OPTIMIZATION OF CHEMICAL KINETIC MECHANISM FOR EFFICIENT COMPUTATION OF COMBUSTION PROCESS IN ADVANCED INTERNAL COMBUSTION ENGINE CONFIGURATIONS

by

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We, the undersigned committee, hereby approve the attached dissertation

OPTIMIZATION OF CHEMICAL KINETIC MECHANISM FOR EFFICIENT COMPUTATION OF COMBUSTION PROCESS IN ADVANCED INTERNAL COMBUSTION ENGINE CONFIGURATIONS

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ABSTRACT

Title: Optimization of Chemical Kinetic Mechanism for Efficient Computation of Combustion Process in Advanced Internal Combustion Engine Configurations

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For the development and optimization of future fuels and automotive engines, computer modeling and simulation has proved itself as an inseparable, efficient and cost effective tool to experimental studies. The traditional reliance of computer models on simplified global reaction steps to simulate the combustion and engine performance parameters, such as in-cylinder pressure, heat release rate and pollutant formation could reduce credibility of the predictions as the global reaction steps depend on arbitrary adjustment of model parameters. This study has incorporated detailed chemistry by augmenting the combustion model of a three dimensional unsteady compressible turbulent Navier-Stokes solver with liquid spray injection by coupling its fluid mechanics solution with detailed kinetic reactions solved by a commercial chemistry solver. Detailed chemistry has been incorporated by constructing a novel reduced mechanism for spark ignition engines. Mechanism reduction is carried out through sensitivity analysis of a skeletal reaction mechanism for compression and power stroke utilizing computational singular perturbation (CSP) method and using the low temperature reaction pathway analysis. To use detailed chemistry and enhance the chemical
kinetics library of the fluid dynamics code, this research is comprised of the development of an interface between fluid dynamics and chemical kinetics codes for study of gasoline mechanism in a premixed spark ignition engine. A well-established surrogate (isooctane) has been selected for this study because gasoline is a complex mixture of various compounds and hydrocarbons. A distinguishing feature of this study is the use of 90% iso-octane and 10% n-heptane as surrogate fuel because this combination best modeled the results. With this novel approach, the reduced mechanism obtained from this study is used to perform a mesh independent study that validated and showed a good agreement of in-cylinder pressure, heat release rate and emissions against the experimental data for a range of equivalence ratio from $\phi = 0.98$ to 1.3 for spark ignition engines.
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<tbody>
<tr>
<td>IC</td>
<td>Internal Combustion</td>
</tr>
<tr>
<td>CFD</td>
<td>Computational Fluid Dynamics</td>
</tr>
<tr>
<td>SI</td>
<td>Spark Ignition</td>
</tr>
<tr>
<td>DI</td>
<td>Direct Injection</td>
</tr>
<tr>
<td>PCCI</td>
<td>Premixed Charge Compression Ignition</td>
</tr>
<tr>
<td>HCCI</td>
<td>Homogeneous Charge Compression Ignition</td>
</tr>
<tr>
<td>GDI</td>
<td>Gasoline Direct Injection</td>
</tr>
<tr>
<td>HRR</td>
<td>Heat Release Rate</td>
