EFFECTS OF HOMOGENEOUS CHARGE COMPRESSION IGNITION (HCCI) CONTROL STRATEGIES ON PARTICULATE EMISSIONS OF ETHANOL FUEL

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Abstract

This thesis presents a systematic investigation into the formation of particulate matter in homogeneous charge compression ignition (HCCI) engines. These engines are representative of the emerging generation of low sooting engine technology. Early research in the field concluded that engines operating with this combustion strategy could offer Diesel like efficiency while simultaneously reducing emissions of particulate matter and the oxides of nitrogen to nearly negligible levels. While quantification of gas phase emissions has changed little through modern regulatory history, the metrics defining particulate emissions and the state of understanding of the research community are rapidly evolving. Advances in technology for characterizing particulate emissions from spark ignition and compression ignition engines have been applied to HCCI emissions and the results indicate the production of significant quantities, by both number and mass, of particles from the HCCI combustion strategy. A relationship has been identified between in-cylinder behavior, and both gaseous and particulate emissions. It has been shown to be valid for 2 different fuels and multiple engine loads. Characteristics of the particulate matter suggest it is formed via gas to particle conversion, or nucleation, of the lighter distillates from the engines lubricating oil.
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Nomenclature

BP ...................................................... Brake Power
τ ........................................................ Brake Torque
k ......................................................... Number of Cylinders
N ........................................................ Engine Speed, Revolutions Per Minute
$V_d$ ..................................................... Volumetric Cylinder Displacement
$\eta_v$ ..................................................... Volumetric Efficiency
F ......................................................... Fuel to Air Ratio
$h_c$ ...................................................... Lower Heating Value
$\eta_c$ ..................................................... Cycle Efficiency
$\eta_m$ ..................................................... Mechanical Efficiency
$\eta_{Th}$ .................................................. Thermal Efficiency
$\eta_{Combust}$ ....................................... Combustion Efficiency
SI ......................................................... Spark Ignition
CI ....................................................... Compression Ignition
IC ....................................................... Internal Combustion
HCCI .................................................. Homogeneous Charge Compression Ignition
CAI ...................................................... Controlled Auto Ignition
PFI ..................................................... Port Fuel Injection
DI ....................................................... Direct Injection
EtOH .................................................. Ethanol
$NO_x$ .................................................. Oxides of Nitrogen
CO ...................................................... Carbon Monoxide
CO₂ ........................................ Carbon Dioxide
PM ........................................ Particulate Matter
HC ......................................... Unburned Hydrocarbons
PM10 ...................................... Particulate Matter <10 µm in diameter
PM2.5 ...................................... Particulate Matter <2.5 µm in diameter
NDIR ...................................... Non-Dispersive Infrared
CLD ...................................... Chemiluminescence
FID ....................................... Flame Ionization Detector
FTIR ...................................... Fourier Transform Infrared
TDC ...................................... Top Dead Center
BDC ...................................... Bottom Dead Center
SOC ...................................... Start of Combustion
CAD ...................................... Crank Angle Degrees
CA10 .................................... 10 % Cumulative Heat Release Location
CA90 .................................... 90 % Cumulative Heat Release Location
MFB50 .................................. 50 % Cumulative Heat Release Location
HRR ...................................... Heat Release Rate
EGR ...................................... Exhaust Gas Recirculation
CR ....................................... Compression Ratio
CN ....................................... Cetane Number
λ ......................................... Excess Air Ratio
Φ ......................................... Equivalence Ratio
γ ......................................... Ratio of Specific Heats
IVO .................................................... Intake Valve Open
IVC .................................................... Intake Valve Close
EVO ................................................... Exhaust Valve Open
EVC ................................................... Exhaust Valve Close
NVO .................................................. Negative Valve Overlap
RON .................................................. Research Octane Number
MON ............................................... Motor Octane Number
IMEP ............................................... Indicated Mean Effective Pressure
BMEP ............................................... Brake Mean Effective Pressure
NMEP ............................................... Net Mean Effective Pressure
Chapter 1  Introduction

Homogeneous Charge Compression Ignition (HCCI) has emerged as a key technology for the future of the internal combustion (IC) engine. It represents an evolutionary step in energy conversion as the classic Diesel and Otto cycles merge and the distinct advantages of both cycles are realized. However, differing from both of these traditional engine cycles, HCCI engines lack a physical event which controls the start of combustion (SOC). Depending only on the thermal history and chemical behavior of the cylinder contents, SOC is manipulated by precise manipulation of these variables through methods such as; intake temperature conditioning, fuel blending, exhaust gas recirculation (EGR), variable cylinder geometry, and variable valve timings. Issues related to energy conversion are broad, sweeping, and leave absolutely no demographic unaffected. In the simplest of terms we as an industrialized society compete for the inputs to live and prosper, and in consequence, must deal with the byproducts of our existence. When we draw analogies in the area of energy conversion and power generation, the questions to be asked are; what goes in to our engines, how efficiently do we convert it to useful work, and what comes out? The HCCI engine has been shown to exhibit flexibility in terms of fuel input, efficiently convert those fuels to useful work, and generate minimal emissions in comparison with current engine technology.

1.1 Motivation

HCCI has seen renewed interest from the research community in recent years. More advanced engine control, volatile fuel prices, and stricter emissions regulations have motivated researchers to put increased resources into this relatively young engine technology. Advanced engine control is allowing the combustion mode, once thought to be impractical for highly variable on-road conditions, to be commercialized in applications varying in size from small motorcycles to heavy duty industrial Diesels. Forms of HCCI have been explored by Honda (Ishibashi, 2000), Nissan (Kimura et al., 1999), and Toyota (Hasegawa and Yanagihara, 2003) in production engines. Both
Nissan and Toyota have recently employed strategies that use multiple fuel injections in Diesel engines at altered timings to enhance mixing thus simulating a premixed burn. Honda has taken an approach much closer to that of Onishi et al. (1979) utilizing the natural EGR present in two stroke engines. HCCI engines are well suited to running at an optimized constant load and speed; with the growing popularity of hybrid vehicles in consumer markets, HCCI technologies could find their way to mass production on a series hybrid within 5 years. With any new technology, it is important that we develop a comprehensive understanding of the mechanisms governing operation and the consequences of manipulation. The clearly understood benefits of HCCI engines are the near Diesel efficiencies achieved with simultaneous mitigation of the particulate matter (PM) and oxides of nitrogen (NO\textsubscript{X}) problems that have historically plagued Diesel engines. As pointed out by Price et al. (2007), PM emissions in HCCI engines are often regarded as negligible. However, few researchers have begun to look in detail at these particulate emissions. The limited work that has been put forth shows evidence of total PM mass being drastically cut, while the total number of particles below 50 nm, or nanoparticles, is observed to increase significantly (Price et al., 2007, Kaiser et al., 2002, Misztal et al., 2009a, Misztal et al., 2009b). These works show limited cases, but they do indicate significant need for more thorough study.

1.2 Statement of Problem

The key to applying HCCI technology is control of the onset of combustion without the aid of a physical event. In Diesel engines, this event is the injection of fuel, in SI engines, the firing of a spark plug. An HCCI engine must draw in fuel and air, and then subject it to such conditions that the mixture auto ignites via compression with the appropriate timing. Various control strategies exist to manipulate the thermal and chemical conditions of the fuel and air charge. A comprehensive examination of the effect of these control strategies on emissions at various operating conditions is lacking.

1.3 Significance

The work presented within this dissertation examines the interactions between common control strategies for HCCI combustion and the effects of these strategies on
emissions. More generally, the body of knowledge gained from the study of gas phase and PM emissions in spark ignition (SI) and compression ignition (CI) engines will be applied to a new type to internal combustion engine. The end goal of the work is to identify optimal control strategies for a variety of conditions in terms of emissions. If HCCI engines are to move into consumer markets they will undoubtedly utilize multiple combinations of the above control strategies. Understanding the effects of different control mechanisms, chemical or thermal, will give researchers and designers a valuable input in developing an optimized control map for a given engine.

1.4 Organization

This dissertation is organized in the following manner. Initially an IC engine background is given in order to gain familiarity with classic reciprocating engines, the thermodynamics governing them, and the defining characteristics of each type. An introductory explanation of HCCI engines is then given in an attempt to relate HCCI engines to classic IC engines, highlight the benefits, and examine the problems associated with them. The history of HCCI engines is also presented along with a thorough examination of the current literature which aids in defining the state of the art and illustrating how the technology has evolved up to this point.

Because the thrust of the work is concerned with examining emissions, specifically PM below 50 nm, an overview of IC engine emissions will also be presented. This is followed by an explanation of the instrumentation used for evaluating PM emissions throughout this work.

Preliminary HCCI modeling has been conducted. These results will be presented, with discussion focused on how they relate to the experimental work executed and the current literature. Preliminary modeling was used to shape the design of the experimental apparatus, which also be presented.

A series of experiments were executed to explore emissions consequences of various start of combustion control strategies and develop and understanding of the formation of emissions in HCCI engines. The results of the experimental work will be presented and discussed. Connections will be made to preliminary modeling and the
current literature. Through discussion of the experimental work, an argument will be
developed with the intent of explaining the origins and behavior of particulate matter in
HCCI engines.
Chapter 2  Background

HCCI combustion is a combustion mode with characteristics resembling both spark ignition (SI) and Diesel or compression ignition (CI) processes. Through a hybrid cycle, the high efficiency of Diesel engines can be obtained with relatively low levels of the PM and NO\textsubscript{X} emissions known to plague them. This is made possible through fully premixed and very lean (\(\lambda>1\) or \(\Phi<1\)) combustion that maintains comparatively low temperatures throughout the process.

2.1 Engine Fundamentals

In order to more easily relate HCCI combustion to conventional reciprocating IC engine cycles, a brief review of engine fundamentals is presented. Conventional IC engines can be split into two groups, each utilizing different gas power cycles to generate power and do work. The first group, SI engines, follows the ideal Otto cycle which is characterized by the following four processes: adiabatic and reversible compression (1-2), constant volume heat addition (2-3), adiabatic and reversible expansion (3-4), and constant volume heat rejection (4-1). The ideal process is illustrated in Figure 1.

SI engines described by the ideal Otto cycle utilize a homogeneous mixture of fuel and air in practice. In the actual Otto cycle, the near stoichiometric fuel and air mixture is compressed from state 1 to state 2. Addition of fuel to the inducted air has historically been accomplished by means of a carburetor, with modern SI engines using a fuel injection system to introduce fuel into the intake manifold. For a very general case, compression ratios are on the order of 10:1, with pre-ignition cylinder pressures of roughly 700 kPa and peak pressures near 2000 kPa (Heywood, 1988). Heat addition takes place from state 2 to state 3 via constant volume heat addition in the form of an exothermic combustion reaction, which is ignited via electric discharge from a spark plug. Ignition timing is controlled exclusively by the spark timing, with any type auto-ignition viewed as undesirable. Moving along the isentrope from state three to state four is the power generation portion of the cycle where the working fluid undergoes
expansion after burning. Finally heat is rejected from the cylinder between states four and one.

![Figure 1: p-v diagram of the ideal Otto cycle](image)

The second group generates power and does work via the ideal Diesel cycle through the following similar processes: adiabatic and reversible compression (1-2), constant pressure heat addition (2-3), adiabatic and reversible expansion (3-4), and constant volume heat rejection (4-1). Figure 2 illustrates the ideal Diesel process.

![Figure 2: p-v diagram of ideal the Diesel cycle](image)
In the case of a CI engine following the Diesel cycle, much of the $p$-$v$ path is the same. The compression ratios are higher however, on the order of 20:1 giving pre-ignition cylinder pressures near 5000 kPa and peak pressures near 15000 kPa (Heywood, 1988). In contrast to the Otto cycle, the Diesel cycle gains heat via constant pressure heat addition from state two to state three. This means that the piston is moving downward and expanding as the mixture burns. The remainder of the piston travel is accomplished between state three and state four as the hot combustion gas expands. Similar to the Otto cycle the Diesel cycle is concluded with constant volume heat rejection in moving from state three to state four. The physical event controlling the start of combustion in a CI engine is the injection of the fuel into the hot compressed air within the cylinder. Because no fuel is present within the cylinder until just prior to the combustion event, much high compression ratios are possible in CI engines.

The most basic analysis of reciprocating IC engines requires consideration of the entire engine as a control volume, with mass crossing the boundary as air, fuel, and exhaust gas, work leaving the system as shaft power, and waste heat also leaving the system. With great simplifications made by considering heat rejection from exhaust gas and waste heat via efficiencies, analysis of fuel and air inputs and their relationship to work output is done through Equation 1. In both groups of engines the thermodynamic cycle must be coupled with the physical processes of introducing charge into the cylinder and expelling exhaust gas from the cylinder. The entire event may be accomplished by either two (2-stroke cycle) or four (4-stroke cycle) strokes of the piston. Air enters the engine and is quantified as a function of $\rho_{\text{air}}$, $k$, $N$, $V_d$, and $\eta_v$, which respectively represent; air density, the number of cylinders, the displacement of a single cylinder, and the volumetric efficiency of the engine at that condition. Fuel entering is quantified via $F$, the ratio of mass of fuel to mass of air, and $h_c$, the lower heating value of the fuel. And work output is given as brake power ($BP$) through mechanical and cycle efficiencies. This equation is used in its presented form for a 4 stroke cycle engine.
Terms commonly used to describe the relationship of actual operating chemistry to stoichiometric chemistry for a given fuel are $\lambda$ and $\Phi$, they are defined below by the mass based ratio between fuel and air, $F$.

$$\lambda = \frac{1}{\Phi} = \frac{\left(\frac{m_{\text{Fuel}}}{m_{\text{Air}}}_{\text{Stoich}}\right)}{\left(\frac{m_{\text{Fuel}}}{m_{\text{Air}}}_{\text{Actual}}\right)}$$

Internal combustion engines vary greatly in displacement and total power output. Mean effective pressure (MEP) has been established as a normalized measure of engine output and is related to engine power through Equation 3.

$$Power = MEP \times V_d \times k \times \frac{N}{2}$$

Either brake power or indicated power can be used in the equation, the corresponding MEP is then either referred to as BMEP or IMEP. Stone (1999) defines IMEP directly as indicated work over the displaced cylinder volume. Indicated parameters and brake parameters are related through the mechanical efficiency of the engine. Because the only work done by the piston is defined by the integration of pressure over a changing volume, IMEP can be calculated directly from in-cylinder pressures via Equation 4.
For the work presented here IMEP will be used to represent engine load. This gives the ability to quantify results with a normalized parameter that is valid for a variety of engine sizes.

Heat release rate HRR is used in quantifying in-cylinder engine phenomena such as SOC, cylinder temperature, and burn duration. Heat release, calculated through the first law of thermodynamics, is the amount of heat energy added to the cylinder contents to produce the measured variation in in-cylinder pressure. Neglecting heat transfer to the cylinder walls, heat release is a function of the internal energy change of the system and the work ($PdV$) done by the piston. In evaluating internal energy changes, the cylinder contents are assumed to be ideal gases. Quantitatively defined through heat release, SOC is the point at which 10% of the total energy is released, burn duration is then defined as the time between 10% fuel energy release and 90% fuel energy release.

2.2 Homogeneous Charge Compression Ignition

HCCI is a next generation engine technology capable of exploiting the primary advantages of both compression ignition and spark ignition engines. The physical process will first be described then be related to classic IC engine thermodynamic cycles. As with both a CI and SI reciprocating engines, the reciprocating HCCI engine is a piston-cylinder device. In four-stroke HCCI the valve train operates in a similar manner as a common four stroke engine. The piston positions and valve events are shown in Figure 3. Stroke 1 consists of the piston moving downward and a mixture of fresh charge, air and fuel, being introduced via the intake valve. The intake valve is then closed and the mixture compressed as the piston approaches top dead center (TDC), shown in position two. As the piston approaches TDC the mixture nears its auto-ignition temperature due to compression heating. Upon reaching its auto-ignition temperature, the mixture will auto-ignite in a series of spontaneous reactions occurring
nearly simultaneously across the cylinder. The device behaves like a homogeneous reactor ignited via compression ignition. Differing from surface pre-ignition there is no traveling flame front creating regions of hot, high pressure burned gas. Additionally, the process avoids uncontrolled knock though highly dilute in-cylinder conditions and much lower fuel to air ratios than those found in traditional SI engines. This limits high rates of heat release responsible for damage in SI knocking. The ignition is controlled solely by chemical kinetics, thus governed by species concentration and mixture temperatures (Najt and Foster, 1983).

![Figure 3: Charge path in a 4 stroke HCCI engine](image)

The third stroke of the cycle represents power generation from expansion of the gas due to heat addition from combustion. After the piston has reached bottom dead center (BDC) the exhaust valve opens and the piston moves up in the fourth and final stroke of the cycle, which is responsible for exhausting the products of combustion.

From a gas power cycle point of view, the HCCI cycle is a variant of the classic engine cycles exhibiting characteristics of both the Otto and Diesel cycles. Like both these cycles, the ideal HCCI cycle begins with adiabatic and reversible compression during stroke one, shown by the isentrope from state 1 to state 2 in Figure 4.
HCCI engines often utilize high compression ratios, similar to those of classic CI engines, along with constant volume heat addition, generally associated with SI combustion. In order to attain such high compression ratios with a premixed fuel and air charge, fuel to air ratios must be very lean or highly dilute, with values of $\lambda$ on the order of 3 to 5 not uncommon.

An understanding of HCCI combustion can be achieved relatively simply. Ignoring for the present the fuel behavior and idealizing the process as polytropic, but still adiabatic and reversible, we can use the pressure volume relation for a polytropic gas to relate change in volume, pressure, and temperature (Moran and Shapiro, 2000).

$$p_1V_1^\gamma = p_2V_2^\gamma$$

Substituting the compression ratio (CR) for $V_1$ divided by $V_2$ we get Equation 6.
\[ \frac{p_2}{p_1} = CR^\gamma \]

If we add the assumption that the working fluid behaves as an ideal gas, the temperature at state 2 becomes a function of the state 1 temperature and the amount the gas is compressed (CR).

\[ T_2 = T_1 CR^{\gamma-1} \]

This analysis illustrates a key concept in HCCI timing control. The fuel and air charge must be elevated above its auto-ignition temperature in order for the mixture to begin burning. Ideal SOC timing occurs at TDC with burn duration kept as short as possible to approximate the constant volume heat addition of the ideal Otto cycle. Controlling \( T_2 \) is accomplished via manipulation of either engine intake temperature or cylinder compression ratio, with intake temperature being the input most easily varied.

It is now pertinent to address the role of charge chemistry HCCI timing. Auto-ignition characteristics, unique properties of fuels, are viewed differently in different types of engines. Auto-ignition is spontaneous ignition of the charge due to its own thermal energy, which is provided by compression from both the piston and rapidly expanding burned gas, rather than consumption of the fuel and air mixture by a traveling flame front. As temperatures increase, reaction rates of chain propagating and branching mechanisms also increase, creating an uncontrolled combustion event known as knock. Auto-ignition is undesirable in SI engines and resistance to it in SI fuels is characterized by the octane number. Octane number is quantified via the research octane number (RON), motor octane number (MON) or an average of the two (ON). With common fuels ranging from 60 to 130 or higher, octane number describes a fuels resistance to knock for a given set of conditions with the highest octane numbers corresponding to the most knock resistant fuels. Analogously CI engine fuels are rated
through cetane numbers with common fuels ranging between 20 and 100, the upper end of which defines very ignitable fuels. Cetane numbers (CN) characterize a particular fuel’s ability to auto-ignite by gauging how readily the fuel auto-ignites after a critical temperature and pressure is reached within the cylinder. Cetane numbers provide a comparative evaluation of the ignition delay, or time between fuel injection and SOC, for a given fuel. The relationship exhibited between cetane and octane numbers is inverse. Because numbers are found empirically the correlation is not exact but follows the general trend shown in Figure 5.

Similar to a knock event in SI engines, HCCI combustion results from auto-ignition of premixed fuel and air due to compression. However, very lean or highly dilute mixtures maintain a controlled burn by absorbing some of the thermal energy released during the reactions.

![Cetane number and octane number relationship](image)

**Figure 5: Cetane number and octane number relationship (Stone, 1999)**
2.2.1 Historical Perspective

Originally given the name Active Thermo-Atmosphere Combustion (ATAC) by Onishi et al. (1979), the HCCI process was developed as a means to reduce emissions and increase fuel efficiency in 2-stroke SI engines at part throttle loads. The authors sought to exploit lean burning auto ignition in 2-stroke engines to minimize the cycle-to-cycle variability which results in misfire. Misfire leads to high HC emissions in 2-stroke engines.

Onishi et al. (1979) contrasted HCCI combustion to standard SI combustion by examining the manner in which the mass of fuel and air mixture is burned. Rather than heat release in abrupt and discrete unit mass reactions across the volume of the cylinder, as in standard combustion, the entire mixture of fuel and air releases its energy in set of simultaneous reactions. Theoretically, this means that there is no stationary or propagating flame front, making the process uniquely different from either standard CI or SI combustion. Although Noguchi et al. (1979) refer to the burning process as flame propagation; they clearly describe a process of multiple ignition sites and a rapidly spreading flame in all directions similar to the observations of Onishi et al. Noguchi also differentiates the process from classic “run on” by presenting Schlieren photography of combustion initiation at multiple sites away from cylinder walls. In a situation of run-on, hot carbon deposits ignite the charge, thus flame propagation starts from the cylinder walls where these deposits are located. Onishi and Noguchi coined distinct terms ATAC and TS (Toyota-Soken) combustion for their discoveries; however they were both documenting the same phenomenon. In both cases significant fuel consumption savings were realized, along with the mitigation of the cycle to cycle variability normally present in 2 stroke SI engines.

One of the significant and unique characteristics of HCCI combustion is the two stage heat release exhibited by most fuels (Stanglmaier, 1999). Noguchi et al. referred to a primary low temperature reaction and secondary combustion reaction along with identifying the importance radicals from previous cycles in controlling the onset of the first stage reaction. It was observed that CHO, HO$_2$, and O radicals were present and behaved as ignition kernels for the initial stage of TS combustion. Upon the formation
of significant numbers of OH radicals, the combustion reaction would commence. Noguchi et al. also hypothesized that the CHO, HO₂, and O radicals originated from chemical cracking of unburned residuals or fresh mixture at the mixing boundary.

HCCI was first researched in a 4 stroke engine by Najt and Foster (1983) under the name compression ignition homogeneous charge (CIHC). Much of the current work has moved from the early roots in two stroke research to four stroke work due to the increased ability to manipulate the details of the gas exchange process. Najt and Foster (1983) reiterate that there is a lack of a flame front in HCCI engines and further elaborate on the nature of the 2-stage combustion reactions. They note that the low cycle to cycle variability seen by Onishi and Noguchi is observed in 4 stroke operation as well. Most importantly they begin to clearly define which operating parameters are most pertinent to HCCI combustion and what effects they have. Theoretical and experimental work clearly showed the advance of combustion timing with increased intake charge temperature. The role played by EGR was investigated in detail and it was concluded that few radicals in the exhaust would survive until the next cycle and the primary effect of EGR on ignition timing is thermal.

The name HCCI was first used by Thring (1989) to summarize earlier efforts by Onishi et al., Noguchi et al., and Foster and Najt, as well as describe his own work. In the ten years preceding the work of Thring and the twenty years since, HCCI has been given at least 10 different titles. The multiple names and acronyms were summarized by Zhao (2007) in the following statement; “Close examination of these names and the rationales behind them shows that all names contain the description of two fundamental characteristics of the new combustion process: 1) premixed fuel and air mixture, and 2) auto-ignited combustion.” Zhao introduced two names to describe all HCCI activities up to the time of publication. They differed in that the first term, HCCI, is used to describe work conducted under a set of circumstances more representative of Diesel combustion, with low octane/high cetane fuels and relatively high compression ratios. The second term CAI (Controlled Auto-Ignition) is then used to describe processes with characteristics showing more similarity to gasoline engine processes, using slightly lower compression ratios and high octane/low cetane fuels. This distinction was made
to illustrate that for high octane/low cetane fuels compression alone is not adequate for ignition, significant heating of the charge is also required and referring to all process as simply compression ignition can be misleading (Zhao, 2007). For the work presented here, HCCI will be used as the name describing the process.

2.2.2 Current Relevant Literature

The current body of knowledge surrounding HCCI engine research has been evolving for thirty years. Relative to the volume of work addressing conventional IC engines, there is limited study, however. As a concept HCCI is well researched with significant amounts of information available from a variety of researchers, however many gaps are still present concerning a full understanding of the field. Current work can be broken into a number of subfields, including development of variable engine geometry, development of HCCI control strategies, chemical and CFD modeling, and fuels research. Three common goals are shared by most researchers. The first is to develop a thorough understanding of the HCCI combustion phenomenon. The second is to use this understanding to exploit a variety of strategies aimed at precisely controlling the start of ignition. And the third, to further expand the attainable speed and load range of HCCI engines. The core limitations of this technology are an inability to control ignition timing and rate of heat release at very low loads and very high loads respectively. These limitations are manifested in misfire (low loads) and knock (high loads).

The most common approach for controlling auto-ignition timing in HCCI research is the use of thermally conditioned intake air. Evolving from early work by Najt and Foster (1983) and Thring (1989) amongst others, which examined steady state conditions, current research is focused on fast response thermal management systems aimed at extending load and speed ranges and transient operation. Realistic sources of thermal energy for HCCI were outlined by Yang (2005) when investigating its use to extend the lower load boundaries for high octane (gasoline) fuels. To achieve the desired intake temperatures while pushing the lower load boundaries, the authors required utilization of the thermal energy from compression heat, residuals, exhaust
gases, and coolant. As an easily varied parameter when compared with compression ratio or valve timing, thermal management maintains its relevance as a control strategy. Steady state heating via resistive elements sees extensive use in research applications, however, they would serve little use under the rapidly changing conditions of real world engine operation. Understanding that a conventional heating system would have far too slow of response due to its high thermal inertia, mixing systems comprised of separate hot and cold streams of intake air have seen significant research and allow rapid adjustment hot and cold proportions based on engine demands. A thermal management system recently developed by Martinez-Frias et al. (2002) and further refined by Flowers et al. (2005) allows for rapid response to changing thermal demands via closed loop feedback controlled mixing valves. In a 6-cylinder HCCI engine Flowers has implemented an advanced intake manifold utilizing independently heated and cool air streams for each cylinder. The closed loop feedback is obtained via combustion timing calculated from in-cylinder pressure. This adiabatic mixing methodology is similar to that of Peng et al. (2007) who utilized a set of mixing valves controlling the proportion of ambient and heated air to a single cylinder engine. Additionally Peng et al. successfully operated this system through the transition between SI mode and HCCI mode. Some fluctuations in engine speed and BMEP were reported at the transition, they lasted only a few engine cycles. The naturally aspirated single cylinder engine used by Peng et al. was fueled with ethanol via port fuel injection and utilized EGR as well as intake heating. Haraldsson et al. (2004) have also developed a rapid response thermal management system. Differing from Flowers et al., Haraldsson et al. developed a mixing system on a five cylinder engine without individual cylinder mixing capabilities. The feedback for the thermal management in this case was an average IMEP across the five cylinders. Cylinder to cylinder variations in IMEP then were mitigated via an additional algorithm that controlled fueling to each cylinder and subtly adjusted individual cylinder fueling to maintain a user determined IMEP. Successful implementation of a thermal management system similar to Peng et al. was reported by Hyvönen et al. (2004) with quantitative findings shown. The authors achieved stability across five cylinders with less than 1 CAD variation in CA50 compared to 11 CAD of
variation in CA50 with constant intake air temperatures. Comparing their work to a cylinder by cylinder fuel management strategy, similar to that of Haraldsson et al., the authors viewed thermal management as a superior methodology. This was justified by examining NO\(_X\) variations from cylinder to cylinder. When fueling was used to bias combustion phasing, the authors reported different loading and pressure rise rates in individual cylinders. The result was elevated NO\(_X\) levels in the cylinders with slightly higher loads.

The second most common approach for SOC control in HCCI engines is modulated EGR. In applications using 2-stroke engines, such as those of Onishi et al. (1979) and Noguchi et al. (1979), EGR provided all necessary thermal energy to facilitate combustion. In 2-stroke applications EGR is present in the form of residuals left in the cylinder between cycles. In the cases of EGR as residuals it is also possible that radicals remain in the burned gas and facilitate combustion reactions. This effect was what early researchers had in mind when coining the term “Active Radical” combustion. When first transferring the technology to a 4-stroke engine, Najt and Foster (1983) and Thring (1989) noted the importance of external EGR due to the lack of hot residuals. Thring also systematically examined EGR as a diluent to eliminate knock. EGR levels, defined by CO\(_2\) volume concentration though Equation 8, were varied from 13 to 33 %. Higher rates generally were required to achieve higher equivalence ratios, which correspond to higher loads.

\[
EGR = \frac{CO_{2,\text{Intake}}}{CO_{2,\text{Exhaust}}} \times 100\% \tag{8}
\]

This work clarified the dual purpose nature of EGR in HCCI engines. The first role of EGR is raising cylinder temperatures through transfer of thermal energy from hot exhaust gases to the cooler intake charge. The second role is that of a thermal sink, controlling the rate of heat release and inhibiting rapid and uncontrollable pressure rise. Insight into this role can be gained by examining the specific heats of the primary
components of exhaust gas and comparing them with the specific heat of air at typical combustion temperatures. Figure 6 shows the specific heats of the primary components of exhaust gas and air. Using EES software to model the specific heats, we assume that air, nitrogen, water, and carbon dioxide are ideal gases at these temperatures. Shown on a molar basis, the clear difference in the specific heats of CO\textsubscript{2} and H\textsubscript{2}O, when compared to air, explain the ability of exhaust gases to limit the rate of pressure rise as described by Thring (1989). Equation 7 is useful clarifying this effect. T\textsubscript{1} and T\textsubscript{2} are related through compression ratio (CR) to the exponent \(\gamma\)-1. For ideal gases in an adiabatic and polytropic process, \(\gamma\) is equal to the ratio specific heats. As this ratio increases, T\textsubscript{2} will exhibit an increase for the same T\textsubscript{1}.

