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APPENDIX A. BACKGROUND ON ENGINE COMBUSTION PROCESSES

Formation of pollutants depends on the mixing and combustion modes in any reaction system. For example because of the different environments, emissions formation in a traditional CI engine is totally different from that in a traditional gasoline engine. In order to meet the stricter pollution control regulations, we first have to know how the various engine combustion processes affect the emissions for different engines.

A 1. CI engine combustion process

In CI engines the liquid fuel is injected at high pressure directly into the combustion chamber when the piston is near compression TDC. The fuel injector nozzles atomize the fuel, which evaporates and mixes with the compressed air in the high-temperature, high-pressure environment. Once the vapor and air mixture forms and the local temperature exceeds the autoignition temperature, this region will ignite undergoing premixed combustion. This partial energy release is followed by a period of mixing controlled combustion which consumes the fuel. Modern compression ignition engines follow neither the constant-volume heat addition nor the constant-pressure heat addition cycle presented in undergraduate thermodynamics courses, rather heat release occurred at both constant volume (pre-mixed combustion) and at constant pressure (diffusive mixture combustion) conditions. Since diesel engine are operated under high compression ratio, the theoretical thermal efficiency of CI is 30-40% larger than SI. In fact a simple switch from SI to CI engines in light-duty trucks would improve the Corporate Average Fuel Economy (CAFE) to 22.2 mpg
from the current 20.7 mpg and allow all the manufacturers to easily meet the requirements for 2007. Therefore, the diesel engine has become a prime candidate for future transportations’ needs because of the increasing threat of limited oil resources and global warming due to CO₂ emissions.

However, although the diesel engine improves fuel economy it has a problem with emissions NOx and Particulate Matter (PM). The high temperature in diesel engines leads to high NOx, while fuel rich oxidation in some regions produces elevated particulate concentrations. Unfortunately it is difficult to reduce these two pollutants simultaneously. A number of sub-system advances are needed in order to meet the emissions regulations, some of these are:

- Improvement in the fuel injection systems by using higher pressures
- Improvements in after-treatment to reduce NOx and particulate levels
- Improvement Exhaust Gas Recirculation (EGR) system
- Improvement in turbochargers that will be faster acting, enhance transient response, and reduce their costs
- Advances in control electronics

Based on the evaluation of the potential of different injection systems, looking particularly at the distributor pump, unit injection system and common rail system, the common rail system is firstly selected, its capability to maintain the constant high pressures during injection, support variable injection timing and duration [Fulton and Leviticus, 1993], and multiple-injection [Lee and Reitz, 2003]. By increasing rail pressure with different nozzle geometries, the experimental
results show significant benefits in NOx/smoke trade off at part load condition with high Exhaust Gas Recirculation (EGR) rate. At full load conditions and low engine speed the mixture formation improves with increased rail pressure in combination with reduced nozzle hole diameter and results show significant benefits in terms of smoke emissions [Schommers et al., 2000]. The extensive research carried out over the last years has led to the consideration of split injection as an effective means to reduce NOx and particulates emissions, in which double-pulse, and even multi-pulse injections were used [Corcione et al., 2002]. By properly timing the separation between pilot and main injection it is possible to minimize both NOx and soot [Chi et al., 2002].

Early models of diesel combustion assumed that a burning diesel jet was composed of a dense fuel-rich core surrounded by a uniformly leaner fuel-air mixture. Autoignition occurred in the near stoichiometric regions. Soot was assumed to form in a narrow region on the fuel-rich side of the diffusion flame. Dec [1997] has proposed a conceptual spray and combustion model of CI engines based on laser imaging of combustion of an atomized spray. Dec suggests two stages of oxidation for both the premixed and the mixing controlled combustion phases. The first stage is partial oxidation of the fuel in a rich premixed reaction, and the second stage is combustion of the fuel-rich, partially oxidized products of the first stage in a near stoichiometric diffusion flame.

As the liquid fuel is injected into the cylinder, it entrains hot cylinder air along the sides of the jet, leading to fuel evaporation. The liquid length of the jet is relatively insensitive to the injection pressure [Siebers, 1998]. With further
injection a vapor head vortex is formed in the leading portion of the jet downstream of the liquid jet. The fuel vapor-air mixture region in the head vortex is relatively uniform. The premixed combustion begins in the vortex, where the equivalence ratio is between 2.0 – 4.0 throughout its cross section, and produces PolyAromatic Hydrocarbons (PAHs) and soot.

Then, a turbulent diffusion flame forms at the edge of the jet around the products of the initial premixed stage. This turbulent diffusion flame begins the transition to the mixing controlled phase, and is near stoichiometric. The diffusion flame causes the formation of larger soot particles at the jet periphery. Finally, the jet reaches a quasi-steady condition in which the general features of the jet do not change significantly as it expands across the combustion chamber.

In addition, combustion chamber shape and in-cylinder air motion including swirl, squashing motion and turbulence in diesel engines are two other prime factors that affect fuel evaporation, mixture, and combustion [Lu et al., 2000]. They are also critical factors influencing the performance of diesel engines and may be optimized in term of higher efficiency and lower emissions.

NOx is formed throughout the entire combustion process due to the reaction of atomic oxygen and nitrogen. The reactions forming NOx are very temperature dependent, so NOx emissions from an engine are proportional to the engine load. NOx is formed in the high temperature regions at the diffusion flame interface where both oxygen and nitrogen are available, and in the postcombustion hot gas regions [Miller and Bowman, 1989].
Due to diffusive combustion of very rich mixtures, even fuel, soot formation is unavoidable. While most of the soot is destroyed in the diffusion flame, the soot that is not oxidized becomes an exhaust emission [Schommers et al., 2000]. The only ways to eliminate soot is through further oxidation during the expansion stroke or by after-treatment.

CO and Unburned Hydrocarbon (UHC) emissions from CI engines are usually lower than those in SI engines. CO is usually oxidized later in the combustion process using the excess air that is always present in CI engines. UHC come primarily from; (1) fuel trapped in the injector at the end of injection that ultimately diffuses out, (2) fuel mixed into air surrounding the burning sprays in regions sufficiently lean that it can not burned, and (3) fuel trapped along the walls by crevices, deposits, or oil due to impingement by the spray [Yu et al., 1980]. UHC and CO can further be oxidized during the exhaust stroke when the UHC emit from the crevices.

### 2. SI engine combustion process

In Port-Fuel-Injected (PFI) SI engines the fuel mixes with air in the intake manifold to form a homogeneous charge with equivalence ratio of about 1.0. When the spark plug fires, a flame kernel is formed and a flame propagates through the homogenous charge. SI engines resemble the constant-volume heat addition cycle presented in thermodynamics texts. In this simple analysis the thermal efficiency depends only on the compression ratio. Unfortunately, the compression ratio is limited due to autoignition of the unburned gases (called “end gas”) ahead of the flame. This autoignition create pressure waves that
travel through the combustion gases. Oppenheim [1984] presented a generic
definition of knock as “an undesirable mode of operation that originates
spontaneously and sporadically in the engine, producing sharp pressure pulses
associated with a vibratory movement of the charge and the characteristic sound
effect from which the phenomena derives its name.” Modern explanations
identify that compression of the end gas by the flame front raises the end gas
temperature beyond the autoignition point. The implication of knock is that it
limits engine efficiency.

In the combustion process of a SI engine, turbulent flame propagation is
always important. Turbulence significantly increases flame propagation speed so
that the end gas has less time to autoignite. As a result, compression ratio may
be increased, resulting in higher thermal efficiency. Turbulence characteristics of
flows in engine cylinders have been measured using both hot-wire anemometry
and laser Doppler velocimetry. In addition to turbulent intensity, to fully
characterize a turbulent flow, one needs to also specify the distribution of the
random vortices that make up the turbulence. There are three scales to describe
different vortices, as following:

The integral scale is the distance where the correlation between the local
velocities at two points is zero. It represents the largest turbulent vortex size.
The Taylor microscale is useful in estimating the mean strain rate of the
turbulence. The Kolmogorov microscale, which is the smallest size viscous
damping will allow.
There are three regimes for turbulent flames. The regimes are wrinkled laminar flame, flamelets in eddies, and distributed reaction. SI engines operate in the wrinkled laminar flame and flamelets in eddies regimes, depending on the engine speed.

