PM from the increased fraction of premixed combustion. **Figure 4-11** shows that the absolute value soot, which remained on the sample filters, was similar for the three fuels during advanced combustion. The most significant differences from the PM emissions and the soot emissions occurred during advanced combustion for injection timings of -2° ATDC and 0° ATDC, where the diesel and HTFT fuels combusted inefficiently. The PM produced from the diesel fuel at -2° ATDC and 0° ATDC was composed of only 8.8% and 3.5% soot, respectively. The total PM mass for LTFT at -2° ATDC and 0° ATDC was composed of much less hydrocarbon, such that the PM was composed of 41% and 78% soot, respectively.
Figure 4-11: Emissions index soot emissions for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.

Figure 4-12 qualitatively presents the PM and ISF emissions. The PM filters were observed to have a brown shade for filters at -8° ATDC and -6° ATDC, indicating a moderate loading of diesel soot. As injection timing retards, the filters for the diesel fuel and to a lesser degree the filters for HTFT began to lighten to a yellow hue at -2° ATDC and 0° ATDC, indicating elevated hydrocarbon emissions which condensed as PM. The LTFT fuel, which combusted efficiently at all injection timings, was not observed to produce a high level of hydrocarbon emissions at the retarded injection timings. The conventional combustion mode with baseline injection timing produced black filters indicating a high soot content in the particulate matter. The LTFT baseline filter was
slightly lighter than the diesel or HTFT filters, indicating less PM. These observations trend exactly with the PM mass measurements presented in Figure 4-10.

The soot filters are slightly lighter in shade than the PM filters. However, the diesel and HTFT filters at -2° ATDC and 0° ATDC drastically changed in color, from deep yellow to nearly white. This observation confirmed the high SOF composition of the diesel and HTFT filters at retarded injection timing.
Figure 4-12: Qualitative observations on filter containing PM (top) and post soxhlet extraction filters containing soot (bottom) for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel, HTFT and LTFT fuels.

4.3.7 Total Hydrocarbon Emissions

Figure 4-13 shows the total hydrocarbon (THC) emissions for the conventional combustion condition and the advanced combustion conditions. Under conventional combustion, the three fuels created similarly low levels of unburned hydrocarbons, with the diesel fuel producing the most (5.41 g/kg fuel). With respect to the diesel fuel, the HTFT and LTFT fuels produced a 3% and a 48% decrease in THC, respectively. The
reductions in THC under conventional combustion with FT fuels were modest in terms of absolute values and reflect trends observed in others studies [43, 64].

The combustion of the three fuels under advanced combustion conditions resulted in more significant variations of the THC emissions, with injection timings near TDC producing dramatically different emissions. The diesel fuel and the HTFT fuel exponentially increased THC emission as SOI approached TDC, while the LTFT fuel produced a nearly imperceptible increase in THC emissions. As SOI retarded the LTFT fuel produced from 63% to 92% less THC emissions, than the diesel fuel at the same SOI timing. With respect to the HTFT fuel, the LTFT produced 61% to 85% less THC.

The high THC emissions produced by the diesel and HTFT, in particular at -2° and 0° ATDC, are related to the high PM emissions at the same SOI timings. These large increases in THC emissions are consistent with observations of diesel advanced combustion [51-55]. The LTFT fuel reduced THC emissions at every advanced combustion SOI timing, compared to the diesel and HTFT fuels. THC slightly increased for the LTFT from 2 g/kg\textsubscript{fuel} at -8° ATDC to 3.68 g/kg\textsubscript{fuel} at 0° ATDC; however, this is very small compared to the exponential increase produced by the diesel and HTFT fuels.
4.3.8 Carbon Monoxide Emissions

As expected, Figure 4-14 shows that the plot for carbon monoxide (CO) emissions index reflects the same trends as the THC emissions in Figure 4-13, for both the conventional combustion and the advanced combustion conditions. However, the variations in CO emissions resulting from the combustion of the three fuels are slightly less than those for the THC emissions. The combustion of diesel fuel in the conventional combustion condition produced 15.12 g/kg\textsubscript{fuel} CO. The HTFT and LTFT fuels produced 10% and 44% less CO emissions.

The combustion of the diesel and HTFT fuels under the retarded advanced combustion SOI timings greatly elevated CO emissions. The LTFT fuel’s CO emissions
are similar to the THC emissions. The LTFT fuel produced between 56% and 80% less CO emissions in comparison to the diesel fuel, and in comparison to the HTFT fuel, the LTFT produced between 49% and 77% less CO emissions.

Figure 4-14: Emissions index CO emissions for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC and conventional diesel combustion at a pilot injection of -13.1° and main injection at 3.9° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.

4.3.9 THC-NOX Trade-off

Conventional diesel combustion is subject to a PM- NOX trade-off. The PM produced in the study was primarily composed of a soluble organic fraction, or condensed hydrocarbons. The plot of THC-NOX trade-off for advanced combustion in Figure 4-15 indicates that the diesel fuel and HTFT fuel have strong inverse relationships between the THC and NOX emissions. The late SOI timings can be easily identified on
the figure as high THC points. The LTFT fuel was observed to avoid the THC-NO\textsubscript{X} trade-off.

![Figure 4-15: Emissions index THC vs. Emissions index NO\textsubscript{X} for advanced diesel combustion at -8°, -6°, -4°, -2°, and 0° ATDC for diesel (○), HTFT (▲) and LTFT (▼) fuels.](image)

### 4.4 Discussion

Figure 4-13 and Figure 4-14 show that PCCI combustion led to significant THC and CO emissions when using the diesel fuel and to a lesser extent the HTFT fuel, while the LTFT fuel produced dramatically lower THC and CO emissions. The apparent rate of heat release data (Figure 4-2) indicated that the combustion of the LTFT fuel varied from the other fuels: a shorter ignition delay and lower maximum rate of heat release in the premixed combustion phase, offset by an increased rate of diffusion combustion. The
reductions in THC and CO emissions by the LTFT fuel can be explained by examining the advanced diesel combustion process.

Dec [67] determined the largest effect of EGR to be the reduction of compressed gas temperature, using a single-zone model with time-varying compression, with full chemical kinetics to simulate HCCI combustion. The low compressed gas temperature effect of EGR which results in simultaneously low NOX-PM emissions was earlier described by Akihama et al. [3]. Dec [67] also indicated that an important secondary effect of EGR was to significantly slow the reaction kinetics, extending the ignition delay for fixed injection timings. The concepts of Dec’s simulation work can be extended to explain phenomena, which occur during diesel PCCI where a significant premixed combustion phase occurs due to EGR. With an extended ignition delay, the premixed charge during advanced diesel combustion can become overly fuel-lean in localized regions, resulting in elevated THC and CO emissions. A high cetane number would shorten the ignition delay, preventing these THC and CO emissions. LTFT fuel’s decreased rate of premixed combustion and increased rate of diffusion combustion reduced the amount of over-leaning of the fuel-air charge.

Advanced diesel combustion is a hybrid combustion mode, which utilizes diesel engine hardware to combust more of the fuel via a premixed fuel-air charge similar to that in spark ignited (SI) combustion. However, the fuel-air charge in diesel advanced combustion is not completely premixed, as the acronym PCCI indicates. According to Cheng et al. [39], THC emissions in a premixed charge can arise from fuel being stored in-cylinder crevices, fuel absorption into the oil layer on the cylinder wall with subsequent desorption, absorption onto cylinder deposits with subsequent desorption,
flame quenching and exhaust valve leakage. It is possible for the liquid fuel jet to penetrate to the cylinder wall during PCCI with very early injection (-40° ATDC) [68]; however with the SOI timing used in this work, the liquid fuel jet impingent would concentrate in the piston bowl instead. Similarly, Colban et al. [69] linked experimental data for THC emissions from diesel LTC to a 1-D engine model, showing that the majority of THC emissions were produced from the quench layers on the cylinder wall and piston top. Lachaux and Musculus [70] found that the formation of formaldehyde coincided with unburned hydrocarbons, and they subsequently performed in-cylinder formaldehyde visualization during low-temperature CI combustion to verify the THC formation mechanism. They suggested that in the event of a long ignition delay, THC would form late in the combustion cycle in the region near the injector. This phenomenon was shown to be created by a fuel-lean mixture due to low-momentum fuel injection during the end of injection [71]. UHC and CO emission are also attributed to rich fuel mixtures, particularly when fuel injection continues to occur into the expansion stroke, thus preventing expansion cooling and adequate combustion temperatures [72].

4.4.1 LTFT Fuel Effects

The literature shows that a major source of high THC and CO emissions produced in PCCI is due to combustion quenching and over-mixing of the fuel-air mixture. The LTFT fuel affected in-cylinder spray, physical ignition delay and chemical ignition delay, which ultimately reduced the degree of over-mixing of the air-fuel charge. Some factors,
which likely caused the LTFT fuel to have lower THC and CO emissions, are suggested below.

The LTFT had a shorter ignition delay, which is a factor that reduced high THC and CO emissions due to over-leaning. Musculus et al. [71] suggested that when ignition dwell (the time from end of injection to start of ignition) was positive, the region near the injector could be too lean at the end of injection and result in unburned hydrocarbons. Conversely, a negative ignition dwell, where injection overlaps with the start of combustion, would prevent the formation of an overly-lean charge produced near the injector at the end of injection. Figure 4-16 shows THC vs. ignition dwell, the LTFT fuel had a negative ignition dwell, while the HTFT and diesel fuels had positive ignition dwells. THC emissions are shown to exponentially increase with a positive dwell. The negative ignition dwell of the LTFT fuel appears to be a major factor, which resulted in a reduction of incomplete combustion. Nevertheless, the contribution of other factors which may have contributed to more complete combustion should still be considered.
The maximum penetration distance of the liquid fuel spray (the liquid length) of the LTFT can be assumed to be shorter than that of the other fuels, based on the lower density and higher volatility of the LTFT fuel. The reduction of liquid length by high volatility fuels has been shown to be magnified under low combustion chamber temperature conditions [15]. The short liquid length of the LTFT fuel reduced the possibility of liquid spray impingement on the cylinder wall or piston bowl, resulting in lower THC or CO emissions.

Highly paraffinic fuels such as the LTFT fuel are seen to have increased low temperature heat release [73, 74]. Pickett et al. [68] has shown evidence that, under LTC conditions, cool flame chemistry occurs upstream of mixing-controlled combustion, even though a low temperature heat release event is not visible in the heat release data.
Furthermore, Musculus [75] recently suggested that diesel LTC, compared to conventional diesel combustion, shows longer liquid length before vaporization and a distinct cool flame event that likely contributes to fuel vaporization. It could then be inferred that the heat produced by the low temperature chemistry of the LTFT fuel enhanced the rate of liquid fuel vaporization, compared to the other fuels. The apparent rate of heat release of the LTFT fuel in Figure 4-2 does not show a low temperature heat release event, because it is masked by the high compression ratio of the engine. The literature shows that the appearance of low temperature heat release can be clearly observed at decreased compression ratios [74].

It has been established that THC and CO emissions, both products of incomplete combustion, can be formed at the piston bowl or cylinder by quenching and over-mixing, as well as by being formed near the injector due to over-mixing in PCCI. The complete combustion of THC and CO emission depends on the availability of hydroxyl radicals, such as in the oxidation of CO given in (R 4-1).

\[ \text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2 \]  \hspace{1cm} (R 4-1)

The primary source of the hydroxyl radicals is from the chain branching reaction during which hydrogen peroxide is decomposed, as given in (R 4-2). According to Westbrook [6], this is the intermediate temperature ignition chemistry in which HCCI and diesel combustion occurs.

\[ \text{H}_2\text{O}_2 + \text{M} \rightarrow \text{OH} + \text{OH} + \text{M} \]  \hspace{1cm} (R 4-2)

It can be hypothesized that the highly paraffinic LTFT fuel creates a larger radical pool than that for the diesel or HTFT fuels, in regions of the combustion chamber where over-mixing or quenching can occur. The ignition process is dependent on localized
conditions reaching the decomposition temperature of hydrogen peroxide. The conjectured increase in low temperature heat release produced by the LTFT fuel provided heat that allowed the hydrogen peroxide to decompose at an earlier time. The LTFT, having more available radicals earlier in the combustion process, is able to more completely consume the air-fuel mixture, reducing THC and CO emissions. Additionally, the LTFT fuel may have a leaner “critical” equivalence ratio, which would have allowed it to autoignite in regions of the cylinder that the diesel and HTFT fuels could not.

In summary, the reduced THC and CO emissions produced during the combustion of the LTFT appear to be linked to the combustion phase due to the fuel’s high ignition quality. Furthermore, the LTFT fuel is hypothesized to be able to combust in localized regions of the cylinder that have temperatures too low or are too over-mixed for the HTFT or diesel fuels to combust. The different aspects of the LTFT fuel noted above are attributed to a combination of density, volatility and cetane number. Many contributing factors to the low THC and CO emissions produced by the advanced combustion of the LTFT fuel have been discussed. The dominant factors, which produce high THC and CO emission during the combustion of the diesel and HTFT fuels, along with the reduction in THC and CO emission for the LTFT fuel, are only speculative given the level of measurements available in this study. An optical diagnostics study would provide greater insight regarding the combustion process of the LTFT fuel.
4.4.2 Optimized Injection Timing

The optimum SOI was calculated to be the minimum relative value when taking the sum of the NOX and PM emissions values normalized by the maximum emissions value of the advanced diesel combustion SOI sweep. The optimum was calculated to be at -4° ATDC for the diesel and HTFT fuels. As an exception, the LTFT produced very low PM emissions even at SOI timings near TDC, which caused the optimum SOI of the LTFT fuel to be a 0° ATDC. However, to make a fair comparison of all three fuels, SOI of -4° ATDC was selected as the SOI timing to compare against the optimized SOI of the HTFT and diesel fuels.

Figure 4-17 shows that at the optimized injection timing there is only a slight variation in brake thermal efficiency (BTE), due to the more advantageous combustion phasing of the higher cetane number fuels. The HTFT fuel increased BTE by 1.4% while the LTFT increased by 1.4% with respect to the diesel fuel.

Figure 4-17 indicates that at the optimized injection timing, the HTFT fuel increased NOX by 13% compared to the diesel fuel. This increase was due to the 3% less EGR recalculated during the combustion of the HTFT fuel, although the HTFT fuel had 0.9° shorter ignition delay. However, the LTFT fuel had a 3.4° shorter ignition delay than the diesel fuel but produced 17% less NOX. This apparent discrepancy was due to the difference in EGR%, but the lower percentage of premixed combustion that the LTFT fuel produced was likely a contributing factor. Similarly, PM emissions for the HTFT fuel increased by 25% while for the LTFT fuel decreased by 63%. These NOX and PM emissions indicated that increasing the fraction of diffusion combustion in advanced
diesel combustion might result in lower cylinder temperatures than a purely premixed combustion phase.

THC and CO emissions reduced quite dramatically, especially for the LTFT fuel. THC for the HTFT fuel reduced 31% and LTFT reduced by 80% compared to the advanced diesel combustion diesel baseline. CO reduced 32% for the HTFT fuel and likewise reduced 75% for the LTFT fuel. It is apparent that the increased cetane number fuels reduced the amount of overly-lean charge that can lead to incomplete combustion.

Figure 4-17: Comparison of optimized start of injection of advanced diesel combustion for brake thermal efficiency, NOX, PM, THC and CO of diesel (□), HTFT (■) and LTFT (■) fuels.

In this work, THC and CO emissions were demonstrated to be dramatically reduced, below conventional combustion levels, during advanced diesel combustion of high cetane number (DCN 81) synthetic fuel. This achievement marks significant progress in advanced combustion from nearly a decade ago, when post-combustion
aftertreatment was thought necessary to make advanced combustion viable [6]. As indicated in the introduction of this paper, modest reductions in THC and CO emissions were shown in advanced combustion with fuels with cetane numbers of ~60. Advanced diesel combustion, specifically HECC, was used in combination with a purely paraffinic synthetic fuel, which produced low NO\textsubscript{X}, PM, THC, and CO emissions without increased fuel consumption, relative to conventional diesel combustion or advanced combustion with the diesel fuel. Based on the synergy observed between a highly paraffinic fuel and the HECC mode, we recommend referring to this combination as Paraffin Enhanced Clean Combustion (PECC).
4.5 Conclusion

A low temperature Fischer-Tropsch (LTFT) fuel with high cetane number enabled low THC and CO emissions along with low PM and NO\textsubscript{X} during advanced combustion. The use of the high cetane fuel in a PCCI advanced combustion mode allowed for large rates of EGR to be utilized to reduce NO\textsubscript{X} and PM emissions, while preventing an excessively long ignition delay from producing an over lean charge, which could lead to incomplete combustion. The PCCI operating mode with enhanced performance through use of a paraffinic fuel (deemed “Paraffin Enhanced Clean Combustion” or PECC) led to the following results at optimized injection timing of -4\degree ATDC:

- Brake thermal efficiency increased by ~1.5%
- NO\textsubscript{X} reduced by ~17% versus standard diesel fuel in PCCI
- PM reduced by ~63% versus the diesel fuel in PCCI mode
- Total hydrocarbons reduced by ~80% versus the diesel fuel in PCCI mode
- Carbon monoxide reduced by ~75% versus the diesel fuel in PCCI mode

Furthermore, a fuel with slightly raised ignition quality (DCN 51) was shown to increase NO\textsubscript{X} and PM, while fuel with a DCN of 81 produced lower NO\textsubscript{X} and PM. The results for the conditions under which the engine was operated, PCCI advanced combustion mode should consist of a significant fraction of mixing-controlled combustion as opposed to a solely premixed combustion phase.
Chapter 5

Effects of Fuel Ignition Quality on Critical Equivalence Ratio

5.1 Introduction

The motivation of this work is to further investigate the dramatic reduction of incomplete combustion observed during the advanced diesel combustion of a high cetane number fuel, described in Chapter 4. In Chapter 4, it is hypothesized that higher cetane number fuel would achieve complete combustion in localized regions of the combustion chamber, while a lower cetane number fuel would not. This hypothesis is based on the work of Musculus et al. [71] which introduced the concept of a “critical” $\Phi$, below which fuel in localized regions of the chamber is potential sources for incomplete combustion.