![Figure 6: Specific heat (\(c_p\)) of primary exhaust gas components and air](image)

EGR effects were more recently examined on a multi-cylinder production Diesel engine modified for HCCI experiments by Au \textit{et al.} (2001). Experiments were conducted that maintained constant intake temperature, effectively removing the thermal role of EGR, and varied overall EGR rate. Burn duration was used to quantify combustion behavior. Au \textit{et al.} defined the burn duration as the number of CAD
required to complete 10-90% of the total heat release. It was found that total burn
duration increased significantly with EGR rate, but SOC had little or no dependence on
EGR rate.

Lü et al. (2005b) examined in detail the effects of cooled EGR on SOC and
combustion duration. In agreement with Au et al. (2001), the authors saw very little
effect of cooled EGR on SOC. These experiments were done for reference fuel blends
ranging in octane number from RON 0 to RON 75. For \( n \)-heptane (RON 0), peak
pressures and total burn duration showed little dependence on EGR as rates. However
higher octane fuels, RON 50 and RON 75, exhibited significant response to increased
EGR rates. In particular with RON 75 fuel, increasing the EGR rate resulted in a shift in
peak pressures later in the cycle by as much as 15 CAD. The results could be observed
for EGR rates ranging from 15% to 45% with the highest rates corresponding to the
greatest CAD shift in peak pressures. In addition, the magnitude of the peak pressure
was drastically cut as more EGR was added. Peak pressures of RON 75 fuel were cut
nearly in half, from 9 MPa to 5 MPa, when 45% EGR was utilized. The authors cited
both the increased heat capacity and lack of oxygen as reasoning for the delay in, and
reduction of, peak pressures. The lack of oxygen was cited as playing an important role
in limiting the primary high temperature chain branching reaction shown in Equation 9.

\[
H + O_2 \Rightarrow O + OH
\]  

Additionally Sjöberg et al. (2007) have clearly demonstrated a retarding effect of
EGR on ignition timing. The primary reasons for the effect are listed as; first, the high
specific heat of the gases reduces the compressed gas temperature, and second,
reductions in oxygen concentrations limit available oxygen for combustion reactions.
The sensitivities of HCCI combustion to each of these drivers were also documented by
Sjöberg et al. (2007) to vary with fuel type.

The third area of HCCI research most pertinent to this work is utilization of fuel
properties to control combustion. Many types of fuels are suitable for HCCI combustion
and a great deal of research examining them has been done. High octane fuels such as gasoline (Thring, 1989), natural gas (Yap et al., 2004), and hydrogen (Gomes-Antunes, 2008) have all seen successful application. High cetane fuels such as Diesel (Tsolakis, 2005) and n-heptane (Lü et al., 2005b) have also been used. Renewable fuels also show promise, ethanol (Mack, 2009), DME (Shudo, 2003), and bioDiesel (Tsolakis, 2005) have all been used as primary fuels in HCCI engines. This is not a comprehensive listing, but rather a sampling to illustrate the flexibility of HCCI technology for combusting a variety of fuels.

Altering the properties of a single fuel during operation is obviously not feasible; however modern port fuel injection systems allow blending of two fuels with different properties on a cycle-to-cycle timescale. Utilization of two fuels allows manipulation of SOC timing by exploiting the different relative tendencies of different fuels to auto-ignite. Logistically having two fuels creates problems in terms of on-board storage and refueling infrastructure. However, work by Deluga et al. (2004) involving autothermal reforming has shown that modest amounts of hydrogen rich gas can be reformed from ethanol with relative ease. More recently, a comprehensive look at various types of reforming bio-ethanol to obtain hydrogen rich gases was given by Ni et al. (2007). Such small scale reformers could be integrated into an engine fuel system so that hydrogen could be used as a supplemental fuel, providing on the order of 20% or less of total energy input. Reforming ethanol to make hydrogen then allows operation of a dual fuel engine requiring only one type of fuel to be filled and stored. The effectiveness of producing hydrogen rich gas by reforming conventional hydrocarbons has spurred a large amount of research in the area of dual fuel engines, particularly dual fuel HCCI engines. HCCI research utilizing dual fuel systems has seen proof of concept level research as well detailed combustion analysis by numerous sources.

Yap et al. (2004) presented modeling results that predicted the start of combustion in an HCCI engine fueled with natural gas and supplemented with varying amounts of hydrogen. As hydrogen content of the fuel was increased from 0% to 20%, the predicted start of combustion advanced by nearly 10 CAD. These results suggested hydrogen addition aided the fuel in igniting more readily so that intake heating requirements
could be relaxed while maintaining constant peak pressure timing. Validating the work experimentally, it was found that the addition of a small amount of hydrogen in the EGR stream allowed the required intake temperatures to be dropped by as much 20°C at low loads. Specifically, these exercises examined the temperature drop that was acceptable with the addition of hydrogen while maintaining a constant indicated mean effective pressure (IMEP). However, the effect was found to be less profound at higher loads. Pressure rise rates were then examined and it was found that hydrogen addition gave slight increases in maximum rates of pressure rise. Again these effects were more pronounced at low loads. Compression ratios on the experimental engine ranged from 12:1 to 14.5:1, with intake heating on the order of 140° to 300 °C used. Yap et al. (2006) expanded on the previous work with additional experimental work examining higher concentrations of hydrogen flow rates in the EGR stream and higher compression ratios. Again, advancement of the start of combustion was shown with increasing amounts of hydrogen addition. This was quantified by examining the 5% burn point, which advanced by roughly 6 CAD at low loads and 3 CAD at high loads. The amounts of hydrogen used here were very small, on the order of 0.5 % to 0.75% of total intake air flow, equating to 3 % to 5 % of the total fuel energy. The authors explained enhancement of combustion via an increase in atomic hydrogen to feed the chain branching mechanism shown in Equation 9.

Hosseini and Checkel (2006) also investigated the effects of hydrogen rich gas (reformer gas) on natural gas fueled HCCI combustion. The hydrogen rich gas used in this work was 75% hydrogen and 25% carbon monoxide. These tests examined compression ratios ranging from 16:1 to 18.5:1 and intake temperatures of 140°C on a single cylinder engine. The hydrogen rich gas tended to advance the SOC, agreeing with the work of Yap. In an unthrottled engine, load is inversely proportional to λ. At λ values ranging from 2.5 to 2.8, it was shown that using reformer gas to comprise 60% of the total fuel mass, which is equal to roughly 75% of fuel energy, would advance the SOC by nearly 6 CAD. Lesser fractions were also evaluated, giving a relatively linear response. Hosseini and Checkel also found that adding reformer gas to natural gas HCCI combustion extended the low load end of the operating window, with higher
proportions of reformer gas showing increasingly significant effects. In these experiments EGR rate and compression ratio were held constant and an operating window was established by varying $\lambda$ until the engine either lost power or knocked.

Hosseini and Checkel assessed reformer gas effects on both high octane fuels (2007a) and low octane fuels (2007b). In the high octane tests PRF fuels with octane numbers of 80 and 100 were tested with compression ratios of 16:1 and 14.4:1 respectively at intake temperatures of 140°C. For the low octane tests, n-heptane which defines ON=0 was used and compression ratios were dropped to 9.5:1 and 11.5:1, with intake temperatures held at 100°C. These results provide interesting insight into the difficulty encountered when trying to develop a general fuel index as explained by Shibata and Urushihara (2007). All of the blends tested were blends of n-heptane and iso-octane primary reference fuels. In contrast with the above work conducted using natural gas, the SOC in all of these tests was delayed with increasing amounts of reformer gas. In the high octane tests with ON=80 fuel, SOC was shifted later by 7 CAD with 30% of the fuel by mass reformer gas when compared to tests with 0% reformer gas. The same trend was observed in the low octane tests and was even more pronounced. SOC for ON=0 fuel burned at a constant $\lambda$, EGR rate, CR, and intake temperature shifted later in the cycle by 12 CAD as reformer gas mass fraction was increased from 0% to 20%. Interestingly these effects are completely opposite of the effects seen by Yap (2004, 2006) as well as Hosseini and Checkel (2006) when natural gas was the primary fuel. The behavior is likely the result of an averaging effect in octane number when the more easily ignited hydrogen is mixed with natural gas which has a RON near 120. Hosseini and Checkel (2008) repeated the earlier experiments with lower levels of hydrogen in the reformer gas, 50% $\text{H}_2$ compared to 75% $\text{H}_2$ in prior studies, in order to more realistically simulate actual reformer gas levels of hydrogen. The results confirmed prior work with natural gas SOC advancing and primary reference fuel blends retarding as reformer gas mass fraction was increased. The experimental results were also modeled in ChemComb-SZM and showed similar trends as the experimental work.
2.3 Emissions

Initially examining the emissions characteristics of SI and CI engines gives a set of base conditions to which comparisons of HCCI emissions can then be made. A summary of general emissions trends of each of the three types of engines operating at steady state is given below. In each section a brief description of gas phase emissions will be presented with greater attention paid to PM emissions.

Engine emission standards regulate a common set of emissions universally agreed upon as having negative effects on air quality. In the gas phase, CO, HC, and NO\textsubscript{X} are regulated, with CO\textsubscript{2} not regulated by most legislation but still viewed as undesirable due to its classification as a greenhouse gas. NO\textsubscript{X} is primarily composed of NO with only trace amounts of NO\textsubscript{2} in SI engines, however in CI engines NO\textsubscript{X} can be composed of up to 30% NO\textsubscript{2} (Hilliard and Wheeler, 1979). Engine emissions are commonly normalized to engine output and presented in the form grams per brake horsepower hour (g/bhp) or grams per kilowatt hour (g/kW hr).

Solid and liquid phase emissions are also regulated and commonly referred to as particulate matter (PM). Differing from gas phase emissions, PM emissions are much more sensitive to sampling conditions and great care must be taken when collecting these samples. As discussed by Kasper (2005), in modern engines, particles due to gas to particle conversions in the exhaust system and PM in dilution air can be more abundant than PM originating from the engine itself. Particulate matter from engines ranges from less than 5 nm to greater roughly 10000 nm in mobility diameter and, when examined in the ambient, is distributed trimodally between a coarse, accumulation, and nucleation modes. The coarse mode contains particles on the order of 1000 to 10,000 nm, the accumulation mode from 30 to 700 nm, and the nucleation mode particles are generally less than 30 nm (Kittelson, 1998).

The two driving forces behind HCCI research are gaining higher efficiency and curtailing regulated emissions. In general CI engines have thermodynamic efficiencies 20% to 30% higher than a comparable output SI engine. This is a benefit of the high compression ratios and lean burn strategies allow by CI. Additionally CI engines
eliminate the throttling losses characteristic of SI engines operating at part load. It is clear from the most elementary combustion chemistry reaction that an increase in efficiency translates directly to a decrease in CO$_2$ per unit power output.

### 2.3.1 Spark Ignition Emissions

SI engines power much of the passenger fleet throughout the U.S. Recent work examining PM source apportionment by Johnson et al. (2005) reports roughly 90% of the traffic flow on a typical urban interstate to be light duty SI powered vehicles on weekdays with that number climbing to 99% on weekends. Operating generally very close to a stoichiometric air to fuel ratio ($\lambda=1$), deviation from these conditions has negative consequences on emissions characteristics. As charge mixtures get progressively more fuel rich, HC and CO emissions tend to increase, while NO$_X$ emissions peak just lean of stoichiometric and drop off with increasing or decreasing $\lambda$. HCs originate in the crevice volumes around piston rings and in the cool boundary layer of oil at the cylinder walls. HC emissions will also increase sharply at very lean conditions as misfire begins to occur (Sher, 1998). CO and NO are both formed in the high temperature, high pressure burned gas behind the flame front (Mattavi and Amann, 1980). As the combustion chamber volume expands and the fuel is consumed, these burned gases cool abruptly, freezing molar concentrations of the radicals. Control of NO concentrations is achieved in part via EGR in SI engines. EGR rates ranging from 10-25% of total intake air are common before combustion becomes unstable. EGR reduces cylinder temperatures in SI engines, therefore curbing NO production rates, by acting as a diluent and soaking up thermal energy (Abd-Alla, 2002). In addition to EGR, implementation of 3-way catalysts in SI exhaust systems is a useful tool in controlling NO$_X$, CO, and HC emissions. However these catalysts require tightly controlled combustion conditions very near to stoichiometric to be effective (Twigg and Wilkins, 1998).

Kayes and Hochgreb (1999a) thoroughly examined PM formation in SI engines and found experimentally that both total mass and number concentration, as well as number weighted mean and mode particle size, were at a minimum near stoichiometric.
All of these descriptors increased as the mixture moved both lean and rich. In the case of total mass concentration, increases of 2 orders of magnitude were observed in the very lean and very rich regions as lambda was swept from .7 to 1.7. The same authors also reported that as engine load increased both PM total mass and total number increased as well. In the same study EGR rates were varied while keeping all other operating parameters fixed. An inverse relationship between EGR rate and total number and mass concentrations was shown. Examining the composition of PM in SI engines more closely, Burtscher et al. (1998) found particles to be in the form of chain agglomerates composed primarily of carbon and a large fraction of volatile material.

Stoichiometric compressed natural gas (CNG) engines have seen limited use as an alternative to conventional gasoline fueled SI engines in recent years in part due higher efficiency gained though high compression ratios, and also due to an overall cleaner burn (Ayar, 2006). Additionally the higher hydrogen to carbon ratio of the fuel creates less CO$_2$ emissions per unit fuel energy (Cho, 2007). Gas phase CNG encounters no mixing problems and will not exhibit the fuel rich jet burning characteristics of direct injection spark ignition (DISI) or CI engines. Additionally, the pooling effects which can create emissions problems in PFI engines are not present in these types of engines because of the gas phase fueling strategy. Recent work by Schreiber (2007) comparing emissions from gasoline fueled SI, Diesel fueled CI, and CNG fueled SI engines showed the CNG fueled engines producing total particle numbers on par with concentrations from a Diesel engine found downstream of the DPF. Both of which were lower than engine out exhaust concentrations in the port fuel injection (PFI) or direct injection (DI) gasoline engines tested. The results were average concentrations from 19 gasoline fueled cars, 12 Diesel fueled cars, and 3 CNG fueled cars, and were based on measurements recorded during the New European Driving Cycle (NEDC). Following similar trends as gasoline fueled SI engines, Ristovski et al. (2000) showed both CMD (count median diameter) and total concentration (particles/cm$^3$) increasing directly with load in natural gas fueled SI engines.
2.3.2 Compression Ignition Emissions

The overall efficiency gain in CI engines comes at a price when examining PM emissions. Furthermore, relatively low exhaust temperatures prohibit the use of catalysts to treat NOX emissions. The excess air of lean burn combustion also contributes to NO production by ensuring a sufficient source of oxygen. However, EGR is used extensively to control NO formation in CI engines. In this case, the reductions in NO concentrations are primarily a result of the displacement of intake air (O2, N2) with exhaust gases (CO2, H2O, N2), thus limiting available oxygen for NO formation (Ladommatos, et al., 1999).

Although the global equivalence ratio is maintained lean in Diesels, the nature of the fuel injection process leads to localized rich regions around the fuel jet as it undergoes diffusion burning during the burn process (Dec, 1997). This localized rich combustion produces the sooty black smoke that comes to mind as one considers a path traveled behind an old Diesel truck. A distinct tradeoff exists between NOX and PM, when utilizing EGR in CI engines. The NOX – PM tradeoff is well documented by numerous authors and summarized by (Ladommatos, et al., 1999), Abd-Alla (2002), and Zheng et al. (2004). The phenomenon is a consequence of the localized rich regions of diffusion burning being further starved of oxygen when EGR displaces intake air.

The composition of CI, or Diesel, PM is reported by Kittelson (1998) to be primarily carbon and unburned hydrocarbons, as well as sulfate, water, and ash. Burtscher et al. (1998) notes that the volatile fraction composing CI particles is much lower than that of SI engines. An early study conducted by Tobias et al. (2001) used thermal desorption particle beam mass spectrometry (TDPBMS) and temperature programmed thermal desorption (TPTD) to investigate Diesel particulate matter composition. They conducted analysis of the organic compounds comprising Diesel particulate matter and found high percentages of alkanes and cycloalkanes. The similarity of the cycloalkanes to alkanes ratios in the PM to those of the lubricating oil led the authors to believe that significant contributions were made from lubricating oil. Sakurai et al. (2003) further investigated Diesel nanoparticle composition through TDPBMS and tandem differential mobility analyzer (TDMA) techniques and found
particles emitted at low to moderate loads were composed of roughly 95% compounds from unburned lubricating oil.

The agglomerative nature of these particles is shown in detail by Park et al. (2003). The structure and packing density of the primary particles has been shown to vary depending on the fuel, engine, and operating conditions. Park et al. (2003) also documented a size dependant difference in effective particle density through a series of experiments using an aerosol particle mass analyzer to relate particle mass to mobility. These authors found a trend of decreasing effective density with increasing particle size ranging from 1.2 g/cm$^3$ at particle sizes near 50 nm to .3 g/cm$^3$ at particle sizes near 300 nm.

In general, due to the abundance of oxygen in lean burning CI engines, CO emissions are negligible. Although CI engine fuels are less volatile, or more difficult to ignite, HC emissions levels are generally lower in CI engine than in SI engines due to high temperatures and global oxygen rich conditions. They often originate from either misfire due to lack of fuel, or under mixed fuel and air which create localized rich regions that are not fully oxidized during combustion (Sher, 1998).

2.3.3 Homogeneous Charge Compression Ignition Emissions

Emissions in HCCI engines show clear advantages over SI and CI engines. The primary hurdle in utilizing HCCI engines, controlling the start of combustion, is also closely tied to the emissions benefits realized in these engines. In-cylinder combustion processes dictate the speed and uniformity in which fuel is oxidized and products are formed. In SI combustion a traveling flame front is initiated at the spark plug and leaves behind it a region of high temperature burned gas that is further compressed and heated as the flame continues across the chamber. As mentioned above CO and NO form in this burned gas. The same start of combustion event is controlled by fuel introduction in CI engines. However combustion time scales are much faster than mixing timescales leading to poorly mixed fuel and air combined with diffusion burning of fuel rich regions. From this diffusion burning precursors to PM formation are created. HCCI combustion has no event to initiate combustion; reactions are simultaneous and as a
result no burned gas effects are present (Zhao, 2007). Additionally fuel and air are premixed, minimizing diffusion burning.

The allure of HCCI combustion is rooted in the Diesel like efficiency exhibited by these types of engines accompanied by ultra low emissions. Resulting from premixed, low temperature combustion, the NO\textsubscript{X} – PM tradeoff prevalent in CI engines is avoided and simultaneous reductions can be achieved. Review papers from Johansson (2007), Juttu \textit{et al.} (2007), Epping \textit{et al.} (2002), and Stanglmaier and Roberts (1999) cite numerous authors noting significant and simultaneous reduction in PM and NO\textsubscript{X}. Although the magnitudes of these reductions vary across engine conditions, fuels, and HCCI control strategies, a clear and well documented trend is indeed present. Figure 7, adapted from the work of Kitamura \textit{et al.} (2002), shows regions of soot and NO\textsubscript{X} formation in combustion processes obtained via modeling. It can be seen that low temperature, lean combustion is the ideal operating regime for minimizing both PM (soot) and NO\textsubscript{X}. The SI and HCCI regions are well defined and easily understood in this figure, however the notion that Diesel flames burn rich when the overall air to fuel proportions are lean, warrants discussion. As mentioned in section 2.3.2, a fuel rich region initially surrounds each evaporated fuel packet in CI combustion. This is a result of evaporation of the fuel upon injection and gives way to rich premixed combustion in that region which located at the upper left most point on the contour path shown. Zhao (2007) defines 3 regions of combustion in Diesel engines that occur after the initial ignition delay, with premixed combustion as the first. As we move down the contour to roughly $\Phi=3$, the mixture begins to burn as a diffusion flame. Due to turbulent mixing, the partially oxidized hydrocarbons and new fuel eventually move past the flame front and are burned at high temperatures as locally stoichiometric conditions are approached. In this burn region maximum temperatures are reached on the contour. After significant burning has occurred, the globally lean conditions continue to supply oxygen as the remaining fuel is burned in an increasingly lean and cool environment until all of the fuel is consumed. It can be seen that inhomogeneities in the fuel mixture of Diesel engines lead to production of both soot and NO\textsubscript{X}, a problem that HCCI specifically addresses.
In beginning the discussion of emissions in HCCI engines it will be helpful to briefly discuss the routes of formation of common harmful emissions during combustion. Thermal NO\textsubscript{X}, formed via the Zeldovich mechanism, is the primary contributor to NO formation during combustion. At ambient pressures the forward reaction rates of Equations 10, 11, and 12 all increase exponentially as temperatures surpass 1600 \textdegree C, giving rise to rapidly increasing NO levels (Zhao, 2007). Just as is the case in SI and CI engines, some of the NO is further oxidized into NO\textsubscript{2} as cylinder temperatures decrease during the expansion stroke. With the combination of these two compounds referred to as NO\textsubscript{X}. HCCI combustion is a type of low temperature combustion and achieves low NO\textsubscript{X} levels by maintaining in-cylinder temperatures near or below the high thermal NO\textsubscript{X} formation regimes. A strategy intended to minimize NO\textsubscript{X} formation in any type of engine must either limit peak temperatures or suppress the reactants feeding the Zeldovich mechanism. Peak temperatures are limited by the minimization of peak pressures and rates of pressure rise. The most significant
reductions in NO in conventional engines are realized with the use of EGR. In the case of Diesel engines, reactants (air) are displaced with exhaust gases containing CO₂ and H₂O. And in the case of SI engines peak temperatures are controlled by the relatively high specific heats of the same compounds.

\[
N₂ + O \leftrightarrow NO + N \quad \textbf{10}
\]

\[
N + O₂ \leftrightarrow NO + O \quad \textbf{11}
\]

\[
N + OH \leftrightarrow NO + H \quad \textbf{12}
\]

Decreasing cylinder temperatures indefinitely is clearly not the answer to cutting emissions, at some point a combustion event will simply not occur and we will be pumping fuel in and fuel out of the combustion chamber resulting in no power output and obviously high HC emissions. However before this most drastic case occurs, notable trends in both HC and CO emissions become evident. As peak cylinder temperatures decrease, increases in HC and CO emissions are encountered. Au et al. (2001) illustrates a tradeoff between NOₓ and both CO and HC emissions. As EGR rates are increased to increase burn duration, NO is observed to fall while CO and HC increase. Oxidation of CO to CO₂ occurs at temperatures above roughly 1200 °C (Zhao, 2007). The HC oxidation reactions also require relatively high temperatures to progress. Unburned hydrocarbons from fuel in crevice volumes and from fuel and oil at the cylinder walls increase as cylinder temperatures reach lower peak values. HCCI combustion temperatures ideally fall in the tightly defined temperature regime that allows maximum oxidation of CO and HCs, but is below temperatures that promote rapidly increasing NO levels. The review papers cited above all note increased CO and HC emissions as a major drawback of HCCI engines. Lü et al. (2005a) show notable differences in CO and HC emissions between high octane and low octane fuels. At the same engine conditions both CO and HC emissions were shown to increase directly
with octane number. Regardless of octane number, CO and HC emissions were also shown to decrease with decreasing $\lambda$ (increasing load). For this particular study CO emissions of all fuels tested converged and showed little sensitivity to $\lambda$ at values below roughly $\lambda = 3$. HC emissions of low octane fuels (RON 0, 25, and 50) also decreased and converged with decreasing $\lambda$. These emissions leveled out around a $\lambda$ value of 4.

For high octane fuel (RON 75) Lü et al. (2005b) has clearly illustrated the ability of increasing EGR to delay combustion and significantly cut in-cylinder peak temperatures. A slight dependence of both CO and HC emissions on EGR rates up 40% was also shown in this work. However an increase of nearly 4 times in HC and CO emissions was found as EGR rates were pushed from 40% to 45%. Prior to the drastic increase, these emissions levels were already high, about .3% by volume CO and .05% by volume HC. These levels are similar to engine out SI levels and far in excess of average CI levels. Modern SI engines however employ a 3-way catalyst to significantly cut both CO and HC emissions as well as NO$_X$. Because exhaust temperatures are lower than SI exhaust temperatures, current oxidation catalyst technology is not effective in removing CO and HC from the HCCI exhaust stream (Epping et al., 2002).

Currently there have been few studies conducted that closely investigate PM emissions in HCCI engines. Kaiser et al. (2002) examined PM emissions of an HCCI engine fueled with gasoline which used an early direct injection strategy at various timings. A SMPS and two stage ejector dilutor setup was used for PM measurements. HCCI combustion was achieved with intake temperatures ranging from 150° to 200°C at a compression ratio of 15.2:1 and $\lambda$ ranging from 2 to about 18. Particle size distributions are presented for 3 HCCI operating conditions ($\lambda=2.35$, 3.25, and 6.77) at a single engine speed of 1100 rpm. In addition, particle size distributions from the same engine running in a DISI ($\lambda=1$) mode and a motored mode are shown. At two of the HCCI conditions, $\lambda=2.35$ and $\lambda=3.25$, accumulation mode number concentrations were higher than that of DISI operation. Additionally the mode itself was found at a larger mobility diameter. The presence of the large accumulation modes was explained by the existence of at least some degree of diffusion burning. This was a consequence of the
DI nature of the fuel injection system and the cool operation of lean burning HCCI combustion which creates the need for longer evaporation and mixing times to fully vaporize and mix the fuel. The $\lambda=6.77$ HCCI condition showed far fewer accumulation mode particles than either of the above mentioned HCCI conditions or the DISI condition. However an order of magnitude increase was seen in nucleation mode number concentrations at this condition when compared with the other conditions. The authors also presented HC emissions data at each condition noted that the HC emissions at the $\lambda=6.77$ condition were an order of magnitude higher than the other HCCI conditions. With extremely lean operation, cylinder temperatures are much cooler, impeding full oxidation of boundary layer and crevice bound hydrocarbons, thus increasing concentrations of hydrocarbon precursors to nucleation. Furthermore, the lower fueling rate at this condition corresponds to shorter injection times. This represents an increase in mixing time which serves to created a more homogeneous mixture and minimize diffusion burning. However, the reduction of accumulation mode particles may have facilitated nucleation of new particulate matter resulting from a lack of adsorption and condensation sites Kittelson et al. (2003).

The authors report a sharp change in the CO/CO$_2$ proportion as a function of $\lambda$, with CO$_2$ most prevalent at $\lambda<4.5$ and CO becoming most prevalent at $\lambda>6.9$. As combustion takes place at leaner conditions, in cylinder temperatures generally decrease due to charge dilution, impeding full oxidation of CO to CO$_2$. Increased hydrocarbon emissions are also seen as a consequence of lower in-cylinder temperatures. Similar results were also reported from a CHEMKIN model by Dec and Sjöberg (2003) and verified experimentally through HCCI engine tests fueled by iso-octane.

A study by Price et al. (2007) reported PM emissions again from a gasoline fueled HCCI engine. In this work, a multiple electrometer based differential mobility particle sizer (Cambustion DMS500) was used to collect PM data. A DI-HCCI fueling strategy very similar to the one of Kaiser et al. (2002) was also used. Valve timings with negative valve overlap (NVO), referring to the exhaust valve being closed early at the end of the exhaust stroke, were used to trap residuals and add thermal energy to the charge. A single $\lambda$ of 1 was used for most testing, with the valve timings and intake
temperature varied and the emissions reported as a function of these parameters. For all of the conditions, composed of varied valve timings and intake temperatures, a bimodal number distribution is reported. A total of 19 different valve timing combinations were examined and each showed a nucleation mode that had a significantly higher particle concentration than the accumulation mode of the same distribution. Comparing one HCCI data set with a SI data set at the same indicated mean effective pressure (IMEP), the authors found a notable increase in accumulation mode particles and decrease in nucleation mode particles in the HCCI data compared with the SI data. These results are in agreement with Kaiser et al. (2002) where the authors noted some degree of diffusion burning is present due to the DI nature of this type of HCCI. The higher cylinder temperatures associated with a propagating flame front aid initial droplet evaporation for the SI cases, giving less diffusion burning and consequently a smaller accumulation mode in the PM distributions.

A more detailed look at HCCI particle size distributions was recently published by Misztal et al. (2009a). Similar to the two previous studies, the fuel injection strategy used was a DI-HCCI system injecting unleaded gasoline directly into the cylinder employing NVO to capture residuals for thermal energy. The authors utilized an electrometer based aerosol measuring system (Cambustion DMS500) preceded by exhaust dilution. However they note that dilution air temperature and humidity were not tightly controlled. Works by Abdul-Khalek et al. (1999, 2000), Mathis et al. (2004), and Rönkkö et al. (2006) all illustrate the sensitivity of nanoparticle formation to dilution temperature and humidity.

The primary focus of this work was to explain the consequences of intake heating on PM emissions. A mixing system for hot and cold intake streams was designed to vary intake temperature. In order to examine multiple intake heating temperatures and different valve timings, a fixed IMEP and engine speed was used for a given case. IVO was then changed and intake temperature was varied to compensate and maintain the same IMEP. The result was an engine condition reached through differing contributions from of NVO and intake heating. An optimization point could then be found where total PM mass was minimized. Because this study was conducted on a DI-HCCI engine
many of the differences in PM signatures are attributed to subtle changes in evaporation and fuel mixing effects. Most interesting is the documentation and explanation of the simultaneous reductions in total PM mass and NO\textsubscript{X} for a fixed speed and IMEP. As EGR rates were increased through delayed IVO, in essence limiting intake air for a fixed amount of residual thus increasing overall EGR percentage, notable drops in both PM and NO\textsubscript{X} could be seen. The reductions in PM are explained by the fuel experiencing more mixing time in the hot recompressed residuals, prior to the introduction of intake air. Insight into NO\textsubscript{X} reductions is gained through the maximum rate of in-cylinder pressure rise for these cases. Lower pressure rise rates are characteristic of longer duration and lower maximum temperature combustion which limits NO\textsubscript{X} production rates.