</tr>
<tr>
<td>CSP</td>
<td>Computational Singular Perturbation</td>
</tr>
<tr>
<td>DRG</td>
<td>Directed Relation Graph</td>
</tr>
<tr>
<td>DRGEP</td>
<td>Directed Relation Graph with Error Propagation</td>
</tr>
<tr>
<td>DRGASA</td>
<td>Directed Relation Graph-Aided Sensitivity Analysis</td>
</tr>
<tr>
<td>PFA</td>
<td>Path Flux Analysis</td>
</tr>
<tr>
<td>QSSA</td>
<td>Quasi-Steady-State Approximation</td>
</tr>
<tr>
<td>$r_{AB}$</td>
<td>Relative error induced to species A by elimination of B</td>
</tr>
<tr>
<td>$I_{A,i}$</td>
<td>Importance Index of species A in ith reaction</td>
</tr>
<tr>
<td>BTDC</td>
<td>Before-Top-Dead-Center</td>
</tr>
<tr>
<td>ATDC</td>
<td>After-Top-Dead-Center</td>
</tr>
<tr>
<td>CA50</td>
<td>crank angle for 50% heat release ATDC</td>
</tr>
<tr>
<td>$S_r$ or $v_r$</td>
<td>Stoichiometric vector of rth reaction</td>
</tr>
<tr>
<td>$F_r$ or $q_r$</td>
<td>Reaction rate of rth reaction</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Net reaction rate</td>
</tr>
<tr>
<td>G</td>
<td>Rate of change of species mass fraction and temperature</td>
</tr>
</tbody>
</table>
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    \item \( G_{\text{fast}} \) \quad \text{Rate of change of species mass fraction and temperature for fast reactions}
    \item \( G_{\text{slow}} \) \quad \text{Rate of change of species mass fraction and temperature for slow reactions}
    \item \( \lambda \) \quad \text{Eigenvalue}
    \item \( T \) \quad \text{Temperature}
    \item \( Y \) \quad \text{Mass fraction}
    \item \( y \) \quad \text{Mass fraction or temperature}
    \item \( J \) \quad \text{Jacobian}
    \item \( \Delta t \) \quad \text{Time step}
    \item \( \text{FA}_{\text{stoic}} \) \quad \text{Stoichiometric Fuel to Air Ratio}
    \item \( \epsilon \) \quad \text{User-defined small threshold}
    \item \( \epsilon_{\text{Reac}} \) \quad \text{User-defined small threshold}
    \item \( \tau \) \quad \text{Characteristic time scale}
    \item \( \tau_{\text{slow}} \) \quad \text{Fastest relevant time scale for slow reaction group}
    \item \( \tau_{\text{fast}} \) \quad \text{Slowest relevant time scale for fast reaction group}
    \item \( \Phi \) \quad \text{Equivalence Ratio}
    \item \( \text{RR} \) \quad \text{Reaction Rate}
    \item \( \text{LWALL} \) \quad \text{Law-of-the-wall}
    \item \( \text{PULSE} \) \quad \text{Way the fuel is injected (pulsed) in the combustion chamber}
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“In the name of Allah, the Most Generous, the Most Merciful”. All praise is due to Allah, the Most Generous, and the Most Merciful. I am His humble servant and I thank Him for His continuous blessings on me and my family. Truly, “And my guidance cannot come except from Allah, in Him I put my trust and unto Him I repent” (Quran, 11:88). I am heartily thankful to my adviser, Dr. Gerald J. Micklow, whose encouragement, guidance and support from the initial to the final level enabled me to develop an understanding of the subject. I would like to extend my thanks to the esteemed Ph.D. committee. I would like to extend special thanks to Dr. Hamid Hefazi, Department Head Mechanical & Aerospace Engineering. I would also like to thank Dr. David Rothamer from University of Wisconsin for the experimental data.