Chapter 4 examines the effect of high ignition quality fuels in a light duty diesel engine operating under advanced diesel combustion. An ultralow sulfur diesel fuel (diesel) with a derived cetane number (DCN) of 45, a synthetic fuel produced in a high temperature Fischer-Tropsch (HTFT) process with a DCN of 51 and a synthetic fuel produced in a low temperature Fischer-Tropsch (LTFT) process with a DCN of 81, were evaluated with a start of injection (SOI) timing sweep. The LTFT fuel of high ignition quality was shown to lower incomplete combustion by enabling an 80% reduction in total hydrocarbon (THC) emissions and a 74% reduction in carbon monoxide (CO) emissions relative to the diesel fuel. Several factors were suggested to contribute to the lower THC and CO emissions which included combustion phasing, ignition dwell and critical $\Phi$ [76]. Petersen et al. [38], in a concurrent study, similarly observed that a higher ignition quality
diesel fuel significantly decreased the UHC and CO emissions during advanced diesel combustion.

The concept of a critical Φ was examined in great detail by Musculus et al. [71] wherein the Φ of a fuel jet was studied optically in a combination of a constant volume chamber and a single cylinder direct-injection heavy-duty diesel engine under typical LTC conditions. A long ignition dwell, the duration from the end of injection (EOI) to the start of combustion (SOC), was shown to produce overly-lean charges. Localized regions of low Φ were observed to occur in particular near the injector at the tail of the fuel jet, where rapid mixing with ambient gases occurred. Localized regions of the combustion chamber where radical pools are not large enough to support the transition to high temperature reaction have been identified in the past to generate incomplete combustion. Radical poor environments occur due to either inadequate conditions where quenching occurs such as at cylinder walls or when inadequate fuel is available to support chain branching reactions [39]. As mentioned above, the unique feature of the work by Musculus et al. [71] is the temporal and spatial quantification of charge mixture which identified the localized region of the spray jet thereby producing potential unburned hydrocarbons.

In a motored engine experiment, Curran et al. [77] examined autoignition chemistry of isomers of gasoline surrogates pentane, hexane, and primary reference fuel mixtures of n-heptane and isooctane under a constant stoichiometric Φ by varying CR. Curran et al. [77] stated, “Below some CR, there is virtually no reaction; as the CR increases, CO concentration and extent of reaction increase until, at some critical value, autoignition is observed, all without spark ignition in the combustion chamber.” The
autoignition is being referred to as the event where high temperature heat release (HTHR) is produced. The study conducted by Curran et al. measures the critical CR, where in-cylinder conditions are not adequate to produce a suitable radical pool that can support chain branching although the air fuel mixture is at unity.

In a later work, Szybist et al. [65] demonstrated in a motored engine at constant \( \Phi \) and increasing CR, that fuels of significant cetane number displayed a two-stage autoignition process with a low temperature heat release (LTHR) event and a HTHR event. Here significant CO emissions were shown to be produced during LTHR. Negligible amounts of CO\(_2\) were shown to be produced due to decarboxylation of ester containing species during LTHR. Battin-Leclerc [11] also reports some CO\(_2\) production from intermediate ether reaction pathways during LTHR. The majority of CO\(_2\) is produced during HTHR by the oxidation of CO [32].

In this study, a modified CFR engine fed with a homogenous charge is used to simulate a localized region in diesel spray jet. A diesel fuel (DCN 43), a HTFT fuel (DCN 51) and a LTFT (DCN 77) as well as single-component surrogates of similar ignition quality are evaluated. Under steady-state conditions and a set of constant CRs, the \( \Phi \) is gradually increased where autoignition due to high temperature chemistry is indicated and defined as the critical \( \Phi \). In contrast to previous work, this study examines the transition from LTHR to HTHR at conditions adequate to support HTHR but with inadequate fuel to produce a significant radical pool, which is the condition shown by Musculus et al. [71]. The lower critical \( \Phi \) of fuels with higher ignition qualities is ultimately proven to be a factor which produces lower emissions from incomplete combustion during advanced diesel combustion with high cetane number fuels. The
determination of critical $\Phi$ to compare fuels is a novel concept, which is based on the concept of critical $\Phi$ developed by Musculus et al. [71]. According to Musculus et al. [71], the “critical” $\Phi$ is a barrier below which fuel in localized regions of the chamber is a potential source of incomplete combustion.

5.2 Experimental

5.2.1 Engine and Test Facility

In the present study, a modified motored CFR (Cooperative Fuel Research) engine was operated at steady-state at 600 rpm, shown in Figure 5-1. The carbureted fueling system was replaced with an electrical heater, set to 260 °C, and a gasoline direct injection fuel injector (GDI). Fuel flow rate was varied by modifying the duration of fuel injection, according to a predetermined calibration for each fuel tested. Fuel was fed to the injector at a pressure of 700 psi. A hot-wire mass airflow (MAF) sensor was used to measure mass flow rate of air. The CFR engine’s knock sensor was replaced with a Kistler 6052B piezoelectric pressure transducer, which measured the crank angle at a resolution of 0.1°. Expanded detail of the modified CFR engine experimental setup can be found in Szybist et al. [12] and in Zhang et al. [74].
Figure 5-1: Modified Cooperative Fuels Research (CFR) engine. Originally printed in Szybist et al. [12] and reproduced in Zhang et al. [74].

In the present study, several additional modifications were made to enhance the stabilization of test parameters. The evaporative steam cooling system, used to maintain water jacket temperatures of the engine, was replaced with an 8 liter 1000 watt refrigerated/heating circulator. Return coolant was additionally passed through a series of air-cooled radiators, which allowed the circulator to maintain operation in heating mode. The water jacket temperature was maintained at 90 °C during both motoring engine operation and engine operation with significant high temperature heat release. Additionally a 6 liter, 1100 watt refrigerated/heating circulator was used to maintain the GDI injector’s mounting plate at a constant 90 °C. As a result, the GDI injector’s mount
was a constant 90 °C during mass measurements for the injector calibration and engine operation, regardless of intake temperature.

5.2.2 Test Condition

In this work, a constant compression ratio (CR) was held at 4, 5, 6 and 8, respectively, as \( \Phi \) was gradually increased. Details of the test conditions used for all fuels tested are given in Table 5-1. The engine motored at 600 rpm throughout all conditions, as well as a constant cooling jacket temperature of 90 °C and a constant intake air temperature of 260°C. Bottled CO\(_2\) and N\(_2\) were delivered upstream of the air intake to simulate exhaust gas recirculation (EGR). Simulated EGR values with 12 vol. % O\(_2\), 7.5 vol. % CO\(_2\) and 80.5 vol. % N\(_2\) were targeted based on the work in Kook et al. [78]. Post-processing revealed that actual simulated EGR was composed of 10.7 vol. % O\(_2\), 8 vol. % CO\(_2\) and 81.3% vol. N\(_2\). The engine was allowed at least one minute to stabilize before data acquisition. Once steady-state operation was verified, data was measured for three minutes at each \( \Phi \) tested.

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<th>Table 5-1: Operational conditions.</th>
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<td>Simulated EGR</td>
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5.2.3 Exhaust Species Analysis

An AVL Combustion Emissions Bench II was used to measure gaseous emissions. CO$_2$ was measured by Rosemount infrared analyzers, and O$_2$ was measured by using a Rosemount paramagnetic analyzer. CO was measured using a California Analytical Instruments infrared analyzer. Significant unburned hydrocarbons and partially-oxidized hydrocarbons were present in the exhaust sample. Three external chillers were connected in series to prevent the contamination of the various analyzer cells. As such, the hot exhaust sample going to the CO, CO$_2$ and O$_2$ analyzers was first chilled to reduce moisture; these emissions were reported on a dry basis. Emissions data were sampled every 10 seconds under steady-state operating conditions.

5.2.4 In-cylinder Pressure Data Analysis

As noted above, the CFR engine’s knock sensor was replaced with a Kistler 6052B piezoelectric pressure transducer, which measured cylinder pressure at a resolution of 0.1° crank angle. A custom LabVIEW data acquisition system was used to acquire 40 cycles of crank angle revolved pressure data, and a single averaged trace was computed. A band-pass filter and a cubic spline algorithm were utilized to smooth the pressure trace without altering its features. A zero-dimensional single zone model given by Heywood [5] was utilized to calculate apparent heat release rate (AHRR) and in combination with the ideal gas law to calculate bulk cylinder temperature. Details of the specific calculations used for the in-cylinder combustion analysis of this experiment’s setup are outlined in previous work conducted by Zhang [7]. Provisions were made in
consideration of the significant residual gas fraction that will affect composition of the in-cylinder charge, as discussed in the results section below.

The typical convention used throughout the literature is to refer to heat release rate calculated through zero-dimensional single zone model as the apparent heat release rate (AHRR). The term *apparent* is added to the heat release rate since its reliance on the first law of thermal dynamics neglects losses and heat transfer. As the engine motors, the AHRR trace indicates negative heat release due to heat transfer. For studies in which high magnitudes of HTHR are produced, the negative heat release due to heat transfer can be negated. However, the negative heat release is more significant in relation to the magnitude of total heat release in studies such as this one, where often only LTHR is produced. For this reason, motored pressure traces were subtracted from the firing pressure traces to calculate what is referred to as the heat release rate (HRR) in this work, per a method similar to the one used in Woschni [79].

**5.2.5 Test Fuels**

The conventional ultra-low sulfur diesel fuel (diesel), the synthetic fuel produced in a high temperature Fischer–Tropsch (HTFT) process, and the synthetic fuel produced in a low temperature Fischer–Tropsch (LTFT) process, previously examined in light-duty diesel engine in Chapter 4, are the focus of the work in this section. However, these fuels have high final boiling points, which are not conducive to intake vaporization and the creation of a homogenous charge. As discussed by Zhang [7], to ensure vaporization, the partial pressure of a given fuel at room temperature should be below the saturation
vapor pressure for a given $\Phi$. This criteria is straightforward for single-component fuels; however, for real multi-component fuels, assumptions must be made.

A fuel preparation method similar to that of Szybist et al. [12] was used to prepare the diesel, HTFT and LTFT, by removing the heaviest 10% of the fuels’ mass, based on simulated distillation analysis, per ASTM method D2887.

![Simulated distillation curves](image)

**Figure 5-2:** Simulated distillation curves of diesel (●), HTFT (▲) and LTFT (♦); using ASTM method D2887, with a 90% of mass cut point (—).

The resultant final boiling point (FBP) fuel and DCN are given in **Table 5-2**. In general, the modification of the fuel resulted in a ~100 °C decrease in the final boiling points of all the fuels. Complete vaporization of the fuels in the 260 °C intake air charge was confirmed by inspecting the heated intake air manifold after high $\Phi$ operation. As such, complete fuel vaporization in the heated intake manifold was assumed for all fuels and $\Phi$ that were examined. However, condensation of the fuel may have occurred in the combustion chamber before significant compression. The 2, 1 and 4 DCN change in ignition quality, for the diesel, HTFT and LTFT fuels, respectively, after distillation, is an
interesting consequence of the reduction of the FBP, even though it did not impact the objective of this study.

Table 5-2: Comparison of final boiling points and DCN of the full boiling fuels and the 1 to 90% mass of the diesel, HTFT and LTFT fuels.

<table>
<thead>
<tr>
<th></th>
<th>diesel</th>
<th>HTFT</th>
<th>LTFT</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Full BP</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final BP (°C)</td>
<td>416</td>
<td>492</td>
<td>405</td>
</tr>
<tr>
<td>DCN</td>
<td>45</td>
<td>51</td>
<td>81</td>
</tr>
<tr>
<td><strong>1 to 90%</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final BP (°C)</td>
<td>329</td>
<td>369</td>
<td>308</td>
</tr>
<tr>
<td>DCN</td>
<td>43</td>
<td>50</td>
<td>77</td>
</tr>
</tbody>
</table>

To confirm that the vacuum distillation process did not result in pyrolysis or cracking of the fuels, the subsequent fractions of the diesel fuel were examined in a GCMS after distillation. Figure 5-3 shows the GCMS chromatograms for the unaltered diesel fuel, the vacuum distilled 1 to 90% temperature boiling points of the diesel mass and the 90 to 100% temperature boiling points of the diesel fuel’s mass. The GCMS chromatograph of the diesel fractions indicates that noticeable cracking did not occur. It should be noted that the GCMS chromatograph intensity is magnified for a cut fraction when it is analyzed alone.
Figure 5-3: Comparison of GCMS chromatograph for the diesel by full boiling range, 1 to 90% of mass removed after vacuum distillation and 90 to 100% of mass separated after vacuum distillation. Note that the response of the 90 to 100% chromatograph is high due to the increased concentration of the fraction after distillation.

The prepared test fuels diesel, HTFT and LTFT are given in Table 5-3, along with single-component ignition quality surrogate fuels, n-hexane, n-heptane and n-dodecane. The n-hexane, n-heptane and n-dodecane fuels were selected to explore the effect of fuel composition on the critical Φ, by comparing single-component and multi-component fuels of similar ignition quality. Furthermore, the trends in critical Φ of the lower boiling point single-component fuels were used to confirm the complete vaporization of the multi-component fuels.

Murphy et al. [80] tabulated values of pure component CN determined through a combination of motored CN measurements (D 6138), DCN (D 6890) measurements, nonstandard method ignition delay and blending. The reported CN values of n-hexane
ranged from 42 to 44.8, while those of n-heptane ranged from 52.5 and 56, and those of n-dodecane ranged from 80 to 87.6.

Collaborative DCN measurements of the n-hexane, n-heptane and n-dodecane are shown in Table 5-3. The n-heptane’s measured DCN of 53 corresponds with the values reported in Murphy et al. [80]. The measured DCN of n-dodecane, 74, is between 7.5% and 14.9 lower than that reported in Murphy et al. [80], which is expected for a fuel of such high ignition quality. However, n-hexane, which is of typical ignition ranges quality, was measured to have a DCN between 12.1% and 19.5% higher than those reported in Murphy et al. [80]. The discrepancy in the ignition quality of n-hexane can affect the interpretation of its critical $\Phi$ when compared to its ignition quality.

<table>
<thead>
<tr>
<th>Table 5-3: Experimental fuels.</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCN</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>diesel</td>
</tr>
<tr>
<td>HTFT</td>
</tr>
<tr>
<td>LTFT</td>
</tr>
<tr>
<td>n-hexane</td>
</tr>
<tr>
<td>n-heptane</td>
</tr>
<tr>
<td>n-dodecane</td>
</tr>
</tbody>
</table>

5.2.6 Residual Gas Fraction

As noted in Curran et al. [77], it is essential to consider the effects of residual gas fraction in a motored engine study where incomplete combustion occurs. In this study, where a premixed homogenous charge is drawn into the cylinder, the mass flow rates of air and fuel should indicate the global and localized $\Phi$, as given by Eq. (5-1).
However, in operations with low compression ratio, significant residual gas will remain after the exhaust stroke. Although relatively low compression ratios are used in this study, the residual fraction is composed mainly of unreacted fuel and air because incomplete combustion was being studied. An approximation of the percentage-reacted charge can be calculated from the pseudo-cumulative heat release percentage, given in Eq. (5-2).

\[
\text{HR\%}_{\text{pseudo}} = \frac{\int_{\text{SOC}}^{\text{EOC}} \text{ARHR} \, d\theta}{Q_{\text{LHV}} * m_{\text{fuel}}} * 100\%
\]  

(5-2)

The pseudo-cumulative heat release percentage, which approximates the fuel conversion percentage to complete combustion products, assumes that the charge no longer contains fuel when all possible energy is released from the fuel and where partially-oxidized products are still assumed to make up some percentage of the total fuel energy. This estimation of charge conversion indicates that though residual fraction may be large, only a small percentage of the residual fraction has been converted until HTHR is reached.

The residual fraction \(f\) is defined as the mass of the residual charge over the mass of total charge as in Eq. (5-3).

\[
f = \frac{m_{\text{residual}}}{m_{\text{total}}}
\]  

(5-3)
In both Heywood [5] and Ferguson and Kirkpatrick [48], similar methods of calculating residual fraction for ideal cycles are given. In practice, these methods are difficult to implement since they rely on explicit knowledge of temperature and pressure during each stroke of the four-stroke cycle. For instance, the cylinder temperature during the intake stroke is difficult to estimate since heat transfer will reduce the intake temperature of 260 °C to a temperature nearing the cylinder wall temperature of 90 °C. This method is based on the four-stroke Otto gas cycle analysis and assumes a constant gamma.

The method presented in Ferguson and Kirkpatrick [48] for calculating the residual fraction in a four-stroke Otto cycle was implemented as a first approximation of the residual fraction. The method assumes a constant gamma and ignores losses. An initial guess of the residual was needed to initiate a “for-loop” calculation.

A second method for calculation of residual fraction was implemented by Zhang [7], where ideal gas law with Eq. (5-3) was used to derive Eq. (5-4).

\[ f = \frac{1}{cr} \times \left( \frac{P_e}{T_e} \right) \left( \frac{T_i}{P_i} \right) \]  

Eq. (5-4) assumes a constant gamma, ignores heat transfer losses and ignores mass of conservation when the combustion chamber values are open.