In the wrinkled laminar flame regime, the flame thickness is thinner than the smallest turbulent eddy thickness, and the turbulent intensity is of the same order as the laminar flame speed. The effect of turbulence in the cylinder therefore is to wrinkle and distort the laminar flame front. The turbulent flame speed can be 3 to 30 times the laminar flame speed, depending on the turbulent intensity.

At higher engine speeds the turbulent flame regimes can transition from the wrinkled sheet to the flamelets-in-eddies regime [Abraham et al., 1985]. In the flamelets-in-eddies regime, the flame thickness is greater than the small eddy thickness, but less than the integral thickness, and the turbulent intensity is much greater than the laminar flame speed. The increased wrinkling can result in the creation of pockets of unburned gases. In this regime, the burning rate is controlled by the turbulent mixing rate, i.e., the integral length scale, not the chemical reaction rate. Swirl, squishing gas motion, and tumbling gas motion are used in order to increase turbulence levels in SI engines.

In addition, the combustion also depends on the combustion chamber geometry. Not surprisingly, the combustion chambers in SI engines are compact to shorten flame propagation distance.
Due to the homogenous mixture the SI engine has no soot emissions. However, there exist other emissions, even more serious than the diesel engines. Formation of NOx emissions is very temperature dependent similar to diesel engines. The dominant component of NOx is nitric oxide, NO. The most significant reaction mechanism forming NO is the Zeldovich mechanism in which NO is formed in the high temperature burned gases behind by the flame front [Miller and Bowman, 1989].

CO appears in the exhaust of rich-running engines since there is insufficient oxygen to convert all the carbon in the fuel to CO₂. The most important engine parameter affecting CO emission is the fuel-air equivalence ratio in each cylinder. Since CO₂ and CO are in equilibrium at high temperature conditions, with temperatures down to around 1800 K in the expansion stroke, the chemistry in C-O-H system starts to become rate limited and is generally frozen by the time burned gases are leaving the cylinder [Heywood, 1976]. CO formation is unavoidable and CO concentration is the highest of all emissions, if 3-way catalysts aftertreatment is not installed.

About 9% of the fuel supplied to an engine is not burned during the normal combustion phase of the power expansion stroke, in which 2% of total fuel will go out with the exhaust, including partial reaction products, such as acetaldehyde, formaldehyde, 1, 3 butadiene, and benzene, etc. [Cheng et al., 1993]. Hydrocarbon emissions represent a decrease in engine thermal efficiency and main air pollutions. Six main sources of UHC emissions are: (1) crevices, (2) oil layers, (3) carbon deposits, (4) cylinder wall flame quenching, and (5) exhaust
valve leakage. Combustion chamber crevices are major sources of UHC emissions, responsible for about 40% of the UHC. Of the combustion chamber crevices, the piston upper crevice volume is the main contributor to engine-out UHC emissions. In general, the sensitivity of the UHC emissions to the combustion-chamber crevices is influenced strongly by the in-cylinder flow field and combustion, which influence the concentration of burned gases in the crevice gases. UHC can further be oxidized during the exhaust stroke when the UHC emit from the crevices and through 3-way catalyst aftertreatment.

A 3. Direct-injection SI engines

Over the past two decades, attempts have been made to develop an internal combustion engine for automotive applications that combines the best features of the SI and the CI engines. The objective has been to combine the specific power of the gasoline engine with the efficiency of the CI engine. Such an engine would exhibit a brake-specific fuel consumption (BSFC) similar to a CI engine, while maintaining the operating characteristics and specific power output of the SI engine. In the same as for the diesel, the power output of the engine is controlled by the amount of fuel injected into the cylinder and the fuel diffuses and mixes with air. By using a spark plug to ignite the stratified fuel/air mixture, many of the requirements of autoignition quality are avoided, which are inherent in fuels for the CI engine. Furthermore, by proper alignment the spark plug and the fuel injector, overall ultra-lean-operation may be achieved. Therefore, the development of spark-ignition engines with fuel injection directly into the
combustion chamber is an important worldwide initiative of the automotive industry [Harada et al., 1997; Noma and Iwamoto, 1998; Kawamoto et al., 2005].

The theoretical advantages of the gasoline-direct-injection (GDI) engine over the PFI engine are summarized as follows, along with the reasons:

- Improved fuel economy, even up to 25%, resulting from:
  - higher compression ratio;
  - less pumping loss (unthrottled, stratified mode);
  - less heat losses (unthrottled, stratified mode);
  - less acceleration-enrichment required;
  - less cold-start over-fueling required.

- improved transient response;
- more precise air–fuel ratio control;
- more rapid starting;
- selective emissions advantages;
- reduced cold-start UBHC emissions;
- reduced CO₂ emissions.

However, there are some disadvantages for the GDI engine, including

- difficulty in controlling the stratified charge combustion over the required operating range;
- complexity of the control and injection technologies required for seamless load changes;
- relatively high UHC emissions at low load conditions;
- relatively high NOx emissions; requiring lean-NOx catalysts;
- increased particulate emissions.

One of the significant advantages of the four stroke GDI engine is a potential reduction in UHC emissions during an engine cold start and warm up. However, due to the stratified nature of GDI engines, increased UHC emissions result from different sources compared with a conventional SI engines [Zhao et al., 1999]:

- flame extinction occurs for the very lean mixtures near the outer boundary of the stratified charge;
- poor combustion occurs in the rich regions near the piston crown or cylinder wall due to spray–wall wetting;
- lower combustion temperature reduces the degree of post-flame oxidation of UHC;
- lower exhaust gas temperatures degrade the conversion efficiency of the catalyst system and significantly reduce the occurrence of UHC oxidation in the exhaust port.

Since GDI engines operates with a stratified charge, the average temperature is low due to the overall lean operation. However, the temperature
within the core reaction zone remains high due to the presence of a stoichiometric or slightly rich mixture, where NOx is produced easily, even at idle condition. In addition, high compression ratio leads to higher combustion temperature, resulting in more NOx production and emission. However, the NOx level of the GDI engine operating without EGR is similar to that of the PFI engine. It will be a major challenge to achieve the regulatory levels of NOx emissions, particularly for the North American market [Ando et al., 2001].

PM can be formed in diffusion burning of either a locally rich, gaseous air–fuel mixture or incompletely volatilized liquid fuel droplets. The latter is a major source for late injection timing and the PM concentration decreases monotonically as the injection timing is advanced. Accordingly, in GDI engines there probably are rich fuel regions to form PM. As a consequence, reducing PM emissions is also a challenge [Maricq et al., 1999].

As we known, a high compression ratio is the most critical to increase thermal efficiency for all engines. No rich fuel region ($\phi<1.0$) in the air/fuel mixture, or homogeneous mixture is necessary to eliminate PM. Finally, lean or diluted mixture is required to attain low combustion temperature and therefore achieve reduced NOx emissions.

A 4. Homogenous Charge Compression Ignition (HCCI) engines

HCCI is an alternative and attractive combustion mode for internal combustion engines that offers the potential for high diesel-like efficiencies and dramatic reduction in NOx and PM [Najt and Foster, 1983; Thring, 1989; Ryan and Callahan, 1996; Odaka et al., 1999; Marriott and Reitz, 2002; Hyvönen et al.,
HCCI occurs as the result of spontaneous autoignition at multiple points throughout the volume of the charge gas and each autoignition may or may not produce a flame front. In order to control the energy release rate to acceptable levels the engine must be operated with high levels of dilution, exhaust or extra air, which results in significantly reduced pumping losses for SI engines and lower peak burned gas temperature. With appropriately higher compression ratio and less heat lose due to low combustion temperature, the thermal efficiency approaches the levels of CI engines. The low combustion temperature also dramatically reduces NOx emissions [Dickey et al., 1998]. Unlike conventional diesel combustion, the charge is well mixed, so PM emissions can be very low. With increasingly stringent emissions legislation, HCCI is the most promising candidate to solve the emissions problem.