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Muzammil Arshad
1. Introduction

1.1. Background

For the development and optimization of future fuels and automotive engines, computer modeling and simulation has proved itself as an inseparable, efficient and cost effective tool to experimental studies. The traditional reliance of computer models on simplified global reaction steps to simulate the combustion and engine performance parameters, such as in-cylinder pressure, heat release rate and pollutant formation could reduce credibility of the predictions as the global reaction steps depend on arbitrary adjustment of model parameters. The desire for higher fuel efficiency has driven the increased use of spark-ignition direct-injection (SIDI) engines in automotive applications over the past two decades [1].

The present study is a detailed, in-depth and multi-pronged study that utilized detailed chemistry by coupling KIVA [2], which is a Reynolds Averaged Navier-Stokes (RANS) solver, and CHEMKIN [3], which is a chemistry solver, and performed sensitivity analysis and reduction of skeletal reaction mechanism using SENKIN [4], which is a sensitivity analysis module of CHEMKIN, and investigated the prediction and validation of engine performance parameters. This comprehensive research strategy attempted to minimize the computational time by using fewer required reactions and species. The reduced mechanism validated the engine performance parameters for equivalence ratio of 0.98 and 1.3 for a premixed
case. This is a novel approach as a single universal reduced mechanism validated engine performance and combustion parameters of in-cylinder pressure, heat release rate, and emissions for a range of equivalence ratios utilizing the low temperature pathway analysis. Also, the primary fuel has been used as iso-octane (90%) but a small amount of n-heptane (10%) [5] has been used for the study. The reason is that due to presence of n-heptane, formaldehyde forms for low temperature reactions. It later consumes as the reactions progresses. Due to this, iso-octane does not consume or burn until the thermal ignition of n-heptane occurs. This allows extended combustion duration and reduced emissions as well [5]. The fuel used during the experimental study in literature was gasoline [6, 7].

Comparative studies were performed by running numerical simulations in KIVA and the interface between KIVA and CHEMKIN. The mechanism reduction is performed by using the computational singular perturbation (CSP) method which has won approval in various studies due to its accuracy [8, 9, 10, 11, and 12]. The predicted results are compared and validated against experimental results already present in the literature. Global and quasi-global mechanisms were taken as a first test case for numerical simulation predictions and then compared the simulation results with experiments, which provided the reason and justification to go ahead and use detailed chemistry. A well-established surrogate (iso-octane) has been selected for study because gasoline is a complex mixture of various compounds and hydrocarbons. The fundamental research will provide the data and mechanistic
understanding needed for the development of a library for detailed mechanisms that can be used to correctly predict engine performance parameters.

1.2. Motivation

With the realization that CFD results for Internal Combustion (IC) engines need to be correctly modeled by numerical simulations using detailed chemistry, it seems inevitable that the fuel reaction mechanism library must be established to correctly predict and model engine performance. Larger mechanisms are computationally expensive, so reduced mechanisms should form the library of mechanisms that can be accessed by researchers.

Gasoline is a mixture of hundreds, if not thousands, of hydrocarbons. A popular approach for solving this problem is to establish a surrogate fuel that represents a “typical” gasoline. A surrogate fuel is a well defined mixture of a few hydrocarbon compounds whose relative concentrations can be adjusted such that the combustion characteristics of the mixtures become similar to those of a typical gasoline. Chemical kinetic models for the surrogate mixture are then developed based on the models established for the individual components of the mixture.

1.3. Objectives

The goal of this dissertation is to develop and utilize a reduced order chemical mechanism for better prediction of combustion parameters. Two engine performance parameters, in-cylinder pressure and heat release rate, were selected to
validate the existing experimental results. Pollutant emission formation was also selected to be validated against the experimental data. This goal will be attained by addressing the following objectives:


2. KIVA-CHEMKIN interface coding by which CHEMKIN library becomes part of KIVA executable.

3. Calculation of in-cylinder pressure & heat release rate using global and quasi-global mechanisms.

4. Comparison of predicted results with the experimental data.

5. Selection of a skeletal mechanism and reducing the mechanism to fewer reactions to enhance computations and efficiency.

6. Calculation of in-cylinder pressure & heat release rate using the reduced reaction mechanism.

7. Comparison and validation of predicted results with the experimental data.

8. Comparison and validation of predicted results for pollutant emission formation with the experimental data.

1.4. Approach

To effectively and correctly predict the combustion parameters of in-cylinder pressure and heat release rate, it was determined that the correct prediction would require detailed combustion chemistry. Numerical simulations were performed with
the global and quasi-global mechanisms for the premixed case. The results obtained from the comparison of global and quasi-global reaction mechanisms showed the need for improvement in the prediction of in-cylinder pressure and heat release rate. To use detailed chemistry, a skeletal mechanism was selected with 296 reactions and 73 species [13]. Since it is more computationally intensive to use large reaction mechanisms, the skeletal mechanism was reduced to 53 reactions and 44 species using the CSP technique. These reactions were selected based on a sensitivity analysis and importance index defined later in Chapter 4. The reduction of the skeletal mechanism performed in this study is novel because it utilized the low temperature reaction pathway analysis which resulted in a controlled combustion process and produced a good agreement of numerical simulations against the experimental results. The results from the reduced mechanism provided a good prediction of in-cylinder pressure and heat release rate. An important aspect of using the reduced mechanism is that the detailed chemistry produced a good agreement of in-cylinder pressure and heat release rate which were over-predicted by the global and quasi-global mechanisms. The reduced mechanism obtained through this study is validated for for $\Phi = 0.98$ and, $\Phi = 1.3$, and is applicable to intake temperature and intake pressure ranges suitable for spark ignition engines. An ongoing literature review was done to find out the experimental data to validate the results.
1.5. Dissertation Layout