In summary, the authors of this work showed decreasing particulate emissions with increasing intake air temperature. The effect was attributed to enhanced fuel evaporation due to higher in-cylinder temperatures during compression. Because evaporation and wall wetting phenomena are unique to DI fueling strategies, it should be noted that this trend is not expected to be characteristic of all HCCI engines. Additionally trends of NO\textsubscript{X} and PM emissions both decreasing with increasing EGR were reported. These trends differ drastically from the widely accepted PM – NO\textsubscript{X} tradeoff found in the Diesel emissions literature, but show good agreement with the simultaneous PM and NO\textsubscript{X} reductions associated with HCCI combustion. Finally, an overall trend of increasing loads and speeds leading to increased PM emissions, as is also characteristic of both CI and SI engines, was shown.

A second publication by Misztal et al. (2009b) examines the role of injection timing in PM formation in the same engine as described above. This work again examines HCCI emissions when operating at very rich fuel to air ratios in terms of HCCI operation, on the order of \( \lambda = 1 \). The emissions data collected were compared to data obtained from the same engine operating in DISI mode. HCCI data is presented from both a single injection strategy and a split injection strategy. In terms of general HCCI operating conditions \( \lambda = 1 \) is very rich and represents very high loads. As with
previous work by Misztal et al., this results in significant accumulation mode particulate matter (soot).

The DI mode of fuel delivery led to a high sensitivity of PM formation to injection timing. Injection timings were reported in terms of end of injection (EOI) and were varied from 250º BTDC to 350º BTDC of the compression stroke. The most advanced timings generally showed the highest PM mass and number emissions even though mixing times were the longest. The authors attributed this to wall wetting effects from impingement of most of the fuel on the piston surface. As timings were delayed, consistent reductions in PM were reported until the trend eventually reversed, this was explained by a lack of mixing time prior to ignition. Optimum timings were found to be those in unison with the intake valve opening event. This relationship was explained by the increased mixing from the induction of fresh air into the cylinder. The authors conclude that PM emissions are very closely coupled to mixture homogeneity for this type of HCCI engine.

Although difficult to achieve, the purest form of HCCI requires fully premixed fuel and air. All of the above PM emissions studies were done with DI fueling systems and as a result show effects of diffusion burning. In order to clearly understand PM formation in HCCI and other low sooting engines it will be very beneficial to examine the most basic cases of premixed compression ignition combustion and employ a fully premixed charge.
Chapter 3 PM Emissions Instrumentation

The sensitivity of particulate emissions measurements to sampling conditions and practices has been examined by numerous authors. Recently Kasper (2005) and Mohr (2005) have evaluated PM emissions sampling practices and examined the magnitudes and sources of possible error. As engine manufacturers are forced to build cleaner engines, the absolute magnitude of PM emissions, both number and mass, falls rapidly leaving the quantities of interest closely approaching noise levels. Kasper (2005) notes in particular the advantages found in both sensitivity and time resolution with modern nanoparticle sampling instrumentation compared to gravimetric analysis.

With HCCI combustion, emissions of PM, or smoke, are frequently described as “near zero” (Juttu, 2007) or “ultra low” (Epping, 2002). However recent work by Kaiser et al. (2002), Price et al. (2007), and Misztal et al. (2009a and 2009b) have shown that although the total mass of PM is indeed drastically reduced, significant numbers of particles remain in the size ranges below 100 nm in mobility diameter. This size range is well within the capabilities of modern nano-particle sampling instrumentation, which is well suited for studies in HCCI PM emissions.

3.1 Size Distribution Characterization

Characterization of combustion exhaust particle size distributions has been thoroughly research by a multitude of SI and CI engine studies. This work will draw from the methodology of previous researchers, applying lessons learned to a new problem, the emissions characteristics of HCCI engines. The primary suite of instrumentation used consists of a Scanning Mobility Particle Sizer (SMPS), Condensation Particle Counter (CPC), Engine Exhaust Particle Sizer (EEPS), and Tandem Differential Mobility Analyzer (TDMA).

3.1.1 CPC

The most basic of these instruments is the continuous flow condensation particle counter (CPC) which possesses only single particle counting capabilities. The basic function of these instruments is to grow fluid droplets around particles initially too
small to detect by light scattering. The droplets are then counted with light scattering methods. To accomplish the droplet growth, the aerosol is first passed though a region of saturated vapor. It is then subjected to a temperature gradient in order to achieve supersaturation of the vapor. Droplet growth initiated due to supersaturation, with the small particles used as condensation nuclei for liquid droplets.

Two types of continuous flow CPCs exist, with the primary difference between them the working fluid (water or butanol). Significant design differences are also present. Continuous-flow, water based condensation particle counters (CPCs) were introduced in 2003 (Hering, et al., 2005). Along with the obvious difference in working fluid of the water-based CPCs, the thermodynamic approach for achieving supersaturated conditions within the growth section also differs from that of a conventional continuous-flow, butanol-based CPC. The ability of any CPC to activate and grow a droplet around a condensation nuclei is characterized by the Kelvin equation [13] (Hinds 1999). A given saturation ratio ($S_R$) corresponds to a distinct particle size or Kelvin diameter ($d^*$) capable of maintaining mass equilibrium under the stated conditions. Where $P_d$ is the partial pressure at the droplet-vapor interface and $P_S$ is the saturation pressure of the vapor. This quantity is defined by the material properties, density ($\rho$), surface tension ($\gamma$), and molecular weight along with the temperature of the system (T) and the universal gas constant (R). Above this diameter, mass flux to the droplet surface is greater than away from it and the droplet grows to a size detectable by light scattering.

$$S_R = \frac{P_d}{P_s} = \exp \left[ \frac{4\gamma MW}{\rho RTd^*} \right]$$

Figure 8 and Figure 9 illustrate the design of butanol and water based CPC growth sections. These schematics are simplified versions taken from the work of Agarwal and Sem (1980) and Hering et al. (2005).
Conventional laminar flow CPCs, referred to from this point forward, as butanol CPCs develop supersaturation by heating liquid butanol in the saturating region to a point significantly above the temperature of the condensing region. The aerosol passes through the saturating region and then enters the condensing region where a thermoelectric cooling device drops the temperature, thus lowering the saturation pressure of the system and leaving the previously saturated butanol vapor in a supersaturated condition. This is made possible by rapid rate of thermal diffusion relative to that of mass diffusion of butanol in air. We know that the Kelvin diameter of a particle decreases with saturation ratio. Increasing supersaturation, by increasing the temperature difference between the saturator and condenser, moves down the minimum particle size that can be activated and grown. The maximum temperature difference is bounded on the by the onset of homogeneous nucleation.
Water based CPCs use a different method to achieve supersaturation. As shown in Figure 9, the aerosol flow initially enters a conditioning region where the temperature is brought to a temperature below that of the growth region and the relative humidity is brought to 100% by way of diffusive mass transfer from a saturated wall wick (Hering et al. 2005). The aerosol then enters a heated growth region, where the saturation pressure of water consequently becomes much higher. According to Hering and Stolzenburg (2005) a region of supersaturation results along the centerline of the growth tube, owing to the relatively high rate of mass diffusion of water vapor in air compared with that of thermal diffusion of air.

Worst case performance evaluations by Hering and Stolzenburg (2005), Hering et al. (2005), and Liu et al. (2006) reported differences in instrument response to sample aerosols of differing composition. In the same studies instrument response improved when examining challenge aerosols with increased hygroscopicity, thus better suited to growth by water condensation. These studies conclude that most aerosols in real-world environments would be adequately hydrophilic to allow proper particle activation and growth. Field studies near roadways by Biswas et al. (2005) and Hering et al. (2005) confirm the aforementioned hypothesis. More recently Mordas et al. (2008) and Hermann et al. (2007) found similar results of increased $D_{50}$ with highly pure hydrophobic aerosols along with better performance with the addition of minute hydrophilic impurities. Ambient atmospheric data from mobile emissions sources has
been presented by Biswas et al. (2005) and Hering et al. (2005). The work conducted here was executed with butanol based CPCs due to availability.

### 3.1.2 SMPS

Initially developed by Wang and Flagan (1990), the SMPS utilizes a Differential Mobility Analyzer or DMA (Knutson and Whitby, 1975) coupled with a CPC. The principle of operation of the DMA is explained below and illustrated in Figure 10.

The DMA portion of the SMPS is used to classify particles by electrical mobility. An electric potential is put on the center rod while the outer tube of the DMA is held at ground. When operated with laminar sheath and aerosol flows a scenario is created where a particle’s trajectory is established from two velocity components. The first, a result of the particles drag, follows the sheath flow in the axial direction, and the second, a result of the particles electric mobility, induced by the applied potential, is in the radial direction. This induced force is balanced with the drag force working against the particle in the radial direction. To predict the velocity in the radial direction the following relations describing these two forces are equated. $C_C$ is the Cunningham slip correction factor, $\mu$ is the dynamic viscosity of the fluid, $d_P$ is the particle mobility diameter, and $V$ is the particles terminal velocity in the radial direction.

\[
neE = \frac{3\pi\mu d_P}{C_C}
\]

Solving for velocity $V$ and simplifying with mechanical mobility, we obtain the following expression for particle velocity, influenced by a given electric field, in a specific fluid.

\[
V = neEB
\]
Where \( n \) is the number of charges on the particle, \( E \) is the strength of the electric field, \( e \)

is a constant for the elementary unit of charge, and \( B \) is the particles mechanical

mobility. Hinds (1999) defines mechanical mobility as the relative ease of producing

steady motion for an aerosol particle. This is defined quantitatively by dividing the

terminal velocity of a particle by the drag force acting on it.

When the above velocity vector is added to the velocity vector of the sheath flow a

unique trajectory is defined for a unique particle mobility diameter. By adjusting the

applied field particles of differing mobility diameters can be given the same trajectory.

This is the desired function of the DMA. An exit path exists so that only particles

following the prescribed trajectory will make their way into the exit geometry. All

others will impact the center rod and stick or be flushed out with the excess air flow.

![DMA flow schematic](image)

**Figure 10: DMA flow schematic**

The DMA operating voltage range is scanned through via an algorithm controlled

high voltage power supply, with the CPC reporting concentrations at a mobility
diameter corresponding to each voltage. A data reduction algorithm then interprets the CPC counts and gives a distribution of concentrations versus mobility diameters. A commercial version of this software, provided by the instruments manufacturer, was used.

Because different CPCs have different performance characteristics, particularly counting efficiency, the software must account for these. Counting efficiency relates the specific instrument response at a given particle size to the true concentration of particles as measured by an external calibration source. As the lower response limit of the CPC is encountered, counting efficiencies fall from near 100 percent to near zero in the span of a few nanometers. The current version of the Aerosol Instrument Manager (AIM) software allows for user inputs of operating parameters so that all pertinent variables for SMPS operation are defined. The AIM software compensates for reduced counting efficiency by referencing a counting efficiency curve for each CPC. This curve is a list of efficiencies and corresponding particle diameters denoted with an “eff” file extension in the AIM program files. The software includes unique counting efficiency curves for each of the manufacturers particle counters that the software supports. If the particle counters are following their expected behavior, the effects of counting efficiency should be fully remedied by this correction. The AIM software also has a correction for diffusion losses within the components and associated plumbing of the SMPS. Brownian diffusion, driven by a concentration gradient between the aerosol stream and the walls where concentrations are effectively zero, leads to significant losses of particles smaller 100 nm as shown by Reineking and Porstendörfer (1986). The diffusion correction employed by the software compensates for these losses. Aside from particle size, residence time within the SMPS flow path is the only input affecting diffusion losses. Each CPC has a specific flow rate and combining this with the defined geometry of the SMPS enables the software to correct for diffusion losses. In principle, these corrections enable the AIM software, regardless of instrument configuration to theoretically calculate homogenous results. It is important to note that at very small particle sizes where diffusion losses are most pronounced and counting efficiency of the instrument is very low, the reported concentrations are highly corrected and based on a
few sporadic particle counts. This leads to a very high sensitivity to false counts and highly inferred data sets which should be closely examined.

Two DMAs were available for use in the SMPS, a long DMA (TSI model 3081) and a nano DMA (TSI model 3085). The nano DMA is optimized for size classification of particles in the 3 to XX nm size range. The long DMA has a range of 10 to 1000 nm. An SMPS comprised of a nanoDMA was used for the majority of the work conducted here. With SMPS sheath and aerosol flows set to 15 and 1.5 lpm respectively for all work conducted, the SMPS was operated with a size range of 3 to 64 nm. Preliminary measurements indicated the absence of particles above this range. These flow rates were selected to give as small as possible minimum particle diameter while maintaining a size range that encompassed all expected particle sizes.

Number concentrations can then be converted to mass through a density and volume calculation at each particle size. For all mass calculations a particle density of 1.0 g/cm$^3$ was used. Schnieder et al. (2005) has shown this to be a reasonable estimate of density for PM originating from engine lubricating oil. This density was also used for PM studies on a gasoline fueled HCCI engine by Misztal et al. (2009a).

### EEPS

Most recently developed of the particle instruments used is the Engine Exhaust Particle Sizer (EEPS), which gives comparatively fast response, on the order of 10 Hz (Johnson et al., 2004). The technology was developed at the University of Tartu and commercialized by TSI Inc. Unlike the SMPS, the EEPS is an electrometer based instrument and does not physically count individual particles. Particles entering the EEPS are initially given a unipolar charge then routed through an annular space with an electric potential applied to a center rod and the outer cylinder held at ground. The outer cylinder of the annulus is comprised of a set of isolated electrometers. Each electrometer corresponds to range of known electrical mobilities and corresponding particle sizes. The instrument sample flow and particle terminal velocity due to electrical mobility allow calculation of a bin of particle sizes that will be detected by
each electrometer. Particle concentrations at a given size are then inferred from currents in corresponding electrometers.

Although the fast time response of the EEPS makes it a valuable tool for PM emissions research, the work conducted here concentrated on steady state engine conditions. In addition the EEPS has poorer sensitivity and size resolution that the SMPS system. Consequentially, the SMPS was used much more extensively in this work.

3.1.4 TDMA

Experimental work carried by Liu, et al. (1978), McMurry, et al. (1983), and Rader et al. (1986) began using two DMAs in series as a means of further understanding chemical and thermo physical properties of aerosol particles. Rader and McMurry (1986) adopted the term TDMA to describe apparatus which feature two or more DMAs operated in series. Application of TDMA to study droplet evaporation and growth has been rigorously characterized by Rader and McMurry (1986). Orsini et al. (1998) have also given a detailed description of adaptation of TDMA for measuring volatile fractions of particles. The TDMA technique published by Orsini (1998) was successfully used by Sakurai (2003) to study Diesel nanoparticle composition. A similar system has been used for this work and is shown in Figure 11. The thermal conditioner was sized in accordance with Orsini (1998) and Sakurai (2003), with temperature monitored continuously at the conditioner outlet. The temperatures used for the thermal conditioner ranged from 40° to 110°C with data collected in 10° increments.
3.2 Dilution

To simulate the process of hot exhaust gases mixing with ambient air and cooling a micro-dilution system very similar to the one developed by Abdul-Khalek (1999) was used. The system draws a small sample of exhaust from the engine outlet and dilutes it in two stages with a variable residence time aging chamber between. The conditions pertinent to aerosol nucleation and growth by condensation are dilution ratio, dilution air temperature, residence time in the aging chamber, and relative humidity. The micro-dilution system allows for easy manipulation and tight control of these variables. A schematic of the system is shown in Figure 12.
A key point to be made here is that HCCI engine exhaust is thought to produce significant number of particles with diameter smaller than 50 nm (Price et al., 2007; Kaiser et al., 2002). When examining detailed characteristics of these particle size distributions, great care must be taken to tightly control dilution conditions due to the sensitivity of nucleation to dilution conditions as shown by Abdul-Khalek (1999). The sensitivity of nucleation mode particles, or nanoparticles, to dilution system residence time was clearly shown at nearly all dilution ratios and temperatures examined. As residence time increased from 100 ms to 1000 ms, the number of nucleation mode particles increase by more than an order of magnitude. Meanwhile accumulation mode particle concentrations remained unchanged. A relationship between primary dilution air temperature and nucleation mode behavior was also established and a trend of falling concentration with rising temperature established. The sensitivity of nanoparticles to dilution conditions was further explored by Abdul-Khalek et al. (2000) and Mathis et al. (2004). Abdul-Khalek et al. isolated particle growth rates and reported them to vary significantly with primary dilution temperature. Additionally strong trends of decreasing growth rate with increased primary dilution ratio were established by Abdul-Khalek et al. (2000). Additionally these authors showed strong trends of decreasing growth rate with increased primary dilution ratio. Total concentration of nucleation mode particles was again shown to steadily drop as primary dilution temperatures were increased. Mathis et al. confirmed these results and reported a
maximum change of more than an order of magnitude exhibited when primary dilution temperatures were increased from 17°C to 40°C. The effects of humidity were also investigated. Mathis et al. found nucleation mode concentrations increasing by an order of magnitude as humidity increased from 2% to 51% RH. Similar sensitivity to humidity was shown via modeling of nucleation mode PM from Diesel combustion by Kim et al. (2002). These authors noted number concentrations increasing by a factor of 6 when relative humidity of the dilution air was increased from 10% to 90%.

Both primary and secondary dilution ratios are set through air flow rates. For this work they were also confirmed initially with NO concentrations at the selected dilution conditions. Due to the sensitivity of nanoparticle formation to primary dilution conditions, the primary dilution ratio was continuously monitored via CO\(_2\) concentrations (ppm) through Equation 16.

\[
DR_{\text{Primary}} = \frac{(CO_{2, \text{Exhaust}} - CO_{2, \text{Ambient}})}{(CO_{2, \text{Primary}} - CO_{2, \text{Dilution Air}})}
\]

Figure 13 shows the sensitivity of ethanol HCCI nucleation mode PM to stage one dilution air temperature. The data was collected with a stage one dilution ratio of 17.7:1, a dilution tunnel wall temperature of 25°C, a stage two dilution ratio of 15:1, and a stage dilution air temperature of 25°C. The engine was operated on pure ethanol fuel, at a low load condition, with a speed of 1500 RPM. At low stage one air temperatures, 25°C, nanoparticle formation increased significantly. However, with stage one dilution air temperatures between 30° and 40°C, formation of the nucleation mode remained relatively stable. Variations in stage 2 dilution air temperature show little effect on nucleation mode formation and are not presented here.
In an effort to more precisely control dilution conditions within the aging chamber, or tunnel, the outer wall was water jacketed and held at a constant temperature equal to that of the stage one dilution air. The following analysis was conducted to ensure air temperatures within the tunnel were reasonably close to tunnel wall temperatures. Taken from Kaminski and Jensen (2005), Equation 17 predicts the exit fluid temperature for a case of internal flow with constant wall temperature.

\[
T_{\text{Exit}} = (T_{\text{Inlet}} - T_{\text{Wall}}) \exp \left( -\frac{hA}{\dot{m}c_p} \right) + T_{\text{Wall}}
\]

Where \(T_{\text{Exit}}\) is the mean fluid exit temperature, \(T_{\text{Inlet}}\) is the temperature of the fluid entering the tunnel, \(T_{\text{Wall}}\) is the dilution tunnel wall temperature, \(h\) is the forced convection coefficient for the system, \(A\) is the cross sectional area of the tunnel, \(\dot{m}\) is the mass flow rate of fluid through the tunnel, and \(c_p\) is the constant pressure specific heat of the fluid in the tunnel. A Reynolds number for the tunnel entrance was
calculated to be roughly 10,500, indicative of a turbulent flow condition. Combined with a Prandtl Number of .696 for air at these conditions, a Nusselt number of roughly 30 was calculated which then allowed a convective heat transfer coefficient (h) equal to 5 W/m² °C to be found. Figure 14 shows exit air temperature profiles at different distances along the length of the 120 cm dilution tunnel, found through Equation 17.

![Figure 14: Mean exit temperature profiles along the length of the dilution tunnel, varied wall temperature, T_in = 50°C, Air flowrate = 80 slpm](image)

An inlet temperature of 50°C was used and is based on a 15:1 dilution ratio of 300°C exhaust air with 35°C dilution air. It can be seen that at roughly half the tunnel length (60 cm) the air temperature is within 3°C of the wall and at the end of the tunnel (120 cm) the air temperature is only 1°C higher than the wall. Measured air temperatures at the exit of the tunnel were within 1°C of predicted and within 2°C of the tunnel wall.

A sensitivity analysis also was conducted to explore the effect of dilution tunnel wall temperatures on particle formation, and find a temperature at which the exhaust aerosol was most stable. For this analysis stage one dilution ratio was held at 17.7:1 and stage two at 15:1. Stage two dilution air temperatures were held at 25°C. At each of two
dilution tunnel temperatures, PM data was collected at three stage one dilution air temperatures. These results of these experiments are shown in

![Graph showing sensitivity of PM formation to dilution tunnel wall temperature](image)

**Figure 15: Sensitivity of PM formation to dilution tunnel wall temperature**

Based on the above sensitivity analyses, it was found that stage one dilution air temperatures of 35°C gave the most stable nucleation mode. Additionally particle formation showed reasonable stability at tunnel wall temperatures of 35°C. Stage one dilution air and tunnel wall temperatures were both held at 35°C throughout all further testing. Stage 2 dilution temperatures were held at 25°C.
Chapter 4 Preliminary Modeling

Identifying the operating conditions suitable for HCCI combustion is a critical step in the development of an experimental apparatus. CHEMKIN® software was utilized to model the chemical and thermodynamic behavior of an idealized system. Using the engine parameters of the actual test engine, a single cylinder of the test apparatus was modeled. The cylinder is modeled as zero-dimensional homogeneous reactor. Fuel and air are assumed to be well mixed and in the gas phase with both the intake and exhaust valves closed at the beginning of the simulation. The charge is modeled in a single zone with the entire contents of the cylinder viewed as a continuum. A very similar approach has been used by Ng and Thomson (2007) and Martinez-Frias et al. (2007). For the preliminary modeling work presented, the system boundaries (cylinder walls) were viewed as adiabatic. Pertinent engine characteristics are shown in Table 1.

<table>
<thead>
<tr>
<th>Engine Model</th>
<th>Isuzu 4HK-1TC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bore (mm)</td>
<td>115</td>
</tr>
<tr>
<td>Stroke (mm)</td>
<td>125</td>
</tr>
<tr>
<td>Crank Length (c, mm)</td>
<td>62.5</td>
</tr>
<tr>
<td>Connection Rod Length (l, mm)</td>
<td>198</td>
</tr>
<tr>
<td>Single Cyl. Displacement (cm³)</td>
<td>1298</td>
</tr>
<tr>
<td>Clearance Volume (cm³)</td>
<td>74</td>
</tr>
<tr>
<td>l/c</td>
<td>3.168</td>
</tr>
<tr>
<td>Compression Ratio</td>
<td>18.5:1</td>
</tr>
</tbody>
</table>

Combustion reaction mechanisms have been developed and published by researchers specifically for the fuels used in this work. The mechanisms consider intermediate species formed as fuels are broken down and oxidized into the products of combustion. Additionally, tabulated thermodynamic properties for the cylinder contents are required for evaluation of cylinder temperature and pressures based on species concentration and cylinder geometry. Thermodynamic properties and the chemical kinetic mechanism for ethanol combustion were taken from the work published by
Marinov (1999). The hydrogen combustion thermodynamic properties and chemical kinetics used were those developed by Conaire et al. (2004). A suitable mechanism for modeling the behavior both fuels was not available however. To examine the effects of dual fueling strategies a mechanism was developed that utilized kinetic data from both of the above reaction sets. Removing the reactions involving hydrogen from the ethanol mechanism of Marinov and replacing them with the more extensive set of reactions encompassed by the work of Conaire et al. gave a reaction set that could more adequately model combustible mixtures of ethanol and hydrogen. The combined mechanism was validated by comparing the results of hydrogen and ethanol combustion modeled independently with their respective mechanisms to hydrogen and ethanol modeled with the combined mechanism. All modeling was done with a time resolution of one half of one CAD. Table 2 shows the important combustion properties of the fuels used in the modeling work, which will also be used in the proposed experiments.

<table>
<thead>
<tr>
<th>Property</th>
<th>Hydrogen</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>H₂</td>
<td>C₂H₅OH</td>
</tr>
<tr>
<td>Molecular Mass (kg/kmol)</td>
<td>2.016</td>
<td>46.068</td>
</tr>
<tr>
<td>Lower Heating Value (kJ/kg)</td>
<td>121,000</td>
<td>29,700</td>
</tr>
<tr>
<td>Density @ 380 K (kg/m³)</td>
<td>.06465</td>
<td>1.477</td>
</tr>
<tr>
<td>Stoichiometric Air to Fuel Ratio</td>
<td>34.06</td>
<td>8.94</td>
</tr>
</tbody>
</table>
The HCCI combustion process of hydrogen has been modeled using three different mechanisms for the same set of engine conditions. From Figure 16 it is clear that the ethanol mechanism does not properly describe hydrogen combustion. Start of combustion, defined here as the point where the pressure trace deviates from the motoring trace, is shown to be delayed by nearly 5 CAD when modeling HCCI combustion of hydrogen with the ethanol mechanism compared to the results obtained with the hydrogen mechanism. Although the ethanol of mechanism of Marinov has a series of 25 reactions dealing with the combustion of hydrogen, the hydrogen mechanism of Conaire et al. has a more detailed set 42 of reactions. The combined mechanism, shown in blue, matches the results of the hydrogen mechanism nearly perfectly. To ensure that the replacement of the hydrogen reaction equations did not affect the overall performance of the ethanol mechanism, a series of ethanol HCCI simulations were executed comparing the ethanol mechanism with the combined
mechanism. The results are shown in Figure 17. Very reasonable agreement between the two mechanisms is also seen with ethanol HCCI combustion. A slight deviation in the pressure traces can be seen near the start of combustion however the deviation is less than 1 CAD and for this work can be viewed as negligible.

![Cylinder pressure traces of simulated HCCI combustion of ethanol fuel with $\lambda=3$, intake temp. of 400 K, and engine speed of 1000 rpm](image)

**Figure 17: Cylinder pressure traces of simulated HCCI combustion of ethanol fuel with $\lambda=3$, intake temp. of 400 K, and engine speed of 1000 rpm**

The most basic purpose for modeling the system is to isolate conditions feasible for combustion in a particular engine. HCCI combustion is bounded on the upper end of the load range by uncontrollable rates of pressure rise resembling knock and on the lower end by misfire. The conditions selected for modeling and experimental work were selected based on their relationship with full rated load of the engine. The IMEP corresponding to maximum rated load for this engine is roughly 14 atm (1400 kPa), if we assume $\eta_M$ to be on the order of 90%, an IMEP of 16 atm (1600 kPa) will result.
Values of \( \lambda \) were selected to cover low and mid load operating conditions. A pressure trace obtained through the model allows IMEP to be calculated for each \( \lambda \) via Equation 4. Table 3 illustrates the modeled \( \lambda \) values used, the corresponding IMEP, and the percentage of IMEP at maximum rated load for the test engine.

A series of range finding simulations were first executed to ensure that each \( \lambda \) was within the limits combustibility for the fuels. After isolating the desired \( \lambda \) values, the response of the model to intake temperatures was investigated. An IMEP sweep was modeled using a fixed fuel flow corresponding to the initial lambda at 370 K. The intake temperature was then changed in 10 K increments. Increasing intake temperature changes the amount of air going into the cylinder through ideal gas behavior, thus the actual lambda falls as temperature rises. In order to maximize efficiency, IMEP is maximized at a fixed fueling rate. For each of the four initial \( \lambda \) values shown in Figure 18, a range of temperatures from 370 K to 410 K was swept through.

<table>
<thead>
<tr>
<th>( \lambda_{\text{Initial}} )</th>
<th>( \lambda_{\text{MaxIMEP}} )</th>
<th>Max IMEP (atm)</th>
<th>( T_{\text{in}} ) for Max IMEP (K)</th>
<th>% IMEP at Rated Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>4.87</td>
<td>3.78</td>
<td>380</td>
<td>24%</td>
</tr>
<tr>
<td>4.0</td>
<td>3.89</td>
<td>4.71</td>
<td>380</td>
<td>29%</td>
</tr>
<tr>
<td>3.0</td>
<td>2.92</td>
<td>6.10</td>
<td>380</td>
<td>38%</td>
</tr>
<tr>
<td>2.0</td>
<td>1.89</td>
<td>8.74</td>
<td>390</td>
<td>55%</td>
</tr>
</tbody>
</table>
Figure 18: Pressure vs. CAD at 5 intake temperatures for each of 4 lambda ranges, EtOH fuel, 1000 RPM

From the pressure traces shown it is clear that increasing the inlet temperatures advances the start of combustion. The results presented here also follow intuitive thought. For a fixed geometry piston and cylinder device, increasing the initial temperature of the system will result in higher temperatures being reached earlier in the stroke. This in turn leads to advancement the start of combustion. As the mixture composition gets richer ($\lambda$ decreases), it can be seen that the pressure traces tend to fall below the motoring trace. Additionally, at the lowest temperature case in the $\lambda_{Initial}=2$ plot, the pressure trace indicates that the mixture does not even ignite. These phenomena are due to the high specific heat of ethanol, which is more than twice that of air. Thus the effect is less noticeable in leaner mixtures which contain far less ethanol.