However, some technical issues limit the application of HCCI and require development:

- combustion phasing – both start of autoignition and control of combustion rate – perhaps the greatest challenges;

- CO and UHC emissions, resulting from low combustion temperature, particularly at lower load conditions, and from crevices and boundary layer [Dec, 2002; Christensen et al., 2001; Easley et al., 2001; Hilditch et al., 2003];

- stability over required operating range;
• high load conditions: detonation and NOx emissions;
• cold start;
• power density;
• transient operation (operating mode transition).

HCCI combustion was first discovered as an alternative combustion mode for two-stroke IC engines by Onishi et al. [1979]. They successfully utilized a perceived drawback of “run-on” combustion with high level of residuals and high initial temperature at light load condition to achieve a stable lean combustion with lower exhaust emissions, specifically UHC, and fuel consumption. This new combustion mythology was named “Active Thermo-Atmosphere Combustion” (ATAC). By observing the combustion process in an optical engine they found that during this combustion mode there was no discernable flame propagating through the chamber, indicating combustion occurred as a multi-center autoignition process. Onishi et al. identified that the critical parameter to obtain ATAC was the initial temperature of the well-mixed charge consisting of fuel, air and residuals.

In the same year Noguchi et al. [1979] conducted a spectroscopic analysis on HCCI combustion in an opposed piston, two-stroke engine. They measured high levels of CHO•, HO2•, and O• radicals within the cylinder prior to autoignition, which demonstrated that pre-ignition chemical reactions had occurred and these reactions contributed to the autoigniton. After autoignition took place, H•, CH•, and OH• radicals were detected, which were indicative of
high-temperature chemical reactions. In a traditional SI engine, these radical species are only associated with end-gas autoignition, namely knock, which confirmed the similarities between the reactions of HCCI and knock in an SI engine.

To investigate the fuel suitability and broaden the stable operation range for HCCI in two-stroke engines, Lida [1994, 1997] and Kojima and Norimasa [2004] performed a series of experiments using fuels such as methanol, dimethyl ether, ethanol, propane and n-butane to investigate fuel adaptation and the composition and the exhaust mechanism of the exhaust gas. In addition, Honda demonstrated the reliability of HCCI engines in a pre-production two-stroke motorcycle engine [Yamaguchi, 1997].

Based on previous HCCI works in two-stroke engines, Najt and Foster [1983] successfully conducted HCCI experiments in a four-stroke engine with blends of paraffinic and aromatic fuels over a range of engine speeds and dilution levels. The intake air had to be heated to a high level to achieve HCCI operation due to the low level of internal residuals inherent in four-stroke engines. From simplified chemical kinetically controlled modeling and heat release analysis, they concluded that HCCI combustion is a chemical kinetic combustion process, in which HCCI autoignition is controlled by the same low temperature (below 1000 K) chemistry as that occurring during SI engine knock and in which most of the energy release is controlled by the high temperature (above 1000 K) chemistry. They realized that HCCI suffers from uncontrolled ignition timing and limited operating range. Thring [1989] extended the work in a four-stroke engine
using fully-blended gasoline and mapped the operating regime as a function of equivalence ratio and External EGR rate. The load range limitations of HCCI were noted and an engine operating strategy was put forward, suggesting use of HCCI mode at part load and transitioning into SI flame mode at high load condition.

HCCI research has continued over the past 20 years. Experiments have been conducted in four-stroke engines operating on fuels as diverse as gasoline, diesel, methanol, ethanol, LPG, natural gas, etc. with and without fuel additives, such as iso-propyl nitrate, dimethyl ether (DME), di-tertiary butyl peroxide (DTBT) etc.. A variety of physical control methods (e.g., EGR) have been examined in an effort to obtain wider stable operation [Odaka et al., 1999; Ryan and Callahan, 1996; Christensen et al., 1997, 1998, 2000; Aceves et al., 1999; Allen and Law, 2002; Nordgren et al., 2004; Caton et al., 2005]. From these investigations and many others in the past five years it appears that the key to implementing HCCI is to control the charge autoignition behavior which is driven by the combustion chemistry.

Even more than in IC engines, compression ratio is a critical parameter for HCCI engines. Using high octane fuels, the higher the compression ratio the better in order to ignite the mixture at idle or near-idle conditions. However, compression ratios beyond 12 are likely to produce severe knock problems for the richer mixtures used at high load conditions. It seems that the best compromise is to select the highest possible CR to obtain satisfactory full load performance from SI fuels [Najt and Foster, 1983]. The choice of optimum
compression ratio is not clear; and it may have to be tailored to the fuel and other techniques used for HCCI control. For early direct-injection diesel-fueled HCCI engines compression ratios must also be limited to mitigate the problem of over-advanced autoignition resulting from pre-ignition chemical reactions [Gray and Ryan, 1997; Ryan et al., 2004; Helmantel et al., 2005]. For these applications other measures should be explored for control of HCCI operation at idle or near idle conditions.

Another critical factor to obtain appropriate combustion phasing in HCCI is EGR [Cairns and Blaxill, 2005]. At lower load conditions for HCCI, especially, using high octane number fuels, the effect of internal EGR is to provide sufficient thermal energy to trigger autoignition of the mixture late in the compression stroke. At higher load conditions for HCCI, especially, using high cetane number fuels cold external EGR is required to retard over-advanced combustion phasing. Effects of external EGR on autoignition of the mixture are different from that of internal EGR even when both the EGR mixtures are at the same temperature [Law et al., 2002].

In four-stroke engines with flexible valve actuation, there are several strategies for internal EGR. One is the rebreathing strategy of Law et al., [2001] where the exhaust valve remains open throughout the intake stroke; another is the exhaust recompression strategy [Zhao et al., 2002]. Milovanovic et al. [2004] demonstrated that the variable valve timing strategy has a strong influence on the gas exchange process, which in turn influences the engine parameters and the cylinder charge properties, hence the control of the HCCI process. The EVC
timing has the strongest effect followed by the IVO timing, while the EVO and IVC timing have the minor effects. Caton [2005] showed that the best combination of load range, efficiency, and emissions may be achieved using a reinduction strategy with variable intake lift instead of variable valve timing. However, no strategy is able to obtain satisfactory HCCI combustion at near-idle loads. Also, under high levels of internal EGR the emissions are re-ingested in the engine and have an extra chance to be burned in the next cycle.

Intake air temperature can be used to modify HCCI combustion phasing, but the controllable range has severe limits. Outside this range the engine volumetric and thermal efficiency are largely reduced due to too advanced autoignition timing. Also variation of intake temperature is generally a slow process, so this method is not really practical, especially under a transient condition [Sjöberg et. al. 2005].

Increasing cylinder pressure through supercharging or turbocharging is an effective means to increase the engine’s IMEP and extend the operational range of equivalence ratio for a HCCI combustion mode. Unfortunately, the higher cylinder pressures make autoignition control at high loads even more critical, which limits its potential application. Christensen et al. [1998] achieved high loads up to 14 – 15 bar and ultra low NOx emissions; and by preheating the intake air CO emission was negligible. However, the typical low exhaust temperatures of HCCI require special care in turbocharger design in order to achieve high load/high efficiency operation. Hyvönen et al. [2003] investigated that the HCCI operation range with both mechanical supercharging and
simulated turbocharging and compared with a natural aspirated SI with gasoline as fuel. The operating range can be more than doubled with supercharging and higher brake efficiency than with a natural aspirated SI is achieved at the same loads.

An alternative solution to extending operating the range is to operate the engine in a ‘hybrid mode’, where the engine operates in HCCI mode at low, medium and cruising loads and switches to spark ignition (SI) mode (or diesel mode-CI) at cold start, idle and higher loads [Milovanovic et al., 2005].

Urushihara et al. [2005] used SI in a stratified charge to initiate autoignition in the main homogeneous lean mixture eliminating the need to raise the temperature of the entire charge. A higher maximum IMEP was achieved with SI-CI combustion than with conventional HCCI combustion. However, nitrogen oxide (NOx) emissions increased due to the SI portion of the combustion process.

Spark ignition has also been used for affecting the HCCI combustion initiation. For the same combustion phasing, compression ratio and inlet air temperature can be decreased with spark assistance. The effect from spark assistance decreases with decreasing equivalence ratio ($\phi$) and can be used low to about $\phi = 0.333$ [Kontarakis et al., 2000; Hyvönen et al., 2005].