On average, the combination of the pseudo-cumulative heat release percentage to both approximations of residual fraction resulted in an \( \Phi \), which was 0.01 lower than the \( \Phi \) calculated from the intake charge alone. This is due to the very low rate of heat release or fuel conversion that occurs before the onset of HTHR when the engine is operating at
low CRs. Furthermore, when the engine was operated at higher CRs, more fuel conversion occurred before the onset of HTHR, but at the high CRs, less residual fraction remained in the combustion chamber after the exhaust stroke. As such, it was found to be reasonably accurate and more convenient to report $\Phi$ solely based on intake mass of air and fuel.

5.3 Results

The following results are intended to support the validity of the criteria used to identify the critical $\Phi$ of n-hexane, n-heptane, n-dodecane, diesel, HTFT and LTFT fuels at the CRs of 4, 5, 6 and 8. Various idiosyncrasies are identified for the test fuels and operational conditions through the heat release analysis, maximum bulk analysis, temperature analysis and emissions analysis. Key figures of interest are presented below to avoid repetition. In general, the n-hexane, n-heptane, n-dodecane, diesel, HTFT and LTFT fuels were consistent in their behavior, which defined variations in critical $\Phi$, regardless of CR.

5.3.1 Critical $\Phi$ Criterion

In this work, critical $\Phi$ is defined as the minimum $\Phi$ at which a motored engine can achieve and sustain HTHR throughout consecutive combustion cycles. A sweep of $\Phi$ is performed by gradually increasing $\Phi$ from low to high. The increasing $\Phi$ sweep prevents any residual reactive species or residual heat from skewing the test with a more
reactive combustion chamber environment. In this study, only two-stage fuels were examined, which produced LTHR at \( \Phi \) before the critical \( \Phi \). At and after the critical \( \Phi \), both LTHR and HTHR events are present. **Figure 5-4** displays an example of the criteria used to determine the critical \( \Phi \) for n-dodecane at a CR of 4, where the critical \( \Phi \) occurs at an \( \Phi \) of 0.35. Raw CO ppm and CO\(_2\) \% exhaust emissions were monitored during the \( \Phi \) sweep. CO emissions increase with an increase of LTHR as more fuel participates in low temperature reactions. Formaldehyde (CH\(_2\)O) produced during low temperature reaction has a hydrogen abstracted to form a formyl radical (HCO\(\cdot\)), which then undergoes another hydrogen abstraction to form CO [32]. Before the critical \( \Phi \), small amounts of CO\(_2\) are produced by decomposition of intermediate cyclic ether and not oxidation [11]. At and after the critical \( \Phi \), CO is oxidized into CO\(_2\), which is represented by a trade-off in the CO and CO\(_2\) exhaust emissions.

Furthermore, the critical \( \Phi \) marks the transition of only LTHR to both LTHR and HTHR, which is signified by an increase of the maximum bulk cylinder temperature. Since a homogeneous charge is being autoignited, the maximum bulk cylinder temperature is representative of localized regions of combustion charge. The maximum bulk cylinder temperature, as seen in **Figure 5-4**, increases from 929 K to 1270 K at critical \( \Phi \) of 0.35. The critical \( \Phi \), where HTHR occurs, producing a bulk cylinder temperature of 1270 K, is in reasonable agreement with Hwang et al. [81], where two-stage fuels were reported to have LTHR producing mass-average temperatures from 760 K to 880 K, ITHR producing mass-average temperatures from 950 K to 1170 K and HTHR occurring with a rapid temperature rise.
Figure 5-4: Example of critical $\Phi$ criterion for n-dodecane at a CR of 4, indicated by CO (●), CO$_2$ (▲), maximum bulk in-cylinder temperature $K$ (♦) and the critical $\Phi$ (—).

In Figure 5-5, the HRR of the $\Phi$ sweep for n-dodecane at a CR of 4, reflects the progression to the critical $\Phi$ identified in Figure 5-4. LTHR is observed to gradually increase with increasing $\Phi$, until $\Phi = 0.33$. At $\Phi = 0.34$, a second stage heat release event occurs, though this $\Phi$ is not the critical $\Phi$. During the operation at $\Phi = 0.34$, it was noted that autoignition occurred intermittently between consecutive combustion cycles. As a result, the 40 cycle of pressure trace contained a combination of cycles where some exhibited only LTHR and some both LTHR and HTHR. Based on the definition of critical $\Phi$ used in this work, the critical $\Phi$ is at an $\Phi$ where sustained HTHR occurs throughout consecutive combustion cycles. Thus, the critical $\Phi$ n-dodecane at a CR of 4 is observed to occur at an $\Phi$ of 0.35, which is in agreement with the CO, CO$_2$ and maximum bulk cylinder temperature data in Figure 5-4.
Critical $\Phi$ for n-dodecane occurs at a leaner $\Phi$ of 0.27 for a CR of 5, than it does for a CR of 4, as seen in Figure 5-6. Furthermore, CO emissions, CO$_2$ emissions and maximum bulk cylinder temperature data indicate that the transition to high temperature autoignition occurs less abruptly at a CR of 5, compared to a CR of 4. The $\Phi$ sweep for n-dodecane at a CR of 5 has a maximum in CO of 1.39% occurring at $\Phi = 0.25$, which is higher than that for CR $= 4$ which has a maximum in CO of 1.21% at $\Phi = 0.34$. It should be noted, though, that maximum in CO at a CR of 4 was likely increased by the intermittent HTHR that occurred between combustion cycles at $\Phi = 0.34$. Additionally, the maximum bulk cylinder temperature as seen in Figure 5-6 increases from 1070 K to 1173 K at the critical $\Phi$ of 0.26.
Figure 5-6: Example of critical $\Phi$ criterion for n-dodecane at a CR of 5, indicated by CO (●), CO$_2$ (▲), maximum bulk in-cylinder temperature K (♦) and the critical $\Phi$ (---).

Figure 5-7 shows the HRR traces of the $\Phi$ sweep for n-dodecane at a CR of 5, where second stage heat release events occur at $\Phi$ well before the critical $\Phi$. For example, the $\Phi$ of 0.25 displays second stage ignition producing a maximum bulk cylinder temperature of 991 K. Figure 5-7 shows six HRR traces produced from single cycle non-averaged pressure trace data at $\Phi = 0.25$. These HRR traces indicate that a second stage heat release event is occurring even though the mass-averaged temperature is below that typical for HTHR. Hwang et al. [81] found, through a combination of formaldehyde chemiluminescence imagining and single-zone kinetic model computation, that a significant amount of heat released during the second stage heat release event was due to ITHR. This would indicate that the second stage heat release event observed in Figure 5-7 is indeed due to ITHR.
Figure 5-7: Example HRR profiles for n-dodecane at a CR of 5 and gradually increasing $\Phi$ of 0.1 (········), 0.2 (-----), 0.24 (-----), 0.25 (-----), 0.26 (-----) and 0.27 (-----).

Figure 5-8: Example HRR profiles for n-dodecane at a CR of 4 and $\Phi$ 0.25 for six individual combustion cycles. The 10 cycles are cycle #1 (-----), cycle #2 (-----), cycle #3 (-----), cycle #4 (-----), cycle #5 (-----) and cycle #6 (-----).
HRR profiles should provide by definition the clearest indication of the critical $\Phi$. This is the case for the lower ignition quality fuels, diesel, HTFT, n-heptane and n-hexane, where a second stage heat release event will abruptly appear, clearly due to HTHR. However, in the case of high ignition quality fuels such as n-dodecane and LTFT, a significant second stage heat release event occurs due to ITHR before the critical $\Phi$. Furthermore, the transition from ITHR to HTHR becomes less clear for CRs of 6 CR 8 with increased motoring pressures and temperature. As such, the decrease of exhaust CO still clearly indicates the critical $\Phi$. This indeed brings doubt to the legitimacy of the critical $\Phi$ for the higher CRs examined because an abrupt increase of HRR does not occur at higher CRs. However, the reproduced critical $\Phi$ trends among the test fuels at all four compression ratios provide a crosscheck to validate critical $\Phi$ at the higher compression ratios. The critical $\Phi$ of the diesel, HTFT, LTFT, n-hexane and n-heptane, were determined using the same criteria used to determine the critical $\Phi$ of n-dodecane.

### 5.3.2 Heat Release Rate

The HRR profiles for the $\Phi$ sweeps indicate how the combustion process of the six test fuels varies before and at their given critical $\Phi$. No attempt was made to control or optimize combustion phasing. Instead, during cylinder motoring, temperature and pressure conditions were determined by the given CR and the fuels were allowed to react accordingly. Figures 5-9, 5-10 and 5-11 show examples of HRR traces from the diesel fuel, HTFT fuel and LTFT fuel, respectively, at a CR of 6. In Figures 5-9, 5-10 and 5-11, the highest $\Phi$ given is the respective critical $\Phi$, where the diesel, HTFT and LTFT
fuels have critical $\Phi$ of 0.4, 0.31 and 0.22, respectively. The diesel fuel, Figure 5-9, and more so HTFT fuel, Figure 5-10, produce some ITHR before the critical $\Phi$. HTFT fuel has DCN that is 8 units higher than that of the diesel fuel and a slight increase in ITHR at the $\Phi$ before the critical $\Phi$. However, the LTFT in Figure 5-11, which has a DCN that is 34 units higher, produces significant ITHR before its critical $\Phi$. The absolute value of LTHR is observed to be higher for the fuels of greater ignition quality, which corresponds to observations made by Szybist et al. [65]. The higher ignition quality fuels produce relatively more LTHR, which increases the in-cylinder temperature and causes the transition to intermediate temperature reaction sooner. Since, the higher ignition quality fuels are producing significant LTHR and ITHR at leaner $\Phi$, the in-cylinder radical pools are a smaller fraction of the potential radical pool. This causes the conditions to linger at that of the intermediate temperature reaction regime, where a uniform transition to HTHR cannot occur.
Figure 5-9: Example HRR profiles for diesel at a CR of 6 and gradually increasing Φ of 0.1 (-----), 0.2 (-----), 0.3 (- - -), 0.38 (-- --), 0.39 (---) and 0.4 (----).

Figure 5-10: Example HRR profiles for HTFT at a CR of 6 and gradually increasing Φ of 0.1 (-----), 0.2 (-----), 0.25 (- - -), 0.29 (-- --), 0.3 (---) and 0.31 (----).
Figure 5-11: Example HRR profiles for LTFT at a CR of 6 and gradually increasing $\Phi$ of 0.1 ($\cdots$), 0.17 (-----), 0.19 (-- --), 0.2 (---), 0.21 (-----), and 0.22 (-----).

Figure 5-12 shows the HRR profiles for all six test fuels for a CR of 6 at $\Phi$ of 0.1, where the fuels’ pre-critical $\Phi$ HRR profiles can be compared regardless of the differing fueling rates. Table 5-4 provides quantitative values for key phasing events and HRR magnitudes for Figure 5-12. Figure 5-12 shows that all six test fuels produce only LTHR at $\Phi = 0.1$. The ignition quality of the fuels can be assessed in terms of CA50, where LTHR having a DCN of 77 has a CA50 at -31.4 °ATDC, and where diesel having the lowest DCN of 43 has a CA50 at -17.8 °ATDC. A SOC algorithm was developed and implemented, where SOC occurs at the inflection point of the HR. Details of the SOC algorithm are given in Appendix A. The SOC do not correlate as strongly with DCN as CA50 does. Figure 5-13 shows CA50 to have an $R^2$ value of 0.957 and SOC to have an $R^2$ value 0.936. The difference between SOC and CA50 can be attributed to the broad range of components found in the diesel, HTFT and LTFT fuels, which will begin
low temperature oxidation non-uniformly. In comparison, the single-component fuels, n-hexane, n-heptane and n-dodecane, begin low temperature uniformly, with variations due to possible thermal and concentration stratification that occurs in-cylinder. As a result, the single-component fuels produced sharp HRR peaks, while the multi-component fuels produce HRR peaks that rise more gradually.

The difference between the low temperature oxidation of the multi-component and single-component fuels is also observed by examination of the maximum HRR and cumulative HRR shown in Table 5-4. The n-hexane and n-heptane are shown to produce more LTHR at $\Phi = 0.1$ than either the diesel or the HTFT produce. The diesel and n-heptane, although of comparable ignition quality to the n-hexane and n-heptane, respectively, have significant contributions from olefins and aromatics which have been shown to produces less LTHR than paraffins [82]. The LTFT with a DCN of 77 is shown in Figure 5-12 and Table 5-4 to have earlier phasing than the n-dodecane with a DCN 74, which is expected due to the difference in DCN. However, the n-dodecane produces more LTHR, 19.6 J, than the LTFT, 18.5 J, even though they are both composed primarily of n-paraffins. The difference in cumulative LTHR is due to the broad array of n-paraffins, which comprise the LTFT fuel. The shorter n-paraffins, which comprise the LTFT fuel, may be too stable to produce LTHR at the given conditions. The longer n-paraffins, which comprise the LTFT fuel, may condense on the cylinder walls early in the intake stroke and may not even react during the HTHR.
Figure 5-12: HRR profiles for n-hexane (---), n-heptane (--), n-dodecane (---), diesel (---), HTFT (---) and LTFT (----) fuels at an Φ 0.1 and CR of 6.

Table 5-4: Key phasing parameters of the HRR traces for diesel, HTFT, LTFT, n-hexane, n-heptane and n-dodecane at a CR of 6 and Φ of 0.1.

<table>
<thead>
<tr>
<th></th>
<th>diesel</th>
<th>HTFT</th>
<th>LTFT</th>
<th>n-hexane</th>
<th>n-heptane</th>
<th>n-dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCN</td>
<td>43</td>
<td>51</td>
<td>77</td>
<td>50</td>
<td>53</td>
<td>74</td>
</tr>
<tr>
<td>SOC LTHR (°ATDC)</td>
<td>-33.8</td>
<td>-34.1</td>
<td>-42.1</td>
<td>-32.8</td>
<td>-35.3</td>
<td>-40.3</td>
</tr>
<tr>
<td>CA50 (°ATDC)</td>
<td>-17.8</td>
<td>-20.0</td>
<td>-31.4</td>
<td>-19.7</td>
<td>-23.3</td>
<td>-28.3</td>
</tr>
<tr>
<td>Cumulative HR (J)</td>
<td>10.0</td>
<td>11.6</td>
<td>18.5</td>
<td>19.2</td>
<td>17.6</td>
<td>19.6</td>
</tr>
<tr>
<td>Maximum HRR (J/deg.)</td>
<td>0.39</td>
<td>0.55</td>
<td>0.96</td>
<td>0.91</td>
<td>0.87</td>
<td>1.07</td>
</tr>
</tbody>
</table>
Figure 5-13: Correlation of SOC LTHR and CA50 to DCN for diesel (●), HTFT (▲), LTHR (♦), n-hexane (×), n-heptane (+) and n-dodecane (■) fuels at a CR of 6 and Φ of 0.1.

Figure 5-14 shows the HRR profiles for all six test fuels for a CR of 6 at Φ of 0.2. The increase of Φ results in a more LTHR for all the fuels which increases cylinder temperatures, resulting in significant second stage heat release for the LTFT and n-dodecane and a less prominent second stage heat release event for the n-hexane and n-heptane. As mentioned in the section above, the work by Hwang et al. [81] would suggest this second stage heat release event to be ITHR. However, since only global measurements were conducted in this study, a stratified combination of ITHR and HTHR, though possible, is unlikely given the calculated bulk cylinder temperatures.

The trends in phasing and cumulative HR for Φ = 0.2 are similar to Φ = 0.1, although there is a major difference in how the LTHR is terminated. At Φ = 0.1, all the LTHR that could be supported by the lean fuel charge is produced. However, at Φ = 0.2, more LTHR occurs, which also increases cylinder temperature for the transition from low
temperature chemistry to immediate temperature chemistry. In general, **Figure 5-12** and **Figure 5-14** show that the higher ignition quality fuels produce more LTHR, which transition to ITHR and ultimately hasten the onset of HTHR.

![Figure 5-14: Heat release rate of n-hexane (--.--), n-heptane (---), n-dodecane (--), diesel (--), HTFT (---) and LTFT (---) fuels at an Φ of 0.2 and CR of 6.](image)
Table 5-5: Key phasing parameters of the HRR traces for diesel, HTFT, LTFT, n-hexane, n-heptane and n-dodecane at a CR of 6 and Φ of 0.2.