The effects of hydrogen on ethanol HCCI combustion were also simulated using the same model as above. In the following simulations, hydrogen proportions were calculated based on a percentage of power input through Equation 18. The mole
fractions of each fuel with respect to total fuel were then varied in order to correspond to 0, 5, 10, 15 and 20 % hydrogen energy supplementing the main ethanol fuel supply.

\[
Total\ Energy\ (KJ) = n_{H_2}LHV_{H_2}\left(\frac{KJ}{kg}\right)MW_{H_2}\left(\frac{kg}{kmol}\right) + n_{EtOH}LHV_{EtOH}\left(\frac{KJ}{kg}\right)MW_{EtOH}\left(\frac{kg}{kmol}\right)
\]

![Cylinder Pressure vs. crank angle for varying hydrogen proportions](image1)

**Figure 19:** Pressure vs. CAD with varying hydrogen proportions for each of 4 lambda ranges, EtOH base fuel, 1000 RPM, intake temperature of 380 K

In these cases we also have a changing cylinder volume left for air with constant fueling as the fuel proportions vary. The variance here is due to the discrepancy in the energy to volume ratios between hydrogen and ethanol. As hydrogen energy is slightly increased, the additional volume required for fuel displaces air and causes a decrease in
From the simulations it can be seen that SOC advances with increasing hydrogen proportion. It is also evident that IMEP is increased although the fuel energy input is held constant. Table 4 shows the optimized IMEP cases for the variable hydrogen energy input simulations. In the two leanest cases, the rate of pressure rise shows a significant increase with increasing hydrogen energy. This behavior agrees well with the findings of Yap et al. (2004), who examined similar amount of hydrogen addition to natural gas HCCI combustion.

Table 4: \( \lambda \), IMEP, and rated power relationship for hydrogen test conditions

<table>
<thead>
<tr>
<th>( \lambda_{\text{Initial}} )</th>
<th>( \lambda_{\text{MaxIMEP}} )</th>
<th>Max IMEP (atm)</th>
<th>% ( \text{H}_2 ) for Max IMEP</th>
<th>% of IMEP at Rated Load</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>4.99</td>
<td>3.72</td>
<td>20</td>
<td>23%</td>
</tr>
<tr>
<td>4.0</td>
<td>3.98</td>
<td>4.59</td>
<td>20</td>
<td>29%</td>
</tr>
<tr>
<td>3.0</td>
<td>2.98</td>
<td>5.98</td>
<td>15</td>
<td>38%</td>
</tr>
<tr>
<td>2.0</td>
<td>1.96</td>
<td>8.59</td>
<td>20</td>
<td>54%</td>
</tr>
</tbody>
</table>

A third set of simulations were run in order to understand the effects of EGR on ethanol HCCI combustion. Again a constant fueling rate was held for each lambda range. Because intake air is being displaced by EGR in these experiments and the fueling is held constant a new lambda is realized with each EGR rate. An intake temperature of 380 K was used for each of the modeling runs. To obtain the proper ratios of combustion reactants, a calculation was made to find intake charge mole fractions from the contributions of fuel, air, and each of the EGR constituent molecules. EGR rates (EGR) as a percentage of the total volume of intake air were used and the amount of fueling was held constant. The only products of combustion to simulate EGR were \( \text{CO}_2 \), \( \text{H}_2\text{O} \), \( \text{O}_2 \), and \( \text{N}_2 \). These mole fractions were calculated at lambda values of 2, 3, 4, and 5 and EGR rates of 0, 10, 25, and 50 % using an EES code. The mole fractions were then used as part of the input set for the CHEMKIN simulations.

A constant intake temperature of 380 K was used for all EGR simulations. In practice this scenario is quite feasible. Although changes in intake charge temperature
will result from the introduction of hot exhaust gases, the intake heater feedback loop samples temperature downstream of the EGR introduction port. As more thermal energy is gained from the exhaust gases, the intake heaters can lessen their contribution and only perform up to the level that is necessary to maintain the temperature set point.

Figure 20: Pressure vs. CAD with varying EGR rate for each of 4 lambda ranges, EtOH fuel, 1000 RPM, intake temperature of 380 K

The simulations with EGR show peak pressures decreasing as EGR rates increase for all lambda cases. The results agree well with the experimental efforts of Lü et al. (2005b) for a high octane fuel. This is a clear result of the increase in mixture specific heats as more CO$_2$ and H$_2$O are added. The above simulations show some dependence of SOC on EGR rates in cases $\lambda=2$ and $\lambda=3$. However, in the $\lambda=4$ and $\lambda=5$ cases less effect is seen on SOC and more of an effect on dP/dCAD materializes. This is consistent with the findings of Au et al. (2001) in showing little effect on SOC and a pronounced effect on dP/dCAD. The explanation behind this differing behavior with $\lambda$
range is unclear. The ability of EGR to limit peak rates of pressure rise is visually quite clear in all of the cases except \( \lambda = 2 \), where rates of pressure rise remain relatively unchanged. Controlling rate of pressure rise is critical in maintaining smooth HCCI combustion and ensuring knock is not encountered. Table 5 summarizes the peak pressures obtained from the EGR modeling exercises.

<table>
<thead>
<tr>
<th>% EGR</th>
<th>( \lambda_{\text{initial}} = 2 )</th>
<th>( \lambda_{\text{initial}} = 3 )</th>
<th>( \lambda_{\text{initial}} = 4 )</th>
<th>( \lambda_{\text{initial}} = 5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Pres. (atm)</td>
<td>IMEP (atm)</td>
<td>Peak Pres. (atm)</td>
<td>IMEP (atm)</td>
<td>Peak Pres. (atm)</td>
</tr>
<tr>
<td>0</td>
<td>113.5</td>
<td>8.50</td>
<td>99.3</td>
<td>5.97</td>
</tr>
<tr>
<td>10</td>
<td>107.4</td>
<td>8.40</td>
<td>97.3</td>
<td>5.83</td>
</tr>
<tr>
<td>25</td>
<td>93.6</td>
<td>8.16</td>
<td>95.4</td>
<td>5.90</td>
</tr>
<tr>
<td>50</td>
<td>47.3*</td>
<td>.23</td>
<td>88.5</td>
<td>5.81</td>
</tr>
</tbody>
</table>

Summarizing the IMEP for the EGR conditions, it can be seen in Figure 20 that increasing EGR rate both delays SOC and limits peak pressures. From these characteristics of the pressure traces it is clear that increased EGR will lead to lower IMEP. This is true provided the combustion trace does not deviate from the motoring trace prior to TDC (0°) in the cycle.

An important assumption that must be justified for this modeling is that the mixture is a thoroughly mixed combination of gases that can be viewed as a homogeneous reactor. Theory of droplet evaporation and diffusion burning are important considerations in Diesel engine (CI) combustion, however in the case of an HCCI engine these issues are not of concern if the preceding assumption is valid. The following analysis aids in the justification of this assumption. Derived from Fick’s law of diffusion, Turns (2000) has developed Equation 19, which relates droplet evaporation time\( (t_d) \) to initial droplet diameter\( (D_0) \) via an evaporation constant \( (K) \).
Through Equation 20, K is defined by the following conditions of the system: droplet density \( \rho_{\text{Droplet}} \), surrounding fluid density \( \rho \), diffusion coefficient \( D_{AB} \), and the transfer number, \( B_Y \). The transfer number relates the mass fractions of vapor at the droplet surface to those of the surrounding fluid and is given by Equation 21.

\[
t_d = \frac{D_0^2}{K}
\]

\[
K = \frac{8\rho D_{AB}}{\rho_{\text{Droplet}}} \ln(1 + B_Y)
\]

\[
B_Y = \frac{Y_{\text{EOH,S}} - Y_{\text{EOH,\infty}}}{1 - Y_{\text{EOH,S}}}
\]

Through this analysis, the lifetimes of ethanol droplets were calculated in the intake runner prior to induction into the cylinder via the valves. If, for simplicity we neglect the latent heat of vaporization of ethanol, and an intake air temperature of 370 K and a droplet temperature 10 K below the boiling point of ethanol are assumed, \( t_d \) in the intake will range from .0001 to .04 seconds for 5 to 100 \( \mu \)m ethanol droplets. Residence times \( (\tau) \) of the fuel-air mixture before entering the combustion chamber have been calculated based on intake geometry and engine speed and assuming the fuel is injected into the moving air stream with the intake valve open. For engine speeds of 1000 RPM and 2500 RPM \( \tau_{\text{Intake}} \) is equal to .018 and .007 seconds respectively. It is clear that evaporation in the intake ports is not sufficient to ensure all of the fuel is in the gas phase at the highest engine speed conditions. Further examining common practices in port fuel injection mixture preparation, we see that the injector is minimally responsible for atomizing fuel. Zhao et al. (1995) describes the design and operating characteristics of modern PFI systems and states that fuel injections are usually timed while the intake valve is still closed. The practice takes advantage of impingement of the spray on interior intake surfaces to promote secondary atomization, giving droplet sizes generally
below 50 µm. Examining the window of time between intake valve closing from one cycle and intake valve opening for the subsequent we can find a residence time of the stagnant air inside the intake port of roughly .024 seconds at 2500 RPM. Summing these two residence times with the in-cylinder evaporation time, roughly another .005 seconds at 2500 RPM, we can see that time for complete evaporation of even very large diameter droplets is sufficient. In addition, the increased temperatures associated with compression further enhance droplet evaporation. Droplet lifetimes were evaluated during the compression stroke at cylinder temperatures and pressures found via modeling. It is shown in Figure 21 that lifetimes fall by nearly 50% as temperatures and pressures approach the SOC condition. These data help to ensure the ethanol droplets will be completely evaporated upon SOC.

![Figure 21: Lifetime of 50 µm ethanol droplets during the compression stroke of Isuzu 4HK1-TC test engine, intake temperature is 370 K, droplet temperature assumed to be 342 K (T_{\text{boil,EtOH}} = 352 K)](image-url)
Chapter 5  Experimental Apparatus

5.1 Multi-cylinder Test Engine

Utilizing a multi-cylinder engine greatly increases the level of difficulty in maintaining uniform HCCI combustion over a single cylinder engine. Variations in-cylinder temperature and charge composition can be caused by: coolant paths, EGR distribution, intake air paths, and charge distribution. In order to precisely control as many of these variables as possible a custom port fuel injection (PFI) intake manifold was designed to replace the stock manifold. The multi-cylinder test engine with modifications is shown in Figure 22.

The engine is based on a production Isuzu 4HK1-TC Diesel engine. The 4HK1-TC is a 4-cylinder, 5.2 liter, turbo charged, direct injection engine. It was originally equipped with common rail fuel injection and met all current emissions standards at the time of production. A series of modifications has been made in order to convert the Diesel engine to an HCCI engine. First the common rail fuel injection system was removed. The injector rail, high pressure pump, and fuel distribution piping are not required and were removed to clear space for new intake manifold. The original intake manifold was very simple and had no separation between cylinder ports. This is an acceptable design for a Diesel engine where only intake air and EGR flows through the manifold, however it is not suitable for HCCI operation. Additionally the stock EGR delivery system was removed, as it was poorly designed for ensuring even EGR flow to each cylinder. The stock 18.5:1 compression ratio, piston design, and valve timings were all maintained.
5.1.1 Intake Manifold

The design of the intake manifold allows for fully independent and isolated control of fuel delivery, charge temperature, and % EGR for each of the four cylinders. This isolated and independent control gives the opportunity to normalize in-cylinder inhomogeneities across the four cylinders in terms of cylinder pressure or ignition delay with one intake variable, while examining the effects of manipulating the other available variables. The intake manifold, shown in Figure 22, couples all of the required
modifications for this HCCI engine. Two sets of fuel injectors, liquid and gaseous, EGR ports, and thermally conditioned air ports are all designed into the manifold.

5.1.1.1 Fuel Injection

The fuel injection system is based on a standard PFI system with four independently controlled, fully variable ethanol injectors. In addition to four liquid fuel injectors, the system is equipped with a supplementary set of four gaseous hydrogen fuel injectors with the same independent control. In order to minimize any effects of intake wall wetting and maintain precise control of $\lambda$, the ethanol injectors are oriented so that their spray pattern is focused on the intake port of the hot engine block. They are timed to inject in advance of intake valve opening, giving adequate time for droplet evaporation. The ethanol, is burned with the assumption that it is completely evaporated and fully mixed with air upon SOC. To help promote complete fuel evaporation, the high pressure injector supply line is preheated to very near the 85°C ambient pressure boiling point of ethanol prior to injection. Additionally, intake air temperatures are also well above this boiling point. Calculation of droplet lifetimes at these conditions, summed with droplet lifetimes during compression, indicated total residence times of the droplet within the intake runner, cylinder head, and combustion chamber to be well in excess of the required time for full evaporation of the fuel droplets. Ethanol fuel flow rates are monitored continuously via mass change in the fuel supply reservoir.

The hydrogen fuel injectors also discharge directly into the respective cylinder intake ports. These injectors are timed to inject during the intake stroke with the intake valves open. Hydrogen fuel flow rates were monitored with a Sierra (Smart-Trak) mass flow meter.

Fuel flow rate for both injector sets can be controlled with injector pulse width and with fuel supply pressure. Fuel injection is timed off the crank and cam shafts of the engine and controlled via an aftermarket engine management system (Intelligent Controls, IC 5420).

The undenatured ethanol fuel composition is shown in Table 6. The hydrogen fuel was UHP/Zero grade with a purity of 99.999%.
Table 6: Ethanol Fuel Composition

<table>
<thead>
<tr>
<th>Fuel Characteristic</th>
<th>Specification</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proof</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>Density @ 20 °C (g/cm³)</td>
<td>.7900-.7932</td>
<td>.7904</td>
</tr>
<tr>
<td>Water Content</td>
<td>0.2 %</td>
<td>0.2%</td>
</tr>
<tr>
<td>Methanol</td>
<td>&lt; 0.1%</td>
<td>&lt; 0.001%</td>
</tr>
</tbody>
</table>

5.1.1.2 EGR

EGR can take two forms, the first, external EGR consists of routing exhaust gases from the exhaust side of the engine back into the fresh air intake. This strategy is commonly used in both SI and CI engines as an emission control device. The second form, where the gas components are often referred to residuals, maintains some level of exhaust gases in the cylinder from the previous cycle. All engines have some level of residuals remaining in the cylinder; however 2-stroke engines carry many more from cycle to cycle due to the lack of dedicated exhaust and induction strokes.

External EGR on the test engine is manually controlled for each cylinder through a set of four gate valves fed from the main EGR distribution manifold. A single branch of the four cylinder EGR loop is shown in Figure 23. Temperature of the EGR manifold is monitored along with exhaust back pressure and temperature. Pressure in the EGR distribution manifold can be adjusted via the exhaust back pressure valve. By adjusting the total back pressure the system, flow through the EGR manifold can be increased. EGR flow to individual cylinders is controlled via an EGR throttle valve on each branch of the EGR loop. Intake temperatures are held constant throughout varied EGR rates by controlling the temperature of the fresh intake air stream. The EGR manifold was also wrapped in an improvised water jacket in order to cool the EGR stream ensuring intake temperatures could be maintained at constant levels.
Accounting for ambient CO$_2$ levels during testing, Equation 22 defines an EGR rate by relating CO$_2$ levels in the engine exhaust and the mixed stream of intake air.

\[
EGR \text{ Rate (\% EGR)} = \frac{\left(\% \text{ CO}_2, \text{ Intake} - \% \text{ CO}_2, \text{ Ambient}\right)}{\left(\% \text{ CO}_2, \text{ Exhaust} - \% \text{ CO}_2, \text{ Ambient}\right)}
\]

5.1.1.3 Thermal Management

The thermal management system consists of independently PID controlled air heaters upstream of the fuel injectors on each intake runner. Closed-loop feedback is given via type K thermocouples located at the intake mounting flange. Prior to the independently controlled heaters, a main set of preheaters elevate the temperature in an initial step to ease the electric current burden on the independent heaters. The bank of preheaters is designed to raise the intake temperature a maximum of 35°C above the inlet temperatures when the engine is operating at a maximum of 3000 RPM. The individual heaters are designed to then take the preheated air to the operating condition. They are capable of creating a maximum $\Delta T$ of 95°C with the engine operating at 3000
RPM. This gives maximum intake temperatures on the order of 155° assuming an ambient temperature of 25°C.

A recent study by Peineke et al. (2006) examined the use of glowing wires for production of nanoparticles. In this series of experiments the wires were heated due to resistance while passing a current through them and as a result metallic material is sublimated. The wire was immersed in a flow of nitrogen and oxygen with temperature controlled downstream of the heated wire via a water jacketed chamber. Utilizing the cooled nitrogen/oxygen flow to induce nucleation, the authors reported size distributions of highly pure metallic particles in the range of 3 to 80 nanometers depending on the nucleation conditions and wire material. They also compiled a list of suitable materials and developed an empirical rule for selecting useable material based on saturation pressure at a given materials melting temperature. Although the precise details of this series of experiments are not of particular interest in relation to the proposed work, the phenomenon of nucleation of small metallic particles from a heated wire is of extreme consequence. These particles, if present in the exhaust, could provide nucleation sites leading to formation of exhaust PM around the metallic seed particles. The exhaust aerosol would not be representative of an aerosol generated solely from engine exhaust. Lee et al. (2006) noted significant differences in the concentrations of metal bearing particles when examining emissions of an engine running on fuel doped with ferrocene ((C$_2$H$_5$)$_2$Fe). As ferrocene concentrations were increased from 20 ppm to 60 ppm, an order of magnitude increase was seen in the nucleation mode of the particle size distribution. Additionally, metal particles were found via single particle mass spectrometry throughout all particle sizes some doping levels. The authors explain the presence of metal containing particles over the entire size range is likely due to three formation and growth mechanisms, self nucleation of metal vapor, condensation onto preexisting carbon particles, and coagulation of small metal containing particles.

The heating elements used in the thermal management system are nickel-chromium (80%/20%) resistive heaters. With the heating element surface dimly glowing, surface temperatures are likely to be in the region of 700-1000 K. At these temperatures investigation is warranted into the production of particles by the resistive heaters. A
A series of experiments was designed to simulate the temperatures and air flow rates the system would encounter during engine operation. A variable speed blower was placed upstream of the heaters simulate air flow normally provided by the engine. The apparatus is shown schematically in Figure 24. The heaters in apparatus are the same heaters as those used on the engine.

Flow rates were selected corresponding to engine operation at 1000, 1500, and 2500 RPM and measured with a laminar flow meter. At each of these flow rates outlet air temperatures of 70°, 110°, and 150°C were examined and compared to the system operating with no heat addition. Temperatures were set using closed loop PID control with feedback from type K thermocouples $T_1$ and $T_2$ respectively. The 70°C data point was chosen in order to examine the system operating only on heater 1, and the 150°C point chosen as the highest expected temperature. PM data collected with an SMPS is presented below. The SMPS sampled from the stainless steel sampling probe and was used in anticipation of a nucleated particle size distribution. Upon testing it became clear that no such size distribution existed and total concentrations are presented. The

![Figure 24: Schematic of intake heating bench test](image)
process air was filtered initially at the blower inlet and again prior to the LFE. The filters used were general purpose automotive air filters and are not HEPA grade, thus some ambient PM is still present in the air stream. However, comparing the no heat (0°) size distribution with those generated at 70°, 110°, and 150°C allows direct examination of the particle generation of the heaters.

Figure 25 clearly shows no significant particle generation at any temperature or flow rate. Total concentrations shown are on the order of 100 to 1000 particles per cm³. For reference the total concentration of particles from 2.5-80 nm in the ambient lab air at the time of testing was roughly 50,000 particles/cm³. In agreement with accepted filtration theory, an increasing trend in total concentration can be observed as airflow rate rises. These particle sizes are primarily captured by Brownian diffusion which is less effective at high flowrates through the filter media (Hinds, 1999).

![Figure 25](image_url)

**Figure 25: Total concentration of particles between 2.5 and 80 nm at heater exit**
Although the heaters were expected to give some PM addition, none was observed. This is explained by the fact that the temperatures seen at the wire surface are far too low to sublimate material. The melting point of the nickel-chromium alloy is approximately 1400°C and the estimated temperature of the wire in the setup is much lower, around 650°C. The work presented by Peineke et al. examined heated wires at temperatures near the melting temperature of the material and noted that evaporation rates are exponentially dependent on temperature. Particle concentrations reported by those authors were on the order of $10^5$ particles/cm$^3$. 
Chapter 6  Effects of Intake Temperature on Emissions From an Ethanol Fueled HCCI Engine

The key to HCCI combustion is controlling the SOC without a physical ignition event. Presented here is the first of a series of experiments designed to characterize the emissions consequences of three SOC control strategies and their relationship to the optimization of engine output, characterized by IMEP and BP. Specifically this work explores thermal conditioning of intake air as a SOC control strategy and the emissions effects realized due to altered combustion phasing.

Utilizing the procedures developed for characterizing nanoparticles from CI and SI engines, data on particles from 3 to 64 nm in mobility diameter from an ethanol HCCI engine will be presented. The instrumentation described above makes possible accurate assessment of particle size distributions and allows meaningful conclusions to be drawn for particles as small as 3 nm. A fully premixed fuel injection strategy will be used to minimize the effects of droplet evaporation and diffusion burning. As noted by Hyvönen et al. (2004), achieving congruent ignition conditions across multiple cylinders in the same engine can prove very difficult. Variations in the gas exchange process, compression ratio, cylinder cooling, fuel supply, and intake air temperature are all present at some level. The test apparatus is well suited to the experiments, with three easily manipulated variables available for control of SOC for individual cylinders: intake temperature, % EGR, and fuel properties.

Adopted in the earliest research efforts (Najt and Foster, 1983), manipulation of intake temperature to control SOC and extend the HCCI load and speed range has been used extensively in many research activities since. The evolution of fast response thermal management systems such as those reported by Flowers et al.(2005), Haraldsson et al. (2004), and Peng et al. (2007) gives credence to the use of thermal management as a means for controlling SOC under rapidly changing engine conditions.

In general, auto-ignition of low cetane fuels requires either unreasonably high compression ratios or preheating of the intake air. Additionally, low load demand for
intake heating in HCCI applications stems from low in-cylinder temperatures which limit the available thermal energy to the system.

The work presented examines the effects seen in both gas phase and PM emissions over a range of loads. At each load condition, intake temperature was varied while holding all other variables constant in order to maximize IMEP. At each intake temperature sub-condition in this optimization process, emissions measurements were made and then related to engine output. Intake temperatures were set and monitored via PID controlled intake heaters. Small variations in intake temperature required for congruent combustion across all cylinders were achieved through the independent intake air heaters. A similar biasing process was developed and successfully executed by Flowers et al. (2005) on a 6-cylinder HCCI engine. This was however, a proof of concept exercise and no emissions work was conducted. Contributions of PM from the heaters have been shown to be insignificant. There are two main goals for this series of experiments. The first is to add to the understanding of PM emissions in HCCI engines. Systematic research was carried out stepping through a set of predefined engine operating parameters. At each condition the engine was allowed to reach steady state and then emissions data were gathered. Resulting from this work is a map of PM characteristics for a high octane biofuel, ethanol, when thermal conditioning is used to control SOC in a HCCI engine. The second goal of this work will be to establish operating conditions that will give stable operation for subsequent testing with fuel blending and EGR used as combustion modifiers. Table 7 outlines the work executed for this set of experiments. The conditions were chosen based on the manufacturers speed corresponding to maximum rated torque with loads representing low and moderate engine operation.

6.1 Experimental Procedure

A significantly modified 2005 5.2 liter Isuzu engine (model 4HK1-TC) is used for these studies. The focus of the experiments is to explore the overall effects and mechanisms in which altering SOC via thermal management is manifested in exhaust emissions. The thermal management system developed for the engine, described in
detail in Section 5.1.1.3, provides a means to precisely control intake air temperature to each of the four engine cylinders independently. The fuel is 200 proof, undenatured ethanol. It is burned with the assumption that the fuel is completely evaporated and fully mixed with air upon SOC. To help promote complete fuel evaporation, the high pressure injector supply line is preheated to very near the 85º C ambient pressure boiling point of ethanol prior to injection. Additionally, intake air temperatures are also well above this boiling point. Calculation of droplet lifetimes at these conditions, summed with droplet lifetimes during compression, indicated total residence times of the droplet within the intake runner, cylinder head, and combustion chamber to be well in excess of the required time for full evaporation of the fuel droplets.

The experiments were conducted with constant fueling, as a result, changing intake air temperature led to small changes in the mass based $\lambda$. This is due to the volumetric nature of air induction into the naturally aspirated engine, and as a consequence, $\lambda$ values are not constant but rather presented as a narrow range. A single engine speed of 1500 RPM was used. This speed corresponded to the manufacturers specified engine speed at rated torque, it was selected to ensure smooth, well balanced engine operation free of resonant vibrations. Table 7 summarizes the three load conditions explored, the intake temperature ranges used, and the performance characteristics of each range.

<table>
<thead>
<tr>
<th>Engine Load</th>
<th>Low</th>
<th>Mid-1</th>
<th>Mid-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda$ range</td>
<td>5.0 - 4.2</td>
<td>4.0 - 3.5</td>
<td>3.2 – 3.0</td>
</tr>
<tr>
<td>Fueling Rate ($g_{EtOH}/sec$)</td>
<td>1.43</td>
<td>1.84</td>
<td>2.24</td>
</tr>
<tr>
<td>Fuel Input Energy Rate (kW)</td>
<td>42.5</td>
<td>54.6</td>
<td>66.5</td>
</tr>
<tr>
<td>Intake Temperature Range (°C)</td>
<td>110-160</td>
<td>90-130</td>
<td>90-110</td>
</tr>
<tr>
<td>Load Range (N·m)</td>
<td>48-55</td>
<td>59-93</td>
<td>118-128</td>
</tr>
<tr>
<td>IMEP Range (kPa)</td>
<td>221 - 236</td>
<td>233 - 318</td>
<td>383 - 403</td>
</tr>
</tbody>
</table>
At each of the loads, data were collected at 10°C intervals within the intake temperature ranges listed in Table 7. In each case, further temperature increases were halted as combustion advanced well before TDC and rates of pressure rise rose sharply. A drop in output power coupled with obvious audible increases in engine noise signified the onset of knock. The low end of the temperature range was bounded by misfire, indicated by intermittent losses in engine output power.

In addition to collection of data on particulate emissions as described in Chapter 3, gas phase emissions data was also collected. During all testing oxides of nitrogen (NO\textsubscript{X}), carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}), and unburned hydrocarbons (HC) were monitored. Gas phase emissions data were collected with conventional combustion gas analysis instruments. A California Analytical instruments model 600-HCLD NO\textsubscript{X} analyzer was used for all NO\textsubscript{X} measurements. The instrument measured wet emissions concentrations and was operated with a range of 0-10 ppm. HC emissions data, also sampled wet, were collected with a J.U.M. Engineering 3-300A hydrocarbon analyzer. CO and CO\textsubscript{2} data were collected dry and corrected via a wet-dry correction factor. The instruments used were a Horiba VIA-510 CO analyzer with an operating range of 0-5000 ppm, and a Rosemont 880 CO\textsubscript{2} analyzer with an operating range of 0-15%. For continuous monitoring of dilution ratios, a second CO\textsubscript{2} analyzer, Sable Systems model CA-10, sampled exhaust gas downstream of stage one dilution and was used to calculate dilution ratios.

Further range finding data was collected based on the conditions presented in Table 7. The engine exhibited stable operation from idle to loads up to 130 Nm. At a fixed load of 90 Nm and a fixed intake temperature of 110 °C, the apparatus operated smoothly at speeds ranging from 1000 RPM to 2250 RPM. Although engine operation was stable at 2250 RPM, oil temperature slowly increased with engine speed and surpasses 115°C at this condition.

### 6.2 Results and Discussion

The experimental results obtained while exploring the effects of intake air temperature on the performance and emissions of an ethanol HCCI engine are presented
below. Initially an analysis of combustion phenomena is conducted, followed by an emissions analysis. The results of both are compared with the literature and relationships between combustion properties and emissions in a dual fuel HCCI engine are then established.

6.2.1 Combustion Analysis

Looking first at the optimization of engine output, quantified here by IMEP, Figure 26 shows clear peaks for each of the load conditions where increased or decreased intake temperature results in a loss of output power. IMEP calculations are derived from the average IMEP across the 4 engine cylinders, each of which is based on 40 cycle averaged in-cylinder pressure data. Error bars represent the standard error of the mean for IMEP data across the 4 cylinders of the engine. BMEP is plotted on the same graph with the position of maxima in agreement with the calculated IMEPs as expected. By comparing an indicated parameter, derived from cylinder pressure, with a direct and external measure of engine output, BMEP, we are able to qualitatively validate the in-cylinder pressure data acquisition and reduction methods used.

![Figure 26: Optimization of engine output with intake temperature, ethanol HCCI, constant fueling, 3 loads, 1500 RPM](image-url)
Further investigation into the in-cylinder behavior will aid in understanding the phenomena producing the changes in engine output. Figure 27, Figure 28, and Figure 29 show the average in-cylinder pressure behavior for the three load conditions as intake temperature is varied. All pressure traces shown represent forty cycle individual cylinder averages, again averaged across the four engine cylinders for a total of 160 cylinder cycles. Error intervals shown represent the standard error of the mean calculated across the four engine cylinders. In agreement with the literature and preliminary modeling, distinct advances in SOC are obvious as intake temperatures increase. Peak pressures also increase with intake temperature at each of the three loads tested.

Also shown in Figure 27, Figure 28, and Figure 29 on the right hand y-axis is heat release rate. In calculating HRR, a single zone model similar to that presented by Stone (1999) is used. The cylinder contents are assumed to behave as ideal gases composed of an initially specified fuel and air mixture. The rates reported are net heat release rates and neglect heat transfer to the cylinder walls. Heat release analysis allows quantitative calculation of SOC timing, defined by the crank angle at which 10% of the heat energy of the fuel has been liberated (CA10) and burn duration CA90-CA10. Additionally in-cylinder temperature is calculated from the heat release analysis.