Recent advances in extending the operational range has utilized stratification at all three parameters: fuel, temperature and EGR.
Fuel injection system determines mixing effect of fuel, air and EGR. For gasoline a conventional PFI injection system can form a good homogeneous mixture [Kontarakis et al., 2000]. Fuel stratification can extend the HCCI low and high load limit. Additionally, by a direct injection accompanied with exhaust recompression strategy [Willand et al. 1998], the fuel injected into exhaust prior to the intake process will undergo pre-ignition reactions and thus promote whole chemical reaction system. As a consequence, the operational range can be extended toward low load conditions. However, the stratified mixture resulting from late injection leads to more NOx and even PM formation.

Stratification of fuel is absolutely necessary for HCCI using diesel type fuels, at high load conditions. Although the HCCI combustion of diesel type fuels can be more easily achieved than with gasoline type fuels because of the diesel fuels’ lower autoignition temperature, overly advanced combustion timing can cause low thermal efficiency and serious knock at high load conditions. In addition, mixture preparation is a critical issue. There is a problem getting diesel fuel to vaporize and premix with the air due to the low volatility of the diesel fuel [Christensen et al., 1999; Peng et al., 2003]. Many of investigators [Ryan and Callahan, 1996; Christensen et al., 1999; Helmantel and Denbratt, 2004; Ra and Reitz, 2005] have indicated the potential for HCCI to reduce NOx and PM emissions. However, premixed HCCI is not likely to be developed into a practical technique for production diesel engines due to fuel delivery and mixing problems.
This has led to the consideration of alternative diesel-like fuel delivery and mixing techniques, such as early direct-injection HCCI and late direct-injection HCCI, which produce a stratification of equivalence ratio.

Early direct-injection has been perhaps the most commonly investigated approach to diesel-fueled HCCI. By appropriate configuration of the cylinder, fuel mixing with air and EGR can be promoted. However, the injector must be carefully designed to avoid fuel wall wetting, which can result in increased UHC emissions and reduced thermal efficiency [Akagawa et al., 1999]. If mixing is not achieved, NOx and PM formation will be enhanced. Combustion phasing remains a critical issue in this kind of HCCI. The UNIBUS (UNIform BUJky combustion System) using early direct-injection, which was introduced into production in 2000 on selected vehicles for the Japanese market, chose a dual-injection strategy [Yanagihara, 2001]. Su et al. [2005] used multi-injection modes. The injection rate pattern, the mass ratios between pulses and the pulse number have been proved to be very important parameters in achieving acceptable results.

One of the most successful systems to date for achieving diesel-fueled HCCI is late-injection DI-HCCI technique known as MK (modulated kinetics) incorporated into their products of the Nissan Motor Company. In the MK system, fuel was injected into the cylinder at about 3 CAD ATDC under the condition of a high swirl in the special combustion chamber. The ignition delay is extended by using high levels of EGR [Mase et al. 1998; Kimura et al., 2001].
The effectiveness of combustion retardation to reduce pressure-rise rates increases rapidly with increasing temperature stratification. With appropriate stratification, even a local stoichiometric charge can be combusted with low pressure-rise rates. Sjöberg et al. [2005] suggested that a combination of enhanced temperature stratification and moderate combustion retardation can allow higher loads to be reached, while maintaining a robust combustion system. The effect of EGR stratification also takes a role in enhancing stability through fuel and temperature stratifications.

Controlling the coolant temperature also extends the operational range for a HCCI combustion mode [Milovanovic et al., 2005]. Additionally, Since MTBE and ethanol have low cetane numbers, two additives mixing in diesel fuel could delay overly advanced combustion phasing [Akagawa et al., 1999]. Moreover, water injection also improved combustion phasing and increased the duration of the HCCI, which can be used to extend the high load limit [Nishijima et al., 2002]. However, UHC and CO emissions increased for all of the cases with water injection, over a broad range of water loading and injection timing.
APPENDIX B. BACKGROUND ON COMBUSTION CHEMISTRY

B 1. Autoignition chemistry studies

Studies of autoignition began in the early 1900’s when knock was identified as a limitation on engine output and fuel efficiency. Most of the work in spark ignition (SI) engines related to autoignition suggests that autoignition is strongly affected by fuel additives and oxidation with heat release ahead of the advancing flame front.

In 1920, Midgley [1920] studied relative knocking characteristics in a firing engine for paraffinic gasoline and kerosene. The connection between the longer chain length of the kerosene and its greater knocking tendency was noted. A variety of pure compounds including ethanol, n-butyl alcohol and benzene showed good knock resistance. As discussed in a review paper [Litzinger 1990], in 1928 Ricardo and Thornycraft investigated the general knocking characteristics of paraffins, naphthenes and aromatics. They found that naphthenes have markedly less knock tendency than paraffins and the neat aromatics could not be made to produce knock.

The first evidence of preflame reactions was presented by Withrow and Rassweiler referred to Litzinger [1990]. From the absorption spectra of end gases in a firing engine, they found absorption lines appear prior to the passage of the flame and become more intense under knocking conditions. Later work identified formaldehyde as the source of some of the spectra observed and thus demonstrated that the fuel was undergoing oxidation reactions ahead of the flame. The preflame reactions were further observed by Egerton et al. [1935]
using a sampling valve to withdraw samples of end gases. Concentrations of oxygen, carbon monoxide, carbon dioxide, total aldehydes and peroxides were obtained as a function of crank angle for commercial gasoline with and without tetraethyl lead (TEL) and for pure benzene. Hydroperoxide was found to exist close to TDC in sufficient quantities to cause knock.

In 1948 Lovell related the chemical structural of hydrocarbons to a fuels tendency to knock [Litzinger, 1990]. For alkanes, Lovell noted that the knock tendency of fuel decreases for alkanes with shorter chains and more branching and for alkenes with the double bond closer to the center of the straight-chain alkene.

Several studies were conducted in 1950’s dealing extensively with the heat release associated with the pre-combustion reactions. A key issue was the role of this pre-combustion heat release in increasing the temperature of the end gases and thereby causing or contributing to knock. Pastell [1950] presented results on the pressure rise associated with pre-combustion reactions in a motored CFR engine. During a study of the two stage autoignition in motored engines, based on a review paper by Litzinger [1990], in 1951 Levendahl and Howard investigated the heat release in the first stage of autoignition for n-hexane, benzene, n-heptane, two heptenes, 1-hexanol and n-heptaldehyde.

The effects of additives on knock were subsequently studied by Downs et al. [1951]. Alkyl peroxides, aldehydes and hydrogen peroxide were investigated. The results seem to demonstrate the key role of alkyl peroxides in the knock process since only these compounds had a significant effect on knock tendency.
at levels that might exist in a firing engine. Thus, the results strongly support the importance of low temperature chemistry which forms the alkyl peroxides. In the aldehyde testing, formaldehyde, acetaldehyde, propionaldehyde, and butylaldehyde were added in molar concentrations of 5% or more to a full boiling gasoline. Interestingly, the formaldehyde acted as an anti-knock and the other aldehydes were only slightly pro-knock.

Davis et al. [1955] found that the motored engine produced quite similar carbonyl species profiles to those obtained in the fired engine. The experiments were conducted in an CFR engine fueled with n-pentane, n-heptane, and iso-octane. On the basis of this similarity, the authors state that “the motored engine is a convenient and valid research tool for combustion research, since apparently it duplicates precombustion reactions which occur in an engine under normal operating conditions”. Since then, the motored engine has been widely used as a research tool for the study of autoignition chemistry.

In the 1960’s, based on numerous studies autoignition chemistry in a variety of facilities, including static reactors, flow reactor, compression machines, and engines, the general oxidation mechanism of alkanes at low and intermediate temperatures was proposed. Significant advances in gas chromatography (GC) technology allowed for detailed speciation of end gas compositions. Thus, the postulated underlying chemical reaction schemes could be validated, corrected and improved.

Walsh [1963] proposed a mechanistic link between knock tendency and fuel structure and suggested that the isomerization of the RO$_2$• radical (where
RH is the original fuel molecule, and $R_\bullet$ is the radical formed by abstraction of one hydrogen atom) plays a critical role in the oxidation of hydrocarbons, since the isomerized radical can lead to a series of chain branching reactions. Thus, the mechanism of the fuel decomposition and oxidation prior to autoignition is helpful to understand the knock behavior of a fuel.