<table>
<thead>
<tr>
<th></th>
<th>diesel</th>
<th>HTFT</th>
<th>LTFT</th>
<th>n-hexane</th>
<th>n-heptane</th>
<th>n-dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>DCN</td>
<td>43</td>
<td>51</td>
<td>77</td>
<td>50</td>
<td>53</td>
<td>74</td>
</tr>
<tr>
<td>LTHR SOC (°ATDC)</td>
<td>-34.1</td>
<td>-32.6</td>
<td>-45.9</td>
<td>-32.3</td>
<td>-34.3</td>
<td>-43.0</td>
</tr>
<tr>
<td>ITHR SOC (°ATDC)</td>
<td>n/a</td>
<td>n/a</td>
<td>-21.4</td>
<td>-5.6</td>
<td>-10.7</td>
<td>-20.0</td>
</tr>
<tr>
<td>Cumulative LTHR (J)</td>
<td>11.8</td>
<td>25.5</td>
<td>31.4</td>
<td>25.5</td>
<td>27.7</td>
<td>35.3</td>
</tr>
<tr>
<td>Cumulative ITHR (J)</td>
<td>n/a</td>
<td>n/a</td>
<td>57.6</td>
<td>15.5</td>
<td>23.3</td>
<td>73.8</td>
</tr>
<tr>
<td>Cumulative HR (J)</td>
<td>11.8</td>
<td>25.5</td>
<td>89.0</td>
<td>40.9</td>
<td>51.0</td>
<td>109.1</td>
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<tr>
<td>CA50 (°ATDC)</td>
<td>-20.0</td>
<td>-18.9</td>
<td>-4.7</td>
<td>-16.3</td>
<td>-15.4</td>
<td>-3.0</td>
</tr>
<tr>
<td>Maximum HR (J/deg.)</td>
<td>0.8</td>
<td>1.2</td>
<td>2.7</td>
<td>1.7</td>
<td>2.0</td>
<td>3.2</td>
</tr>
</tbody>
</table>

5.3.3 Maximum Bulk Cylinder Temperature

Figures 5-15, 5-16 and 5-17 show maximum bulk cylinder temperature with an increase Φ sweep at CRs of 4, 5, 6 and 8 for the fuels of primary interest in this study: diesel, HTFT and LTFT. The maximum bulk cylinder temperature provides a mass-averaged approximation of the highest global temperature that occurred in the combustion chamber. The bulk cylinder temperature is not a direct measurement of temperature, but rather it is calculated from in-cylinder pressure data.

In Figure 5-15, the maximum bulk cylinder temperature of diesel fuels indicates an abrupt increase in temperature as Φ is gradually increased, due to HTHR, which indicates the critical Φ. At a CR of 4, the diesel fuel does not transition to HTHR during the sweep of Φ, where it is shown in Figure 5-15 to produce only up to ~820 K. The
diesel fuel is not reactive enough to achieve high temperature ignition in the conditions resulting from a CR of 4. In contrast, the diesel fuel is shown to transition abruptly from \(~890\) K to \(~2000\) K during high temperature ignition at a CR of 5. The diesel fuel at a CR of 6 is shown to achieve HTHR at \(\Phi = 0.23\), with a temperature of \(~1480\) K. The increase of CR results in a lower critical \(\Phi\) and a lower maximum bulk cylinder temperature at the critical \(\Phi\), since less fuel is in the combustion chamber. In addition, the pre-critical \(\Phi\) temperatures are elevated with the increase in CR, where the CRs of 5 and 6 are shown to have temperatures of \(~890\) K and \(~920\) K, respectively. The transition to HTHR is relatively more gradual for the diesel fuel at a CR of 8. As noted in the earlier sections, significant ITHR is produced by all fuels at elevated CRs, but is greater for the higher ignition quality fuels. The CO and CO\(_2\) exhaust emissions data are used to confirm that the critical \(\Phi\) of the diesel fuel is at \(\Phi = 0.23\), where it produces temperatures of \(~1180\) K.
The maximum bulk cylinder temperature for the HTFT fuel at CRs of 4, 5, 6 and 8 shown in Figure 5-16 indicates that the HTFT fuel produces similar trends as the diesel fuel with respect to the CR; however, the HTFT fuel has a significantly leaner critical $\Phi$ than the diesel fuel. The 7 DCN points higher ignition quality of the HTFT fuel as compared to the diesel fuel is apparently related to the lower critical $\Phi$ of the HTFT fuel. The HTFT fuel is shown in Figure 5-16 to achieve high temperature ignition at an $\Phi$ of 0.76 for a CR of 4, producing a temperature of ~1600 K, unlike the diesel fuel, which did not achieve HTHR at a CR of 4. The HTFT fuel at CR = 5 produces HTHR at an $\Phi$ of 0.46 which occurs at a significantly leaner $\Phi$ than the diesel fuel at an $\Phi$ of 0.63. In general, the HTFT fuel at its critical $\Phi$ produces a lower maximum bulk cylinder temperature than the diesel fuel at the same compression ratio, since less fuel is in the combustion chamber at the critical $\Phi$. 

Figure 5-15: Maximum bulk cylinder temperature of diesel fuel with an increase $\Phi$ sweep at CR of 8 (●), CR of 6 (×), CR of 5 (+) and CR of 4 (■).
Figure 5-16: Maximum bulk cylinder temperature of HTFT fuel with an increase Φ sweep at CR of 8 (●), CR of 6 (×), CR of 5 (+) and CR of 4 (■).

Figure 5-17 shows the maximum bulk cylinder temperature for the Φ sweep for the LTFT fuel where the transition to HTHR is relatively smoother at all CRs. The LTFT fuel is a more reactive fuel, having a DCN which is 35 units greater than that of the diesel fuel. At a CR of 4, the LTFT fuel achieves high temperature ignition with a discernible step change in temperature, with an increase from ~900 K to ~1240 K. However, at a CR of 5, the LTFT fuel was noted to produce intermittent knocking at Φ of 0.25 and 0.26 before the critical Φ of 0.27, where constant high temperature ignition produced a temperature of ~1290 K. The LTFT fuel produced a very gradual transition to HTHR at CRs of 6 and 8 even though pre-critical Φ knocking was not observed. The bulk cylinder temperature transitioned at CR = 6, from ~1110 K to 1231 K at the critical Φ of 0.23 and at CR = 8 transitioned from ~1190 K to 1210 K at the critical Φ of 0.17. A temperature of 1190 K is above the temperature of the ITHR regime, according to the work of Hwang.
et al. [81], meaning that the critical $\Phi$ may actually have occurred at an $\Phi$ of 0.16 for $\text{CR} = 8$. However, the bulk cylinder temperature calculation is only an approximation of the true in-cylinder temperature. Furthermore, the CO exhaust emissions were used ultimately to discern the critical $\Phi$ to be 0.17.

![Graph](image)

**Figure 5-17:** Maximum bulk cylinder temperature of LTFT fuel with an increase $\Phi$ sweep at $\text{CR}$ of 8 (●), $\text{CR}$ of 6 (×), $\text{CR}$ of 5 (+) and $\text{CR}$ of 4 (■).

### 5.3.4 CO and CO$_2$ Emissions

The $\Phi$ sweep was extended well past the critical $\Phi$, where the fall-off of CO emissions indicated complete combustion, at a $\text{CR}$ of 8, for the diesel, HTFT and LTFT fuels. The extended $\Phi$ sweep was conducted at a $\text{CR}$ of 8 since less fuel would be consumed at a high $\text{CR}$, and more importantly, because lower and safer pressure raise rates would occur in-cylinder. **Figure 5-18** shows the volumetric exhaust CO emissions for the diesel, HTFT and LTFT fuels at a $\text{CR}$ of 8. The volumetric exhaust CO emission trends in **Figure 5-18** are representative of the volumetric exhaust CO emissions for the
diesel, HTFT and LTFT fuels at CRs of 4, 5 and 6. **Figure 5-18** shows, at a given Φ, through CO emissions, that the LTFT is the most reactive fuel, followed by the HTFT fuel and finally the diesel fuel. The LTFT fuel initially produces higher CO emissions than the HTFT fuel, followed by the diesel fuel at a given Φ. Then at the Φ of 0.17, the LTFT fuel begins to produce HTHR where CO is converted to CO₂ primarily through the path shown in (R 5-1).

\[
\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2 \quad \text{(R 5-1)}
\]

At the critical Φ, the LTFT, HTFT and diesel fuels are in the midst of low temperature reaction regime. The HTFT fuel achieves high temperature ignition at Φ = 0.2, and later the diesel fuel does at Φ = 0.23. More fuel is in the cylinder at each of the successive critical Φ, resulting in elevated CO emissions. Heat release is dominated by HTHR at Φ = 0.3, where CO emissions are nearly that of the initial Φ of 0.05.

![Figure 5-18: Volumetric exhaust CO (ppm) emissions over an Φ sweep diesel (●), HTFT (▲), LTHR (♦) fuels.](image)
The volumetric exhaust CO$_2$ emissions at a CR of 8 are not typical of the CO$_2$ emissions at CRs of 4, 5 and 6. As shown previously in Figures 5-4 and 5-6, n-dodecane volumetric exhaust CO$_2$ emissions abruptly increased at the critical $\Phi$. CO$_2$ production during LTHR has been reported to be produced by secondary cyclic ether reactions, without CO oxidation [11]. The sudden increase in CO$_2$ is due to the oxidation of CO, per (R 5-1), which occurs during the HTHR. The multi-component fuels and single-component fuels alike produced significant CO$_2$ before their critical $\Phi$, at a CR of 8. The HRR profiles and bulk cylinder temperatures indicate that all the fuels at CR = 8 produced a second stage heat release event, which was assumed to be ITHR.

Furthermore, the heat release assumed to be ITHR was identified to repeatedly occur for individual combustion cycles. Further experimentation is necessary to determine whether the second stage heat release event is ITHR or is due to thermal stratification, where locally some HTHR produces CO$_2$. If the second stage heat release event is ITHR, then ITHR may have enhanced the production of CO$_2$ through decomposition of LTHR intermediate species. Regardless of the possible evidence for ITHR, a definite critical $\Phi$, where global HTHR occurs, can be identified for all the fuels at a CR of 8.
Figure 5-19: Volumetric exhaust CO₂ (%) emissions over an Φ sweep diesel (●), HTFT (▲), LTHR (♦) fuels.

5.3.5 Low Temperature Fuel Reactivity

CO is produced in localized regions of the combustion chamber in which low temperature reaction pathways are active. However, CO production will occur globally in an ideal homogenous charge combustion environment. CO is an indication of low temperature fuel reactivity through the normalization in the variation in fueling rate along the Φ sweep. Low temperature fuel reactivity of the n-hexane, n-heptane, n-dodecane, diesel, HTFT and LTFT fuels are shown over the Φ sweep via emission index CO in Figures 5-20 and 5-21, at CR = 4 and CR = 6, respectively. Figures 5-20 and 5-21 indicate similar trends in fuel reactivity between CR = 4 and CR = 6. In general, a higher CR is shown to lead to higher low temperature reactivity before the critical Φ. At any CR, the low temperature reactivity of the fuels, follows the ranking:

n-dodecane > LTFT >> n-heptane > n-hexane >> HTFT > diesel.
**Figure 5-20** shows the low temperature reactivity of the n-dodecane and LTFT fuels to increase exponentially to their given critical Φ where an abrupt drop in low temperature reactivity takes place. The low temperature reactivity of the n-heptane, n-hexane, HTFT and diesel fuels follow horizontal trends, until their critical Φ, with the exception of the diesel fuel.

![Graph showing emission index CO for various fuels](image)

**Figure 5-20**: Emission Index CO of n-dodecane (■), LTFT (♦), n-heptane (✚), n-hexane (×), HTFT (▲) and diesel (●), at a CR of 4, over an increasing Φ sweep.

**Figure 5-21** shows that n-dodecane, LTFT n-heptane and n-hexane produce parabolic trends in their low temperature reactivity. These fuels exhibit a decline in low temperature reactivity past the pinnacle of the parabolic trends, although the critical Φ does not occur until the abrupt decrease in low temperature reactivity. The HTFT and diesel fuels display an exponential increase in reactivity during the Φ sweep at a CR of 6. **Figures 5-20 and 5-21** indicate that low temperature reactivity is higher for fuels solely composed of n-paraffins and with longer average chain lengths, as expected.
Figure 5-21: Emission Index CO of n-dodecane (■), LTFT (♦), n-heptane (+), n-hexane (×), HTFT (▲) and diesel (●), at a CR of 6, over an increasing Φ sweep.

5.3.6 Summary of Critical Φ under Ambient Air Composition

The HRR profiles, maximum bulk cylinder temperatures and exhaust emissions convey the Φ resolved transition to HTHR and indicate the difference in reactivity produced by diesel, HTFT, LTFT, n-hexane, n-heptane, and n-dodecane fuels. Ultimately, the focus of this work is the measurement of the critical Φ for the various test fuels. Great care was placed in the description of the criteria used to identify the critical Φ. The determination of critical Φ to compare fuels is a novel concept based on Musculus et al. [71] which introduced the concept of a “critical” Φ, below which fuel in localized regions of the chamber is a potential source for incomplete combustion.

A summary of critical Φ vs. DCN is shown in Figures 5-22 through 5-25 for CRs of 4, 5, 6 and 8, respectively. The blend-derived CN of n-hexane, 42, is also indicated in
the critical $\Phi$ summary figures, since it affects the interpretation of the single-component fuels’ critical $\Phi$. Critical $\Phi$ is plotted against DCN to determine if there is a direct correlation between critical $\Phi$ and a reduction in complete combustion, since in Chapter 4 high ignition quality fuels were shown to reduce incomplete combustion.

Figures 5-22 through 5-25 show a monotonic trend between critical $\Phi$ and DCN for all the test fuels, when the blend-derived CN value of n-hexane is ignored. However, if the DCN value for n-hexane is ignored, distinct monotonic trends are observed for the single-component and multi-component fuels. The distribution of critical $\Phi$ decreases with the increase in CR, yet the trends in critical $\Phi$ are retained with the increase in CR. At CR = 4, the critical $\Phi$ of the fuels varies between 0.35 and 0.76. At CR = 5, the critical $\Phi$ of the fuels varies between 0.27 and 0.63. At CR = 6, the critical $\Phi$ of the fuels varies between 0.23 and 0.4. At CR = 8, the critical $\Phi$ of the fuels varies between 0.17 and 0.23.
Figure 5-22: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 4. Note that the blend-derived cetane number of n-hexane is shown for comparison.

Figure 5-23: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 5. Note that the blend-derived cetane number of n-hexane is shown for comparison.
Figure 5-24: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 6. Note that the blend-derived cetane number of n-hexane is shown for comparison.

Figure 5-25: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 8. Note that the blend-derived cetane number of n-hexane is shown for comparison.
5.3.7 Effect of EGR on Critical \( \Phi \) Ratio

Simulated EGR was introduced into the combustion chamber through air dilution with \( \text{N}_2 \) and \( \text{CO}_2 \). Intake charge \( \text{O}_2 \) dilution was used to examine the effects of an advanced combustion environment on critical \( \Phi \). An intake charge was composed of 12 vol. % \( \text{O}_2 \), 7.5 vol. % \( \text{CO}_2 \) and 80.5 vol. %\( \text{N}_2 \), targeted at condition used by Kook et al. [78] in which simulated EGR was utilized. However, post-processing revealed that a lower \( \text{O}_2 \) intake mixture was introduced to the combustion chamber. The actual charge was composed of 10.7 vol. % \( \text{O}_2 \), 8 vol. % \( \text{CO}_2 \) and 81.3% vol. \( \text{N}_2 \).

The monotonic trend of critical \( \Phi \) between the test fuels was similar to that of the critical \( \Phi \) results for ambient air. The distribution of critical \( \Phi \) among the test fuels at a CR of 8 increased significantly with simulated EGR, with critical \( \Phi \) between 0.38 and 1.0.
Figure 5-26: Critical $\Phi$ vs. DCN for n-dodecane, LTFT, n-heptane, n-hexane, HTFT and diesel fuel at a CR of 8 and simulated EGR. Intake charge was composed of 10.7 vol. % $O_2$, 8 vol. % $CO_2$ and 81.3 vol. % $N_2$. Note that the motored cetane number of n-hexane is shown for comparison.

5.4 Discussion

Musculus et al. [71], who first presented the concept of critical $\Phi$, stated that “UHC emissions may arise from jets that ignite before EOI (negative ignition dwell) if the mixtures near the injector become too lean either to autoignite in the time available or to support propagation of the downstream reaction zone into the near-injector region.” In Chapter 4, it was conjectured that a factor which resulted in lower emissions of incomplete combustion products for the LTFT fuel was that the LTFT was able to transition to second stage ignition in localized regions of the combustion chamber while the HTFT and diesel fuel could not. In the current chapter, a homogenous charge was used to simulate a localized region in a diesel spray jet. Fuels of different ignition quality were fed into the combustion chamber in an $\Phi$ sweep to determine their critical $\Phi$. 
The summary of critical $\Phi$, shown in Figures 5-22 through 5-25, clearly indicates that fuels of higher ignition quality have lower critical $\Phi$. The distribution among the critical $\Phi$ decreases significantly with the increase of CR. This would indicate that the critical $\Phi$ of fuels would vary little for compression ignition engines with CR between 12 and 24 and that critical $\Phi$ is not an important metric [5]. However, as Figure 5-27 indicates, simulated EGR significantly increases the distribution of critical $\Phi$ of the fuels tested at a CR of 8. Indeed, intake air with 10.7% $O_2$ represented an aggressive level of EGR, but it can be assumed that lower rates of EGR would expect a less dramatic but still significant effect on critical $\Phi$. Thus, critical $\Phi$ is an important metric to indicate combustion behavior and eliminate incomplete combustion emission in both HCCI and PCCI advanced combustion modes, which utilize EGR.

Figure 5-27: Summary of critical $\Phi$ of diesel (■), HTFT (■), LTFT (■), n-hexane (/), n-heptane (/) and n-dodecane (/) at CR 4, CR 5, CR 6 CR 8 and CR 8 with EGR.
The correlation between critical $\Phi$ and ignition quality is not linear. Therefore, the relationship between critical $\Phi$ and ignition quality is unclear. **Figure 5-28** shows the critical $\Phi$ vs. DCN at CRs of 4, 5, 6 and 8 with second order polynomial trend lines. The second order polynomial between critical $\Phi$ and DCN at a CR of 8 is plausible, with an $R^2$ value of 0.922. The correlations between critical $\Phi$ and DCN at CR of 5 and 6 are even stronger, with $R^2$ values of 0.937 and 0.958, respectively. However, the second order polynomial for the CRs of 4, 5 and 6 produces a parabolic trend, which indicates that fuels with DCN between 65 and 70 would have lower critical $\Phi$ than the dodecane and LTFT. Critical $\Phi$ cannot be correlated to DCN even with a second order polynomial, which is in contrast to ignition delay and DCN that correlates with a first order polynomial in ASTM method D6890 [83].