Compared with modeled behavior, much slower pressure rise as combustion occurs is shown here. Through these differences, the limitations of the model are made obvious. The sharp rates of pressure rise exhibited by the model are due to its single zone assumption with heat transfer neglected. In reality, wall cooling plays a significant role in absorbing energy from combustion and all reactions are not taking place in a perfectly simultaneous manner. Transfer of energy through the cylinder walls to the engines coolant system leads to temperature distribution with cooler areas igniting later. This leads to the slower rates of pressure rise seen in empirical in-cylinder pressure data.
Figure 27: In-cylinder pressure behavior of ethanol HCCI combustion, fixed fueling, $\lambda = 5.0-4.2$, 1500 RPM, varying intake temperature

Figure 28: In-cylinder pressure behavior of ethanol HCCI combustion, fixed fueling, $\lambda = 4.0-3.5$, 1500 RPM, varying intake temperature
Shown in Table 8 is a summary of the parameters used to characterize the combustion process. These data were calculated from the same 160 averaged in-cylinder pressure cycles shown in Figure 27, Figure 28, and Figure 29. It can be clearly seen that at all engine loads studied elevating intake temperatures leads to advances in SOC. More advanced combustion in turn leads to higher peak heat release rates. With more heat released prior to or very near TDC, the physical volume in which the energy is released becomes smaller, and due to engine geometry, does not change as much per CAD. This causes higher cylinder pressures and consequentially higher temperatures. The behavior is clearly represented at each load. Variability of the combustion data was shown to be low with the standard error of the mean in peak pressure timing calculated across the four cylinders of the engine ranging from .10 to .18 CAD. The coefficient of variation of the IMEP data across the 4 cylinders ranged from 0.5% to 5.3%.
Table 8: Summary of combustion properties, ethanol HCCI with varying intake temperature, 1500 RPM, 3 loads

<table>
<thead>
<tr>
<th>Intake Temp. (°C)</th>
<th>IMEP (kPa)</th>
<th>SOC (°ATDC)</th>
<th>Burn Dur. (CAD)</th>
<th>Peak HRR (J/CAD)</th>
<th>Peak Temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low Load</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>230</td>
<td>-2</td>
<td>10</td>
<td>80</td>
<td>1380</td>
</tr>
<tr>
<td>120</td>
<td>230</td>
<td>-3</td>
<td>8</td>
<td>90</td>
<td>1430</td>
</tr>
<tr>
<td>130</td>
<td>240</td>
<td>-5</td>
<td>7</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>140</td>
<td>230</td>
<td>-6</td>
<td>6</td>
<td>100</td>
<td>1500</td>
</tr>
<tr>
<td>150</td>
<td>230</td>
<td>-8</td>
<td>5</td>
<td>100</td>
<td>1540</td>
</tr>
<tr>
<td>160</td>
<td>220</td>
<td>-9</td>
<td>6</td>
<td>110</td>
<td>1560</td>
</tr>
<tr>
<td><strong>Mid Load 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>230</td>
<td>5</td>
<td>12</td>
<td>60</td>
<td>1220</td>
</tr>
<tr>
<td>100</td>
<td>310</td>
<td>1</td>
<td>9</td>
<td>110</td>
<td>1450</td>
</tr>
<tr>
<td>110</td>
<td>320</td>
<td>-2</td>
<td>7</td>
<td>130</td>
<td>1546</td>
</tr>
<tr>
<td>120</td>
<td>310</td>
<td>-4</td>
<td>5</td>
<td>140</td>
<td>1590</td>
</tr>
<tr>
<td>130</td>
<td>300</td>
<td>-6</td>
<td>5</td>
<td>150</td>
<td>1630</td>
</tr>
<tr>
<td><strong>Mid Load 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>90</td>
<td>380</td>
<td>5</td>
<td>10</td>
<td>130</td>
<td>1440</td>
</tr>
<tr>
<td>100</td>
<td>400</td>
<td>0</td>
<td>6</td>
<td>170</td>
<td>1630</td>
</tr>
<tr>
<td>110</td>
<td>380</td>
<td>-3</td>
<td>5</td>
<td>180</td>
<td>1690</td>
</tr>
</tbody>
</table>

Two efficiencies characterizing engine performance are shown in Figure 30. The first is combustion efficiency ($\eta_{\text{Combust}}$), calculated via Equation 23 from exhaust gas components, inlet fuel flow, and intake air flow. It represents a measure of the unused chemical energy carried out of the engine via the exhaust stream. In Equation 23, $y_i$ is the exhaust gas mass fraction of each combustible species, $h_{C,i}$ is the heat of combustion (LHV) for the given species, and $m$ represents inlet mass flows of fuel and air. Hydrogen, carbon monoxide, and unburned hydrocarbons are considered in this analysis. Although PM contains combustible materials, it was neglected. PM mass concentrations in the exhaust gas are roughly three orders of magnitude less than those of CO and HCs resulting in a minimal contribution to combustion efficiency. The second measure of efficiency shown for the engine is cycle efficiency, shown in Equation 24, and defined as the indicated power output divided by the fuel chemical energy input rate.
As the engine intake temperatures are increased, the most notable jumps in combustion efficiency are seen near the lowest intake temperatures. At these temperatures the fuel conversion begins to deteriorate as in-cylinder temperatures, in the coolest regions of the combustion chamber fall below those required for full oxidation of the fuel.
6.2.2 Emissions Analysis

Figure 31 summarizes brake specific emissions of CO, HC, NOX, and PM for ethanol HCCI at the low load operating condition. A total of 6 data sets were collected at 10° C intervals ranging from 110° to 160°C. Number weighted particle size distributions are shown in Figure 32 and mass weighted distributions in Figure 33. For all mass calculations a particle density of 1.0 g/cm³ was used. Schnieder et al. (2005) has shown this to be a reasonable estimate of density for PM originating from engine lubricating oil. This density was also used for PM studies on a gasoline fueled HCCI engine by Misztal et al. (2009a).

For all particulate matter distributions presented here, the error bars represent confidence intervals established at the 90% level using a t-distribution, sample sizes vary by data set from three to fifteen. Total levels of particulate number and mass show significant sensitivity to intake temperature, with mass levels spanning nearly 3 orders of magnitude. To clearly illustrate these variations and the details of the individual distributions, particle mass data is shown on a log-log plot.

Following expected trends, brake specific CO and HCs at the low load condition decrease as higher intake temperatures lead to higher in-cylinder temperatures through advanced combustion. These thermal conditions, promoting more complete oxidation of hydrocarbons, also lead to increasing NOX levels. Johansson (2007) describes the thermal window above 1500 K, the temperature necessary to oxidize CO to CO₂, and below 1800 K the point at which NOX formation increases exponentially, as the optimal operating arena for HCCI. Brake specific particulate emissions initially decrease with intake temperature reaching a poorly defined minimum between 130 and 150°C, and then increase. Referring to Table 8, the combustion parameters behave differently and follow continued trends in the same direction throughout the temperature range at every load. The reason for erratic PM emissions behavior at this condition is not fully understood. However the particle mass distributions shown in Figure 33 are all similar in shape with overlapping error bands. At the low load conditions distinguishing between the magnitudes of the mass distributions with 90% confidence is difficult due to high variability.
Figure 31: Brake specific emissions from ethanol HCCI combustion with varying intake temperature, fixed fueling, $\lambda = 5.0-4.2$, 1500 RPM

Figure 32: Mobility size distributions from ethanol HCCI combustion with varying intake temperature, fixed fueling, $\lambda = 5.0-4.2$, 1500 RPM
The brake specific CO, HCs, and NO\textsubscript{X} emissions trends at the mid load 1 condition are similar to those at the low load condition. Increasing intake temperature leads to significant in-cylinder temperature increases through advanced combustion. This promotes more complete hydrocarbon oxidation, but also promotes NO\textsubscript{X} formation. It should be noted however that although NO\textsubscript{X} values show notable increases with intake temperature, they remain extremely low over all conditions and intake temperatures tested. The BSCO and BSHC values start out much higher than at the low load condition, but as combustion temperatures increase, they fall dramatically until on par with the low load levels. Lean burn HCCI combustion has excess oxygen available for oxidation CO and HCs, but slow reaction rates prevent complete oxidation fuel due to low in-cylinder temperatures.

Brake specific PM emissions are lower than at the low load condition, and like NO\textsubscript{X}, increase strongly with intake temperature, opposite the trend shown for CO and HCs. Particle number and mass distributions presented in Figure 35 and Figure 36.
respectively show increasing concentration and size with increasing intake temperature. Error bars show considerable fractional variability, especially at low temperatures.

Figure 34: Brake specific emissions from ethanol HCCI combustion with varying intake temperature, fixed fueling, $\lambda = 4.0-3.5$, 1500 RPM
Figure 35: Mobility size distributions from ethanol HCCI combustion with varying intake temperature, fixed fueling, $\lambda = 4.0-3.5$, 1500 RPM

Figure 36: Mass distributions from ethanol HCCI combustion with varying intake temperature, fixed fueling, $\lambda = 4.0-3.5$, 1500 RPM
The mid load 2 brake specific emissions data in Figure 37, show similar behavior in brake specific CO, HC and NO\(_X\) emissions to the previous two loads. Like the mid load 1 number size distribution data, Figure 38 shows increases in number concentration as intake temperatures are increased. However a decrease in mobility diameter at an intake temperature of 110°C causes mass concentrations to decrease.

**Figure 37:** Brake specific emissions from ethanol HCCI combustion with varying intake temperature, fixed fueling, \(\lambda=3.2-3.0\), 1500 RPM
Figure 38: Mobility size distributions from ethanol HCCI combustion with varying intake temperature, fixed fueling, $\lambda = 3.2-3.0$, 1500 RPM

Figure 39: Mass distributions from ethanol HCCI combustion with varying intake temperature, fixed fueling, $\lambda = 3.2-3.0$, 1500 RPM
The particle characterization work presented in Chapter 9 demonstrates that nearly all the particles measured in this work were volatile. Furthermore, no measurable concentration of solid accumulation mode particles has been observed. In the absence of solid nucleation mode particles to act as adsorption sites the only gas to particle conversion processes available for organic vapors in the exhaust as it dilutes and cools are homogeneous nucleation and condensation. This leads the formation of volatile nucleation mode particles. Tobias et al. (2001) reports that the composition of volatile nucleation mode particles emitted by a CI engine shifts towards characteristics more indicative of lubricating oil as loads increase. This suggests that higher in-cylinder temperatures led to more lubricating oil related nucleation mode particle. For all loads examined in the current HCCI study, the highest in-cylinder temperatures led to the highest total mass of PM. Sakurai et al. (2003) later found that in diesel engines running at light to moderate loads, volatile particulate matter was composed of at least 95% compounds originating from unburned lubricating oil. Although different from standard CI engines, HCCI engine have many characteristics in common; first, the charge is ignited via compression, second, combustion generally occurs in a globally lean environment, third, exhaust temperatures are usually much cooler than those found in SI engine operation, and fourth, a similar configuration of the piston, piston rings, and lubrication system is used. Thus delivery of lubricating oil to the combustion chamber and its processing by the combustion system may be similar. With undenatured ethanol used as the fuel in these tests, fuel contributions of sulfur, heavy hydrocarbons, trace metals, and other impurities are virtually nonexistent. Although the HC emissions relatively high, FTIR measurements showed them to be mainly unburned ethanol along with smaller quantities of methane, ethylene, and low molecular weight aldehydes, all of which are too volatile to condense under sampling conditions used here. Furthermore, unburned HC decrease at higher intake air temperatures while PM emissions increase.

Examining a hydrogen SI engine, Miller et al (2007) noted that as in-cylinder temperature increased, organic carbon levels in the PM also increased. The authors
thought this was likely due to more complete breakdown of the oil lining the cylinder walls. Data collected in this HCCI work suggests similar behavior is taking place here.

A multiple regression analysis was performed on all of the variable intake temperature ethanol HCCI data to examine the dependence of total particulate mass on select combustion parameters. The influence of the independent variables; SOC, combustion duration, peak temperature, and peak heat release rate on the dependant variable, total particulate mass, was analyzed. The size of the sample set used for analysis was 14, which led an $R^2$ value of .44. This relatively low $R^2$ value reflects a high degree of variability in the data. Examining the brake specific data presented in Figure 31, Figure 34, and Figure 37 gives insight into the primary contributor to a high degree of variability. The low load BSPM results, show in Figure 31 clearly exhibit a high degree of variability with little apparent trend over the intake temperature spanned. Comparing the $R^2$ value for the entire data set with the one calculated without the low load data included we see a significant change. The new data set had a sample size of 8 and yielded a $R^2$ value of .95. These results indicate the possibility of errors in the low load data set, the cause of which is unknown at this time.

### 6.3 Conclusions

Both gas phase and particulate brake specific emissions exhibit very clear dependencies on intake air temperature. For each of the three loads tested, emissions of CO and HC were highest at the lowest intake temperatures. These temperatures also corresponded to points with significant losses in engine output power and efficiency, suggesting incomplete combustion.

A dependence of total particle mass and number on intake temperature was observed at all loads. Pure HCCI combustion is not base on flame propagation and produces no locally rich burning, so that soot formation is generally avoided. With no soot agglomerates acting as organic vapor sinks, these vapors act as precursors to nucleation and lead to significant numbers of nucleation mode particles. Although some variation is seen, in most cases the total particulate mass increases with peak HRR or peak in-cylinder temperature. The dependence of total PM mass on peak temperatures
suggests that PM formation in fully premixed HCCI engines is associated with organic carbon vapor from vaporized or atomized lubricating from the cylinder walls and piston ring pack. Advanced SOC leads to higher heat release rates and higher in-cylinder temperatures leading to elevated cylinder liner temperatures which increase the vapor pressures and evaporation rates of organic compounds in the lubricating oil.

These results provide useful information on the influence of intake temperature at various loads. However in later experiments it was found that particulate emissions were lower at the same operating conditions as investigated here. The new findings were found to be repeatable over all of the three loads. The subsequent testing spanned three months and included multiple data sets. A possible explanation for these differences is given below. The engine used in these test was originally configured and used extensively as a conventional Diesel engine. The variable intake temperature experiments were the first one conducted after the engine was converted to HCCI operation. It is possible that the engine itself was not adequately broken in to remove valve, ring, and piston deposits associated with its previous history. After a rigorous period of operation at moderate loads and speeds up to 2250 RPM, the engine exhibited the drop in PM emissions. After this drop the engine showed excellent repeatability throughout all further experiments. All further data presented was collected after this rigorous break in period.
Chapter 7  The Effect of EGR on Emissions in an Ethanol Fueled HCCI Engine

Because EGR serves two purposes in HCCI engines, adding thermal energy to the uncompressed mixture and acting as an energy sink to slow oxidation kinetics, it is widely used for extending the HCCI operating range. Since the earliest studies by Onishi et al. (1979), Noguchi et al. (1979), Najt and Foster (1983), and Thring (1989), at least some level of EGR has been utilized in nearly all HCCI experiments. Recently, work by Au et al. (2001) and Lü et al. (2005b) has contributed to the understanding of SOC effects and burn duration effects of EGR. More modern applications like those explored by Milovanovic (2004) take advantage of rapid response variable valve timing to alter in-cylinder residual levels during transient engine operation. These applications show promise for commercialization by altering effective compression ratio, EGR rate, and ultimately SOC.

The goal of this work is to determine the influence of using EGR to control SOC on the emissions from an ethanol fueled HCCI engine. PM emissions are closely examined in order to explore the relationship between EGR and PM formation. Data are presented on combustion behavior, gas phase emissions, and particulate phase emissions and a relationship between EGR, combustion behavior, and emissions is established.

7.1  Experimental Procedure

In conventional SI and CI engines, EGR has significant effects on emissions of both PM and NOx. This work closely examines the relationship between EGR and PM formation in HCCI engines. A global EGR rate is initially set at 0, 10, 25, and 50% of intake air volume. This is accomplished by measuring CO₂ concentrations in the exhaust, the intake downstream of EGR mixing, and the ambient intake air. An EGR rate is then calculated using Equation 22. The maximum output condition from the thermal conditioning experiments was used as the starting point (0% EGR) for this work. Consistent with the thermal conditioning experiments, fuel flows were kept
constant for each load throughout the EGR work. The feedback to the thermal management system is located downstream of the EGR inlet allowing a constant intake temperature to be maintained as the flow of hot exhaust gas to the intake was varied. Although EGR cooling was in place, it is necessary to note that at the mid load 2 condition, with 25% and 50% EGR, the EGR cooler was not able to maintain temperatures below the PID set point temperature. This resulted in elevated intake temperatures at these conditions. Table 9 shows the test conditions examined. EGR rates, realized lambdas calculated via carbon balance, and intake temperature set points are shown.

Table 9: Test conditions for ethanol HCCI with varying EGR experiments

<table>
<thead>
<tr>
<th>Low Load</th>
<th>Mid Load 1</th>
<th>Mid Load 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>T\text{Intake} = 130 °C</td>
<td>T\text{Intake} = 110 °C</td>
<td>T\text{Intake} = 100 °C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>EGR Rate</th>
<th>\lambda_{C-Bal}</th>
<th>EGR Rate</th>
<th>\lambda_{C-Bal}</th>
<th>EGR Rate</th>
<th>\lambda_{C-Bal}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0 %</td>
<td>4.35</td>
<td>0.0 %</td>
<td>3.63</td>
<td>0.0 %</td>
<td>3.06</td>
</tr>
<tr>
<td>10.9 %</td>
<td>3.68</td>
<td>10.9 %</td>
<td>3.02</td>
<td>10.7 %</td>
<td>2.61</td>
</tr>
<tr>
<td>25.0 %</td>
<td>3.16</td>
<td>25.9 %</td>
<td>2.56</td>
<td>23.3 % *</td>
<td>2.10</td>
</tr>
<tr>
<td>50.9 %</td>
<td>1.83</td>
<td>49.3 %</td>
<td>1.53</td>
<td>48.8 % *</td>
<td>1.21</td>
</tr>
</tbody>
</table>

*Intake temperatures exceeded set point values due to EGR cooler limitations

The same modified 2005 5.2 liter Isuzu engine (model 4HK1-TC) as was used in the thermal management work is employed for these studies. The engine was operated at a speed of 1500 RPM. This speed corresponded to the manufacturers specified engine speed at peak rated torque, it was selected to ensure smooth, well balanced engine operation free of resonant vibrations. The same loads were investigated here as in the previous thermal conditioning experiments. They were selected at reasonable intervals representing low to moderate engine loads. The highest load condition was bounded by the onset of engine knock. The fuel was 200 proof, undenatured ethanol.

These exercises required cylinder to cylinder biasing to establish a base level of uniform EGR distribution and combustion across all cylinders. Fine tuning of EGR rates was accomplished with independently controlled gate valves on the intake of each
cylinder. Precise measurement of individual EGR rates was possible via measurement ports downstream of the EGR inlet on each intake runner, illustrated in Figure 23. Small variations in individual cylinder intake temperature were dealt with through the subtle use of the thermal management system. Because changing EGR rate affected CO$_2$ levels in the exhaust gas, an iterative approach was required to compute final EGR proportions. Actual EGR levels were considered acceptable if they were within 10% of the target EGR proportion.

Due to lean operation of the engine, significant oxygen remains available in the exhaust after combustion. In order to obtain actual lambda values, both fresh air and oxygen originating from the exhaust must be accounted for. Müller (2010) presents a method of calculating fuel to air ratio with the inclusion of oxygen from EGR. Internal EGR, or residuals, are neglected for this analysis. The engine is a high compression four stroke with modest valve overlap, leaving little residual gas in the cylinder from cycle to cycle.

7.2 Results and Discussion

As perhaps the most universal tool for combustion control in HCCI engines, EGR limits rates of pressure rise and controls peak pressures. Additionally, through the addition of thermal energy to the fuel and air charge, it can also serve to advance combustion. The experimental results obtained through varying the EGR rate to an ethanol HCCI engine at three loads are presented here. Initially an analysis of combustion phenomena is conducted, followed by an emissions analysis. The results of both are compared with the literature and relationships between combustion properties and emissions in a dual fuel HCCI engine are established.

7.2.1 Combustion Analysis

Figure 40, Figure 41, and Figure 42 show in-cylinder pressure behavior from the three engine loads tested. The limiting effect of EGR on peak pressures and rate of pressure rise is evident from examination of these figures. The increase in specific heat of the mixture due to EGR is also made clear by the compression behavior documented in these figures. In Figure 42, which is for the highest load condition, the limitations of
the EGR cooler are made clear through the details of the pressure behavior. The dual thermal and chemical effects of EGR in HCCI engines are clearly evident. Initially, at low EGR levels, the EGR cooler can maintain a constant intake temperature, allowing documentation of purely the chemical effect of EGR. It then becomes apparent that intake temperatures are increasing due to the SOC advance shown in the 25 and 50% EGR cases. Measured intake temperatures for these cases were 110° and 140° respectively for these conditions, compared to the 100°C set point used at this load.

Also shown in Figure 40, Figure 41, and Figure 42 on the right hand y-axis is heat release rate. In calculating HRR, a single zone model similar to that presented by Stone (1999) is used. The cylinder contents are assumed to behave as ideal gases composed of an initially specified fuel and air mixture. The rates reported are net heat release rates and neglect heat transfer to the cylinder walls. Heat release analysis allows quantitative calculation of SOC timing, defined by the crank angle at which 10% of the heat energy of the fuel has been liberated (CA10) and burn duration CA90-CA10. Additionally in-cylinder temperature is calculated from the heat release analysis.

Figure 40: In-cylinder pressure behavior of ethanol HCCI combustion with varying EGR rate, fixed fueling, low load, 1500 RPM, 130° intake temperature
Figure 41: In-cylinder pressure behavior of ethanol HCCI combustion with varying EGR rate, fixed fueling, mid load 1, 1500 RPM, 110° intake temperature

Figure 42: In-cylinder pressure behavior of ethanol HCCI combustion with varying EGR rate, fixed fueling, mid load 2, 1500 RPM, 100° target intake temperature
Table 10: Summary of combustion properties, ethanol HCCI with varying EGR rate, 1500 RPM, 3 loads

<table>
<thead>
<tr>
<th>EGR Rate</th>
<th>IMEP (kPa)</th>
<th>SOC (ºATDC)</th>
<th>Burn Dur. (CAD)</th>
<th>Peak HRR (J/CAD)</th>
<th>Peak Temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low Load</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>240</td>
<td>-5</td>
<td>7</td>
<td>100</td>
<td>1510</td>
</tr>
<tr>
<td>10%</td>
<td>240</td>
<td>-4</td>
<td>8</td>
<td>90</td>
<td>1540</td>
</tr>
<tr>
<td>25%</td>
<td>250</td>
<td>-4</td>
<td>8</td>
<td>90</td>
<td>1500</td>
</tr>
<tr>
<td>50%</td>
<td>240</td>
<td>-2</td>
<td>10</td>
<td>80</td>
<td>1600</td>
</tr>
<tr>
<td>Mid Load 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>320</td>
<td>-1</td>
<td>6</td>
<td>120</td>
<td>1530</td>
</tr>
<tr>
<td>10%</td>
<td>320</td>
<td>0</td>
<td>8</td>
<td>120</td>
<td>1560</td>
</tr>
<tr>
<td>25%</td>
<td>330</td>
<td>1</td>
<td>9</td>
<td>110</td>
<td>1520</td>
</tr>
<tr>
<td>50%</td>
<td>320</td>
<td>1</td>
<td>10</td>
<td>100</td>
<td>1650</td>
</tr>
<tr>
<td>Mid Load 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>390</td>
<td>0</td>
<td>6</td>
<td>160</td>
<td>1590</td>
</tr>
<tr>
<td>10%</td>
<td>400</td>
<td>5</td>
<td>11</td>
<td>130</td>
<td>1540</td>
</tr>
<tr>
<td>25%</td>
<td>410</td>
<td>4</td>
<td>9</td>
<td>140</td>
<td>1650</td>
</tr>
<tr>
<td>50%</td>
<td>390</td>
<td>-1</td>
<td>7</td>
<td>130</td>
<td>1820</td>
</tr>
</tbody>
</table>

Table 10 summarizes the combustion properties calculated from in-cylinder pressure data at each test condition. Variability of the combustion data was shown to be low with the standard error of the mean in peak pressure timing calculated across the four cylinders of the engine ranging from .18 to .34 CAD. The coefficient of variation of the IMEP data across the 4 cylinders ranged from 1.0 % to 4.0 %. The role of EGR in increasing burn duration and limiting peak rates of heat release is shown to be in good agreement with the literature. Rahbari (2008) modeled the effects of EGR on ethanol HCCI and found increasing EGR delays SOC, extends burn duration, and limits peak cylinder temperatures. Reasonable agreement was also found with the work of Au et al. (2001) and Lü et al. (2005b). However, these authors did not show significant delay in SOC with increasing EGR rate. Dec et al. (2009) have found that in order to maintain a constant MFB50, which refers to the point in the cycle where 50 percent of the fuel has been burned, increasing intake temperatures were required as EGR rate was increased. This translates into increasing EGR rates leading to delayed SOC at constant intake temperature. Additionally Sjöberg et al. (2007) have clearly demonstrated a retarding effect of EGR on ignition timing. The primary reasons for the effect are listed as; first, the high specific heat of the gases reduces the compressed gas temperature, and second, reductions of O₂ concentration limits available O₂ for combustion reactions.
Figure 43 shows the response of cycle and combustion efficiency to changes in EGR at three engine loads. In all cases, cycle efficiency remains relatively constant showing only a slight drop at the highest levels. A similar trend was recently documented by Swami-Nathan et al. (2010) for varying EGR rates in an acetylene fueled HCCI engine.

Combustion efficiency does show a slight decreasing trend as EGR rates are increased at each load condition. EGR is employed in SI engines to act as a diluent and soak up thermal energy during combustion (Abd-Alla, 2002). EGR should have a similar effect in the cases studied here. For all loads shown, peak pressures fall as EGR rates are increased. Because the combustion regime is near the low temperature limit for the oxidation of CO to CO$_2$, 1400-1500 K, lower in-cylinder temperatures lead to increasing levels of CO in the exhaust, which is most prominently shown in the Mid load 2 emissions data. This is one of the reasons for reduced combustion efficiency. Emissions trends for CO and HCs at the Low Load and Mid Load 1 conditions do not agree with the decreases in combustion efficiency shown in Figure 43. This is likely due to the contributions of hydrogen in the exhaust stream to combustion efficiency. Because hydrogen was not directly measured for the EGR experiments, the assumption of a fixed water-gas equilibrium constant was used to calculate hydrogen emissions in the carbon balance process outlined by Müller (2010). The increases in calculated hydrogen emissions at higher EGR rates lead to decreases in combustion efficiency which may be an artifact of this assumption.
7.2.2 Emissions Analysis

A summary of brake specific emissions from the low load EGR tests is shown in Figure 41. It can be seen that brake specific NO\textsubscript{x} and PM both decrease as EGR is increases, but CO and HC fall only slightly. The relatively small influence of EGR on CO and HC emissions is due to the competing influences of temperature and oxygen concentration. As EGR is increases, peak in-cylinder temperature generally rises as shown in Table 10 but oxygen decreases due to increasing lambda as shown in Table 9. Oxygen in the exhaust is reduced by nearly 60% at all loads from the 0% EGR condition to the 50% EGR condition. Response of CO and HC emissions to EGR at mid load 1 shown in Figure 44 is similar to low load.
Figure 44: Brake specific emissions from ethanol HCCI combustion with varying EGR rate, 1500 RPM, 130°C intake temperature, low load

For all particulate size distributions presented here, confidence intervals are established at the 90% level using a t-distribution, sample sizes vary by data set from five to twenty. Error bars shown for BSPM in Figure 44, Figure 47, and Figure 50 also represent a 90% confidence interval. Error bars shown for brake specific gas phase emissions represent the standard error of the mean for each data point. Sample sizes ranged from 2 to 7. Particle number and mass show significant sensitivity to EGR, with mass levels spanning nearly 3 orders of magnitude. To clearly illustrate these variations and the details of the individual distributions, particle mass data is shown on a log-log plot.

Figure 45 and Figure 46 show size and mass distributions respectively for the low load condition. Although little difference is seen in particulate emissions at low EGR levels, as EGR reaches 25% and then 50%, a significant drop in both number and mass is clear at each level. Taking into account the fixed fueling rate and relatively stable cycle efficiencies, there are no detrimental effects of high EGR levels on engine performance or emissions. Stable engine output coupled with the sharp drop in total
particulate mass leads to sharp drops in brake specific PM as EGR increases as shown in Figure 44.

![Figure 45: Mobility size distributions with varying EGR rate, ethanol HCCI combustion, fixed fueling, 1500 RPM, 130° intake temperature, low load](image)

For the low load and mid load 1 conditions, increasing EGR levels lead to downward trends in both total number and particle mobility diameter. The number concentrations for each of these loads are shown in Figure 45 and Figure 48 respectively. The combined effect of these two characteristics is a very significant reduction in particle mass concentration. The corresponding mass distributions are shown in Figure 46 and Figure 49.