Bradow and Alperstein [1967] conducted measurements of chemical species produced in the end gas of a fired CFR engine supplied with iso-octane and iso-octane/diisobutylene (DIB) mixtures. The authors presented a discussion of the chemical paths accounting for the major species observed. Maynard et al. [1967] analyzed the exhaust gases from a motored CFR engine fueled with iso-octane with and without the additive tetra-ethyl lead (TEL). Nineteen oxidation products were measured along with the total acids (as HCOOH) and total peroxides (as HOOH). A reaction mechanism was presented to explain the detected products.

Luck et al. [1973] used a novel high-speed multiple sampling system in a single cycle in a fired engine using n-heptane to make measurements with a resolution of 5 CAD at 800 rpm. They concluded that the “work greatly strengthens the correlation between cool flame and knocking combustion and clearly supports the theory that knock is a spontaneous ignition process”.

The first quantitative, spectroscopic measurement in the end gas of a firing engine was made by Abata et al. [1978]. The hydroxyl radical concentration was measured in the end gas of a firing engine fueled with ethane. Unfortunately,
the experiments were not conducted over a very broad range of conditions due to the extremely difficult nature of using this technique.

Since 1980 most of the studies have been designed to allow development of detailed chemical models. Cernansky et al. [1986] studied the pre-ignition reactions using n-butane and iso-butane. The end gas was isolated in the center of the combustion chamber by simultaneous ignition of four equally spaced spark plugs mounted in the cylinder wall. Gas samples were extracted from the end gases at times just prior to knock and analyzed by gas chromatography. The species data were compared to those obtained from a detailed chemical kinetic model. The relative distribution of intermediate products produced by the model is in good agreement with the experiments. The chemical reactions leading to formation of the relevant species were identified and chemical kinetic differences between the autoignition of n-butane and iso-butane were discussed.

Used the same engine system as Cernansky et al. [1986], Green et al. [1987a, 1987b] studied the chemical aspects of autoignition of iso-butane and n-butane both experimentally and theoretically with detailed chemical kinetic simulations. The experimental results indicate that the heat release prior to ignition is critical for the end-gas temperature to increase and cause hot ignition. Furthermore, in a ‘skip fired’ (the engine was fired then motored for two cycles) experiment with n-butane, the recycled residual products via the motored cycle pre-ignition reactions demonstrated a significant influence on the end gas reactions of the fired motored cycle.
Beginning in the late 1980's, Leppard [1987, 1988, 1989, 1991, 1992] studied the autoignition chemistry of a series of paraffins, olefins, and oxygenates in a motored CFR engine. Comprehensive species data of the exhaust products were measured at various compression ratios up to the point of autoignition. The data were analyzed to determine the chemical routes accounting for the measured stable species. The experimental results of n-butane and C4 olefins were compared to a detailed model by Pitz et al. [1988; 1991].

At Drexel University, initial experiments by Henig et al. [1989] using n-butane, iso-butane and blends employing the same skip-fired strategy as Green et al. [1987a, 1989b] were conducted to investigate the effects of fuel structure on autoignition. Products sampled from the end gas in fired cycles confirmed the importance of low and intermediate temperature chemistry prior to autoignition and examined the interaction between n- and iso-butane. The heat release and chemical species in the second motored cycles were examined in a later investigation by Addagarla et al. [1989a]. Chemical pathways were discussed based on the species data. Wilk et al. [1990] modeled the species data using a detailed chemical kinetic model.

Addagarla et al. [1989b] measured the critical inlet fuel/air conditions of temperature and pressure which induce autoignition for n-pentane, n-hexane, and the primary reference fuels under motored engine conditions. Then, based on gas composition measurements in the engine prior to ignition Addagarla [1991] studied the n-pentane mechanism.
Filipe et al. [1992] examined the preignition reactivity and autoignition behavior of several PRF blends under motored conditions. Time resolved concentration profiles of fuels and light intermediate species (C≤4) were measured. The experimental results indicated that significant amount (up to 40-50%) of both n-heptane and iso-octane reacted during the cycle.

Li et. al. [1994,1995] conducted experiments in a motored research engine fueled with neat PRF’s, an 87 octane blend of PRF’s (PRF 87), and PRF 87 blended with methyl tert-butyl ether (MTBE), ethyl tert-butyl ether (ETBE), methyl tert-amyl ether (TAME), diisopropyl ether (DIPE), methanol and ethanol. Detailed evolution profiles of reactants, molecular intermediates, and products were measured prior to autoignition via in-cylinder sampling combined with gas chromatographic analysis. An oxidation mechanism was assembled to describe the chemical processes responsible for the measured species and ignition behavior. Some key reactions were examined and discussed in detail based on the species concentration measurements. In addition, the interaction between n-heptane and iso-octane oxidation was addressed using the results of PRF 87. The effects of adding the oxygenates on the oxidation and autoignition of PRF 87 were identified. The results showed that all of the ethers and alcohols were effective in reducing preignition reactivity and retarding autoignition, and mechanistic explanations for the behavior were proposed.

Since 1998 HCCI studies have been conducted both experimentally and theoretically. Using PRF 20 fuel Yang [2002] measured species evolution profiles at different equivalence ratio, additives, such as 1-pentene and toluene, and
major EGR components, such as CO\textsubscript{2} and NO. The results were used to elucidate the chemical kinetics controlling HCCI operation.


Mechanisms of hydrocarbon oxidation are evolutionary products of chemists' thought and experiments and, as such, they may change with time as new insights are developed. Thus, when we discuss a particular mechanism, we are not referring to the mechanism in the same sense that we refer to the first law of thermodynamics, or other well-known conservation principles.

In 1882, Perkin first observed cool flames [Lignola et al., 1987]. A negative temperature coefficient behavior was found when Pease was studying oxidation of propane in a flow reactor in 1929. The early concept (pre-1930) of non chain type schemes for hydrocarbon oxidation could not explain the rapidity of low –temperature hydrocarbon oxidation, “cool flame” behavior, nor the negative temperature coefficient of the low-temperature oxidation rate. A wide and exhaustive study of chain theory was initiated in the late 1920s by Semenov and his coworkers. The basic premise of chain theory is that active centers (free radicals and atoms) play a leading role in the destruction of reactant molecules.

In 1926-1929 Semenov discovered the very important fact that some (in fact most) chain reactions can undergo branching, which is self-accelerative behavior, depending on external parameters (pressure, temperature, heat release, etc.). A branched chemical reaction system is very much like the nuclear fission process. The overall chemical reaction rate can be moderated similarly, namely, by affecting the total pool of reactive centers.
In order to explain the chemical induction phenomena, in the early 1930s Semenov proposed the concept of degenerate branching, in which the further reactions of intermediate products formed in the reaction will follow one of two paths depending on external parameters: one is non-chain branching to form stable molecules and other is chain branching to form highly reactive free radicals. The existence of this process, along with the relative overall temperature dependence and exothermicity of the reaction process, leads to the very complex kinetic behavior associated with the chemical induction period, cool flames, and the negative temperature coefficient effects.