![Second order polynomial of critical $\Phi$ and DCN](image)

**Figure 5-28: Second order polynomial of critical $\Phi$ and DCN at a CR of 8 (●), CR of 6 (×), CR of 5 (+) and CR of 4 (■).**

Several fundamental differences between the DCN and critical $\Phi$ should be considered. Foremost, the DCN measurement of ASTM method D6890 [83], as with any
other method to empirically determine ignition quality, is subject to a physical ignition
delay which precedes the chemical ignition delay. In contrast, the critical $\Phi$ is not subject
to physical fuel effects, because the air and fuel are premixed. The premixing of the fuel
and air during critical $\Phi$ measurement also allows a longer time scale for reaction in the
low temperature regime to occur, which begins early in the compression stroke as
temperature and pressure increase. In both the motored CN test and the IQT DCN test
alike, chemical reactions only initiate when fuel, which was directly injected, is
vaporized. Furthermore, comparably little time is available during ignition quality tests
for low temperature reactions to occur before increased temperature shifts the ignition
chemistry into a high temperature regime.

Another fundamental difference between the DCN measurement and critical $\Phi$
measurement is the $\Phi$ at which each measurement produces high temperature
autoignition. OH concentrations have been shown to be highest in regions with
near-unity $\Phi$, in a diesel-like direct injection system where there is fuel stratification
[71]. For a DCN measurement, high temperature autoignition will first occur in the
radical rich regions of the combustion chamber with near-unity $\Phi$ in the fuel jet. In
contrast, high temperature ignition is first detected in the critical $\Phi$ measurement at the
minimum $\Phi$, which will support a transition to high temperature ignition. Critical $\Phi$ is in
this manner more strongly dependent on LTHR, which hastens the onset of HTHR.
However, LTHR has been shown to be dependent on ignition quality [12]. Thus, critical
$\Phi$ is indirectly dependent on fuel ignition quality through LTHR.

The initial analysis in this discussion examined the three multi-component fuels
and three single-component fuels as a single fuel set. However, the multi-component and
single-component fuels should also be analyzed as independent fuel sets. The critical $\Phi$ of the multi-component fuels and single-component fuels at a CR of 5 are shown in shown Figure 5-29 with lines to distinguish the fuel sets. In addition, a three fuel set is shown in Figure 5-29 with the blend-derived CN value for n-hexane.

![Diagram](image)

**Figure 5-29:** Critical $\Phi$ vs. DCN of n-dodecane, LTFT, n-heptane, n-hexane, and HTFT and diesel fuel at a CR of 5. Note that the motored cetane number of n-hexane is shown for comparison. Lines shown to connect the multi-component fuels (---), single-component fuels with blend-derived CN value of n-hexane (---) and single-component fuels with DCN value of n-hexane (----).

The multi-component fuels and the single-component fuels both independently indicate that higher ignition quality fuels have leaner critical $\Phi$, seen in Figure 5-29. However, the single-component fuels yield leaner critical $\Phi$ than the multi-component fuels. Above, an attempt was made to correlate all six fuels with DCN, which is reasonable since the DCN correlation with ignition delay in ASTM method D6890 [83] was developed with a single-component fuel as a reference for calibration. The multi-component fuels and single-component fuels appear to behave inherently
differently in the critical $\Phi$ measurement, which is in contrast to the DCN measurement where single-component and multi-component fuels are measured.

The interpretation of single-component fuel data is made more difficult due to the uncertainty in ignition quality of the n-hexane fuel. The measured DCN of n-hexane in the present work is 50.2 and the two reported blend-derived CN values of n-hexane are 42 and 44.8 [80]. The DCN of n-hexane was expected to be near the average of the two blends derived CN values. There are two likely reasons for this discrepancy. Either there is an inherent flaw in the DCN to ignition delay correlations in ASTM method D6890 when measuring light single-component fuels, or significant hexane isomers contaminated the “n-hexane” samples used in the blend-derived CN measurement tests, lowering the CN. However, it is unlikely that the two independent values reported in Murphy et al. [80] were both produced with contaminated n-hexane.

Assuming that the true ignition quality of n-hexane is that of the reported blend-derived CN value of 42, Figure 5-29 then indicates that the single-component and multi-component exhibited very different behaviors in terms of correlating critical $\Phi$ to DCN. The distinctively different correlation provides stronger evidence that the critical $\Phi$ is not directly related to ignition quality.

The difference in critical $\Phi$ behavior between the single-component and multi-component fuels is likely due to the difference in how single-component and multi-component fuels behave during low temperature combustion. Perez [82] concluded that hydrocarbons in blends oxidize independently and only chemically interact through small radical pools. The single-component fuels are composed of only one n-paraffin each. n-Paraffins have been shown to be the most reactive species during low
temperature oxidation [84]. In contrast, the diesel and HTFT fuels are composed of n-paraffins along with aromatics, olefins and iso-paraffins, which are known to produce less LTHR [9]. Simple blends have been shown to have antagonistic effects among their differing components [82]. It would be logical to assume that complex blends, such as the diesel and HTFT also have antagonistic blending effects. Further evidence that composition affects critical $\Phi$ is given by the LTFT fuel, which is composed primarily of n-paraffins. The LTFT fuel shares the nearest critical $\Phi$ with its surrogate, n-dodecane. Similar trends are shown in Figures 5-20 and 5-21, which indicate low temperature fuel reactivity through emission index CO.

5.5 Summary and Conclusions

A novel experiment was conducted in which the critical $\Phi$ was determined for a conventional ultralow sulfur diesel fuel (diesel), a synthetic fuel produced in a high temperature Fischer-Tropsch (HTFT) process, and a synthetic fuel produced in a low temperature Fischer-Tropsch (LTFT) process, as well as n-hexane, n-heptane and n-dodecane. The intention of the critical $\Phi$ measurement was to determine if a high cetane number fuel would have a lower combustion lean limit than a lower cetane number fuel, which would indicate that the low critical $\Phi$ of a high ignition quality fuel is a factor, which reduces incomplete combustion during advanced diesel combustion.

A homogenous charge was fed into a modified Cooperative Fuels Research (CFR) Octane Rating engine to simulate a localized region in a diesel spray jet. Fuel rate was gradually increased to determine the critical $\Phi$ at which HTHR was supported. The
critical $\Phi$ was determined at compression ratios of 4, 5, 6 and 8 with the intake manifold
temperature at a constant 260 °C. The following conclusions were produced from the study:

- At the highest compression ratio of 8, the critical $\Phi$ of the fuels began to converge,
indicating that critical $\Phi$ may not be a factor that governs incomplete combustion.
However, in the presence of simulated EGR at a compression ratio of 8, the critical $\Phi$
diverged dramatically. Critical $\Phi$ is important in advanced combustion operations where
EGR is utilized.

- A high cetane number fuel was determined to have a lower critical $\Phi$ ratio, which is
a factor that contributes to reduced incomplete combustion. However, a direct
relationship between critical $\Phi$ and ignition quality cannot be made.

The comparison of multi-component fuels, which contain aromatics, paraffins and
olefins, and single-component fuels, which only contain n-paraffins, indicates that critical
$\Phi$ is driven by the effects of fuel composition on low temperature fuel reactivity. Low
temperature fuel reactivity is higher for fuels solely composed of n-paraffins and with
longer average chain lengths.
Chapter 6

Effects of Fuel Composition on Critical Equivalence Ratio

6.1 Introduction

In Chapter 5, a fuel of higher ignition quality was shown to have a leaner critical $\Phi$ than lower ignition quality fuels. This result confirmed the corollary hypothesis of this dissertation that a fuel having a lower critical $\Phi$ will lead to less CO and THC emissions. However, questions remain regarding fuel compositional effects on the critical $\Phi$. The goal of this section is to examine how hydrocarbon composition affects critical $\Phi$. This line of inquiry will ultimately identity fuel compositions which can lower THC and CO emissions when operating an engine under an advanced combustion mode.

In the present study, critical $\Phi$ is measured for two fuel sets to examine compositional effects on critical $\Phi$. The first set contains three fuels, a blend of n-dodecane/toluene, a blend of n-dodecane/iso-octane, and pure n-heptane. The blends were prepared such that they have ignition quality parity with n-heptane. This fuel set is intended to examine the effect of n-paraffins, iso-paraffins and aromatics on critical $\Phi$.

The second fuel set consists of the low cetane number (CN) fuels of the FACE fuels matrix. These four fuels have equivalent CN, but vary over a single plane of the FACE Fuels matrix by volatility and aromatic content. The FACE fuels are ideal to study the composition effects on critical $\Phi$, though the FACE fuels are “real” multi-component fuels. The physical and chemical makeup of the FACE fuels has been well documented in CRC Report No. FACE-1 [85].
6.2 Experimental

6.2.1 Engine and Test Facility

In the present study, a modified motored Cooperative Fuel Research (CFR) octane rating engine was operated with the experimental setup described in Chapter 5. The engine was operated at 600 rpm at steady-state conditions. Fuel and heated air were introduced into the combustion with a gasoline direct injector (GDI) and electrically heated air manifold, which replaced the carbureted fueling system. Fuel was introduced into the intake manifold where it vaporized. The injector and engine cooling jacket were maintained at a temperature of 90 °C via a set of refrigerated/heating circulators. Air mass was measured with a hot-wire mass air flow (MAF) sensor. The CFR engine’s knock sensor was replaced with a Kistler 6052B piezoelectric pressure transducer, which measured the cylinder pressure at a resolution of 0.1° crank angle.
6.2.2 Exhaust Species Analysis and In-cylinder Pressure Data Analysis

Both exhaust species analysis and in-cylinder pressure data analysis were conducted using the same equipment and analysis techniques specified in Chapter 5.

6.2.3 DCN Parity Blends

An n-dodecane/toluene blend and an n-dodecane/iso-octane blend were blended to have a derived cetane number (DCN) approximately that of n-heptane. ASTM method
D6890 was performed iteratively on blends of n-dodecane / toluene and n-dodecane / iso-octane to measure DCN and to match the DCN of the blends to the DCN of n-heptane. The DCN of the blends was confirmed by a final measurement with ASTM method D6890. The resulting blends and corresponding DCN measurements are given in Table 6-1.

**Table 6-1: Composition and DCN of n-heptane, D61/T39 and D50/I50 fuels.**

<table>
<thead>
<tr>
<th></th>
<th>n-heptane</th>
<th>D61/T39</th>
<th>D50/I50</th>
</tr>
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<tr>
<td>n-heptane</td>
<td>100%</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>-</td>
<td>61%</td>
<td>50%</td>
</tr>
<tr>
<td>toluene</td>
<td>-</td>
<td>39%</td>
<td>-</td>
</tr>
<tr>
<td>iso-octane</td>
<td>-</td>
<td>-</td>
<td>50%</td>
</tr>
<tr>
<td>DCN</td>
<td>53.7</td>
<td>53.4</td>
<td>53.9</td>
</tr>
</tbody>
</table>

The abbreviations D61/T39 and D50/I50 were adopted for n-dodecane/toluene and n-dodecane/iso-octane blends, respectively, based on their volumetric blend ratios. The DCN of D61/T39 was 0.3 units lower, or 0.6% lower, than the DCN of n-heptane. The DCN of D50/I50 was 0.2 units higher, or 0.4% higher, than the DCN of n-heptane. Both these values are well within the repeatability range given in ASTM method D6890 [83] (repeatability of 0.96), for a fuel with a DCN of 55.

**Test Condition for DCN Parity Blends**

Test conditions at which the critical Φ of the DCN parity blends were measured are given in Table 6-2. The DCN parity blends were examined under a constant compression ratio (CR) of 8 and with a simulated EGR sweep. The EGR values were
based on those utilized by Kook et al. [78]. Intake air temperature and the cooling jacket
temperature were maintained at a constant 260 °C and 90 °C, respectively.

Table 6-2: Operational conditions for DCN parity blends. Value for simulated
EGR based on Kook et al. [78].

<table>
<thead>
<tr>
<th></th>
<th>O₂ (%)</th>
<th>CO₂ (%)</th>
<th>N₂ (%)</th>
<th>Compression Ratio</th>
<th>Cooling Jacket (°C)</th>
<th>Air intake (°C)</th>
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</thead>
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<tr>
<td>Ambient Air</td>
<td>21</td>
<td>0</td>
<td>79</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Simulated EGR</td>
<td>17</td>
<td>3.5</td>
<td>79.5</td>
<td>8</td>
<td>90</td>
<td>260</td>
</tr>
<tr>
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<td>15</td>
<td>5</td>
<td>80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Simulated EGR</td>
<td>12</td>
<td>7.5</td>
<td>80.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Simulated EGR</td>
<td>10.7</td>
<td>8</td>
<td>81.3</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

6.3 FACE Fuels

The Fuels for Advanced Combustion Engines (FACE) are a matrix of fuel blends
developed by the Coordinating Research Council (CRC) Advanced Vehicle / Fuel /
Lubricants Committee’s FACE Working Group. The FACE Working Group developed
the FACE fuels by targeting ignition quality, volatility and aromatics content as
properties of primary importance to the performance of advanced combustion engines.
As shown in Figure 6-2 the targeted fuel properties are CN of 30 and 55, a T90 of 270
and 340 °C; and aromatics content of 20% and 45%. A centroid fuel, the ninth FACE
fuel, was designated to represent an average marketplace value of the three fuel
properties.
The aromatic, cetane number and volatility values of the FACE fuels, which were measured by ChevronPhillips Chemical Company, are shown in Table 6-3. In this work, the individual FACE fuels will be referred to with the abbreviation FF along with their numerical designation. Table 6-3 shows the actual values of the properties of the FACE fuels and how they differ from the target values. In particular, the actual CN value of the high CN fuels varied greatly from the target values. This is primarily because the high aromatic content of FF7 and FF8 decrease their CN. The high CN FACE fuels varied from the target CN of 55 by as much as 10 units. In contrast, the low CN FACE fuels varied in CN by less than 2 units.
Table 6-3: Comparisons between target and actual values of cetane number, T90 distillation point, and percent aromatics composition for the Face Fuels matrix. Target values are those reported from ChevronPhillips Chemical Company in the CRC Report No. FACE-1 [85].

<table>
<thead>
<tr>
<th>Cetane number</th>
<th>FF1</th>
<th>FF2</th>
<th>FF3</th>
<th>FF4</th>
<th>FF5</th>
<th>FF6</th>
<th>FF7</th>
<th>FF8</th>
<th>FF9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Target</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>55</td>
<td>45</td>
</tr>
<tr>
<td>Actual</td>
<td>29.9</td>
<td>28.0</td>
<td>32.0</td>
<td>28.4</td>
<td>54.2</td>
<td>53.3</td>
<td>44.3</td>
<td>50.0</td>
<td>45.0</td>
</tr>
<tr>
<td>T90 (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Target</td>
<td>270</td>
<td>340</td>
<td>270</td>
<td>340</td>
<td>270</td>
<td>340</td>
<td>270</td>
<td>340</td>
<td>320</td>
</tr>
<tr>
<td>Actual</td>
<td>269</td>
<td>336</td>
<td>270</td>
<td>337</td>
<td>276</td>
<td>341</td>
<td>267</td>
<td>342</td>
<td>321</td>
</tr>
<tr>
<td>Aromatics (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Target</td>
<td>20</td>
<td>20</td>
<td>45</td>
<td>45</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>45</td>
<td>33</td>
</tr>
<tr>
<td>Actual</td>
<td>22.2</td>
<td>19.4</td>
<td>45</td>
<td>46.6</td>
<td>19.5</td>
<td>21.3</td>
<td>42.3</td>
<td>43.3</td>
<td>32.5</td>
</tr>
</tbody>
</table>

In Chapter 5, DCN was used as the metric of ignition quality to which critical $\Phi$ was compared. The DCN values of the FACE fuels measured using ASTM method D6890 at the Pennsylvania State University are shown in Table 6-4. The DCN measurements of the FACE fuels confirmed the large variations in ignition quality of the high CN FACE fuels. Critical $\Phi$ was only measured for the low CN FACE fuels, due to the lack of ignition quality parity of the high CN FACE fuels. The low CN FACE fuels are a set of fuels which permit a comparison of critical $\Phi$ for complex multi-component fuels with similar ignition qualities.

Table 6-4: Derived cetane number (DCN) of FACE Fuels measured with ASTM method D6890.

<table>
<thead>
<tr>
<th>Derived Cetane Number</th>
<th>FF1</th>
<th>FF2</th>
<th>FF3</th>
<th>FF4</th>
<th>FF5</th>
<th>FF6</th>
<th>FF7</th>
<th>FF8</th>
<th>FF9</th>
</tr>
</thead>
<tbody>
<tr>
<td>Derived Cetane Number</td>
<td>34.9</td>
<td>34.6</td>
<td>32.1</td>
<td>33.1</td>
<td>54.5</td>
<td>53.4</td>
<td>44.5</td>
<td>49.7</td>
<td>43.7</td>
</tr>
</tbody>
</table>

The compositions of the FACE fuels were measured and were quantitatively separated into major hydrocarbon structural composition types through two-dimensional gas chromatographic analysis with a flame ionization detector (2-D GC-FID) and were
reported in the CRC Report No. FACE-1 [85]. Table 6-5 shows the quantitative values of n-paraffins, iso-paraffins, cycloalkanes and aromatics in peak area percent response of the detector. The FACE fuels were blended with little to no olefins, which is reflected in Table 6-5.