The NO\(_X\) - PM tradeoff, summarized by Ladommatos, *et al.* (1999), Abd-Alla (2002), and Zheng *et al.* (2004), in traditional CI engines is clearly not present in these HCCI data. This behavior represents an important advantage of the HCCI engine and is consistent with overall findings in the HCCI literature.
Figure 46: Mass distributions with varying EGR rate, ethanol HCCI combustion, fixed fueling, 1500 RPM, 130° intake temperature, low load

Figure 47: Brake specific emissions from ethanol HCCI combustion with varying EGR rate, 1500 RPM, 110°C intake temperature, mid load
Figure 48: Mobility size distributions with varying EGR rate, ethanol HCCI combustion, fixed fueling, 1500 RPM, 110° C intake temperature, mid load 1

Figure 49: Mass distributions with varying EGR rate, ethanol HCCI combustion, fixed fueling, 1500 RPM, 110° C intake temperature, mid load 1
Figure 47 is a plot of brakes specific emissions against EGR for mid load 2. This operating condition shows somewhat different emissions behavior from the lighter load conditions. Both CO and HC emissions peak at 10% EGR and then fall, but CO rises again after 25% EGR while HC continues to fall. The heat release data in Table 10 show that peak in-cylinder temperature initially falls between 0 and 10% EGR but then increases. On the other hand, lambda and exhaust oxygen decrease steadily as EGR increases. The opposing effects of in-cylinder oxygen and temperature may explain the observed trend of CO but the opposite trends in CO and HC at the highest EGR rates suggests that HC oxidation may be more temperature dependent that CO oxidation. However another effect may be playing a role. Although peak in-cylinder temperatures are at their highest, peak heat release rates fall significantly in the 50% EGR case. Due to the slower rate of heat release for this condition, wall heat transfer may have more of an opportunity to cool the mixture in the cylinder wall boundary layer leading to slow oxidation in this region. However this does not explain the opposite trends in CO and HC emissions at the highest EGR rates. In this scenario global cylinder temperatures can remain high as the mixture combusts reasonably close to TDC. However as indicated by the burn duration and HRR, the combustion process is relatively slow, allowing the CAD timescale of combustion and timescale of heat transfer to approach parity.
Figure 50: Brake specific emissions from ethanol HCCI combustion with varying EGR rate, 1500 RPM, 100°C intake temperature*, mid load 2

Figure 51: Mobility size distributions with varying EGR rate, ethanol HCCI combustion, fixed fueling, 1500 RPM, 100°C intake temperature*, mid load 2
Figure 52: Mass distributions with varying EGR rate, ethanol HCCI combustion, fixed fueling, 1500 RPM, 100°C intake temperature*, mid load 2

The trends in NOx and PM emissions shown in Figure 47 are somewhat more complex than for the light load cases. Both show a local minimum between 10 and 25% EGR followed by an increase and then a slow decrease. The trends in peak in-cylinder temperature and peak HRR rate are also complex with a general increase in temperature with EGR but with a dip in temperature a 10% EGR while HRR, like PM and NOx, falls, rises, and then fall again as EGR increases. Although the relationship between in-cylinder temperatures and PM mass is not obvious, a clear relationship between HRR and PM mass is apparent. Increased HRR caused total PM mass to trend upwards. This represents similar behavior to that reported in SI engines by Kayes and Hochgreb (1999), assuming higher loads are indicative of higher peak HRRs. Like the lighter load conditions, a PM-NOx tradeoff with respect to EGR (Ladommatos, et al, 1999; Abd-Alla, 2002; Zheng et al., 2004) is not present, the two emissions respond in the same way to EGR, although the response of PM is stronger.

Just as in the variable intake temperature cases examined in Chapter 6 the particle data are consistent with the view that particles emitted from pure HCCI combustion, at least for the pure ethanol fuel used here, are mainly formed from partially burned
lubricating oil. Thus the findings of Tobias et al. (2001) and Sakurai et al. (2003) that the volatile components of PM are very similar to lubricating oil may also apply here. The difference is that unlike a Diesel engine there are no solid accumulation mode particles to adsorb the oil so the resulting particles are nearly entirely volatile.

7.3 Conclusions

The effects of EGR on an ethanol fueled HCCI engine were studied at constant speed and three loads. Data were collected on performance, in-cylinder behavior, and emissions. At all loads the effect of increasing EGR leading to longer burn duration was confirmed. This is in good agreement with multiple published findings. In most cases studied, increases in EGR led to decreases in both NOx and total PM mass and number emissions. The mid load 2 condition showed a slightly more complex trend with a general trend of decreasing PM and NOx emissions with increasing EGR but local minima for both pollutants between 10 and 25% EGR. This was a consequence of an underperforming EGR cooler that led to more advanced combustion and elevated heat release rates and in-cylinder temperatures at high EGR rates.

The influence of EGR on combustion behavior was as expected, extending burn duration, limiting rates of pressure rise, and minimizing peak rates of heat release. Cooler combustion led to small reductions in NOx as EGR rates were increased. CO and HC emission remained relatively stable at each condition throughout varying EGR rates most likely due to competition between increased cylinder temperatures promoting oxidation and decreasing air to fuel ratios limiting oxygen available.

PM emissions appear to be formed from lubricating oil. In general, increased rates of EGR led to lower PM number and mass concentrations and smaller particle diameters. These reductions are thought to be due to the lower peak rates of heat release leading to less heat transfer to cylinder walls and reductions in the rates of evaporation of oil films from in-cylinder surfaces.

Conducting a multiple regression analysis on the entire ethanol HCCI with variable EGR rate data set illustrates the dependence of total particulate mass on select combustion parameters. The influence of the independent variables; SOC, combustion
duration, peak temperature, and peak heat release rate on the dependant variable, total particulate mass, was analyzed. The size of the sample set used for analysis was 12, which led an R2 value of .83.
Chapter 8 The Effects Fuel Blending on Emissions in an Ethanol and Hydrogen Fueled HCCI Engine.

The advanced capabilities of onboard engine ECUs enable dual fuel technology to be feasible for implementation in the transportation sector. Although the research community has not agreed upon a scale to quantitatively gauge fuel ignition properties in an HCCI mode, analogous to cetane in CI mode or octane in SI mode, there are obvious fuel effects governing SOC. Utilizing an intake charge blended from two distinct fuels gives a scenario of easily altered and precisely controlled global fuel properties. This can enable the operator to manipulate charge properties easily by varying the proportions of the two fuels. The interactions of fuel blending with combustion timing are complex and vary significantly with the fuels selected. For this study hydrogen and ethanol were chosen as the fuel pair to be studied because hydrogen rich gases can be made relatively easily onboard by reforming ethanol. As reported by Hosseini and Checkel (2007) different effects can dominate the interactions giving hydrogen the ability to have directly opposite effects on ignition timing depending on the base fuel. These effects are not the focus of this study which will be limited to the influence of hydrogen addition on overall combustion timing and duration quantified via combustion parameters; SOC, burn duration, peak heat release rate, peak temperature, IMEP and emissions.

The goal of this work is to look at fuel blending as a fast response means of controlling combustion phasing and the corresponding influences on emissions. The SOC advances reported by Yap et al. (2004, 2006), Hosseini and Checkel (2006, 2008) altered timings on the order of 0 to 6 CAD. Although these are significant timing changes, they do not offer adequate ignition enhancement to mitigate the need for thermal conditioning of intake air. For the engine used in the current work operating the engine in a HCCI mode still required some level of intake heating. The work described in Chapter 6 explored optimization of engine output with intake temperature control. These optimized intake temperature conditions are used as the starting point, or zero hydrogen energy condition, for a series of fuel blending experiments. Changes in the
combustion process are quantified and the relationships between hydrogen energy proportion and emissions characteristics are explored.

8.1 Experimental

Ethanol and hydrogen fuels were selected due to their viability as renewable fuels. Ethanol, though controversial by source, is easily utilized through existing infrastructure and is left with few barriers in terms of engine technology. Hydrogen as a primary fuel faces many logistical and technological barriers. However on-board auto-thermal reforming can provide the small amounts hydrogen rich gas from a variety of liquid fuel sources. This series of experiments examines the effects seen in emissions as a range ethanol and hydrogen proportions are tested. Testing was conducted at three load conditions, with the previously optimized intake temperatures for neat EtOH HCCI used in two of the three. At the Mid-Load 2 condition high rates of pressure rise, indicating the onset of engine knock, were encountered with 25% H$_2$ energy when the optimized 100°C intake temperature was used. The intake temperature was lowered to 95° to allow a constant intake temperature to be maintained while only hydrogen energy proportion was altered. A summary of the operating conditions is given in Table 11. Engine speed was selected corresponding to the manufactures rated torque speed in order to ensure smooth engine operating. Loads were selected at reasonable intervals representing low to moderate engine loads. The highest load condition was bounded by the onset of engine knock. Because of the different heating values of the two fuels, different blends of ethanol and hydrogen require slightly different global fuel to air ratios to maintain constant engine output.
Table 11: Fuel Blending Test Conditions

<table>
<thead>
<tr>
<th>Engine Load Condition</th>
<th>Low</th>
<th>Mid 1</th>
<th>Mid 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intake Temperature (°C)</td>
<td>130</td>
<td>110</td>
<td>95</td>
</tr>
<tr>
<td>λ-Range</td>
<td>4.35-4.42</td>
<td>3.32-3.62</td>
<td>2.98-3.11</td>
</tr>
<tr>
<td>Load (Nm)</td>
<td>53</td>
<td>89</td>
<td>125</td>
</tr>
<tr>
<td>IMEP Range (kPa)</td>
<td>224-231</td>
<td>310-317</td>
<td>383-403</td>
</tr>
<tr>
<td>% Hydrogen Output Energy Range</td>
<td>0-25</td>
<td>0-25</td>
<td>0-25</td>
</tr>
<tr>
<td>Flow Rate Range of EtOH Energy In (kW)</td>
<td>42.5-38.9</td>
<td>54.6-47.8</td>
<td>65.9-58.5</td>
</tr>
<tr>
<td>Flow Rate Range of H₂ Energy In (kW)</td>
<td>0-3.47</td>
<td>0-8.34</td>
<td>0-8.16</td>
</tr>
</tbody>
</table>

In order to maintain constant engine output while varying the H₂:EtOH proportion, the following procedure was used.

- First, steady operation of the HCCI engine was achieved on neat ethanol fuel.
- Data was then collected at this condition to use as the 0% hydrogen energy baseline.
- The fuel injector pulse width was then shortened, reducing fuel flow, until the desired percentage of torque, or output energy, was removed.
- Last, hydrogen flow was turned on to the hydrogen injectors and the supply pressure adjusted until the engine was again running at the initial output torque.
8.2 Results and Discussion

The experimental results of supplementing ethanol HCCI combustion with hydrogen fuel are presented below. Initially an analysis of combustion phenomena is conducted, followed by an emissions analysis. The results of both are compared with the literature and relationships between combustion properties and emissions in a dual fuel HCCI engine are established.

8.2.1 Combustion Analysis

Figure 53 through Figure 55 show in-cylinder pressure behavior with the addition of supplemental hydrogen to ethanol HCCI combustion. Each plotted data set was computed via 40 cycle average and then again averaged across each of the 4 cylinders. There is little change in the compression behavior because H2, N2, and O2, all diatomic gases have essentially the same ratio of specific heats, $\gamma$. Ethanol is polyatomic and has a lower value of $\gamma$ but the fractional replacement of ethanol by hydrogen is small and does not appreciably influence the overall value of $\gamma$ during compression. Also shown in Figure 53, Figure 54, and Figure 55 are plots of heat release rate versus crank angle derived from the pressure data. In calculating HRR, a single zone model similar to that presented by Stone (1999) is used. The cylinder contents are assumed to behave as ideal gases composed of an initially specified fuel and air mixture. The rates reported are net heat release rates and neglect heat transfer to the cylinder walls. Heat release analysis allows quantitative calculation of SOC timing, defined by the crank angle at which 10% of the heat energy of the fuel has been liberated (CA10) and burn duration CA90-CA10. Additionally in-cylinder temperature is calculated from the heat release analysis.

At the low load condition the combustion effects of hydrogen were very modest; however as loads increased, clear trends developed showing a distinct advance in SOC timing with increased % hydrogen energy. These timing advances lead to higher peak pressures and increased rates of pressure rise in all cases examined.
Figure 53: In-cylinder pressure behavior of EtOH and H$_2$ HCCI combustion, varying H$_2$ output power, 1500 RPM, low load, 130° intake temperature

Figure 54: In-cylinder pressure behavior of EtOH and H$_2$ HCCI combustion, varying H$_2$ output power, 1500 RPM, mid load 1, 110° intake temperature
The general trends of the in-cylinder pressure behavior from ethanol HCCI with supplemental hydrogen fueling agree well with those found during preliminary modeling exercises. In both modeled and experimental work the effects of hydrogen were modest but did serve to advance combustion. Increases in hydrogen energy resulted in advancement of SOC. Differences between experimental and modeled behavior due to heat loss to the cylinder walls is also evident here and show similar trends as the intake temperature and EGR comparisons.

Exploring the in-cylinder pressure trends in Figure 53 to Figure 55 we see clear agreement with the work of Yap et al. (2004) where increased hydrogen energy leads to advances in combustion timing. We are however reporting more pronounced effects at higher engine loads, differing from the findings of those authors. Yap et al. (2004) were using natural gas as the primary fuel in an engine with compression ratios in the range of 12 to 15:1. The IMEP range reported was from 200 to 350 kPa. This falls close to the IMEP range of the current study which ranged from 220 to 400 kPa. Hosseini and Checkel (2006) have presented similar work with natural gas fueled HCCI.

Figure 55: In-cylinder pressure behavior EtOH and H₂ HCCI combustion, varying H₂ output power, 1500 RPM, mid load 2, 95° intake temperature
supplemented by hydrogen rich reformer gas that also shows advances in SOC due to hydrogen addition. The work of Hosseini and Checkel (2006) was done at IMEP values ranging from 150 to 200 kPa with compression ratios ranging from 16.5 to 18:1.

A summary of combustion parameters is given in Table 12 for each of the three loads tested. Start of combustion, quantified by CA10 is shown to advance by at most 3.5 crank angle degrees. Variability of the combustion data was shown to be low with the standard error of the mean in peak pressure timing calculated across the four cylinders of the engine ranging from .15 to .53 CAD. The coefficient of variation of the IMEP data across the 4 cylinders ranged from 0.9 % to 4.1 %.

<table>
<thead>
<tr>
<th>Hydrogen Energy</th>
<th>IMEP (kPa)</th>
<th>SOC (ºATDC)</th>
<th>Burn Dur. (CAD)</th>
<th>Peak HRR (J/CAD)</th>
<th>Peak Temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low Load</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>230</td>
<td>-5</td>
<td>7</td>
<td>90</td>
<td>1530</td>
</tr>
<tr>
<td>5%</td>
<td>230</td>
<td>-5</td>
<td>7</td>
<td>100</td>
<td>1530</td>
</tr>
<tr>
<td>10%</td>
<td>230</td>
<td>-5</td>
<td>7</td>
<td>100</td>
<td>1530</td>
</tr>
<tr>
<td>15%</td>
<td>230</td>
<td>-5</td>
<td>6</td>
<td>100</td>
<td>1530</td>
</tr>
<tr>
<td>20%</td>
<td>230</td>
<td>-5</td>
<td>7</td>
<td>90</td>
<td>1530</td>
</tr>
<tr>
<td>25%</td>
<td>230</td>
<td>-5</td>
<td>6</td>
<td>100</td>
<td>1550</td>
</tr>
<tr>
<td><strong>Mid Load 1</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>310</td>
<td>-2</td>
<td>6</td>
<td>130</td>
<td>1580</td>
</tr>
<tr>
<td>5%</td>
<td>320</td>
<td>-3</td>
<td>6</td>
<td>130</td>
<td>1580</td>
</tr>
<tr>
<td>10%</td>
<td>310</td>
<td>-3</td>
<td>6</td>
<td>130</td>
<td>1590</td>
</tr>
<tr>
<td>15%</td>
<td>320</td>
<td>-3</td>
<td>6</td>
<td>130</td>
<td>1600</td>
</tr>
<tr>
<td>20%</td>
<td>320</td>
<td>-3</td>
<td>5</td>
<td>140</td>
<td>1620</td>
</tr>
<tr>
<td>25%</td>
<td>310</td>
<td>-4</td>
<td>5</td>
<td>160</td>
<td>1650</td>
</tr>
<tr>
<td><strong>Mid Load 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0%</td>
<td>400</td>
<td>3</td>
<td>9</td>
<td>140</td>
<td>1600</td>
</tr>
<tr>
<td>5%</td>
<td>390</td>
<td>1</td>
<td>7</td>
<td>150</td>
<td>1590</td>
</tr>
<tr>
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<td>6</td>
<td>160</td>
<td>1650</td>
</tr>
<tr>
<td>25%</td>
<td>380</td>
<td>-1</td>
<td>5</td>
<td>170</td>
<td>1700</td>
</tr>
</tbody>
</table>

Note that as combustion is advanced in each case, peak HRR and peak in-cylinder temperatures also increase. It can be seen that burn duration decreases as SOC
advances. The increases in peak cylinder temperatures result from very rapid combustion occurring over a small interval near TDC. If we imagine discrete piston movement near TDC and consider the consequences of liberating energy in a small number of these discrete increments the relationship between burn duration peak HRR, and peak temperature becomes more clear. Figure 56 shows plots of combustion efficiency and cycle efficiency plotted against hydrogen energy fraction for the three loads. Combustion efficiency increases with increasing hydrogen fraction. This is likely related to the increases in peak temperatures with hydrogen addition. As peak cylinder temperatures increase, more complete oxidation of the fuel to CO$_2$ drives reductions in CO and HC emissions, as manifested in increases $\eta_{\text{Combust}}$. Increases in combustion rates are also likely due to the chain branching step cited by Yap et al. (2004) associated with the reaction of atomic hydrogen and diatomic oxygen to form O and OH radicals. At each load cycle efficiencies are almost independent of hydrogen addition rate. This is surprising because cycle efficiency is usually proportional to combustion efficiency. It may be that increases in heat transfer shifts in combustion timing offset gains due to increased combustion efficiency.

![Figure 56: Response of combustion and cycle efficiencies to variations in H$_2$:EtOH proportion, dual fuel HCCI combustion, 3 loads, 1500 RPM](image-url)
Combustion efficiency increases at each load as more hydrogen fuel is added. Calculated in part from emissions of CO and HCs, combustion efficiency is a result of lower emissions of these species and more complete oxidation of the fuel. These results reflect the lower CO and HC emissions at higher hydrogen proportions shown in Figure 57, Figure 60, Figure 63. It should be noted however that hydrogen emissions considered in these efficiencies are calculated from a carbon balance and not directly measured.

8.2.2 Emissions Analysis

Figure 57 through Figure 64 give brake specific emissions along with detailed particle mobility size distributions for the three load conditions tested. Confidence intervals on the particle size and mass distributions were established using students t-distributions at the 90% confidence level. Sample size varied from five to ten depending on the test condition. Error bars on the BSPM data are based on the same 90% confidence interval. Errors bars shown for gas phase emissions data represent the average standard error of the mean for the respective pollutant. These values were compiled from data taken at all three loads.

Resulting from the minimal combustion changes seen in Figure 56 and Figure 53, brake specific emissions shown in Figure 57 remain relatively stable. These results show consistency with the stable combustion parameters calculated at the low load condition in Table 12. Particle mass and number distributions also remain relatively unchanged throughout the six hydrogen energy proportions at this load as shown in Figure 58 and Figure 59.
Figure 57: Brake specific emissions from EtOH and H₂ HCCI combustion with varying H₂ energy, 1500 RPM, low load, 130°C intake temperature

Figure 58: Mobility size distributions from EtOH and H₂ HCCI combustion with varying H₂ energy, 1500 RPM, low load, 130°C intake temperature
Brake specific emissions data from the mid load 1 condition are shown in Figure 60, and number and mass weighted particle size distributions are shown in Figure 61 and Figure 62, respectively. The combustion behavior summarized in Table 12 shows a stronger response to hydrogen fraction that in the low load case with significant increases in both peak temperatures and heat release rates with increasing hydrogen fraction. In direct response to increased cylinder temperatures and heat release rates, NO$_x$ emissions increase by nearly a factor of three and PM emissions by more than a factor of five as hydrogen energy is increased from 0 to 25 percent. On the other hand, CO and HC emissions fall as increasing cylinder temperatures promote more complete oxidation of the fuel, which is also reflected in the combustion efficiency trends. In addition, there is less fuel to form CO and HC as ethanol is replaced by hydrogen.
Figure 60: Brake specific emissions from EtOH and H₂ HCCI combustion with varying H₂ energy, 1500 RPM, mid load 1, 110°C intake temperature

Referring to Figure 61, particle number concentrations shift to a smaller peak mobility diameter while increasing in concentration as hydrogen energy proportion is increased. Although particle sizes are shifted to small diameters, the increases in number concentrations drive mass concentrations up as well.
Figure 61: Mobility size distributions from EtOH and H₂ HCCI combustion with varying H₂ energy, 1500 RPM, mid load 1, 110°C intake temperature

Figure 62: Mass distributions from EtOH and H₂ HCCI combustion with varying H₂ energy, 1500 RPM, mid load 1, 110°C intake temperature
The emissions for the mid load 2 condition are plotted in Figure 63. The general trends are similar to those of mid load 1. Again an increase in brake specific NO\textsubscript{X} emissions of roughly three fold is shown as peak in-cylinder temperatures climb by 100 K from the 0 to 25 percent hydrogen energy conditions. Expected behavior is shown in CO and HC emissions and consequentially reflected in combustion efficiency. Following similar trends as the mid load 1 condition, the mid load 2 tests show BSPM increasing with increased hydrogen energy. However the increase in PM is much more modest than in the previous case.

![Graph showing brake specific emissions](image)

**Figure 63: Brake specific emissions from EtOH and H\textsubscript{2} HCCI combustion with varying H\textsubscript{2} energy, 1500 RPM, mid load 2, 95°C intake temperature**

Particle size and mass distributions are shown in Figure 64 and Figure 65. Although a general trend towards decreased mobility diameter is shown, total PM mass is still increased through elevated particle concentrations.
Figure 64: Mobility size distributions from EtOH and H₂ HCCI combustion with varying H₂ energy, 1500 RPM, mid load 2, 95°C intake temperature

Figure 65: Mass distributions from EtOH and H₂ HCCI combustion with varying H₂ energy, 1500 RPM, mid load 2, 95°C intake temperature
Faster burn rates lead to elevated peak in-cylinder temperatures, which are directly responsible for increases in NO$_X$ emissions due to the sensitivity of NO formation to temperature. Additionally the higher peak temperatures associated with increased hydrogen energy explain reductions in CO and HC emissions as a result of faster oxidation.

These reductions of CO and HC emissions may also be in part due to displacement of hydrocarbon energy with hydrogen energy. To separate the effects of hydrogen enhancing ethanol combustion rather than hydrogen displacing the base fuel, a set of ethanol fuel normalized CO and HC emissions parameters have been calculated in a manner similar to Bika et al. (2009). Figure 66 shows CO and HC emissions normalized to ethanol fueling rate. To further clarify the analysis each supplemental hydrogen condition is normalized to the initial pure ethanol CO and HC emissions level. For each of the three load conditions, a significant increase in oxidation of CO is shown with increasing hydrogen energy. The trends are less pronounced for HC emissions, likely due to the origination of hydrocarbons in the quench zone, where lower local temperatures are less sensitive to changes in peak temperature.

![Graph showing normalized CO and HC emissions](image)

**Figure 66: Ethanol fueling rate specific CO and HC emissions normalized with respect to 0% hydrogen fueling**
Conducting a multiple regression analysis on the entire ethanol with supplemental hydrogen fueling data set brings to light a strong dependence of total particulate mass on select combustion parameters. Again, the influence of the independent variables; SOC, combustion duration, peak temperature, and peak heat release rate on the dependant variable, total particulate mass, was analyzed. The size of the sample set used for analysis was 18, which led an $R^2$ value of .90. Comparing this value to the $R^2$ values obtained through the variable intake temperature and variable EGR data, we see the strongest correlation here. A major contributor to the strength of this correlation is the low variability of the data set. Hydrogen flowrates were easily set to each cylinder and precisely controlled through the engine controller. Hydrogen flow was recorded throughout all testing via a mass flow meter which measured to precision levels at around .1% of the measured flow rate.

Looking in more detail at the relationship between combustion parameters and emissions data, Figure 67 and Figure 68 illustrate the dependency of CO, NO$_X$, and PM emissions on in-cylinder temperatures and heat release rate. The relationship between CO and NO$_X$ emissions and peak in-cylinder temperature behaves as expected as a result of the dependency of reaction rate constants on temperatures, however the trend exhibited by PM emissions is less clear. Nucleation mode particulate matter in CI engines forms via homogeneous nucleation of sulfates and hydrocarbons during dilution and cooling of the exhaust gas (Abdul-Khalek et al., 2000; Kim et al., 2002; Vaaraslahti et al., 2005; Ristimäki et al., 2007). Vaaraslahti et al. (2005) has suggested that as fuel sulfur content diminishes, sulfur and hydrocarbons originating from the lubricating oil become increasingly important as nucleation mode precursors. Gas to particle conversions generate critical clusters, eventually growing via condensation to measurable particles. Nucleation behavior, driven by saturation ratio (Kim et al., 2002) would be significantly affected by the availability of additional precursor material in the exhaust stream. Increased peak cylinder temperatures are indicative of higher overall temperatures throughout the cycle, a condition that leads to elevated evaporation rates of engine lubricating oil from atomized oil droplets and the cylinder walls (Yilmaz et al., 2002; Yilmez et al., 2004; Audeete & Wong, 1999; Gilles et al., 2007).
Figure 67: Brake specific emissions vs. peak in-cylinder temperature, ethanol HCCI with 0 to 25% supplemental hydrogen fueling, 1500 RPM, 3 loads

Figure 68: Brake specific emissions vs. peak heat release rate, ethanol HCCI with 0 to 25% supplemental hydrogen fueling, 1500 RPM, 3 loads
An early study conducted by Tobias et al. (2001) used thermal desorption particle beam mass spectrometry (TDPBMS) and temperature programmed thermal desorption (TPTD) to investigate Diesel particulate matter composition. Tobias et al. (2001) conducted analysis of the volatile organic compounds comprising Diesel particulate matter and found high percentages of alkanes and cycloalkanes. The similarity of the cycloalkanes to alkanes ratios in the PM to those of the lubricating oil led the authors to believe that significant contributions were made from lubricating oil. Sakurai et al. (2003) further investigated Diesel nanoparticle composition through TDPBMS and tandem differential mobility analyzer (TDMA) techniques and found volatile particles emitted at low to moderate loads under steady state conditions were composed roughly 95% compounds from unburned lubricating oil. Additionally, an investigation by Miller et al. (2007) into exhaust PM from pure hydrogen fueled SI engines noted that as in-cylinder temperature increased, organic carbon levels in the PM also increased. The authors thought this was likely due to more complete breakdown and oxidation of some lubricating oil components at elevated temperatures. This HCCI work suggests very similar behavior is taking place here.

### 8.3 Pure Hydrogen HCCI

To further develop an understanding of the HCCI combustion process and its emissions, an investigation was made into the behavior of pure hydrogen fueled HCCI combustion. Hydrogen was selected due to its purity as a fuel. The fuel used for this work was research grade high purity hydrogen; it was specified to have > 99.999% purity.

Recent work has demonstrated hydrogen as a viable HCCI fuel. Caton and Pruitt (2009) explored hydrogen HCCI operating conditions from compression ratios of 17:1 up to 20:1 and were able to maintain controlled combustion at $\lambda$ values ranging from roughly 7 up to 2.5. Intake temperatures tested were in the rage of 80 °C to 100°C. Operation was bounded on the high load end by advanced combustion leading to knock and on the lower load end by drastic drops in efficiency. These efficiency losses are due to inability of the combustion process to fully oxidize the fuel at the lowest loads tests.
Gomes – Antunes (2008) also explored hydrogen HCCI and noted that the high rates of pressure rise found limited its use to relatively light load applications. Compression ratios of 17:1 were used for this work and the engine ran successfully at $\lambda$ values ranging from 6 to 3. Intake temperatures ranged from 85°C to 110°C.

The work of Tobias et al. (2001) and Sakurai et al. (2003) points towards lubricating oil as the primary contributor of precursors to nucleation mode particles in lean burning CI engines. Miller et al. (2007) has also drawn similar conclusions from SI engines running on pure hydrogen fuel. Eliminating fuel bound hydrocarbons and operating an HCCI engine on hydrogen will provide a means to further verify the hypothesis that a similar case can be made for fully premixed HCCI engines. In eliminating fuel bound impurities and hydrocarbons, the precursors to nucleation mode PM are constrained and further speculation into precisely what compounds form this PM in HCCI engines can be made.

### 8.3.1 Experimental

The same modified 5.2 liter Isuzu engine described in earlier experiments was used here. For comparative purposes, the engine was operated with a load near 52 Nm at 1500 RPM, the same load and speed as all of the low load ethanol work. These conditions also resulted in an IMEP range within that of the low load ethanol work. A range of three intake temperatures were swept through to assess the effects intake temperature variation. For all test cases hydrogen fueling was held constant. Table 13 gives the pertinent details of the experimental conditions.

Because conventional gas phase emission instrumentation concerned with HC, CO, and CO$_2$ are of little use when studying hydrogen fueled combustion, different exhaust gas analysis equipment was used for the hydrogen HCCI work. A laser multi-gas spectrometer (Atmosphere Recovery Inc.) was used to obtain concentrations of H$_2$, H$_2$O, O$_2$, and N$_2$ in the exhaust stream. A chemiluminescence NO$_X$ analyzer (California Analytical Instruments, 600 HCLD) was also used to collect NO$_X$ data during this work.

The temperatures of the two stage dilution system were maintained at 35°C, 25°C, and 35°C, for stage 1 dilution air, stage 2 dilution air, and the dilution tunnel water jacket
respectively. Dilution ratios were set to the average dilution ratios obtained during the ethanol and hydrogen work; \( S_1 = 15.6 \) and \( S_2 = 18.8 \). A SMPS (TSI 3080) comprised of a nano DMA (TSI 3085) and ultra fine CPC (TSI 3025), with the sheath and aerosol flows set to 15 and 1.5 lpm, was used for all particle measurements.