Chapter 2 deals with a detailed literature review of the premixed and direct injection in Spark Ignition (SI) engines, gasoline surrogates, and experimental data for engine performance parameters including in-cylinder pressure and heat release rate, mechanism reduction techniques and KIVA-CHEMKIN interface.

Chapter 3 deals with the introduction to KIVA and CHEMKIN and the development of KIVA-CHEMKIN interface. The first part in chapter 3 presents the introduction to CHEMKIN and KIVA. Next, chapter 3 explains the KIVA-CHEMKIN coding and details about how to use the code. Chapter 4 covers the sensitivity analysis which was performed using SENKIN [4] code, extraction of the sensitivity data from SENKIN using KINALC [14] and perform mechanism reduction using the computational singular perturbation (CSP) method in KINALC. Numerical simulations and validation of numerical data against experimental data is performed in Chapter 5. Simulations are performed and the predicted engine performance parameters of in-cylinder pressure and heat release rate (HRR) are validated in Chapter 5. Pollutant emissions data is also validated in Chapter 5. Chapter 6 discusses the conclusions and the recommendations for the future development of this research.
2. Literature Review

In Computational Fluid Dynamics (CFD), many simplifications and assumptions are made to the mathematical models to make them computationally affordable. With the rapid development of computer processors and expansion of allowable memory, scientists and engineers are able to revisit some of the assumptions in effort to enhance the predictive capabilities of a model; a trend which is often observed in engine simulation tools. For this research, the goal is to shift from using multi-step global reactions to a manageable number of elementary reaction steps which governs the kinetics of fuel oxidization.

2.1. Engine Performance: In-Cylinder Pressure and Heat Release Rate

2.1.1. Direct Injection

For the development of future fuels and the optimization of automotive engines, computer modeling and simulation has proved itself as an inseparable tool alongside experimental studies. Traditionally, computer models rely on simplified global reaction steps to simulate the combustion and pollutant formation inside the internal combustion engine due to computational limitations. With the current interest in advanced combustion modes and injection strategies, this approach could reduce credibility of the predictions for advanced concepts since it depends on arbitrary adjustment of model parameters. The desire for higher fuel efficiency has driven the increased use of spark-ignition direct-injection (SIDI) engines in
automotive applications over the past two decades. Estimates in 2013 indicated that up to 60% of the light duty automotive market in the United States utilizes SIDI engines [6].

Gatowski et al. [15] developed, tested and applied a heat release analysis procedure for use with cylinder pressure data from spark ignition (SI) engines. Reasonable agreement was found between the heat release calculated by the model and the fuel energy introduced into the cylinder.

Experiments were conducted at stoichiometric conditions in a single cylinder Direct Injection Spark Ignition (DISI) engine with optical access which was used to investigate the effects of ethanol/gasoline blends on in-cylinder formation of particulate matter (PM) and fuel spray characteristics [16]. Similarly, research conducted in [17] presented the experimental results of the effects of blending ethanol with gasoline on advanced combustion strategies in internal combustion engines. Various fuels were tested and studied for the properties of spray, combustion, ignition and soot formation in a direct injection spark ignition (DISI) engine with an optical access. A decrease in the soot formation was observed while using ethanol blends. Chemical, physical and thermal properties of ethanol/gasoline blends were used to improve the performance and emissions of advanced engine technologies such as, gasoline direct injection (GDI) also known as the direct injection spark ignition (DISI).
Osei-Owusu et al. [18] performed a study on controlled auto-ignition (CAI) for compression ignition and spark ignition engines. Factors affecting combustion were studied such as local temperature, the local composition of the air/fuel mixture, time and pressure. The influences of the above-mentioned factors were investigated using a commercial Computational Fluid Dynamics (CFD) engine simulation package, FLUENT [19], fitted with real optical research engine geometry. Comparison of local predicted and measured flow velocities showed better agreement around the center of cylinder. The results also showed that the numerical simulations and mesh adequately captured the gas mixing processes between the fresh charge of air-fuel mixture and the trapped exhaust gas recirculation (EGR) in the cylinder of the engine.