Table 6-5: Quantitative hydrocarbon speciation by peak area percent of the FACE fuels measured with a 2-D GC-FID, reported in the CRC Report No. FACE-1 [85].

<table>
<thead>
<tr>
<th></th>
<th>FF1</th>
<th>FF2</th>
<th>FF3</th>
<th>FF4</th>
<th>FF5</th>
<th>FF6</th>
<th>FF7</th>
<th>FF8</th>
<th>FF9</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Paraffins</td>
<td>6.78</td>
<td>3.32</td>
<td>10.49</td>
<td>4.36</td>
<td>31.39</td>
<td>30.32</td>
<td>23</td>
<td>10.96</td>
<td></td>
</tr>
<tr>
<td>iso-Paraffins</td>
<td>52.28</td>
<td>58.53</td>
<td>27.48</td>
<td>48.52</td>
<td>31.79</td>
<td>49.12</td>
<td>16.63</td>
<td>22.57</td>
<td>35.89</td>
</tr>
<tr>
<td>Total paraffins</td>
<td>59.06</td>
<td>61.85</td>
<td>37.97</td>
<td>52.88</td>
<td>63.18</td>
<td>62.58</td>
<td>46.95</td>
<td>45.57</td>
<td>46.85</td>
</tr>
<tr>
<td>Cycloalkanes</td>
<td>12.17</td>
<td>14.66</td>
<td>6.19</td>
<td>3.38</td>
<td>7.97</td>
<td>7.78</td>
<td>4.25</td>
<td>3.02</td>
<td>7.65</td>
</tr>
<tr>
<td>Identifiable aromatics</td>
<td>8.08</td>
<td>9.58</td>
<td>6.55</td>
<td>11.53</td>
<td>7.18</td>
<td>1.56</td>
<td>9.4</td>
<td>1.10</td>
<td>11.76</td>
</tr>
<tr>
<td>Unidentifiable aromatics</td>
<td>19.97</td>
<td>13.36</td>
<td>48.01</td>
<td>31.15</td>
<td>19.72</td>
<td>26.01</td>
<td>38.73</td>
<td>48.73</td>
<td>32.04</td>
</tr>
<tr>
<td>Total aromatics</td>
<td>28.05</td>
<td>22.94</td>
<td>54.56</td>
<td>42.68</td>
<td>26.9</td>
<td>27.57</td>
<td>48.13</td>
<td>49.83</td>
<td>43.8</td>
</tr>
<tr>
<td>Total</td>
<td>99.28</td>
<td>99.45</td>
<td>98.72</td>
<td>98.94</td>
<td>98.04</td>
<td>97.92</td>
<td>99.33</td>
<td>98.42</td>
<td>98.30</td>
</tr>
</tbody>
</table>

6.3.1 Test Condition of the FACE Fuels

Table 6-6 shows the test conditions under which the critical Φ of the low CN FACE fuels was measured in the modified CFR engine. The critical Φ of the low CN FACE fuels was measured with ambient air. The cooling jacket and the intake air were held at constant temperatures of 90 °C and 260 °C, respectively. A CR of 7 was selected after exploratory measurements, because a CR of 7 was found to provide reasonable resolution between the fuels’ critical Φ.
Multi-Cylinder Engine Test Conditions for the FACE Fuels

Gaseous exhaust emissions of the FACE fuels were produced by a GM 1.9 L, 4-cylinder common rail direct injection diesel engine, which was located at the Fuel, Engine and Emissions Research Center at Oak Ridge National Laboratory. The engine was a Euro 5 compliant light-duty diesel engine with a variable geometry turbocharger (VGT). Specifications of the GM 1.9 L engine are given in Table 6-7.

### Table 6-7: Specifications of the GM 1.9 L Engine.

<table>
<thead>
<tr>
<th>Engine</th>
<th>General Motors DI Diesel Engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement</td>
<td>1.9 L</td>
</tr>
<tr>
<td>Bore</td>
<td>82.0 mm</td>
</tr>
<tr>
<td>Stroke</td>
<td>90.4</td>
</tr>
<tr>
<td>Rated Power</td>
<td>110 kW @ 4000 rpm</td>
</tr>
<tr>
<td>Injection system</td>
<td>Common Rail</td>
</tr>
<tr>
<td>Valve/Cylinders</td>
<td>4</td>
</tr>
</tbody>
</table>

The engine was operated at steady-state conditions at 1500 rpm and 2.6 bar BMEP under an advanced combustion mode, specifically high efficiency clean combustion (HECC). The HECC mode was achieved with a single early fuel injection with increased rail pressure and EGR at ~40%. Specifications of the engine’s operational conditions are given in Table 6-8. Total hydrocarbons (THC) and carbon monoxide (CO) emissions were measured with a flame ionization detector (FID) and non-dispersive
infrared (NDIR) analyzers, respectively. More details on the experimental setup of the 1.9 L GM engine and its operation are given in Cho et al. [58].

**Table 6-8: Specification of the engine operational conditions.**

<table>
<thead>
<tr>
<th>Specification</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Engine seed</td>
<td>1500 rpm</td>
</tr>
<tr>
<td>BMEP</td>
<td>2.6 bar</td>
</tr>
<tr>
<td>EGR fraction</td>
<td>~41 %</td>
</tr>
<tr>
<td>Intake oxygen concentration</td>
<td>~15.6 %</td>
</tr>
<tr>
<td>Intake mixture temperature</td>
<td>108 kPa</td>
</tr>
<tr>
<td>Coolant temperature</td>
<td>85 °C</td>
</tr>
<tr>
<td>Injection Pressure</td>
<td>875 bar</td>
</tr>
<tr>
<td>Injection timing</td>
<td>varying</td>
</tr>
</tbody>
</table>

**6.4 Results**

The critical $\Phi$ of the fuels shown in the following results was determined by using the same criteria and methodology described in detail in Chapter 5. The critical $\Phi$ of the DCN parity blends and the FACE fuels provides insight into fuel composition effects on the lean limits of high temperature ignition.

**6.4.1 Critical $\Phi$ vs. Fuel Composition**

The critical $\Phi$ of n-heptane, D61/T39 and D50/I50 at CR of 4, 5, 6 and 8 are shown in Figure 6-3. The distribution of the critical $\Phi$ for n-heptane, D61/T39 and D50/I50 is larger at lower CRs, as was also observed for the fuels in Chapter 5. At a CR of 4, n-heptane is shown to have a critical $\Phi$ of 0.49, while both D61/T39 and D50/I50 have a critical $\Phi$ of 0.62. n-Heptane and the two blends have virtually the same DCN, as noted in the experimental section. The DCN of D50/I50 is 0.2 units higher than that of
n-heptane; however, n-heptane has a significantly lower critical $\Phi$. The difference in DCN between n-heptane and D50/I50 may be negligible, but the difference between their critical $\Phi$ is not. Figure 6-3 shows that a single-component fuel n-heptane has a lower critical $\Phi$ than a binary blend D50/I50, regardless of ignition quality. This result is analogous to that of Chapter 5 in which the single-component fuels had lower critical $\Phi$ than the multi-component fuels, regardless of ignition quality.

![Graph](image)

**Figure 6-3: Critical $\Phi$ vs. DCN for n-heptane (+), D61/T39 blend (△) and D50/I50 blend (●) at CR of 4, 5, 6 and 8.**

The critical $\Phi$ of n-heptane, D61/T39 and D50/I50 was determined with decreasing concentrations of intake oxygen at a CR of 8, as shown in Figure 6-4. The mixtures of simulated EGR used at each percentage of intake oxygen are shown above in Table 6-2. Figure 6-4 shows, at ambient oxygen concentrations, the critical $\Phi$ of n-heptane, D61/T39 and D50/I50 to be 0.17, 0.18 and 0.19, respectively. The critical $\Phi$ of n-heptane becomes significantly leaner than that of the blends at an intake oxygen
concentration of 17%, where its critical $\Phi$ is 0.22, and both blends have a critical $\Phi$ of 0.27. A similar, trend occurs between the three fuels at an intake oxygen concentration of 15%. However, at an intake oxygen concentration of 12%, the critical $\Phi$ for D61/T39 is significantly leaner than for D50/I50, with respective critical $\Phi$ of 0.41 and 0.49. This alteration in critical $\Phi$ is also shown at an intake oxygen concentration of 10.7%, where the critical $\Phi$ of D61/T39 of 0.55, is nearer to that of n-heptane, $\Phi$ of 0.53, and diverges from that of D50/I50, $\Phi$ of 0.62.

![Figure 6-4: Critical $\Phi$ vs. intake $O_2$ percentage for n-heptane (+), D61/T39 blend (▲) and D50/I50 blend (●) at CR of 8.](image)

The Emission Index CO provides a means to compare the low temperature reactivity of the fuels at any measured $\Phi$, by normalizing CO mass emissions to the fuel mass flow rate. The low temperature reactivity of n-heptane, D61/T39 and D50/I50 at intake oxygen concentrations of 21%, 17%, 15%, 12% and 10.7% is given in Figures through 6-9.
**Figure 6-5** shows n-heptane to have more low temperature reactivity than the D61/T39 and D50/I50 at lean Φ, for intake oxygen concentrations of 21%. n-Heptane at its apex produces 1050 g/kgFUEL of CO while D61/T39 and D50/I50 are shown to process 1026 and 1016 g/kgFUEL of CO, at their respective apexes. The trends in low temperature reactivity of the three fuels reflect the behavior of critical Φ shown in **Figure 6-4**.

![Figure 6-5](image)

**Figure 6-5: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (▲) and D50/I50 blend (●) over an Φ sweep at CR of 8 with 21 vol. % intake O₂.**

The low temperature reactivity of n-heptane, D61/T39 and D50/I50 at an intake oxygen concentration of 17%, shown in **Figure 6-6**, displays a similar trend as the three fuels at an intake oxygen concentration of 21%. However, the absolute CO emissions values of the three fuels exhibit a wide distribution. n-Heptane, D61/T39 and D50/I50 at their respective apexes of CO emissions were 1148, 981 and 976 g/kgFUEL.
Figure 6-6: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (▲) and D50/I50 blend (●) over an Φ sweep at CR of 8 with 17 vol. % intake O₂.

Figure 6-7 shows a noticeable difference in low temperature fuel reactivity D61/T39 and D50/I50, where D61/T39 is seen to produce CO at an increasingly leaner Φ than D50/I50, at an intake oxygen concentrations of 15%. n-Heptane is shown to still have more low temperature fuel reactivity at leaner Φ than D61/T39 and D50/I50, such that n-heptane, D61/T39 and D50/I50 have the respective apexes of CO emissions of 1072, 937 and 900 g/kgFuel. However, the difference in low temperature reactivity between D61/T39 and D50/I50 was not reflected in their critical Φ, which was at an Φ of 0.32 for both fuels.
Both Figure 6-8, which depicts the low temperature fuel reactivity at an intake oxygen concentration of 12%, and Figure 6-9, which depicts the low temperature fuel reactivity at an intake oxygen concentration of 10.7%, show a significant difference in CO trends for D61/T39 and D50/I50. The apex of CO emissions from D61/T39 occurs at a significantly leaner $\Phi$ than D50/I50 and with a higher magnitude of CO at both oxygen concentrations. n-Heptane, D61/T39 and D50/I50 yielded at their respective apexes of CO emissions of 905, 800 and 725 g/kg\textsubscript{Fuel} at an intake oxygen concentration of 15%; while, n-heptane, D61/T39 and D50/I50 yielded at their respective apexes of CO emissions of 887, 706 and 725 g/kg\textsubscript{Fuel} at an intake oxygen concentration of 10.7%. The trend in low temperature fuel reactivity of the three fuels at intake oxygen concentration of 12% and 10.7% corresponds to their critical $\Phi$ shown in Figure 6-4.

Figure 6-7: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (▲) and D50/I50 blend (●) over an $\Phi$ sweep at CR of 8 with 15 vol. % intake O$_2$. 

Figure 6-8: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (▲) and D50/I50 blend (●) over an Φ sweep at CR of 8 with 12 vol. % intake O₂.

Figure 6-9: Emission Index CO indicating low temperature fuel reactivity for n-heptane (+), D61/T39 blend (▲) and D50/I50 blend (●) over an Φ sweep at CR of 8 with 10.7 vol. % intake O₂.
Discussion of DCN Parity Blends

n-Heptane was shown through its critical $\Phi$ and low temperature fuel reactivity to be more reactive than the blends at all the intake oxygen concentrations tested. D61/T39 and D50/I50 produced similar critical $\Phi$ and produced similar low temperature fuel reactivity at intake oxygen concentrations of 21% and 15%. However, at intake oxygen concentrations of 15%, 12% and 10.7, D61/T39 had a leaner critical $\Phi$ and had more low temperature fuel reactivity than D50/I50. First and foremost, the simulated EGR critical $\Phi$ measurements of n-heptane, D61/T39 and D50/I50 were shown to trend similarly to critical $\Phi$ measurements at low CR. The simulated EGR produced a low oxygen concentration environment with triatomic CO$_2$ that acted as thermodynamic dead weight. Dec [67] reported EGR’s largest effect in an HCCI engine is to reduce the temperature of the compressed gas. Thus, the simulated EGR environment was shown to be analogous to a low CR environment where compressed gas temperatures would be reduced. Critical $\Phi$ of a fuel can be concluded to have a tangible effect on combustion in production engines with high CRs operating in advanced combustion modes.

The above results clearly demonstrate that critical $\Phi$ is not directly related to ignition quality, but that critical $\Phi$ is dependent on fuel composition. Indeed, ignition quality is also dependent on fuel composition, but critical $\Phi$ can be concluded to be affected by fuel composition differently. The differences between the combustion conditions, which lead to the difference in behavior between critical $\Phi$ and ignition quality, were discussed in Chapter 5.
As indicated by Table 6-1, n-heptane is composed of 100% of n-paraffins, D61/T39 is composed of 61% n-paraffins and 39% aromatics and D50/I50 is composed of 50% of n-paraffins and 50% iso-paraffins. In general, n-paraffins are reported to be more reactive than iso-paraffins, while aromatics are the least reactive [41]. D61/T39 and D50/I50 were blended to have the same DCN as n-heptane, which was accomplished by combining a high ignition quality component with a low ignition quality component. n-Dodecane is an n-paraffin, which is very reactive, and was measured to have a DCN of 74. Toluene and iso-octane have such low ignition qualities that it is necessary to blend them with fuels of higher and known ignition qualities in order to determine their ignition qualities. Toluene was reported to have blended CN which varies from -5, 9 to 18.3 [80], while iso-octane was indicated to have a higher ignition quality with blended CN which varies from 12, 14 and 17.5 [80]. Based on the difference in ignition qualities of iso-octane and toluene, the I50/I50 blend was expected to have a leaner critical Φ if a difference was observed.

Shibata et al. [9] concluded that hydrocarbon composition hastens HTHR reactions in the following order, by a series of HCCI experiments:

n-paraffins > iso-paraffins > olefins > naphthenes = aromatics.

The above reactivity order would also suggest that the D50/I50 should have been more reactive than the D61/T39. Shibata et al. [9] also suggested a LTHR inhibitor effect was produced by aromatics, some naphthenes and some olefins. Shibata et al. [9] suggested the inhibitor effect was due to the pi-bond which allows an aromatic to remain stable after dehydrogenation. The extracted hydrogen would react with OH radicals, removing OH from the radical pool and forming water which lowers LTHR [9]. This
would suggest that the aromatic content in the D61/T39 blend would inhibit LTHR, causing D61/T39 to have a richer critical $\Phi$.

Perez [82] reported antagonist interactions in an iso-octane/toluene blend. Somewhat in contrast to Shibata et al. [9], Perez [82] argued that the antagonistic effect was not due to the deactivation of OH radicals by toluene, but was rather due to the more reactive iso-octane removing OH radicals from the radical pool. Perez [82] also reported strong synergistic interaction in an n-heptane/iso-octane blend, which was indicated by an increase of heat release compared to pure component blends. This would suggest that the D50/I50 blend used in this study could be more reactive than the n-heptane, though the critical $\Phi$ measurements indicated otherwise under the conditions tested.

Neither of the aforementioned antagonistic or synergistic blending effects can be used to properly explain why the critical $\Phi$ of the D61/T39 blend was leaner compared to the D50/I50. As such, a simple and straightforward explanation is proposed. The D61/T39 blend had a leaner critical $\Phi$ than the D50/I50 blend because the D61/T39 contains 11% more n-paraffins by volume. Szybist et al. [12] showed that high cetane fuels, which are primarily composed of n-paraffins, produce more LTHR. This result was also reflected in the aforementioned study by Shibata et al. [9] where the n-paraffins were suggested to hasten HTHR reactions faster than other hydrocarbon families. However, the explanation that the large n-paraffin content of D61/T39 caused it to have leaner critical $\Phi$ neglects the possible antagonistic effects by either toluene or iso-octane. Rather, here it is suggested that the toluene and iso-octane are relatively inert during the LTHR chemistry of n-dodecane and only act as thermodynamic dead weight, similar to CO$_2$ in EGR. Iso-Octane and toluene are larger molecules than CO$_2$ and will have larger
heat capacities to rob heat produced from n-dodecane’s LTHR. iso-Octane is shown in Figure 6-10 to produce LTHR in a constant volume chamber, well after n-heptane completes its second stage ignition. In Figure 6-10, iso-octane does produce LTHR, but at a time scale which is later than that of n-heptane. Perez [82] noted that the main interaction between blends is by the shared radical pool. During the critical $\Phi$, n-dodecane will begin producing LTHR before iso-octane and the less reactive toluene do little more than absorb heat. The toluene and iso-octane from the D61/T39 and D50/I50 blends can be confirmed to be inert for the $\Phi$ leaner than the critical $\Phi$, by performing a gaseous species analysis using the method described in Zhang et al. [74].