In 1965, Benson introduced a general oxidation mechanism for low molecular weight alkanes (C₂'s and C₃'s) in the low temperature regime based on the work of Semenov [Benson 1981]. According to Dryer [1991], this mechanism can be written as follows,

\begin{align*}
\text{RH} + \text{O}_2 &+ \text{M} = \text{R} \cdot + \text{HO}_2 \cdot + \text{M} \quad \text{(R1)} \\
\text{R} \cdot + \text{O}_2 &\cdot = \text{RO}_2 \cdot \quad \text{(R2)} \\
\text{R} \cdot + \text{O}_2 (\text{+ M}) &\Rightarrow \text{olefin} + \text{HO}_2 \cdot (\text{+M}) \quad \text{(R3)} \\
\text{RH} + \text{RO}_2 \cdot &\Rightarrow \text{ROOH} + \text{R} \cdot \quad \text{(R4)} \\
\text{RO}_2 \cdot &\Rightarrow \text{R'}\text{CHO} + \text{R"O} \quad \text{(R5)} \\
\text{RH} + \text{HO}_2 \cdot &\Rightarrow \text{HOOH} + \text{R} \cdot \quad \text{(R6)} \\
\text{ROOH} &\Rightarrow \text{RO} \cdot + \text{OH} \cdot \quad \text{(R7)}
\end{align*}
OH• + RH = H₂O + R• \hspace{1cm} (R8)

R’CHO + O₂ = R’CO• + HO₂• \hspace{1cm} (R9)

RO₂• → destruction \hspace{1cm} (R10)

HO₂• → destruction \hspace{1cm} (R11)

and extended to higher temperature with

HOOH + M = OH• + OH• \hspace{1cm} (R12)

and for larger alkanes

RO₂• = QOOH• \hspace{1cm} (R13)

Olefin + HO₂• = epoxide + OH• \hspace{1cm} (R14)

QOOH• + O₂ = R’CHO + ketone + 2OH• \hspace{1cm} (R15)

where RH and R’CHO represent the fuel and aldehydes, respectively, and reaction R1 to R11 describe the low temperature oxidation mechanism for C₂'s and C₃'s alkanes, along with other reactions having to be added as temperature increases (e.g., R12) and as the initial fuel hydrocarbon molecule larger than 3 carbon atoms (e.g., R13-R15). Some of these reactions are not elementary processes (e.g., R15) but represent a combination of several elementary reactions.

A brief description of this mechanism is as follows. In general, alkanes are essentially unreactive below 400 K unless either chemical or photochemical
initiators are active. Above 420 K oxidation is initiated by the removal of a hydrogen by molecular oxygen (R1). However, this step, called an abstraction reaction, is highly endothermic, roughly 45-55 kcal/mol depending on the bond energy of the abstracted H atom. Therefore, as the rate is characterized by an activation energy proportional to the endothermicity, it is very slow. Due to the variations in the bond energies, the abstraction process is very selective as to which hydrogen is removed and depending on the abstraction site, a different alkyl radical \( R^\bullet \) will be formed [Westbrook et al., 1991; Leppard, 1992]. In the low temperature regime, the next step is addition of the oxygen molecule to the alkyl radical \( R^\bullet \) forming alkylperoxide radicals, \( RO_2^\bullet \) (R2). \( RO_2^\bullet \) subsequently produces the chain branching agent \( ROOH \) (R4), which decomposes to form two radicals \( OH^\bullet \) and \( RO^\bullet \) (R7). The reactions (R4 and R7) represent small molecule chain branching. For larger hydrocarbon molecules (\( > C_3 \)), reaction (R13), an important isomerization reaction, will occur and chain branching follows. Reaction (R15) represents the overall result of this branching, the consumption of the parent fuel molecule is accomplished by reactions (R4, R6, R8). Due to the high reactivity of the hydroxyl radical \( OH^\bullet \), the fuel is consumed primarily by the attack of radicals such as \( OH^\bullet \) via (R8). As temperature increases, reaction (R2) becomes effectively reversible, and another oxidation path of \( R^\bullet \) radical, (R3), becomes important. Since R3 produces alkenes and \( HO_2^\bullet \), relatively stable species at these temperatures, it has an inhibiting effect on the overall reaction rate. The mechanism shift explains the decrease of overall reaction rate with the increase of temperature (due to effectively reversible reaction (R2) and non-chain...
branching reaction (R3)), known as negative temperature coefficient (NTC) behavior. For many hydrocarbons, there is such a NTC temperature range, which is usually between 600 K to 800 K. As the temperature is further increased into the intermediate temperature regime, the decomposition of hydrogen peroxide becomes the dominant chain branching path (R12) and the reaction again accelerates.

In addition to the above mechanism, Koert [1990] reviewed a hydrocarbon oxidation scheme when temperature is above 500 K. Among these reactions is an alternative mechanism of alkyl radical reaction with oxygen, which can be written as (R2a)-(R2c),

\begin{align*}
R\cdot + O_2 & = RO_2\cdot^* \quad \text{(R2a)} \\
RO_2\cdot^* & = \text{Olefin} + HO_2\cdot \quad \text{(R2b)} \\
RO_2\cdot^* + M & = RO_2\cdot + M \quad \text{(R2c)}
\end{align*}

where \( RO_2\cdot^* \) is an energized alkylperoxide radical. At low temperatures, the alkyl radical reacts with molecular oxygen to form \( RO_2\cdot^* \) (R2a), which leads to the various phenomena like cool flames, NTC and two stage ignition. The energized alkylperoxide radical can be de-energized by collision with a third body to form the conjugate olefin and hydroperoxy radical or decompose back to reactants (R2b, R2c). This mechanism was suggested by the work of Slagle et al. [1984a, 1984b]. The difference between these two mechanisms, as Slagle et
al. [1984a] noted, is that the alternative mechanism implies a negative
temperature coefficient of the overall reaction rate of R• which is consistent with
the experimental observations, whereas the first mechanism implies a positive
temperature coefficient of this rate.

Recent work in our laboratory [Wang et al., 1999] identified negative
temperature coefficient (NTC) behavior for neopentane. This requires an
alternative to the traditional conjugate olefin pathway to NTC behavior, as
neopentane does not have a conjugate olefin. Detailed modeling indicated that
NTC behavior of neopentane is caused by the β-scission of the neopentyl radical
reaction and the chain propagation reactions of the hydroperoxyl-neopentyl
radical reactions [Wang et al., 1999]. Therefore it is logical to account for such
reactions for all large, branched alkanes.

Development of the alkane hydrocarbon oxidation mechanisms is ongoing
project. For propane and larger alkanes an improvement to the mechanism has
been suggested by Curran et al. [1995, 1998, 2002] and Ranzi et al. [1994, 1995,
1997].

1. Enhancing QOOH• decomposition:

\[
\text{QOOH}^\bullet = \text{QO} + \text{OH}^\bullet \quad \text{(cycle ether formation)} \quad \text{(R16)}
\]

\[
\text{QOOH}^\bullet = \text{Olefin} + \text{HO}_2^\bullet \quad \text{(R17)}
\]

\[
\text{QOOH}^\bullet = \text{R'OH} + \text{R''CHO} \quad \text{(R18)}
\]
QOOH• = Olefin + R’CHO + OH•  \hspace{1cm} \text{(R19)}

QOOH• rapidly breaks down to form various intermediates such as cyclic ethers (R16), conjugate alkene (R17), carbonyls, and lower molecular weight alkenes (R19). These reactions reduce the tendency to follow chain branching path and lead to NTC region for fuels such as neopentane.

2. Redefining branching paths:

\[ \text{QOOH•} + \text{O}_2 = \text{OOQOOH•} \hspace{1cm} \text{(R20)} \]

\[ \text{OOQOOH•} = \text{OQ'OOH} + \text{OH•} \hspace{1cm} \text{(R21)} \]

\[ \text{OQ'OOG} = \text{Oxygenated radical species} + \text{OH•} \hspace{1cm} \text{(R22)} \]

In addition to QOOH• decomposition, the QOOH• radical may react with molecular oxygen to form the OOQOOH• radical (R20). Further, OOQOOH• may isomerize and decompose by breaking the O-O bond to form a hydroxyl radical and a ketohydroperoxide (OQ’OOH). Since ketohydroperoxide (OQ’OOH) is a relatively stable intermediate and will remain until the temperature increases sufficiently to decompose, this two-step approach retards chain branching until higher temperatures.

As temperature is raised HOOH production become more significant via reactions
QOOH• = Olefin + HO2•  \hspace{1cm} (R17)

RH + HO2• = R• + HOOH  \hspace{1cm} (R23)

HO2• + HO2• =HOOH +O2.  \hspace{1cm} (R24)

HO2• can also be formed from other paths, such as

R’CHO +O2 = R’CO• +HO2•  \hspace{1cm} (R25)

with further increases in temperature, there is a continued increase in the reverse of reaction (R2), and an increasing importance of reaction,

HOOH + M = OH• + OH•.  \hspace{1cm} (R12)

Thus, HO2• and OH• become the dominant chain-carrying radicals. Functionally, hydroperoxy radical replaces RO2•, while HOOH replaces ROOH. This mechanism is responsible for the termination of the NTC regime. Benson has referred to inception of this regime as the occurrence of “hot ignition.” Since the temperature (at which the NTC regime begins) increases and the inception of intermediate temperature regime tends to lower temperature with increasing
pressure, it is possible that at some higher pressure, the NTC regime may disappear completely.