<table>
<thead>
<tr>
<th>Intake Temperature (^{\circ})C</th>
<th>95°</th>
<th>100°</th>
<th>105°</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fueling Rate ( \text{g}_{\text{H}_2}/\text{sec} )</td>
<td>.314</td>
<td>.314</td>
<td>.314</td>
</tr>
<tr>
<td>Fuel Input Energy Rate ( \text{kW} )</td>
<td>38.0</td>
<td>38.0</td>
<td>38.0</td>
</tr>
<tr>
<td>( \lambda )</td>
<td>5.09</td>
<td>5.06</td>
<td>4.97</td>
</tr>
<tr>
<td>Load ( \text{N}\cdot\text{m} )</td>
<td>52</td>
<td>54</td>
<td>52</td>
</tr>
<tr>
<td>IMEP ( \text{kPa} )</td>
<td>230</td>
<td>230</td>
<td>230</td>
</tr>
</tbody>
</table>

**8.3.2 Combustion Analysis**

The range of temperatures were selected in an effort to optimize IMEP for the given engine load and speed condition. From Table 13 it can be seen that this occurs with the intake temperature at 100 \(^{\circ}\)C.

Figure 69 shows in-cylinder pressure data gathered at each intake temperature. Consistent with the ethanol data, peak pressures and SOC both show a direct relationship with intake temperature for the intake temperature range shown.
Figure 69: In-cylinder pressure traces of hydrogen HCCI combustion, fixed fueling, $\lambda = 5.08 - 4.97$, 1500 RPM, varying intake temperature

Also shown in Figure 69 are plots of heat release rate versus crank angle derived from the pressure data. In calculating HRR, a single zone model similar to that presented by Stone (1999) is used. The cylinder contents are assumed to behave as ideal gases composed of an initially specified fuel and air mixture. The rates reported are net heat release rates and neglect heat transfer to the cylinder walls. Heat release analysis allows quantitative calculation of SOC timing, defined by the crank angle at which 10% of the heat energy of the fuel has been liberated (CA10) and burn duration CA90-CA10. Additionally in-cylinder temperature is calculated from the heat release analysis. Table 14 shows pertinent combustion parameters for the hydrogen HCCI tests with varying intake temperature. Variability of the combustion data was shown to be low with the standard error of the mean in peak pressure timing calculated across the four cylinders of the engine ranging from .18 to .4 CAD. The coefficient of variation of the IMEP data across the 4 cylinders ranged from 1.8 % to 3.0 %. It can be clearly seen that at all engine loads studied elevating intake temperatures leads to advances in SOC. More advanced combustion in turn leads to higher peak heat release rates. With more heat
released prior to or very near TDC, the physical volume in which the energy is released becomes smaller, and due to engine geometry, does not change as much per CAD. This causes higher cylinder pressures and temperatures. IMEP values are very near those of the low load ethanol testing allowing relevant comparisons between the two tests to be made.

Table 14: Summary of combustion properties, hydrogen HCCI with varying intake temperature, 1500 RPM, 54 Nm Load

<table>
<thead>
<tr>
<th>Intake Temp. (°C)</th>
<th>IMEP (kPa)</th>
<th>SOC (°ATDC)</th>
<th>Burn Dur. (CAD)</th>
<th>Peak HRR (J/CAD)</th>
<th>Peak Temp. (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low Load</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>230</td>
<td>3</td>
<td>10</td>
<td>80</td>
<td>1300</td>
</tr>
<tr>
<td>100</td>
<td>230</td>
<td>2</td>
<td>8</td>
<td>90</td>
<td>1330</td>
</tr>
<tr>
<td>105</td>
<td>230</td>
<td>0</td>
<td>6</td>
<td>100</td>
<td>1390</td>
</tr>
</tbody>
</table>

SOC values, calculated via net heat release, increase from 3°ATDC to TDC as intake temperatures are increased from 95° to 105°C. With this advanced combustion comes higher peak heat releases rates, higher peak in-cylinder temperatures, and higher peak pressures. Burn durations also become significantly shorter as intake temperatures increase. In low temperature combustion processes like HCCI, peak cylinder temperatures are kept relatively low through globally lean fuel and air mixtures. As a consequence, combustion efficiency, which is dependent on partially oxidized fuel, can be low. Thus action taken to increase peak combustion temperatures will lead to increased combustion efficiency through more complete oxidation of the fuel.

Combustion and cycle efficiencies were calculated in a manner similar to that described in 6.2.1 and are shown in Figure 70. A notable difference is the omission of CO and HCs from the analysis. With hydrogen as the sole fuel, emissions of the carbon based pollutants, CO and HCs, were well below the sensitivity of the exhaust gas analyzers. PM emissions do however indicate that the exhaust stream is clearly not completely void of hydrocarbons, however, on a mass basis they are negligible have no effect on this analysis. Although cycle efficiencies remain relatively constant at these temperatures, combustion efficiency exhibits a direct relationship, increasing more than
1% as temperatures are raised from 95° to 105°C. The range of combustion efficiencies found are in very good agreement with those reported by Caton and Pruitt (2009) for a hydrogen HCCI engine with similar geometry.

![Figure 70: Effect of intake temperature on combustion and cycle efficiency, hydrogen HCCI combustion, fixed fueling, \( \lambda = 5.08 - 4.97 \), 1500 RPM](image)

### 8.3.3 Emissions Analysis

Figure 71 summarizes the brake specific emissions and their response to variations in intake temperature of the hydrogen fueled HCCI engine. BSNO\textsubscript{X}, BSH\textsubscript{2}, and BSPM are given at each temperature. Increasing intake temperature leads to increased BSPM emissions and decreased BSH\textsubscript{2} emissions. However, BSNO\textsubscript{X} emissions remain relatively stable. Decreases in hydrogen emissions, and the resulting increases in combustion efficiency, are caused by more advanced combustion leading to higher in-cylinder temperatures, which promote more complete burning of the fuel. Advanced combustion and high in-cylinder temperatures lead to higher PM emissions, showing good agreement with earlier findings in Sections 6.2, 7.2, and 8.2. Full particle size and
mass distributions are given in Figure 72 and Figure 73 respectively. Particle size and mass distributions obtained when motoring the engine are also presented. The motored engine was operating hot with 120°C intake air, resulting in 80°C exhaust, and 96°C oil temperatures.

Comparing hot motored emissions from the engine enables exploration into the role of lubricating oil in HCCI emissions. Total mass concentration of motored PM emissions from the HCCI engine is roughly 4600 µg/m³. This is more than two times the highest levels present during the hydrogen HCCI testing. The primary reason for elevated particulate emissions during motoring, which stems from high oil consumption, is the inability of the piston rings to seat properly during the sharp pressure drop during motored expansion. Furthermore temperatures are still high enough to evaporate hydrocarbons from the lubricating oil to form nucleation precursor material.

A simple polytropic compression model like that presented in Equation 7 gives an idea of the range of temperatures encountered during motored compression in this engine. Using a compression ratio of 18.5, an initial temperature of 120°C, and a γ value of 1.3, gives peak cylinder temperatures around 950°C. Temperatures calculated for this engine through in-cylinder pressures analysis are also very close to that. This indicates that throughout a significant portion of the compression and expansion strokes during motoring, gas temperatures are well above those required for evaporation of engine oil.

An additional contributor to the significantly elevated hot motored PM emissions is the inability of the sub 1000°C motored cylinder temperatures to oxidize any of the evaporated hydrocarbons. This results in all of the evaporated volatile material from the lubricating oil being available as precursor to nucleation.
Figure 71: Brake specific emissions from hydrogen HCCI with varying intake temperature, fixed fueling, \( \lambda = 5.08 - 4.97 \), 1500 RPM

From Figure 72 is evident that increased intake temperatures lead to higher number concentrations of particulate matter and larger mobility diameter particles. These increases both contribute to increases in total mass, as illustrated by BSPM emissions in Figure 71, and PM mass distributions shown in Figure 73. Error bars for the BSPM data shown in Figure 71 represent 90% confidence intervals. For the BSNO\(_x\) data, error bars shown represent the average standard error of the mean for data taken during the EtOH and \( \text{H}_2 \) fuel blending experiments.
Figure 72: Mobility size distributions from a hydrogen fueled HCCI engine, $\lambda = 5.08 - 4.97$, 1500 RPM, varying intake temperature

Figure 73: Mass distributions from a hydrogen fueled HCCI engine, $\lambda = 5.08 - 4.97$, 1500 RPM, varying intake temperature
Conducting two single linear regression analyses on the hydrogen HCCI with variable thermal conditioning data set illustrates the dependence of total particulate mass on select combustion parameters. Because of the limited number of data points, and previous analyses pointing to peak temperature and peak HRR as the most significant drivers of PM formation, the influence of these two variables on the dependant variable, total particulate mass, were analyzed separately. The size of the sample set used for the analysis was three. These data are shown in Figure 74 with peak in-cylinder temperature shown on the lower axis and peak HRR shown on the upper axis. Increased intake temperatures lead to more advanced combustion giving higher in-cylinder temperatures and higher rates of heat release with hydrogen HCCI in a similar manner as in ethanol HCCI combustion. Also similar to ethanol HCCI combustion, PM emissions rates from hydrogen HCCI increase with increasing in-cylinder temperatures and peak HRRs.

![Figure 74: BSPM vs. peak HRR or peak temperature, neat hydrogen HCCI, 1500 RPM, low load, 3 intake temperatures](image)

- $R^2 = 0.9766$
- $R^2 = 0.8377$
If we recall that the intake temperature for the 0% hydrogen energy condition in the ethanol with supplemental hydrogen fueling tests was found by optimizing output torque with intake temperature in earlier experiments, a useful analysis can be developed by comparing those results to the intake temperature optimized peak torque condition using pure hydrogen fuel for HCCI combustion found here. For hydrogen HCCI the peak output condition, indicated by both torque and IMEP, corresponds to a 100°C intake temperature. The load, speed, and IMEP are the same for both the ethanol and pure hydrogen cases. From Figure 75 it can be seen that the number and mass concentration of particulate emissions are also strikingly similar. This insensitivity of particulate emissions to fuel, especially when a hydrocarbon free fuel such hydrogen is used, suggests the primary contributor to PM emissions in fully premixed HCCI combustion are hydrocarbons evaporated from atomized lubricating oil droplets and the cylinder wall. Miller et al. (2007) has made a similar conclusion for a hydrogen fueled SI engine, noting that formation of primary soot particles, composed of elemental carbon, generally takes place in a flame where carbon containing fuel is burned in a locally oxygen starved environment. Miller et al. also presents the argument that organic carbon emissions, found to be increasingly present at elevated loads during hydrogen combustion, result from more complete breakdown of the lubrication oil at higher in-cylinder temperatures. They also cited possible impurities in the fuel and sources of seed particles for nucleation. In an attempt to minimize any fuel contributions to PM formation, >99.999% pure hydrogen was used for the HCCI testing done here.
8.4 Conclusions

A study on the combustion and emissions effects of supplemental hydrogen fueling in a HCCI engine using ethanol as the primary fuel was conducted. The results clearly indicated that combustion phasing is advanced with increasing hydrogen energy proportion. Additionally, the effect became more pronounced at higher engine loads. The advances in combustion phasing were in agreement with published findings for another high octane fuel, natural gas.

Examining emission trends between loads, increased load generally led to higher BSNO\textsubscript{X} and BSPM emissions. Within every load condition, a general trend of increases in hydrogen energy proportion giving increased BSNO\textsubscript{X} and BSPM emissions was present. PM present at all loads was composed entirely of nucleation mode particles, with number concentrations virtually nonexistent above 60 nm in mobility diameter.

Significant reductions of ethanol fuel specific CO emissions were reported at all loads as more hydrogen energy was added. These reductions, which measured more than 50% at moderate loads with the highest hydrogen fueling rates, have been
attributed to enhanced oxidation of CO due to radicals produced via hydrogen chain branching reactions. Modest reductions in ethanol fuel specific HC emissions were also observed.

The sensitivity shown of PM to cylinder temperatures and HRR indicate the primary source of precursor material is likely lubricating oil evaporated from atomized droplets created by reverse gas flow through the ring pack, or evaporated directly from cylinder walls during expansion. Because particulate matter is solely present in the nucleation mode it is likely not originating from the soot forming regions found within locally fuel rich combustion flames.

Additionally a similar engine condition fueled by neat ethanol or neat hydrogen yielded nearly identical particulate emissions. These results strongly suggest lubricating oil as the primary, if not sole contributor, to nucleation mode particulate matter in fully premixed ethanol HCCI combustion. In both ethanol fueling supplemented with hydrogen and pure hydrogen fueled HCCI combustion, emissions of NO\textsubscript{X} and PM increased with increases in peak heat release rate and peak in-cylinder temperature. Associated with the increased in-cylinder temperatures were shorter burn durations, decreasing CO and HC emissions, and increasing combustion efficiency.
Chapter 9    Advanced Characterization Techniques for Emissions from an Ethanol Fueled HCCI Engine

After establishing in previous chapters that particulate emissions in fully premixed HCCI combustion are primarily formed from unburned lubricating oil, it becomes necessary to further elucidate details of what components of the oil eventually reside in exhaust PM. Utilizing TDMA techniques with a thermal conditioning section allow particle volatility to be investigated. Additionally a much more detailed map of gas phase emissions has been drawn through FTIR analysis of ethanol HCCI emissions.

9.1 TDMA Experiments

To gain additional insight into the composition of the particles formed during HCCI combustion, a set of TDMA experiments were conducted at four engine loads and a fixed engine speed of 1500 RPM. The loads corresponded to the low load, mid load 1, mid load 2, and motoring conditions described in earlier experiments.

Taking the pioneering TDMA work of Liu, et al. (1978), McMurry, et al. (1983), and Rader et al. (1986), and applying it to engine exhaust particles, has enabled researchers to gain a great deal of insight into their composition. Orsini (1998) and Sakurai (2003) have used TDMA techniques with thermal conditioning to study Diesel nanoparticle composition and volatility.

Recently, Surawski et al. (2010) have utilized TDMA techniques to investigate the details of particle composition in a Diesel engine with supplemental ethanol fumigation. At all loads tested they found the addition of ethanol greatly increased the volatile volume fraction of accumulation mode particulate matter in a compression ignition engine. The increases in volatile volume fraction also followed directly as higher percentages of ethanol energy were substituted.

Sharp increases in nucleation mode particles with increasing ethanol are explained by a deficit in adsorption sites created through the mitigation of the accumulation mode. Kittelson et al. (2002) explains the role of accumulation mode particles, composed of carbonaceous agglomerates, as that of a condensation and adsorption sink for organic
vapors. When clean burning combustion processes lead to reduction of the accumulation mode, these supersaturated vapors are left as precursors for nucleation of new particulate matter.

9.1.1 Experimental

To isolate volatility fractions of the PM sampled from the engine, the exhaust aerosol was studied with a TDMA apparatus that utilized a thermal conditioning section (Orsini, 1998; Sakurai et al., 2003; Surawski et al., 2010). A schematic of the apparatus is shown in Figure 11. The setup employed a long DMA (TSI 3081) as the fixed voltage DMA which is used to size select particles prior to the thermal conditioning section. Engine exhaust was initially sampled at each load condition with the fixed voltage (long) DMA bypassed and the thermal conditioning section at ambient temperatures to collect full particle size distributions. After determining the mode of the particle size distribution from this data, the aerosol path was then routed through the fixed voltage DMA, with its voltage set to correspond to the mode of the initial size distribution. At each of the three fired engine loads, and a fourth motored load, particle size distribution modes were found and the fixed voltage DMA set in a similar manner.

The nano DMA (TSI 3085) was operating downstream of the thermal condition section in combination with a CPC having a $D_{50}$ of 3.0 nm (TSI 3025), these two instruments were operated as an SMPS and used to collect a size distribution of the initially classified aerosol after being passed through the thermal conditioning section as shown in Figure 11. The methodology allows a particle size change in the monodisperse aerosol due to evaporation of volatile material from the particle surfaces in the thermal conditioning section to be documented.

Both DMA columns were operated with a sample flow of 1.5 lpm and a sheath flow of 15 lpm. At this flow rate, residence time in the thermal conditioning section was about 0.25 seconds. The thermal conditioner was sized to give residence times in accordance with Orsini (1998) and Sakurai (2003), with temperature monitored continuously at the conditioner outlet.

Samples were then taken with thermal conditioning temperatures ranging from 40° to 110° C in 10° increments. The thermal conditioning section was given adequate time
to stabilize at each increment and monitored with a type K thermocouple throughout the testing.

Engine operating parameters of the three fired loads corresponded to the peak IMEP intake temperature conditions which were isolated in earlier experiments and are summarized in Table 15. The operating details of the motoring load condition are also shown. For the fired loads the engine was operating on ethanol with the fuel content specifications listed in Table 6. In order to maintain as high of particle counts as possible the exhaust aerosol was sampled after one stage of dilution. The dilution ratio was held at 15.6:1 throughout all testing. Stage one dilution air temperature was held at 35°C, as was the dilution tunnel water jacket.

Table 15: Engine operating parameters tested in TDMA analysis of ethanol HCCI combustion

<table>
<thead>
<tr>
<th>Condition</th>
<th>Speed (RPM)</th>
<th>Load (Nm)</th>
<th>IMEP (kPa)</th>
<th>Intake Temp. (°C)</th>
<th>λ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Motoring</td>
<td>1500</td>
<td>-</td>
<td>-</td>
<td>120</td>
<td>-</td>
</tr>
<tr>
<td>Low Load</td>
<td>1500</td>
<td>53</td>
<td>230</td>
<td>130</td>
<td>4.3</td>
</tr>
<tr>
<td>Mid Load 1</td>
<td>1500</td>
<td>89</td>
<td>320</td>
<td>110</td>
<td>3.5</td>
</tr>
<tr>
<td>Mid Load 2</td>
<td>1500</td>
<td>128</td>
<td>400</td>
<td>100</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Because two different model DMAs were used, subtle differences in DMA geometry, flow rate and power supply performance could lead to differences in overall DMA performance. The following exercise was conducted to gauge how closely the classifying performance of the long DMA agreed with that of the nano DMA. First, a polydisperse dioctylsebacate (DOS) in isopropyl alcohol aerosol was generated with a Collison atomizer. The aerosol was then diluted and passed through a diffusion dryer containing activated carbon, leaving a pure DOS aerosol. The pure DOS particle size distribution had a mode diameter of 60 nm with total concentrations near $2.5 \times 10^6$ particles/cm$^3$. Next the fixed voltage (long) DMA was set to classify a particle size from the polydisperse DOS aerosol. Finally the scanning voltage (nano) DMA was used to report a measured mobility diameter. Diameters of 25 nm and 35 nm were selected as modes representative of the ethanol HCCI particulate matter. The reported modes are
given in Table 16, an average offset correction of + 0.9 nm has been calculated and will be applied to all TDMA data. The average offset is computed from three SMPS scans at each of the two selected particle diameters.

<table>
<thead>
<tr>
<th>Classified Mobility Diameter (nm)</th>
<th>Measured Mobility Diameter (nm)</th>
<th>Offset (nm)</th>
<th>Measured Mobility Diameter (nm)</th>
<th>Offset (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>23.3</td>
<td>-1.7</td>
<td>24.1</td>
<td>-0.9</td>
</tr>
<tr>
<td>35</td>
<td>34.6</td>
<td>-0.4</td>
<td>34.2</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

Engine exhaust was initially sampled at each load condition with the fixed voltage (long) DMA bypassed and the thermal conditioning section at ambient temperatures to collect full particle mobility size distributions. The aerosol path was then routed through the fixed voltage DMA with its voltage set to correspond to the mode of the initial mobility size distribution. At each of the four engine loads a new mode was found and the fixed voltage DMA set in a similar manner.

Samples were then taken with thermal conditioning temperatures ranging from 40° to 110° C in 10° increments. The thermal conditioning section was given adequate time to stabilize at each increment and monitored with a type K thermocouple throughout the testing. The setup and flow paths of the TDMA apparatus are illustrated in Figure 11.

9.1.2 Results and Discussion

The four data sets collected are shown below, each has the initial full particle size distribution shown for reference along with the TDMA data collected at every temperature increment. The data shown is corrected for a 0.9 nm offset between the long and nano DMAs. The right hand scale of each graph corresponds to the full distributions, with the TMDA classified concentrations read from the left hand scale.
Figure 76: Full distribution and TDMA data, motoring load, 1500 RPM

Figure 77: Full distribution and TDMA data, low load, 1500 RPM
Figure 78: Full distribution and TMDA data, mid load 1, 1500 RPM

Figure 79: Full distribution and TMDA data, mid load 2, 1500 RPM
From Figure 77, Figure 78, and Figure 79, it is clear that each of the three fired load data sets show distinct increases in particle concentrations at the 90°, 100°, and 110°C TDMA temperature settings. A possible explanation lies in the thermodynamics of the system downstream of the thermal conditioning section. As a result of the elevated temperatures of this section of the TDMA, volatile materials are evaporated from the surface of the particles with more material evaporated as temperatures increase. At the highest temperatures, 90°, 100°, and 110°C, very few particles remain to adsorb the condensable volatile matter that has been evaporated into the gas stream. With concentrations of volatile material increasing and no available sites for adsorption, homogeneous nucleation is becomes likely to occur at the exit of the thermal condition section where temperatures abruptly fall creating a region of super saturation.

Figure 80 shows the change in mode versus TDMA thermal conditioning temperature for the data collected. It can be seen that data from the fired engine loads exhibits similar evaporative behavior. For each of these three cases, the primary changes in mobility diameter occur below 90°C with a very similar trend shown for each load. Data from the motoring condition however, exhibits a very different trend. Particle growth here exhibits a negative, nearly linear trend. Change in particle diameter for droplets composed of pure compounds C_{28}, C_{30}, and C_{32} are also shown. Growth rates for these hydrocarbons were calculated using Equation 25. In this equation taken from Hinds (1999), the growth rate is expressed in terms of molecular weight (MW), a condensation coefficient (α_C), vapor pressure of the liquid (p_d), density of the liquid (ρ−ρ_p), Avogadro’s constant (N_A), single molecule mass (m), Boltzmann’s constant (k), and temperature (T). The equation is valid for particles with diameter smaller than mean free path.

\[
\frac{d(d_p)}{dt} = \frac{2MW\alpha_C(-p_d)}{\rho_p N_A \sqrt{2\pi mkT}}
\]

Sakurai et al. (2003) modeled evaporation profiles of pure hydrocarbons C_{24}, C_{28}, and C_{32} and found similar trends of PM evaporation profiles closely agreeing with pure hydrocarbon droplets.
The distinct difference in the motored and fired evaporation profiles leads to the hypothesis that some of the less volatile components in the lubricating oil are either burned or broken down to more volatile compounds during combustion. Differences in the total diameter change of fired load data are simply a result of differing initial particle diameter and a constant percentage of particle volume boiled off. The leveling off behavior exhibited at the three fired loads is an artifact of the droplet being fully evaporated which means no further loss in diameter can occur.

To further illustrate how these profiles affect total volume of PM, Figure 81 presents the remaining particle volume as a fraction of the initial particle volume found at 40°C. Due to laboratory conditions, this temperature is the minimum temperature that could be stably maintained by the PID controlled heater.
Figure 81: Remaining volume fraction of PM in ethanol HCCI exhaust after thermal conditioning during TDMA analysis, 4 loads, 1500RPM

It is shown in Figure 81 that roughly 98% of particle volume (or mass) is composed of volatile material at fired engine loads. Contrasting these results with motored operation, we see a much higher fraction of low volatility material. The volume fraction curve for the motored operating indicates that nearly 20% of this particulate matter is composed of much less volatile components.

Previous work by Tobias et al. (2001), Sakurai et al. (2003), and Vaaraslahti et al. (2005) examining the origins of PM in compression ignition engines has indicated a significant contribution from lubricating oil in the formation of high volatility exhaust aerosols. Comparing the data in Figure 81 with the results presented by Sakurai et al. (2003), very similar behavior can be seen. Although a completely different fuel, engine, and combustion mode were used in the Sakurai study, the trends in remaining volume fraction of PM closely agree with those presented here. In both cases roughly 90% of particle volume is evaporated between 50° and 100°C.

After showing that nearly all of the particulate matter from this combustion process is composed of volatile components likely originating from lubricating oil, the
The following analysis is intended to aid in understanding the mechanism by which volatile species are drawn from lubricating oil on the piston walls, top land area, and ring pack.

Figure 82 illustrates the piston and cylinder wall interface. For our purposes, the combustion zone will be assumed to exist as a homogeneous single temperature zone through which heat is added to the system. The boundaries are shown in red with the oil film on the cylinder liner shown in green. Note that the oil film does not extend completely around the inside of the cylinder liner. Because the film is dispersed each stroke by the piston motion, the upper most regions of the cylinder do not receive a fresh oil coating and thus provide no film surface area for evaporative transport. Shin et al. (1983) list oil film thicknesses between the top piston ring and the cylinder wall on the order of 1 to 8 µm, with a dependence shown on piston position.

![Figure 82: Fuel and air charge, piston, and cylinder liner interface](image)

A recent investigation by Yilmaz et al. (2004) into engine oil consumption has defined five possible routes of oil consumption in SI engines. The first, throw off, is due
to mechanical transport of oil from the top land and upper compression ring caused by the inertial forces of the reciprocating piston. The second, transport via reverse gas flow, is caused by a reversed pressure difference between the combustion chamber and trapped volume between piston rings during expansion. In this mechanism of oil consumption oil is initially driven past the first piston ring by high combustion pressures. During expansion, pressure in the combustion chamber quickly falls while pressure behind the first ring remains high, creating a pressure difference which forces combustion gas and entrained oil through the small ring crevices. The third route, known as blow by, becomes significant when crankcase fumes are directed back into the intake manifold, bringing entrained oil droplets with the air flow. The fourth route is evaporative mass transport of oil from the piston and cylinder liner. And the final route is bulk mass transport via valve leakage between the valve and valve guide. However the authors state this route has essentially eliminated by modern valve seals. A more detailed examination of evaporative mass transfer from the piston and cylinder liner by Yilmaz et al. (2002) suggested that it was the primary contributor to total engine oil consumption during normal engine operation.

Of these routes, throw off, reverse gas flow, and evaporative mass transfer are likely active contributors during both motoring and firing engine operation of the HCCI engine studied here. A simple model of polytropic compression gives an idea of the range of temperatures encountered during motored compression in this engine. Using the engines compression ratio of 18.5, an initial temperature of 120°C, and a $\gamma$ value of 1.3, gives peak cylinder temperatures around 950 °C. This would indicate that throughout a significant portion of the compression and expansion strokes gas temperatures are well above engine oil and coolant temperatures, thus ensuring heat flow to the cylinder wall. This heat flow causes significant evaporation of oil from the cylinder liner oil film. Furthermore, motoring pressures were measured near 5 MPa, high enough to providing a significant pressure gradient to drive reverse gas flow processes. Additionally, oil throw off, a function of inertial effects due to piston motion contributes to atomization of oil during motoring operation. The engine was motored at
1500 RPM, the same speed as the fired conditions giving a similar set of driving forces for oil throw off in all tests.

With higher in-cylinder temperatures expected during the combustion processes associated with the fired loads, the reduced particulate emissions as compared with the motored load seems initially counterintuitive. However these results could be partially attributed to breakdown and oxidation of the volatile material evaporated from the oil as part of the combustion process. Additionally, Yilmez et al. (2004) reports oil transport via reverse gas flow through the ring pack is high at idle and drops as load is increased to roughly 50% load where it stabilizes. The increase in reverse gas flow is attributed to a decrease in blow by as load is decreased which leaves more oil available on piston ring and top land surfaces for transport into the cylinder via reverse gas flow. Yilmez also reports total oil consumption rates to reach a minima at about 50% load due to competing effects from evaporation, blow by, throw off, and reverse gas flow. Furthermore, piston rings are generally designed to seat best when operating at high engine loads, thus high in-cylinder pressures. At very low loads, such at motoring, ring seating is likely at its worst.

Particle size distributions collected with and without a catalytic stripper are shown in Figure 83. Data is shown for a representative ethanol HCCI condition and a motoring condition on the same engine. The details of the engine operating conditions are listed in Table 15. The data is intended to give further insight into the differences between the volatile fractions of particles generated during fired and motored engine processes. Looking at the motored data, a clear distribution can be observed in the catalytic stripper data with a mode near 7 nm and a total concentration of $2.81 \times 10^7$ particles/cm$^3$. Without the catalytic stripper, the motored size distribution has as mode near 20 nm with total concentrations near $4 \times 10^8$ particles/cm$^3$. Apple et al. has shown lubricating oil to have roughly 1.0 % ash content from trace metals, which is likely the solid core evident in our data as well. Apple also showed that particle diameters above 30 nm contribution disproportionately more to total ash concentrations than smaller particles. With motoring distributions showing significantly higher numbers of large particles than fired distributions, the work of Apple et al. provides a good explanation
for why particles from motored loads have a significant solid fraction and those from fired loads do not. The total PM mass concentrations from motoring operating are nearly 3300 µg/m³ with solid ash contributing roughly 0.1% of that. The significant levels of solid residue are a result of high oil consumption during motoring. From the Mid Load 1 size distribution collected with the catalytic stripper, it is clear that there were too few particles to develop a size distribution. Using the catalytic stripper to collected data from the Low Load and Mid Load 2 engine conditions gave similar results.

Gilles et al. (2007) found that oils with larger fractions of high volatility materials led to higher rates of oil consumption when examining consumption of numerous different lubricating oils in a 2.2 liter DI Diesel engine. The findings were similar across all loads and speeds tested. Oil consumption rates reported by Gilles et al. (2007) were in the range of 30 to 45 g/hr for a DI Diesel engine running at 75 and 100% load, with
each load evaluated at 3000 and 4000 RPM. Normalizing the consumption rate to engine displacement give rates of 14-21 g/hr liter. Consumption rates reported by Yilmaz et al. (2004) were over a much wider operating range from no load to full load at engine speeds ranging from 2500 to 5000 RPM. These authors found oil consumption for a 2.0 liter, 4 cylinder engine to range from 7 to 82 g/hr. Again normalizing to displacement gives rates of 4 to 41 g/hr liter. The highest rates were consistently found at high loads and high speeds in both studies. Modeling vaporization rates alone, rather than total oil consumption, Audette and Wong (1999) gave base vaporization rates on the order of 1 g/hr per cylinder (.73 g/hr liter) for an engine operating at 2200 RPM and full load with a similar bore, stroke, and compression ratio as the Isuzu 4HK1-TC used in this HCCI work. Further analysis of reasonable mass transfer parameters used in the study gave evaporation rates for the \(\pm 20\) K liner temperature window ranging from .1 to 10 g/hr per cylinder (.073 to 7.3 g/hr liter) for the 1.38 liter displacement single cylinder engine modeled. The range of evaporation rates spanning 2 orders of magnitude while temperatures only span 40°C shows the sensitivity of evaporation rates to liner temperatures.