![Figure 6-10: Apparent heat release rate of n-heptane (---) and iso-octane (---), calculated from pressure traces produced in the IQT constant volume combustion chamber.](image)
6.4.2 FACE Fuels Ignition Quality

The critical $\Phi$ of the low CN FACE fuels were measured due to their consistent ignition quality and detailed composition analysis given in CRC Report No. FACE-1[85]. Figure 6-11 shows comparisons of the FACE fuels’ ignition quality, comparing CN measured with ASTM method D613 by ChevronPhillips Chemical Company (CPChem) and by Southwest Research Institute (SwRI), with DCN measured with ASTM method D6890 by the National Renewable Energy Laboratory NREL and by the Pennsylvania State University (PSU). The comparisons of ignition quality values from CPChem, SwRI and NREL were previously compared in CRC Report No. FACE-1[85]. However, Figure 6-11 contains the addition of the PSU DCN values of the FACE fuels measured for this study. Figure 6-11 show the two CN measures and two DCN measurements of FF5, FF6, FF7, FF8 and FF9 to be relatively consistent among the four measurements. FF7 had the largest standard deviation for its four ignition quality measurements, which was 0.8. In contrast, Figure 6-11 shows the two DCN measurements of FF1, FF2 FF3 and FF4 to be consistently lower than the two CN measurements. As a result, FF3 had the lowest standard deviation of the four low CN fuels, which was 1.3.
The average of the two DCN ignition quality measurements and the average of the two CN ignition quality measurements are shown in Figure 6-12. The averaged difference between the DCN and CN for the low CN fuels, FF1, FF2, FF3 and FF4, is 4.28 units. In contrast, the averaged difference between the DCN and CO for the low CN fuels FF5, FF6, FF7 and FF8 is 0.04 units. The discrepancy between the CN and DCN measurements for FF1, FF2, FF3 and FF4 reflects the discrepancy between DCN values and blended CN values for n-hexane mentioned in Chapter 5. The ignition delay to DCN correlation of ASTM method D613 is observed to differ from CN values measured with ASTM method D613, between 5.0 % and 22.0% for fuels with CN between 28.5 and 31.4. n-Hexane, a pure component, was shown to have a greater discrepancy of 19.5%, between CN and DCN, in Chapter 5.
Figure 6-12: Average CN value (■) of CPChem and SwRI, as well as Average DCN value (□) of NREL and PSU.

6.4.3 Effect of Ignition Quality on Critical $\Phi$

The correlations between critical $\Phi$ and ignition quality measured by CPChem, SwRI, NREL and PSU are shown in Figures 6-13 to 6-16, respectively. The DCN measurements of the FACE fuels should follow similar trends as the CN measurements, though not the same absolute value as the CN measurements, because the DCN correlation is linear with ignition delay [83]. CPChem, SwRI, NREL and PSU ignition quality measurements are shown to correlate to critical $\Phi$ with $R^2$ values of 0.976, 0.699, 0.003 and 0.425, respectively. The CN measurements show the strongest correlation with critical $\Phi$, while the DCN measurements corrections are much weaker. ChevronPhillips Chemical Company manufactured and sold the FACE fuels [85]. The CPChem measurements of ignition quality are likely the most representative of the FACE fuels
directly after production. However, degradation of the FACE fuels samples was possible preceding the SwRI, NREL and PSU measurements.

Johnson et al. [86] reported that chemical changes of a diesel fuel were dominated by evaporative losses rather than fuel degradation. Mono-aromatics populate the majority of the lower boiling range of FF1, FF2 FF3 and FF4. Evaporative losses of the mono-aromatics could explain the variation in ignition quality observed. Regardless, the ignition qualities of FF1, FF2, FF3 and FF4 prior to the critical Φ measurements were conducted by PSU, shown in Figure 6-16, and are most representative of the FACE fuels samples used to measure critical Φ. A weak correlation between critical Φ and DCN is shown for FF1, FF2, FF3 and FF4, having an R² values 0.425 in Figure 6-16. Furthermore, the results of DCN parity blends indicate that critical Φ and DCN are not strongly related.
Figure 6-13: Critical Φ vs. CPChem CN for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4 (○) at CR of 7.

Figure 6-14: Critical Φ vs. SwRI CN for FACE Fuel 1 (■), FACE Fuel 2 (□), FACE Fuel 3 (●) and FACE Fuel 4 (○) at CR of 7.
Figure 6-15: Critical $\Phi$ vs. NREL DCN for FACE Fuel 1 (■), FACE Fuel 2 (▲), FACE Fuel 3 (●) and FACE Fuel 4 (○) at CR of 7.

Figure 6-16: Critical $\Phi$ vs. PSU DCN for FACE Fuel 1 (■), FACE Fuel 2 (▲), FACE Fuel 3 (●) and FACE Fuel 4 (○) at CR of 7.

6.4.4 Effect of n-Paraffins on Critical $\Phi$

In the DCN parity blends section, it was suggested that the D61/T39 blend had a leaner critical $\Phi$ than the D50/I50 blend because the D61/T39 blend contained 11% more
n-paraffins. n-Paraffins have been shown to increase the percentage of LTHR contribution to the total heat release [9, 12]. Critical Φ of FF1, FF2, FF3 and FF4 are correlated to peak area percent n-paraffins in Figure 6-17. The coefficient of determination, R^2, of the critical Φ and peak area percent n-paraffins is 0.985. The strong correlation between critical Φ and peak area percent n-paraffins indicates that critical Φ of a fuel is governed by the fraction of n-paraffins, which increases LTHR. This result is logical since a conclusion of Chapter 5 is that higher CN fuels produce more LTHR, which hastens the onset of HTHR.

![Figure 6-17: Critical Φ vs. peak area percent n-paraffins for FACE Fuel 1 ( ■ ), FACE Fuel 2 ( □ ), FACE Fuel 3 ( ● ) and FACE Fuel 4 ( ○ ) at CR of 7.](image)

The n-paraffin content, shown in Figure 6-17, was measured by GC-FID peak as peak area percent and reported in the CRC Report No. FACE-1 [85]; however, a standard was not used to quantify and identify the composition. Peak area percent only provides a relative quantification of the n-paraffins for a given fuels sample, which can be skewed if
the fuels compared were prepared with a different concentration of solvent. Mass percent of the n-paraffins was also reported in the CRC Report No. FACE-1 [85], through a combination of PIONA and GC-FIMS. The PIONA analysis, ASTM method D5443 [87], identifies and quantifies hydrocarbon group-type composition for distillates up to 200 °C. The PIONA analysis of the FACE fuels was supplemented with a non-standard method of analysis using Gas Chromatography-Field Ionization Mass Spectrometry (GC-FIMS) to analyze distillates above 200 °C. It was noted in CRC Report No. FACE-1 [85] that the PIONA measurement underrepresented the n-paraffins in FF1 and FF2, and also that underrepresentation of n-paraffins occurred for all the fuels at the transition from PIONA to GC-FIMS analysis. n-Paraffin mass percent distribution for hydrocarbons from C3 and C21 is given in Figure 6-18 for the low CN FACE fuels. The transition from PIONA to GC-FIMS analysis is at C11. Figure 6-18 shows that the low CN FACE fuels vary greatly in n-paraffin chain length and mass concentration.
Critical $\Phi$ correlation with mass percent n-paraffins for the low CN FACE fuels is shown in Figure 6-19. The correlation of critical $\Phi$ and mass percent n-paraffins is strong, with an $R^2$ coefficient of 0.949. The correlation of critical $\Phi$ and mass percent n-paraffins as well as the correlation of critical $\Phi$ and peak area percent n-paraffins provided collaborating evidence that critical $\Phi$ directly related to a fuels n-paraffin concentration. The strong correlation between the two n-paraffin analysis and critical $\Phi$ is in contrast to the four ignition quality measurements of the FACE fuels, where only the CPChem CN measurement suggested a strong correlation.
6.5 Comparison of Critical Φ to Emissions of Incomplete Combustion from a Multi-Cylinder Engine

An irrefutable correlation between critical Φ and n-paraffin content of a fuel has been shown. It is theorized that a fuel of leaner critical Φ, or high n-paraffin content, should produce less THC and CO emissions in an advanced diesel combustion mode. Figure 6-20 and Figure 6-21 show CO and THC emission from a multi-cylinder engine operating under advanced diesel combustion mode, specifically HECC. CO and THC emissions were measured during a start of injection (SOI) timing sweep varying from -20 -18.5, -17, -15.5 and -14 °ATDC, for FF1, FF2, FF3 and FF4. Linear fits were calculated between critical Φ and CO, as well as critical Φ and THC. The R^2 correlation coefficient, the coefficient of determination, is shown in Figure 6-22 for THC and CO emissions for each of the SOI timings.
Critical $\Phi$ is shown to have the strongest correlation with THC and CO emissions for early SOI timings, which cause overly-lean charges. The $R^2$ of CO and THC at the
SOI of -20 °ATDC are 0.846 and 0.685, respectively. The interpretation of the R² for CO at the SOI of -20 °ATDC is that 84.6% of the variation in CO emissions among the fuels with varying critical Φ can be predicted from the relationship between critical Φ and CO emissions. Conversely, 15.4% of the variation in CO emissions among the fuels with varying critical Φ cannot be predicted from the relationship between critical Φ and CO emissions.

The R² of the correlation between critical Φ and CO emissions decreases with the retardation of SOI timing from 0.846 at -20 °ATDC to an R² of 0.050 at -14 °ATDC. The weakening of the relationship for both CO and THC with critical Φ is due to the later SOI timing producing less over-leaning of the fuel air charge. Early start of injection leads to long ignition delay in which fuel air charges can become overly-lean [71]. A leaner critical Φ would only be beneficial to reduce incomplete combustion under conditions where significant over-leaning of the fuel air mixture has occurred. Logically, the late SOI timings produced a stratified mixture was richer than that of the stratified mixture produced by the earlier SOI timings. Figure 6-22 indicates the critical Φ will only have a notable effect on the reduction of incomplete combustion under conditions where significant over-mixing occurs.

The low CO emissions show a stronger relationship with critical Φ than with the THC emissions. Figure 6-22 shows at SOI timings of -20 and 18.5 °ATDC the R² of THC is ~20% of that of CO, while at SOI timings of -17 and -15.5 °ATDC the R² of THC is ~40% that of CO. CO emissions have been shown to dramatically increase as combustion efficiency falls, while THC emissions increase to a less extent, during advanced combustion modes [1]. A fuel with a leaner critical Φ has a great effect on the
reduction of CO emission over THC emissions. This is logical since THC avoids combustion by condensing through the combustion chamber [39], while CO will remain a gas.

![Figure 6-22: R² coefficient of the correlation between critical Φ and emissions index CO (■) as well as the correlation between critical Φ and emissions index THC (□) at SOI times -20, -18.5, -17, -15.5 and -14 °ATDC](image)

6.6 Discussion

Critical Φ measurements from both the DCN parity fuel set and the low CN FACE fuels suggest that critical Φ is directly related to the n-paraffin content of a fuel. In fact, a strong correction was shown between critical Φ and mass percentages of n-paraffins in the FACE fuels. Though this correlation was strong, R² of 0.949, the correlation only contained four data points. The addition of the high CN FACE fuels, FF5, FF6, FF7 and FF8, along with FF9 would strengthen this correlation. The critical Φ of the high CN FACE fuels were not originally measured due to the large variation in CN
among the high CN FACE fuels. However, this work has provided evidence that CN and critical $\Phi$ are not directly related; thus the addition of the high CN FACE fuels would further increase the validity of a correlation between critical $\Phi$ and n-paraffin content.

A comparison of the critical $\Phi$ values to CO and THC emissions from the low CN FACE fuels produced from an engine operating in PCCI is suggestive of a relationship. Low to high CO and THC emissions were observed to trend with lean to rich critical $\Phi$, during the two earliest SOI timings. This result goes a step beyond the motivating hypothesis of this work, that a high cetane number fuel will have a lower combustion lean limit than a lower cetane number fuel, thus avoiding incomplete combustion, because a fuel of equivalent CN with other fuels was observed to have a leaner critical $\Phi$ and produce less THC and CO emissions.

However, the relationship between lower CO and THC emission with a leaner critical $\Phi$ was only strong at early injection timings. Musculus et al. [71] concluded a mixture too lean to achieve complete ignition arose from a long ignition dwell, the time from SOI to SOC. The relationship between lowered CO and THC emissions with a leaner critical $\Phi$ was not apparent at the later SOC timings, because less over-mixing of the fuel air charge occurred at the later SOI timings. However, significant CO and THC emissions still formed at the later SOI timings, but likely not only due to an overly-lean mixture. CO and THC emissions have also been shown to be produced in rich $\Phi$ regions of the combustion chamber, during operation in partially premixed combustion modes [72]. The source of the CO and THC emissions likely shifts from localized regions of overly-lean mixtures to localized regions of overly rich mixtures, as the SOI timing sweep was retarded. A leaner critical $\Phi$ would only beneficially decrease CO and THC emissions.
in localized regions too lean to achieve complete combustion. The shift of the source of the CO and THC emissions at the later SOI timing caused the weakening of the relationship between critical $\Phi$ and emissions in Figure 6-22.

The potential correlation between CO and THC emissions reduction and fuels n-paraffins content has implications for fuel selection for both PCCI and HCCI. Currently, low ignition quality fuels are being studied in advanced combustion modes to control combusting phasing and allow for higher brake thermal efficiency. Two examples of this are gasoline fuel partially premixed combustion [61] and Reactivity Controlled Compression Ignition (RCCI) which utilizes gasoline / diesel dual fueling [88]. These advanced combustion modes, which utilize low ignition quality fuels, produce elevated THC and CO emissions at low load operations where over lean charges are produced. Hypothetically, a fuel can be blended with increased n-paraffin content and balanced with low ignition quality components to maintain low ignition quality. The increased n-paraffin content allows the fuel to achieve complete combustion in regions where otherwise overly-lean mixtures are formed, reducing THC and CO emissions.

The concept of a fuels’ “$\Phi$-sensitivity” was studied to optimize combustion phasing and prevent high maximum pressure rise rates during HCCI [89]. Yang et al. [90] define $\Phi$-sensitivity as the “advancement of combustion phasing for an increase in equivalence ratio”. Yang et al. compared the $\Phi$-sensitivity of single-stage fuel [90], iso-octane, and two-stage fuel [89], PRF 73, to tailor heat release profiles. The two-stage fuel was found to produce lower maximum pressure rise rates than the single-stage fuel with the same combustion phasing. Furthermore, a PRF 73 with 73 vol. % iso-octane and 27 vol. % n-heptane was found to be more $\Phi$-sensitivity than a PRF 80 with 80 vol. %
iso-octane and 20 vol. % n-heptane [89]. This suggests that even though critical Φ and Φ-sensitivity are different metrics they are related through fuel reactivity, such that a lean critical Φ will have strong Φ-sensitivity. As such, the work of Yang et al. [89, 90] indicates another benefit of a lean critical Φ, or a fuel with high n-paraffin content. A lean critical Φ is a two-stage fuel, which will likely produce a lower maximum pressure rise rate in HCCI combustion.

6.7 Summary and Conclusions

DCN Parity Blends

Critical Φ, which was established in Chapter 5 as a measure of a fuel's ability to achieve complete combustion in lean fuel air charge, was used to examine fuel sets of similar ignition qualities in this section. Blends of n-dodecane/toluene and n-dodecane/iso-octane were prepared to have the same DCN as n-heptane. Critical Φ measurements of the two blends and n-heptane revealed that critical Φ could vary for fuels with the same DCN, or ignition quality. Furthermore, simulated EGR was found to have an effect on critical Φ, which was analogous to a lowered compression ratio. The n-dodecane/toluene blend was found to have a leaner critical Φ than the n-dodecane/iso-octane blend under low reactivity conditions. It was concluded that the 11% greater paraffin content of the n-dodecane/toluene blend compared to the n-dodecane/iso-octane with the same DCN, resulted in more LTHR and a leaner critical Φ.
Low CN Number FACE Fuels

Critical $\Phi$ of the low CN number FACE fuels was measured. The low CN number FACE fuels were manufactured to have a target CN of 30, which all four fuels closely met. Four independent measurements of the low CN number FACE’s ignition quality showed variation. Two DCN measurements (ASTM D 6890), one of which was measured in this study, showed ignition quality generally higher than that of the two CN measurements (ASTM D613). In concert with the parity blends, the results suggest a weak relationship between critical $\Phi$ and ignition quality of four fuels with virtually the same ignition quality.

A linear correlation with an $R^2$ of 0.949 was found between critical $\Phi$ and n-paraffin mass percent, for the low CN FACE fuels. This result collaborates with the conclusion that the n-dodecane/toluene blend had a lean critical $\Phi$ because of its higher n-paraffin content. In other words, the critical $\Phi$ of a fuel is governed by the fraction of reactive components (n-paraffins), which increases LTHR.

The critical $\Phi$ measurements were compared to CO and THC emissions from a multi-cylinder diesel engine operating in PCCI with the low CN FACE fuels. Low CO and THC emission from early SOI timings are suggestive of a correlation with lean critical $\Phi$ measurements. It was concluded that the relationship between low CO and THC emissions and lean critical $\Phi$ is only present when early SOI produces over-mixing of the fuel-air charge. It was conjectured that the contribution of CO and THC from overly rich regions becomes larger, and a fuel with a leaner critical $\Phi$ would not reduce these emissions. These results suggest that a fuel can be blended to have a low ignition
quality, which is desired for high efficiency advanced combustion operations and with a high n-paraffin content to reduce CO and THC and reduce maximum pressure rise rates.