In the intermediate temperature regime two important issues have been raised as the hydrocarbon increases in size [Dryer, 1991]:

1. Alkyl radicals ($R\cdot$) decompose into a lower molecular weight alkene and small alkyl radical by $\beta$-scission. $\beta$-Scission refers to the breakage, or scission, of the C-C bond one removed from the carbon atom bearing a radical, the beta bond. Small alkyl radicals continue to decompose into smaller alkyl radicals also by $\beta$-scission.

2. $H\cdot$ atom is formed via following reactions,

\[
CH_3\cdot + HO_2\cdot = CH_3O\cdot + OH\cdot \quad (R26)
\]

\[
CH_3O\cdot + M = CH_2O + H\cdot + M \quad (R27)
\]

Additionally, another decomposition reaction becomes possible

\[
R\cdot + M = Olefin + H\cdot + M \quad (R29)
\]
H• atom is a critical species to trigger branching reactions in the high temperature regime. However, in the intermediate temperature regime the reaction

\[ \text{H•} + \text{O}_2 + \text{M} = \text{HO}_2\text{•} + \text{M} \quad (\text{R30}) \]

competes with

\[ \text{RH} + \text{H•} = \text{R•} + \text{H}_2. \quad (\text{R31}) \]

As temperature increases, the fastest branching reaction is

\[ \text{H•} + \text{O}_2 = \text{OH•} + \text{O•} \quad (\text{R32}) \]

which dominates over reaction (R30). In this regime, however, the reactions

\[ \text{H•} + \text{O}_2 = \text{OH•} + \text{O•} \quad (\text{R32}) \]

\[ \text{H}_2 + \text{OH•} = \text{H}_2\text{O} + \text{H•} \quad (\text{R33}) \]

\[ \text{H}_2 + \text{O•} = \text{OH•} + \text{H•} \quad (\text{R34}) \]
\[ \text{H}_2\text{O} + \text{O}^\bullet = \text{OH}^\bullet + \text{OH}^\bullet \]  
(R35)

control the relative concentrations of \( \text{O}^\bullet, \text{OH}^\bullet \), and \( \text{H}^\bullet \) available to react with all large and small hydrocarbon species and oxygenated hydrocarbons.

Reaction mechanisms for hydrocarbon fuel are built in a hierarchial manner with submechanisms for \( \text{H}_2 \) and \( \text{CO} \) oxidation forming the core of the overall reaction mechanism [Ranzi et al., 1994]. These submechanisms are tested independently, and additional reactions and chemical species are incorporated as the complexity of the fuels dictate. In this way reactions for formaldehyde (\( \text{CH}_2\text{O} \)), ethane (\( \text{C}_2\text{H}_6 \)), methane (\( \text{CH}_4 \)), ethane (\( \text{C}_2\text{H}_6 \)), ethylene (\( \text{C}_2\text{H}_4 \)), acetylene (\( \text{C}_2\text{H}_2 \)), acetaldehyde (\( \text{CH}_3\text{CHO} \)), and \( \text{C}_3 \) species were added to the \( \text{CO}-\text{H}_2-\text{O}_2 \) base mechanism. For carbon numbers \( \geq 3 \) degenerate branching and \( \beta \)-scission mechanisms of the initial fuel based radicals are added along with reactions with \( \text{OH}^\bullet, \text{O}^\bullet, \text{H}^\bullet \), and other small species resulting from degenerate branching and \( \beta \)-scission mechanisms. At each step, new reactions and species are tested through comparisons with experimental data.

Considering that some phenomena still cannot be explained and predicted very well, such as the NTC behavior and oxidation characteristics in lower temperature regimes, more research work providing experimental species evolution data and developing kinetic models to improve current mechanisms are necessary.
B 3. Mechanisms of Aldehyde Oxidation

Aldehydes are a major intermediate species formed during the oxidation of alkanes, alkenes, and aromatics. The primary degenerate branching mechanism for low temperature aldehyde oxidation is shown below [Cavanagh et al., 1990]:

\[
\begin{align*}
R'\text{CHO} + O_2 & \leftrightarrow R'\text{CO} \cdot + \text{HO}_2 \cdot & \text{(R36)} \\
R'\text{CHO} + \text{HO}_2 \cdot & \leftrightarrow R'\text{CO} \cdot + \text{HOOH} & \text{(R37)} \\
R'\text{CHO} + \text{OH} \cdot & \leftrightarrow R'\text{CO} \cdot + \text{H}_2\text{O} & \text{(R38)} \\
R'\text{CO} \cdot + \text{O}_2 & \leftrightarrow R'\text{COO}_2 \cdot & \text{(R39)} \\
R'\text{COO}_2 \cdot + \text{RH} & \leftrightarrow R'\text{COO}_2\text{H} + R \cdot & \text{(R40)} \\
R'\text{COO}_2\text{H} & \leftrightarrow R' \cdot + \text{CO}_2 + \text{OH} \cdot & \text{(R41)} \\
R'\text{CO} \cdot + \text{M} & \leftrightarrow R' \cdot + \text{CO} + \text{M} & \text{(R42)}
\end{align*}
\]

While oxidation of RCHO starts to occur at a measurable rate at temperature around 425 K, where peracetic acid is a major product, at temperatures \( \geq 500 \text{ K} \), significant amounts of \( \text{HO}_2 \cdot \) are produced from the relatively fast reaction between molecular oxygen and an aldehyde, (36). The \( \text{HO}_2 \cdot \) radical can continue to react with another aldehyde to form hydrogen peroxide, (37), and \( \text{HOOH} \) is a critical branching agent into the intermediate temperature regime (hot ignition). Aldehyde can easily consume \( \text{OH} \cdot \) (38),
competing with other species, to form R’CO•. Reactions (39) and (30) formed the branching agent R’COO₂H that decomposes into two radicals, R’• and OH• so as to accelerate reactivity. When temperature increases, the reaction (42) is favored over the reaction (39) and the branching reaction (41) is less important thereby lowering the concentration of radicals and slowing in whole reaction system.

Aldehyde oxidation steps are the major source of carbon monoxide via reaction (42) and carbon dioxide via reactions (41) and (43)

\[
R''CO• + HO2• \leftrightarrow R''• + CO2• + OH• \quad (41)
\]

\[
CO + OH• = CO₂ + H• \quad (43)
\]

in the low and intermediate temperature regime.

As a major intermediate species and major source of CO formation, aldehyde decomposition must be included in any alkane, alkene, or aromatic mechanism. The mechanism outlined above has been used extensively in current models to describe the decomposition of aldehydes [Cavanagh et al., 1990]. However, additional research should be conducted to examine the oxidation of larger aldehyde compounds.

Actual fuels consist of many components and the mechanism of the actual fuel is not simply addition of components’ mechanism. Hence autoignition in IC
engines using practical fuels cannot be fully described in terms of autoignition chemistry at the moment. For this thesis we conducted initial experiments of n-heptane, iso-octane, and propionaldehyde blends in a PFR in order to study preignition behavior of blends; details are provided in Chapter 10.

B 4. Hydrocarbon Oxidation Models

There are five categories of chemical kinetic models: detailed, lumped, reduced, skeletal and global, and these have the general characteristics shown in Table 5-1.

In 1984, Westbrook and Dryer [1984] introduced a detailed chemical kinetic mechanism for oxidation and pyrolysis of propane and propene. This model was later extended to lower temperatures and to much more complex fuels [Pitz et al., 1988]. Since then there have been efforts to develop detailed models for butane, pentane, up to n-heptane and iso-octane [Curran et al., 1998 and 2002]. Detailed models try to include all of the important elementary reactions and individual species using the best available rate parameters and thermochemical data. However, there are uncertainties in the selection of reactions and rate parameters, and detailed models are often developed for a single hydrocarbon and only validated over a rather limited range of conditions. Detailed models of hydrocarbon fuel oxidation, consisting of hundreds of chemical species and thousands of reactions, for an engine simulation require tremendous computational resources if coupled with engine CFD models. Several modeling studies simulating HCCI conditions using detailed chemical mechanisms have been reported. Some used a single-zone model [Aceves et al.,
1999; Kraft et al., 2000] and others used multi-zone CFD [Aceves et al., 2000; Easley et al., 2001]. Even for relatively simple multi-zone models, use of detailed mechanisms is computationally expensive, so that the most effective way to lessen the burden is to develop smaller models [Bourdon et al., 2004].