Distillation curves of the oils used in the studies above were presented by all three authors. The oil studied by Yilmaz et al. (2002) showed the most sensitivity to temperature in the interval from 640 K to 740 K. In this temperature interval the percent of total oil mass evaporated jumped from 10% to 80%. The ten different oil tested by Gilles et al. (2007) showed very similar distillation profiles, with the bulk of the oil evaporated between 625 K and 750 K. Audette and Wong (1999) presented a very similar set of distillation curves for two different 15W-40 grade oils, the same grade of oil as was used for the current HCCI work. The distillation curves presented by all authors also show significant evaporation of mass, up to 10 %, below 600 K. Although cylinder walls are at temperatures near 400 K - 450 K, the combustion gas temperatures approach 1500 K. If a scenario of transient heat conduction is taking place in the cylinder with each engine cycle, temperature distributions will fall between 400 K and 1500 K. Understanding this along with the distillation data support the likelihood that
oil vapor from both cylinder liner evaporation and mechanically generated droplet evaporation within the hot cylinder gases occurs.

The total PM mass rate for ethanol testing ranged from .01 to 4.5 g/hr. The total PM mass rate found during the pure hydrogen HCCI experiments ranged from .1 to .7 g/hr. With the lowest in-cylinder temperatures consistently corresponding to the lowest exhaust PM mass rates. Motored PM mass rates are near .8 g/hr at 1500 RPM. Comparing the mass rate of exhaust PM to the oil consumption rates found by Yilmaz et al (2004) and Gilles et al. (2007) we see an inequality. A simple correlation between oil consumption and PM total mass is not expected however, due to a number of points that can be made to explain the difference. First, it should be pointed out that both authors found a strong direct dependence of oil consumption on both engine load and speed. The consumption rates reported by Yilmaz et al. (2004) were obtained at 75 and 100% rated load, and engine speeds of 3000 and 4000 RPM. The range of covered by Gilles et al. (2007) extended from 2500 RPM to 5000 RPM over all engine loads. HCCI work conducted here was done so at a low engine speed of 1500 RPM and low to moderate engine loads. Second, blow-by will make significant contributions to oil consumption in a high compression engine. The HCCI test engine had a crankcase vented to ambient with a compression ratio of 18.5:1. The vented crankcase dumps crankcase fumes and entrained oil to the ambient which adds to total oil consumption, but would make no contribution to total particulate matter in the exhaust.

9.1.3 Conclusions

Particulate matter in the exhaust stream of a fully premixed ethanol HCCI engine was characterized via TDMA analysis with thermal conditioning. Thermal conditioning temperatures were swept from 40 to 110°C with maximum temperatures dictated by the disappearance of measurable particles. Emissions from three fired loads were examined along with a hot motoring condition. TDMA analysis has shown nucleation mode particulate matter from this engine is composed of more than 98% volatile material. These results are consistent across all load conditions. Particulate matter generated via hot motoring of the engine has less volatile fraction, on the order of 85% at 110°C.
Combining this analysis with the results found in Sections 6.2.2, 7.2.2, 8.2.2, and 8.3.3, evidence suggests that particulate matter from this type of engine forms primarily from lubricating oil and is highly dependant on cylinder temperatures and heat release rates, thus independent of fuel. These results have shown changes in particulate emissions can be induced via multiple SOC control strategies and emissions consequences of each strategy consistently exhibit a dependence on peak cylinder temperature and heat release rate.

Comparing the motored and loaded particle evaporation profiles and volatile volume fractions, they author would like to put forth the hypothesis that a change in the lubricating oil occurs during combustion. The lubricating oil in the engine is primarily composed of hydrocarbons ranging in carbon number from C$_{20}$ to C$_{40}$ (Morgan, 2010). As these hydrocarbons decompose into lighter components, vapor pressures of the compounds will increase giving way to increased volatility. A non-sooting HCCI engine creates exhaust conditions lacking carbonaceous soot on which to condense and adsorb these organic vapors. They instead form nano-particles via homogeneous nucleation during dilution and cooling of the exhaust.

9.2 FTIR Data

As advanced engine technology continually cuts regulated emissions, the exhaust species once thought to be negligible begin to develop a significant contribution to the whole of exhaust emissions. Recent studies by Reyes et al. (2006), Dukulis et al. (2009), Kar and Cheng (2009), and Wallner and Frazee (2010) have all shown the usefulness of FTIR techniques for engine emissions work. Reyes et al. (2006) cites ammonia, formaldehyde, and nitrous oxide as species of particular interest. Additionally, Wallner and Frazee (2010) highlight the rising concerns of oxygenated biofuels leading to increases in aldehydes and alcohols in the exhaust stream. These findings, combined with Kar and Cheng (2009) reporting the diminished response of FID analyzers when used to examine highly oxygenated fuels, create a clear need for more thorough examination of unregulated exhaust species. Although shortfalls in practicality of FTIR as an engine exhaust analysis tool hindered widespread adoption at
its introduction in the late 1980’s, advances in the technology have lead to widespread use and acceptance. According to Adachi (2000), the major obstacles FTIR faced when compared to conventional NDIR, FID, and CLD instrumentation were; cross sensitivity, response time, and accuracy of concentration. Adachi also notes that continued development of the method has addressed many of these deficiencies, resulting in tools and techniques that are now widely used across the automotive industry. Furthermore, Reyes et al. (2006) notes several regulatory and standardization agencies that have validated the technique for extractive gas sampling.

9.2.1 Experimental

Considering the data presented thus far, with particle size distributions composed entirely of nucleation mode particles and understanding that these particles are formed solely through gas to particle conversions, it is clear that a detailed examination of gas phase exhaust components will aid in understanding PM formation and growth in HCCI engines. FTIR data was collected during the TDMA experiments, with the engine operating as previously explained. In addition to giving true “wet” concentration of components in the exhaust stream, FTIR responds to a much wider variety of chemical species than single component gas phase engine analyzers (CO, CO$_2$, NO$_X$, UHCs, O$_2$). Data on the chemical species listed in Table 18 were collected.

FTIR data was collected simultaneously with the TDMA data, Section 9.1 can be referenced for engine operating conditions pertinent to this work. The FTIR instrument, AVL model SESAM (System for Emission Sampling and Measurement), was operated with reference spectra developed by the manufacturer specifically for ethanol fuel. The spectrometer was operated with a sample flow of 10 lpm pulled through a heated filter and sample line maintained at 185 °C. Before commencing data collection at each operating condition, the engine was run for a minimum of fifteen minutes to ensure stable operation. FTIR data was then collected at 1 hertz for the duration of the TDMA experiments, roughly one and a half hours per engine load condition.

Comparisons are made to data obtained via conventional gas analyzers at the same test conditions. Pertinent specifications of theses analyzers are shown in Table 17.
Table 17: Conventional gas analyzer descriptions

<table>
<thead>
<tr>
<th>Analyzer</th>
<th>Manufacturer</th>
<th>Model</th>
<th>Method</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>Horiba</td>
<td>VIA-510</td>
<td>NDIR</td>
<td>0-5000 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>Rosemont</td>
<td>880</td>
<td>NDIR</td>
<td>0-15%</td>
</tr>
<tr>
<td>NO/NO₂</td>
<td>California</td>
<td>600-HCLD</td>
<td>CLD</td>
<td>0-10 ppm</td>
</tr>
<tr>
<td></td>
<td>Analytical</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Instruments</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCs</td>
<td>J.U.M. Engineering</td>
<td>3-300A</td>
<td>FID</td>
<td>0-1000 ppm</td>
</tr>
</tbody>
</table>

9.2.2 Results and Discussion

Along with the chemical species examined, Table 18 shows the coefficient of variation for the data collected at each load condition. Chemical species with negative concentrations were considered to be at the noise level of the instrument and were omitted. Most COVs were well below ten percent. The notable exceptions were nitric oxide, nitrogen dioxide, and propene. The absolute magnitudes of these species are very low, less than 1 ppm. At these levels, the signal to noise ratio of the instrument was quite high, resulting in a high degree of variation in the data. An acceptable degree of variation in the data can be found at species concentrations above 1 ppm. Species with concentrations below the sensitivity of the instrument are considered not measurable and noted in Table 18.
Table 18: Chemical Species Examined via FTIR Spectroscopy

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Abbreviation</th>
<th>COV_{LowLoad}</th>
<th>COV_{MidLoad 1}</th>
<th>COV_{MidLoad 2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>H$_2$O</td>
<td>0.2%</td>
<td>0.3%</td>
<td>0.2%</td>
</tr>
<tr>
<td>Carbon Dioxide</td>
<td>CO$_2$</td>
<td>0.5%</td>
<td>0.2%</td>
<td>0.3%</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>CO</td>
<td>0.9%</td>
<td>1.0%</td>
<td>2.4%</td>
</tr>
<tr>
<td>Nitric Oxide</td>
<td>NO</td>
<td>11.8%</td>
<td>7.4%</td>
<td>4.1%</td>
</tr>
<tr>
<td>Nitrogen Dioxide</td>
<td>NO$_2$</td>
<td>159.1%</td>
<td>141.0%</td>
<td>4.7%</td>
</tr>
<tr>
<td>Nitrous Oxide</td>
<td>N$_2$O</td>
<td>3.3%</td>
<td>3.0%</td>
<td>2.4%</td>
</tr>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>n/m</td>
<td>n/m</td>
<td>n/m</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>HCHO</td>
<td>0.9%</td>
<td>0.9%</td>
<td>1.9%</td>
</tr>
<tr>
<td>Methane</td>
<td>CH$_4$</td>
<td>1.1%</td>
<td>1.1%</td>
<td>2.7%</td>
</tr>
<tr>
<td>Acetylene</td>
<td>C$_2$H$_2$</td>
<td>5.5%</td>
<td>5.0%</td>
<td>8.1%</td>
</tr>
<tr>
<td>Ethylene</td>
<td>C$_2$H$_4$</td>
<td>0.8%</td>
<td>0.9%</td>
<td>2.3%</td>
</tr>
<tr>
<td>Propene</td>
<td>C$_3$H$_6$</td>
<td>19.7%</td>
<td>98.0%</td>
<td>30.3%</td>
</tr>
<tr>
<td>Biethylene</td>
<td>C$_4$H$_6$</td>
<td>n/m</td>
<td>n/m</td>
<td>n/m</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>MECHO</td>
<td>1.2%</td>
<td>0.7%</td>
<td>2.7%</td>
</tr>
<tr>
<td>Acrylaldehyde</td>
<td>C$_3$H$_4$O</td>
<td>n/m</td>
<td>n/m</td>
<td>n/m</td>
</tr>
<tr>
<td>Ethanol</td>
<td>ETOH</td>
<td>0.8%</td>
<td>0.4%</td>
<td>0.5%</td>
</tr>
<tr>
<td>Methanol</td>
<td>MEOH</td>
<td>4.1%</td>
<td>4.7%</td>
<td>6.9%</td>
</tr>
<tr>
<td>Hydrogen Cyanide</td>
<td>HCN</td>
<td>1.1%</td>
<td>1.1%</td>
<td>2.7%</td>
</tr>
</tbody>
</table>

Figure 84 shows FTIR spectroscopy data collected at three fired engine loads and a motoring load. Results are presented on a ppm basis. To aid in comparison, emissions data gathered via conventional gas bench analysis has also been converted to a ppm basis. Motored data shows significant levels of H$_2$O, CO, CO$_2$, HCN in the air being pumped through the engine. The water is a result of high humidity conditions in the lab at the time of testing. Elevated levels of CO, CO$_2$, and HCN found in the ambient laboratory air result from inadequate lab ventilation and improperly sealed exhaust lines on various test apparatus being used during or just prior to data collection. CO and CO$_2$ are common exhaust gas species Additionally, Karlsson (2004) recently document significant levels of HCN in engine exhaust.
Figure 84: Average emissions data collected via FTIR spectroscopy from ethanol fueled HCCI combustion, 4 loads, 1500 RPM

For comparative purposes Table 19 summarizes data collected via conventional gas bench analysis for NOX (CLD), CO (NDIR), CO2 (NDIR), HC (FID), and H2O (calculated), at the same engine conditions. A 95% confidence interval was established using a t-distribution. Data for calculating the confidence intervals were collected over the course of 3 months with sample sizes of 10, 14, and 7 for the low, mid-1, and mid-2 loads respectively. Both analyses show data as ppm on a wet exhaust basis. H2O exhaust fraction is based on the carbon balance relationship developed by Heywood (1988). Because CO and CO2 were measured dry, a wet/dry correction has been applied to them using the same technique.

A chemical balance assuming complete combustion was also used to calculate expected CO2 and H2O values. Humid air was considered for this balance and the results are shown in the columns of Table 19 labeled “Calc”. The calculated CO2 values
are very close to measured values, however calculated and measured H₂O value exhibit a larger discrepancy. This is a result of the bench measured H₂O values actually coming from a hydrogen balance calculation based on fuel flows and measured hydrocarbon values which assumed dry intake air.

Table 19: Average ethanol HCCI exhaust gas composition as measured by conventional gas analyzers

<table>
<thead>
<tr>
<th>Exhaust Gas Component</th>
<th>Load Condition</th>
<th>Load Condition</th>
<th>Load Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOₓ (ppm)</td>
<td>.5 ±0.1</td>
<td>1.2±0.1</td>
<td>7.1 ±1.7</td>
</tr>
<tr>
<td>CO (ppm)</td>
<td>1970 ±70</td>
<td>1380±50</td>
<td>790 ±100</td>
</tr>
<tr>
<td>CO₂ (ppm)</td>
<td>28650 ±440</td>
<td>31110</td>
<td>35840 ±140</td>
</tr>
<tr>
<td></td>
<td></td>
<td>37950</td>
<td>43740 ±980</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>44000</td>
</tr>
<tr>
<td>H₂C (ppm, C₂)</td>
<td>810 ±50</td>
<td>1090±60</td>
<td>1320 ±60</td>
</tr>
<tr>
<td>H₂O (ppm)</td>
<td>45040 ±620</td>
<td>59940</td>
<td>55210 ±180</td>
</tr>
<tr>
<td></td>
<td></td>
<td>70110</td>
<td>66450 ±1450</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>79090</td>
</tr>
</tbody>
</table>

Table 20 shows the ratio of FTIR data divided by data collected with conventional gas analyzers for each of the species shown. The significant variation in the NOₓ data is due to the very low levels of NO, NO₂, and N₂O measured by the FTIR. With total concentrations on a single ppm scale, measurements are approaching the noise level of the instrument. Total hydrocarbons represent all compounds shown in Figure 84 from formaldehyde to hydrogen cyanide.
Table 20: Ratio of ethanol HCCI exhaust gas measurements made via FTIR compared with those collected through conventional gas analysis

<table>
<thead>
<tr>
<th>Exhaust Gas Component (PPM)</th>
<th>Low Load</th>
<th>Mid Load 1</th>
<th>Mid Load 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOx</td>
<td>1</td>
<td>166%</td>
<td>1</td>
</tr>
<tr>
<td>CO</td>
<td>2120</td>
<td>108%</td>
<td>1550</td>
</tr>
<tr>
<td>CO₂</td>
<td>25340</td>
<td>88%</td>
<td>31090</td>
</tr>
<tr>
<td>HC (C₂:EtOH)</td>
<td>800</td>
<td>98%</td>
<td>1110</td>
</tr>
<tr>
<td>THC (C₂:HCs)</td>
<td>1050</td>
<td>130%</td>
<td>1400</td>
</tr>
<tr>
<td>H₂O</td>
<td>58260</td>
<td>129%</td>
<td>66860</td>
</tr>
</tbody>
</table>

Kar and Cheng (2009) have shown similar under reporting when comparing fast response FID measurements to gas chromatograph (GC) data for an SI engine running on ethanol. When blending oxygenates with gasoline they also found that the under reporting of the FID shows a dependence on oxygenate concentration in the blend. For the HCCI tests conducted here the hydrocarbons in the exhaust stream were 76%, 80%, and 84% ethanol for the low, mid-1, and mid-2 load conditions. Comparing these proportions with those reported by Kar and Cheng for pure ethanol SI operation at a similar operating condition, 1500 RPM and 3.8 bar IMEP, we see almost twice as much ethanol in the HCCI exhaust stream. The primary contributor to the high proportion of ethanol species in the HCCI exhaust is the lesser ability of low temperature combustion to oxidize all of the fuel in the cylinder. The likelihood that an HCCI engine has far more unburned fuel than partially oxidized intermediates is higher than that of a hotter burning SI engine. The second contributor is the more thorough measurements of the GC, the authors list a calibration gas set consisting of 23 species of hydrocarbons. The FTIR reference spectra used for HCCI analysis consisted of only 11 hydrocarbon species.

Significant concentrations of formaldehyde and acetaldehyde, 40-60 ppm for each compound, were also found at each operating condition. Schuetzle et al. (1994) have identified methanol and ethanol as primary fuel precursors to formaldehyde and acetaldehyde respectively. Wallner and Frazee (2010) report little dependence of formaldehyde emissions on fuel oxygen content (alcohol proportions) for gasoline and
ethanol blends. However they do show a clear and direct dependence of acetaldehyde emissions on oxygenated fuel proportion for both ethanol and butanol blends in a DI-SI engine.

Wallner and Frazee also report much closer agreement between FTIR and CLD measured NO$_X$ emissions, however this is at NO$_X$ levels nearly 2 orders of magnitude higher than those found in our HCCI engine. The major NO$_X$ differences found in our work are clearly an artifact of trying to measure ultra low NO$_X$ levels near the minimum detection limit of the FTIR. In the same study Wallner and Frazee also presented NDIR and FTIR obtained CO$_2$ comparisons. They reported NDIR measurements on the order or 5-10% below FTIR measurements at a variety of CO$_2$ levels (engine loads) in the range of 700 to 1200 g$_{CO2}$/kW hr. The HCCI work conducted here does not agree with those findings. In our work, FTIR measured CO$_2$ was consistently 12% lower than NDIR measurements. For this study CO$_2$ levels were also close to those examined by Wallner and Frazee. Comparing our NDIR and FTIR measured CO$_2$ data with calculated values of CO$_2$ expected for complete combustion we see very reasonable agreement between NDIR data and calculated values. Examining CO measurements, our data shows FTIR response on the order of 10-20% higher than NDIR methods. The Wallner and Frazee study reported a difference of 5% lower. The cause for these discrepancies is currently unknown.

9.2.3 Conclusions

FTIR spectroscopy techniques have emerged as a popular tool for investigating regulated and non-regulated emissions in greater detail. The work presented here applies these techniques to emissions from an HCCI engine running on ethanol fuel at 3 fired loads. Comparisons have also been made to conventional exhaust gas analyzers used to examine CO, CO$_2$, HCs, and NO$_X$ (NDIR, FID, and CLD).

The limitations of the FID for estimating total HC concentration are shown to be relatively constant across all operating conditions with the FTIR reporting THC$_s$ nearly 30% higher than FID (C$_2$) measurements. These hydrocarbons were primarily alcohols, but significant fractions of aldehydes, methane, and ethylene were also present.
Increases in aldehyde formation in the emissions from alcohol fuels when compared with non-oxygenated fuels are consistent with SI engine literature (Kar and Cheng, 2009).

When examining CO$_2$, the FTIR based instrument tended to underreport the NDIR based instrument results by about 12%. These results did not show good agreement with other comparisons in the literature, however the body of literature is examining these types of comparisons is very limited. Reasonable agreement was not found when examining NO$_X$, however this is likely due to the ultra low NO$_X$ levels encountered with range of .5-5 ppm. Finally CO measurements were compared and gave results that were within reason, however, also not in full agreement with the literature.

Current combustion emissions literature is in general agreement that the addition of oxygenates to hydrocarbon fuels aids in cutting tailpipe HC emissions. To ensure that the literature is correct in reporting significant decreases in unburned hydrocarbons, when measured by FID techniques, it is important to develop an understanding of the technique and possible limitations it may have.
Chapter 10  Summary and Conclusions

A 2005 model 4HK1-TC Isuzu, 5.2 liter, 4 cylinder Diesel engine was modified for studies on HCCI combustion and emissions. A series of tests investigating three common strategies for controlling SOC in HCCI engines were conducted. The primary focus of the work was on the emissions consequences of these strategies. Brake specific emissions of CO, HCs, NO\textsubscript{X}, and PM were presented along with detailed PM size and mass distributions. Detailed analysis of the combustion process, gauged quantitatively through SOC (CA10), burn duration (CA90 – CA10), peak in-cylinder temperature, and peak heat release rate was also presented.

10.1 HCCI Combustion

The first of the experiments investigated the effect of intake temperature on combustion phasing of ethanol fueled HCCI at 3 loads and documented emission trends. Additionally, a similar set of experiments examining hydrogen fueled HCCI at 1 load were executed. All testing was conducted at an engine speed of 1500 RPM. In agreement numerous published works and modeling exercises, increases in intake temperatures led to advanced SOC and shorter burn durations at all loads for both fuels. Shorter burn durations and similar combustion efficiencies require higher rates of heat release as was shown in the data. These higher rates of heat release gave increasing peak in-cylinder temperatures in response to increased intake temperature across all test cases.

The second set of tests examined changes in combustion parameters and emissions trends in response to EGR rates. EGR rates were varied from 0 to 50 % of intake air by volume. Again 3 ethanol fueled engine loads were tested at 1500 RPM. The findings of the current literature were again validated, with increasing EGR rates leading to lower rates of in-cylinder pressure rise. More retarded SOC was also encountered along with longer combustion duration due to increased rates of EGR. Longer combustion durations gave way to lower values of peak heat release. In-cylinder temperatures remained relatively stable at low loads and increased with increasing EGR rates at higher loads.
The third set of experiments conducted characterized combustion and emissions when 2 fuels were used in varying proportions. Three loads were again examined at an engine speed of 1500 RPM. The engine was operated in an HCCI mode with ethanol as the primary fuel. Ethanol fueling was then removed, and the loss of power compensated for by supplementation of hydrogen energy in amounts of 0, 5, 10, 15, 20, and 25 % of engine output energy. Throughout all loads tested, as hydrogen energy proportion was increased, SOC advanced. The advance was increasingly pronounced as load went up, with the largest advance in SOC around 2.5 CAD. Compared to the other SOC control strategies like intake temperature and EGR rate, supplemental hydrogen fueling produced more modest changes in SOC timing. Along with more advanced combustion, increased hydrogen fueling proportions led to shorter burn durations and higher peak rates of heat release. Higher in-cylinder temperatures contributed to increasing combustion efficiency as hydrogen fueling was increased.

10.2 HCCI Emissions

HCCI shows great promise as a low emissions combustion strategy for internal combustion engines. The above research has systematically investigated some of the most common SOC control strategies and documented their emissions consequences. In an effort to clarify the root cause of changes in emissions behavior, emissions response to the combustion parameters peak HRR, and peak temperature are shown. Data in Chapter 6, Chapter 7, and Chapter 8 point to these as the primary drivers of emissions behavior. Because different control strategies can be utilized to influence in-cylinder combustion, the following summary plots illustrate the relationships between emissions and control strategies. The relationships are independent of the control strategy itself. The results show that emissions can be related to combustion parameters, although these parameters are altered via diverse means. Presented below is a summary of the emissions behavior of an ethanol and hydrogen fueled HCCI engine. The responses of brake specific gas phase emissions to in-cylinder temperatures are shown in Figure 85, Figure 86, and Figure 87. The data is from all of the testing conducted on both ethanol and hydrogen fueled HCCI combustion.
The temperature dependence of the chemical kinetics which form these pollutants is clearly shown in each figure. The beginnings of the exponentially increasing rate of NO formation around 1800 K (Johansson, 2007) can be seen as in-cylinder temperatures approach this level. Examining Figure 86 and Figure 87, we see the lower limit for optimum combustion temperature highlighted. As in-cylinder temperatures climb above 1500 K clear reductions in CO are seen. Further oxidation of hydrocarbons to CO₂ or hydrogen to water is also evident in Figure 87 as temperatures increase. These trends are also manifested in increasing combustion efficiency. In all cases examined, the combustion efficiency, calculated from unburned fuel, peaked at the highest in-cylinder temperatures. Combustion efficiencies ranged from 70 to 95% for ethanol HCCI and from 94 to 96% for hydrogen HCCI. The lowest combustion efficiencies represented cases of intermittent misfire.

![Figure 85: BSNOₓ v. peak cylinder temperatures for ethanol and hydrogen HCCI with SOC controlled by multiple strategies](image)

Figure 85: BSNOₓ v. peak cylinder temperatures for ethanol and hydrogen HCCI with SOC controlled by multiple strategies
Figure 86: BSCO v. peak cylinder temperatures for ethanol and hydrogen HCCI with SOC controlled by multiple strategies.

Figure 87: BSHC of BSH\textsubscript{2} v. peak cylinder temperatures for ethanol and hydrogen HCCI with SOC controlled by multiple strategies.
Inspecting all BSPM data, the clearest relationship was shown between BSPM and peak HRR. It is shown in Figure 88 with the highly variable intake temperature data, especially at low loads, highlighted.

![Figure 88: BSPM v. peak HRR for ethanol and hydrogen HCCI with SOC controlled by multiple strategies](image)

A multiple regression analysis examining the relationship between total particulate mass and the combustion parameters; SOC, combustion duration, peak temperature, and peak heat release rate was conducted. Utilizing ethanol HCCI data from the variable intake temperature, variable EGR, and hydrogen supplemented HCCI tests, an initial $R^2$ of .51 was found with a sample size of 44. As in the earlier regression analysis examining only the variable intake temperature data, this analysis was repeated with the omission of the highly variable low load condition. The new regression gave a $R^2$ of .66 with sample size of 38. Taking into account the sporadic behavior of the variable intake temperature data explained in section 6.3, a final regression was conducted omitting all of this data. The final $R^2$ jumped sharply to .82. Omitting all of the variable intake temperature data still left a sample size of 30, due to the contributions of the EGR and supplemental hydrogen data.
Table 21 is a correlation matrix showing the relationship of emissions to common combustion parameters. The trends were established through the analysis of ethanol HCCI, ethanol HCCI with supplemental hydrogen fueling, and pure hydrogen HCCI. In the BSFC column an optimization point was found in most cases, where increases in the independent variable lead to decreases in BSFC initially, however a minima was eventually reached and BSFC started to increase with increasing SOC. The arrows indicate the response of the emissions characteristics to increases in peak temperature, peak heat release rate, and combustion duration respectively. In the case of SOC the arrows indicate the response of the emissions characteristics to delays in SOC.

### Table 21: Correlation matrix relating emissions to combustion properties in fully premixed HCCI combustion of ethanol and hydrogen

<table>
<thead>
<tr>
<th></th>
<th>PM Total Mass (µg/m³)</th>
<th>BSPM (g/kW hr)</th>
<th>BSFC (g/kW hr)</th>
<th>BSHC (g/kW hr)</th>
<th>BSCO (g/kW hr)</th>
<th>BSNOₓ (g/kW hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Temp (K)</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>Peak HRR (J/CAD)</td>
<td>↑</td>
<td>↑</td>
<td>↓</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
</tr>
<tr>
<td>SOC, CA 10 (*ATDC)</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
<td>↑*</td>
<td>↑*</td>
<td>↓</td>
</tr>
<tr>
<td>Duration (CAD)</td>
<td>↓</td>
<td>↓</td>
<td>↑</td>
<td>↑*</td>
<td>↑*</td>
<td>↓</td>
</tr>
</tbody>
</table>

*Trends are not clearly defined when EGR is employed to control combustion phasing

Analysis of particle volatility was conducted through TDMA techniques to gain further understanding of the composition, and ultimately sources, of fully premixed ethanol HCCI particulate matter. The results suggested lubricating oil as the primary contributor to particulate matter in these types of engines.
Analysis of the lubricating oil consumption literature points to oil vaporization from the cylinder walls, reverse gas flow and piston throw-off as the primary routes of oil consumption at the load conditions found throughout our study. A relative insensitivity of the oil film to combustion gas temperatures, in terms of cycle by cycle resolution, in CI and SI engines has been published in the literature is likely true for this HCCI work as well. The cylinder liner temperature will however increase as increases in in-cylinder temperatures require more heat flow to the coolant circuit. Furthermore increased bulk cylinder gas temperatures enhance evaporation of oil droplets generated via reverse gas flow and piston throw-off.

Total particulate mass rates found here were somewhat less than published oil consumption rates. A direct match in these rates was not expected however. Because the higher volatility fractions of the oil are evaporating at the highest rate, the likelihood that these species achieve full or partial oxidation in a low temperature combustion environment is reasonable. This hypothesis combined with the substantial blow-by of the high compression test engine, which routes crankcase fumes out to the ambient, serves to compensate for the difference between published oil consumption rates and the total particulate mass rates found here.

In summary, these findings strongly suggest that although essentially free of accumulation mode (soot) particles, nucleation mode particulate matter is present in significant mass and number in the exhaust of fully premixed HCCI engines. These results are also indicative of the behavior to be expected from other modern low sooting engines. Precursors to this particulate matter are primarily derived from more volatile species in the lubricating oil. The abundance of volatile precursor and lack of adsorption and condensation sites create ideal conditions for homogeneous nucleation.
Aakko, P., & Nylund, N. Particle emissions at moderate and cold temperatures using different fuels.


distributed generation. *Internal Combustion Engine Division of ASME 2005 Fall Technical Conference, Ottawa, Canada.*


Morgan, N. (2010). *Composition of shell rotella 15W-40 lubricating oil*