6.8 Acknowledgements

Kukwon Cho, Manbae Han, C. Scott Sluder and Robert M. Wagner must be acknowledged for their major contribution to GM 1.9 L emissions data, which was measured at Oak Ridge National Laboratory’s Fuel, Engine and Emissions Research Center. I participated in the measurements, during a Post-Masters appointment at Oak Ridge National Laboratory in Fall of 2008. The measurements were published in SAE paper 2009-01-2669. The emission index emissions data shown in Chapter 6 were derived from the same measurements as those given in SAE paper 2009-01-2669, but have not been published to date.
Chapter 7

Conclusions and Recommendations

7.1 Summary of Dissertation

In this dissertation, the primary hypothesis was tested on a light-duty turbodiesel engine and resulted in the novel finding that a fuel of high ignition quality will avoid incomplete combustion during an advanced combustion process. The corollary hypothesis was derived to support and explain the novel finding of the primary hypothesis. The corollary hypothesis was tested in a motored engine experiment and resulted in the novel finding that a high cetane number fuel will have a leaner critical $\Phi$ than a low cetane number fuel, thus avoiding incomplete combustion.

The corollary hypothesis of this dissertation was satisfied, but a question remained regarding fuel compositional effects on critical $\Phi$. As such, a follow-up motored engine experiment was performed and indicated that a fuel’s critical $\Phi$ is strongly correlated to its n-paraffin content, which increases LTHR. The critical $\Phi$ of fuels were compared to light-duty turbodiesel engine emissions data, bringing this dissertation full circle from fundamental ignition study to an applied combustion study. In a light-duty turbodiesel engine operating under PCCI, lean critical $\Phi$ fuels (fuels with higher n-paraffin contents) were shown to have a potential correlation between CO and THC emissions. The suggested correlation between critical $\Phi$ and of CO and THC emissions has implications for fuel formulations for advanced combustion modes to reduce emissions from incomplete combustion.
7.2 Conclusion from Chapter 4, Advanced Diesel Combustion of a High Cetane Number Fuel with Low Hydrocarbon and Carbon Monoxide Emissions

A low temperature Fischer-Tropsch (LTFT) fuel with high cetane number enabled low THC and CO emissions along with low PM and NO\textsubscript{X} during advanced combustion, in a light-duty turbodiesel engine. The THC and CO emissions of the LTFT fuel were compared against THC and CO emission of high temperature Fischer-Tropsch (HTFT) fuel and conventional ultra-low sulfur diesel fuel (diesel). THC and CO emissions were observed to reduce with the increase of cetane number.

- The PCCI operating mode with enhanced performance through use of a paraffinic fuel (deemed “Paraffin Enhanced Clean Combustion”, PECC) led to the following results at optimized injection timing of -4\textdegree ATDC:
  - Brake thermal efficiency increased by ~1.5%
  - NO\textsubscript{X} reduced by ~17% versus standard diesel fuel in PCCI
  - PM reduced by ~63% versus the diesel fuel in PCCI mode
  - Total hydrocarbons reduced by ~80 % versus the diesel fuel in PCCI mode
  - Carbon monoxide reduced by ~75% versus the diesel fuel in PCCI mode

- The results indicate that for the conditions, which the engine was operated at PCCI advanced combustion mode, should consist of a significant fraction of mixing-controlled combustion as opposed to a solely premixed combustion phase.
7.3 Conclusion from Chapter 5, Fuel Ignition Quality Effects on Critical $\Phi$

Many factors were suggested which contribute to the lower THC and CO emissions produced by the combustion of a high cetane fuel. Among the factors was the theory that a high cetane number fuel will have a lower combustion lean limit than a lower cetane number fuel, thus resisting incomplete combustion. This theory was examined in a subsequent study where the critical equivalence ratio ($\Phi$), the minimum $\Phi$ at which a fuel can autoignite, was identified for the diesel, HTFT and LTFT fuels along with surrogate fuels n-hexane, n-heptane and n-dodecane. The critical $\Phi$ of the fuels were measured at CRs of 4, 5, 6 and 8.

- Higher ignition quality fuels produced leaner critical $\Phi$ at all CRs tested. The critical $\Phi$ of the three multi-component fuels and the three single-component surrogates began to converge at higher CRs, indicating that critical $\Phi$ variations may not be significant at CRs of production engines. However, in the presence of simulated EGR at a CR of 8, the critical $\Phi$ diverged dramatically. Critical $\Phi$ was concluded to be an important measure of a fuel’s tendency to avoid incomplete combustion, during advanced combustion operations, which utilize EGR.

- A high cetane number fuel was determined to have a leaner critical $\Phi$ and is a factor, which contributes to reduced incomplete combustion. However, a direct relationship between critical $\Phi$ and ignition quality cannot be made.

- The comparisons of multi-component fuels to single-component fuels, which only contain n-paraffins, indicates that critical $\Phi$ is driven by fuel composition effects on low
temperature fuel reactivity. Low temperature fuel reactivity is higher for fuels solely composed of n-paraffins and with longer average chain lengths.

7.4 Conclusion from Chapter 6, Fuel Compositional Effects on Critical Equivalence Ratios

The corollary hypothesis of this dissertation was satisfied, but a question remained regarding fuel compositional effects on critical $\Phi$. The critical $\Phi$ of n-heptane and two DCN parity blends (fuels blends with matched DCN), along with the critical $\Phi$ of the low cetane number FACE fuels were measured to examine the effects of fuel composition on critical $\Phi$.

- n-Dodecane 61 vol. % / toluene 39 vol. % blend (D61/T39) and n-dodecane 50 vol. % / iso-octane 50 vol. % blend (D50/I50) were prepared to have the same DCN as n-heptane. The critical $\Phi$ of n-heptane, D61/T39 and D50/I50 were observed to vary irrespective of the small variation in DCN. n-Heptane had the leanest critical $\Phi$, followed by D61/T39 and finally D50/I50. D61/T39 was suggested to have a leaner critical $\Phi$ than D50/I50 because it contained 11% more n-paraffins, which led to additional LTHR.

- The critical $\Phi$ of the low CN FACE fuels were measured to further examine the effect of composition on critical $\Phi$. A higher mass percentage of n-paraffin content was shown to correlate with a leaner critical $\Phi$ among the low CN FACE fuels. The experimental study of critical $\Phi$ was brought full circle with emission measurements of the low CN FACE fuels during advanced combustion in a light-duty turbodiesel engine. The comparisons of CO and THC emissions produced from advanced combustion with
critical $\Phi$ suggested a correlation during early SOI timings, when over mixing occurred. The relationship between CO and THC emissions and critical $\Phi$ becomes disconnected at later SOI timing, where overly-rich fuel-air mixtures become sources of CO and THC emissions.

- The suggested correlation of critical $\Phi$ with CO and THC emissions implies that fuels can be produced for advanced combustion modes with larger fractions of n-paraffins to reduce CO and THC emissions produced from overly-lean charges.

### 7.5 Recommendations for Future Work

The following recommendations for future work have been formulated based on the investigations in this dissertation:

- PECC was demonstrated to enable a reduction of NO$_X$, PM, THC and CO emission with a DCN 81 fuel, in a light-duty direct injection diesel engine. It is recommended to determine if PECC can be achieved with fuels of DCN below 81.

- It is recommended to examine the effect of incomplete combustion for fuels with differing cetane numbers and similar ignition dwells. This would involve matching phasing in a light-duty direct injection diesel engine or the use of a constant volume combustion chamber.

- It is recommended to quantify the effect that critical $\Phi$ has on CO and THC emissions produced from a light-duty turbodiesel engine, under PCCI operations. Specifically, it is recommended to quantify the effect of ignition dwell vs. critical $\Phi$. 

• It is recommended to measure the critical $\Phi$ of single-stage fuels. Only two-stage fuels have been examined in this dissertation. The critical $\Phi$ of a single-stage fuel will rely on ITHR rather than LTHR to achieve complete combustion.

• This work has identified the critical $\Phi$ as measurement of fuel behavior during advanced combustion operations. It is recommended to standardize the measurement of critical $\Phi$. It may be necessary to operate an engine with various conditions (i.e., CR, intake temperature, intake oxygen diluent, etc.) depending on the fuel’s reactivity. A normalized critical equivalence ratio value would be necessary.
References


13. Lu, X.-C., W. Chen and Z. Huang, A fundamental study on the control of the HCCI combustion and emissions by fuel design concept combined with controllable


82. Perez, P. L. Effects of the chemical structure and composition on the controlled autoignition of hydrocarbon fuels. The Pennsylvania State University, University Park PA, 2010.


Appendix A

Start of Combustion Algorithm

An algorithm was developed and executed in LabVIEW data acquisition software to identify crank angle resolved events. These events include the start of first stage combustion (SOC1), start of second stage combustion (SOC2), and end of combustion (EOC). Such an algorithm is necessary to calculate the percentage of low temperature heat release (LTHR) and high temperature heat release (HTHR) in a repeatable and unbiased procedure. The algorithm was developed to analyze different combustion scenarios, such as single-stage combustion, two-stage combustion where the first stage combustion is of greater magnitude, and a two-stage combustion where the second stage of combustion is of greater magnitude. The steps in the algorithm are as described below:

**Filter and smoothing**

The algorithm relies on locating peaks and troughs of the averaged pressure trace and averaged HRR or AHRR. Erroneous peaks are often identified due to the high frequency noise in the traces. A combination of cubic splines and low pass filters was implemented to eliminate the noise without alteration of the features of the pressure trace.
Start of Combustion

The simplest definition for SOC is the crank angle where the HR increases past zero HR. Unfortunately, signal noise, even with filtering, makes this point unclear. Furthermore, heat losses, unaccounted for in the heat release calculation, can cause offsets, which lower the entire trace. Often, start of combustion is chosen as a threshold percentage of total heat release such as the crank angle where 5% of the AHRR occurs (CA 5) [58]. In this study, a more robust criterion for determining SOC was desired due to the significance of the percentage of LTHR vs. HTHR in the present study. SOC was calculated using a criterion posed in which SOC is defined in Eq. (A-1) [91].

\[
SOC = \frac{d^3 p}{d\theta^3}
\]  

(A-1)

In Eq. (A-1), \( p \) is the crank angle resolved in-cylinder pressure and \( \theta \) is the crank angle. This criterion indicates SOC as being the inflection point at the beginning of the HRR trace. In the case of single-stage combustion, this point is taken to be the only start of combustion. However, in the case of two-stage combustion, this point is taken to be SOC1 or the start of cool flame heat release.

The transition between first and second stage combustion is often not clear. In situations where there is a long delay between the end of first stage combustion and the start of second stage combustion or a significant Negative Temperature Coefficient (NTC) regime, it is necessary to distinguish between the end of first stage combustion and the start of second stage combustion. However, it is also possible to have a situation where the start of second stage combustion occurs immediately after the peak of the first
stage combustion. As a compromise to these two different two-stage combustion scenarios, SOC2 is defined as the crank angle where the minimum value of the HR occurs between the peak of first stage combustion and the peak of second stage combustion.

**End of Combustion**

As combustion ends, two scenarios often occur. Either the heat release decreases at a gradual rate well into the expansion stroke, or the heat release ends abruptly at a fast rate. When the heat release rate lowers gradually, an inflection point does not appear in the trace. In either scenario, the EOC can be defined as the point where the HRR crosses from positive to negative. Though the definition for EOC can be affected by the noise and offset, the EOC phasing is a less important indicator of phasing combustion, and an insignificant difference is made to the cumulative heat release.
Appendix B

Error Analysis of the Light-Duty Turbodiesel Engine Test Stand

The error analysis method used in this dissertation was based on the error analysis method used by Hess [92] and adapted in Lilik [93]. The data acquisition system logged speed, load, temperatures, pressures, mass air flow, fuel mass and emissions every 10 seconds under steady-state conditions. A five minute sampling period was selected for data analysis for a total of 30 sample points. The points were then analyzed using the Student t-test to calculate the error between the 30 data points sampled at steady-state, as given in Eq. (B-1). The Student t-test multiple used was 2.045, due to the 30 samples taken and based on a 95% confidence interval.

$$\text{Percentage Error}_{\text{Student}} = \frac{t_{\alpha \cdot \sigma}}{\sqrt{n \cdot \bar{X}}} \cdot 100\% \quad (B-1)$$

Where:

- $t_{\alpha}$, Student t-test multiplier (1.96)
- n, number of data points (30)
- $\bar{X}$, Mean
- $\sigma$, Standard deviation
The major sources of intermittent error that effect gaseous and PM emissions are given in Table B-1 and Table B-3, respectively. The systematic errors, which affected both the gaseous and PM emissions measurements, are presented in Table B-3.

**Table B-1: Major sources of instrument errors, which affect gaseous emissions.**

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<th>Abbreviation</th>
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<th>Percent error (%)</th>
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<tr>
<td>NOX%_Inst</td>
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<td>NO%_Inst</td>
<td>NO analyzer error of linearization</td>
<td>0.308</td>
</tr>
<tr>
<td>NO2%_Inst</td>
<td>NO2 analyzer error of linearization</td>
<td>0.308</td>
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<tr>
<td>CO%_Inst</td>
<td>CO analyzer error of linearization</td>
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<td>CO2%_Inst</td>
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<td>FCE%_Inst</td>
<td>Fuel scale</td>
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<td>RME%_Inst</td>
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**Table B-2: Major sources of instruments errors, which affect PM emissions.**

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<td>Fuel scale</td>
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<td>Engine rotational speed measurement</td>
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**Table B-3: Major sources of systematic errors, which affect gaseous and PM emissions.**

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<th>Percent error (%)</th>
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</thead>
<tbody>
<tr>
<td>ERSM%_sys</td>
<td>Engine rotational speed measurement</td>
<td>0.032</td>
</tr>
<tr>
<td>ELM%_sys</td>
<td>Engine load measurement</td>
<td>0.227</td>
</tr>
<tr>
<td>MAFM%_sys</td>
<td>Mass air flow measurement</td>
<td>0.739</td>
</tr>
<tr>
<td>FM%_sys</td>
<td>Fuel measurement</td>
<td>0.812</td>
</tr>
</tbody>
</table>
The instrument and systematic errors for the emission measurements were combined using the root-sum-square (RSS) method, per Hess [92]. An example of the RSS calculation for gaseous CO is given in Eq. (B-2).

\[
\text{RSS}_{\text{Percent}} = \left(\%\text{Error}_{\text{student}}^2 + \text{CO}_{\text{Instr.}}^2 + \text{FCE}_{\text{Instr.}}^2 + \text{RME}_{\text{Instr.}}^2 + \text{ERMS}_{\text{sys.}}^2 + \text{ELM}_{\text{sys.}}^2 + \text{MAFA}_{\text{sys.}}^2 + \text{FM}_{\text{sys.}}^2 \right)^{1/2}
\]  \hspace{1cm} (B-2)

The relative error was calculated from the percent error value with Eq. (B-3).

\[
\text{Error}_{\text{Relative}} = \frac{\text{RSS}_{\text{Percent}}}{100\%}
\]  \hspace{1cm} (B-3)

The error bar value was calculated by multiplying the mean emissions value by the relative error, as in Eq. (B-4).

\[
\text{Error}_{\text{Bar}} = \bar{X} \cdot \text{Error}_{\text{Relative}}
\]  \hspace{1cm} (B-4)
Appendix C

Repeatability of Critical $\Phi$ Measurement

A repeatability study was performed for the critical $\Phi$ measurement of n-heptane at a CR of 8. CR of 8 was chosen for a repeatability study since the majority of the critical $\Phi$ measurements were conducted at a CR of 8 and because a variation in $\Phi$ at a CR of 8 will have the largest relative effect on the measured critical $\Phi$. Figures C-1, C-2, C-3 and C-4, show four individual trials of critical $\Phi$ measurement of n-heptane conducted on different days. The magnitude of the CO emissions in trial 4 is higher than in the other three, because in trial 4 a different CO analyzer was used.

The critical $\Phi$ of n-heptane in trial 1, 3 and 4 was determined to be 0.18, while the critical $\Phi$ of n-heptane in trial 2 was determined to be 0.17. The average of the four trials is 0.178 and the standard deviation is 0.005. The percentage error is 6.998 using Eq. (B-1). The relative error is 0.070, which is only based on the standard deviation of the four trials. The averaged values of the four trials and absolute error are $0.178 \pm 0.012$, based on Eq. (B-4).
Figure C-1: Trial 1 of critical \( \Phi \) repeatability study for n-heptane at a CR of 8, indicated by CO (●), CO\(_2\) (▲), maximum bulk in-cylinder temperature (K) (■) and the critical \( \Phi \) (—).

Figure C-2: Trial 2 of critical \( \Phi \) repeatability study for n-heptane at a CR of 8, indicated by CO (●), CO\(_2\) (▲), maximum bulk in-cylinder temperature (K) (♦) and the critical \( \Phi \) (—).
**Figure C-3:** Trial 3 of critical $\Phi$ repeatability study for n-heptane at a CR of 8, indicated by CO (●), CO$_2$ (▲), maximum bulk in-cylinder temperature (K) (♦) and the critical $\Phi$ (—).

**Figure C-4** Trial 4 of critical $\Phi$ repeatability study for n-heptane at a CR of 8, indicated by CO (●), CO$_2$ (▲), maximum bulk in-cylinder temperature (K) (♦) and the critical $\Phi$ (—).
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