The other four model types are all driven by the desire to minimize the model size. The lumped model [e.g., Violi et al., 2002; Agosta et al., 2004] uses a simplified description of the primary propagation reactions and primary intermediates for large species and then treats the reactions of smaller species with a detailed elementary kinetic scheme, so that the model involves fewer intermediate species than a full detailed model.

The detailed models can be culled to produce a second type of model, a reduced model, which contains only the most critical elements of the full mechanism. A number of different methods have been developed to systematically reduce detailed reaction mechanisms [Frenklach and Wang, 1991; Bhattacharjee et al., 2003; Tang and Pope, 2002; Ren and Pope, 2004; Lu and Law, 2004]. Recently, Patel et al. [2004] modeled the ignition delay data of n-heptane and analyzed a baseline mechanism (40 species and 165 reactions) to identify important reactions. They formulated a reduced mechanism consisting of 29 species and 52 reactions, which satisfactorily predicted the experimental data. However, this may still be too large for detailed CFD calculations.

A fourth type of model is the skeletal model that consists of a sequence of composite kinetic steps representing the reaction progress. These kinetic steps can be elementary, generic, or global reactions. Rate parameters and
thermochemistry are based on the best information but represent “classes” of reactions. Griffiths [1995] has made a comprehensive review of reduced kinetic models and their applications. A brief description of the models which are relevant to the current work follows.

In the 1970s, one of the earliest skeletal kinetic models, based on degenerate-branched-chain and class chemistry concepts, was developed at the Shell Thornton Research Center by Halstead et al. [1975, 1977]. This model consisted of 8 generalized reactions and 5 species (fuel, oxygen, total radical population, a branching agent B, and an intermediate species Q which forms B), where the primary interest is the ignition delay and the phenomenological complexity of hydrocarbon oxidation, such as cool flames, two stage ignition and NTC behavior were considered to be of secondary importance. A mathematical model of 6 coupled differential equations was developed and rate parameters were fitted for several fuels including primary reference fuel blends (iso-octane, PRF 90 and PRF 70) using ignition delay data obtained from a rapid compression machine. The rate of heat release was calculated assuming each CH$_2$- group is oxidized to form CO, CO$_2$, and H$_2$O, which were not consistent with the oxidation products of CO, oxygenates and hydrocarbons in the first stage ignition. This work formed the basis for later developments and the model is widely used in engine applications.

Based on the existing knowledge of the alkane oxidation Cox and Cole [1985] formed a skeletal chemical kinetic model, which consists of 15 reactions and 10 active species and the rate of heat release was calculated in the same
way as in the Shell model. The model was tested against the ignition data using iso-octane and PRF 90 in the Thornton rapid compression machine. The advantages of this model are a better representation of the chemical reactions and the reasonable rate parameters compatible with the existing kinetic information on the type of elementary processes involved.

Hu and Keck [1987] further developed a skeletal chemical kinetic model of 18 reactions and 13 active species. Keeping a better representation of the chemical reactions similar to Cox and Cole model, Hu and Keck treated exothermicity as enthalpy change in each of the elementary reactions. The rate parameters were calibrated using measured explosion limits in a combustion bomb. The fuels studied were C$_4$-C$_8$ straight chain paraffins and iso-octane. The effects of fuel structure are reflected in the rate parameter of the RO$_2^-$ isomerization reaction. The model was applied to predict selected data of ignition delay measured in the Thornton rapid compression machine.

The previous work on skeletal chemical kinetic models showed that a relatively small number of rate limiting reactions can simulate two stage ignition processes and that models can generally reproduce the ignition delay for a specific hydrocarbon of interest based on simple adjustments of a fuel specific equilibrium constant. However, significant physical features such as pre-ignition fuel consumption, cumulative heat release, and key species concentrations were not modeled very well. To resolve these issues, an extended skeletal kinetic model was developed by Li et al. [1992 and 1996] for application to PRF 87 (87% iso-octane and 13% n-heptane) and PRF 63 at selected engine conditions. The
characteristics of this model were that small species oxidation was considered and a formation path for CO was provided. This model, consisting of 13 active species and 29 reactions, predicted the ignition delay and the pre-ignition heat release for these fuels to within 15%. The model was further modified to reflect the oxidation chemistries of butanes. The results indicate that this reduced model can be applied to predict the preignition reactivity of butanes.

The model has been further developed and successfully applied to prediction of HCCI pre-ignition behavior including temperature, pressure, ignition delay and heat release for PRF 20 and PRF 50 fuels [Zheng et al., 2001]. This model has been extended to incorporate low, intermediate, and high temperature chemistry. We have used such skeletal models for pre-ignition behavior, ignition time, and combustion rate in HCCI engines [Zheng et al. 2002]. These results have shown that skeletal models (69 reactions and 45 species in these cases) can be a useful tool to study HCCI engine operation. Nonetheless, if the kinetic model is to be combined with a CFD code, even simpler models are desirable to maintain acceptable computation times. A more detailed explanation for HCCI modeling is presented in Chapter 3 and 4, and an improved preignition model is explained in Chapter 6.

Global models describe the chemistry in terms of a few of the principal reactants and products in one or more overall functional relations. The concept of a model that has a minimal number of variables is extremely attractive, e.g. in CFD calculations, but it is essential that the underlying kinetic and thermal properties of the combustion system be encapsulated in the structure, if the
model is to have the potential for practical application. In general, one- and two-
step, even multistep, global models have successfully described high
temperature chemistry [Dryer, 1991]. However, there also have been a few
efforts to include the low, intermediate and high temperature phenomena in such
models as well. A 4-reaction model [Müller et al., 1992] and a 5-reaction model
[Schreiber et al. 1994] were developed in which two reactions represent the high
temperature chemistry and the others try to represent the low and intermediate
temperature chemistry. In reference [Müller et al., 1992] the prediction of ignition
throughout the entire temperature range rests exclusively on thermal feedback.
Neither of these global models can reflect the behavior in the Negative
Temperature Coefficient (NTC) regime, since NTC behavior inherently involves
intermediate species (for example, HOOH) that provide branching at 900-1100 K
based on the species concentrations. Hence these two global models were only
used to predict ignition delays, and they are not suitable for prediction of the full
HCCI behavior that occurs with PRF fuels. Bourdon et al., [2004] proposed an
optimized 5-step model for HCCI applications; however, further development is
required.

As part of thesis a 7-step global reaction model has been developed; it is
explained in detail in Chapter 5
VITA

Jincai Zheng was born in Hebei Province, P. R. China, where he attended elementary, middle, and high school. In the fall of 1978 Jincai Zheng enrolled Tianjin University at Tianjin P.R. China as an undergraduate student majoring in Mechanical Engineering with the specialization in IC engines. After obtaining his Bachelor of Science degree in 1982, Jincai Zheng continued his education at the same school for his Master degree. His M.S. thesis work was completed in thermo-energy institute in 1985, and he received his Master of Science degree, emphasizing IC engine combustion. Since then Jincai Zheng worked in Tianjin University as a faculty member. He engaged in studying turbulent flame, fuel spray atomization and combustion, low heat rejection diesel engine, reduction of HC and CO emissions, combustion model for gasoline and diesel engines and so on in National Engine Combustion Laboratory.

In the fall of 1998, Jincai Zheng came to the United States for his Ph. D. degree in Mechanical Engineering at Drexel University. He has co-authored 7 technical refereed papers (5 archival, 1 pending) about HCCI engines and 7 additional conference papers in the area of autoignition chemistry while his studying in Drexel University. During this period he also co-authored 6 technical refereed papers in Chinese about his works in Tianjin University.

After receiving his Ph. D. degree, Jincai Zheng plans to work in institutes or industry, engaging in IC engine research, development, and production.