Stricter restrictions for emissions from diesel engines have increased the research towards alternative fuels. Alternative fuels that can be used directly on already existing engines are a topic of active research to compare their performance with conventional fuels. Analysis of the combustion process in engines makes it necessary to take into account the changes in the composition and thermodynamic properties of the working medium. This makes the analysis of the in-cylinder process more accurate. Small fluctuations in the pressure measurements cause big fluctuations in the calculated reaction rate and rate of heat release (ROHR) [20]. Results showed that the calculation of heat, heat loss, indicated work and efficiencies from the pressure measurements gave good results.
Chemical energy of the air-fuel mixture is converted into sensible energy in an Internal Combustion (IC) engine. To convert this sensible energy to useful work, it increases the in-cylinder pressure [15]. A procedure was developed to perform the heat release analysis by using the cylinder pressure data for premixed spark ignition engines. The paper [21] used engine speed measurements to estimate the in-cylinder pressure and combustion heat release for Spark Ignition (SI) engines. This research was applied for engine diagnostics. An estimation of heat release rate by the model helped in predicting cylinder misfire or incomplete/abnormal combustion problems. By using thermodynamic principles, Kuo [22] described a method to predict the cylinder pressure in a spark-ignition engine. The model incorporated 4-stroke engine processes including intake, compression, combustion, expansion and exhaust. Comparative analysis with the pressure data from experiments showed the model to have a high degree of accuracy. Evaluations based on the ability to predict the angle of spark firing and burn duration was also performed. Results showed that the burn duration angle increased and a delay in ignition was observed with increasing load. Delay in ignition due to increase in inlet pressure was found according to the prediction.

A two-stroke DISI engine was used to perform a numerical study with multi-dimensional modeling for an air-fuel ratio of 30:1, medium load and injection timings of 271, 291 and 306 ATDC [23]. The effects of injection timings were investigated on mixture formation, ignition and combustion. Results from this study indicated more fuel evaporation occurred at the earlier injection time for this
particular load. The study resulted in a good agreement between the measured and computed combustion results of average in-cylinder pressure and NOx. The injection case at 306 ATDC produced lower NOx emission and higher CO emission. The reason behind this phenomenon was due to poor mixing. The results were in agreement with experimental measurements. The model could not predict accurately the hydrocarbon emissions. Only the total unburned fuel and total CO emissions agreed with their respective experimental values.

Investigations were performed [24] in a direct injection spark ignition engine on the effects of augmented mixing through the use of an auxiliary gas injection. The engine was operated at a 22:1 overall air-fuel ratio, but with retarded injection timing. The effect of the delayed injection is that the combustion occurs in a locally rich mixture. It was observed by the elevation of CO emissions. NOx emissions decreased at these conditions. Two gas compositions, nitrogen and air, were utilized and the gas supply temperature was ambient. A 25% reduction in CO emissions was observed when a low temperature, inert gas (nitrogen) is injected during the latter portion of the heat release phase. Reduced emissions are due to increased mixing rate of the rich combustion products and excess air during high temperatures which promotes rapid oxidation. Significant reduction in the NOx emissions was also observed. The results confirmed that the auxiliary gas injection (AGI) orientation was effecting changes in the in-cylinder processes. The results pointed in the direction that local rich combustion and low NOx emissions are due to the fact that the design of DISI combustion chamber made to promote significant
late-cycle mixing. Current engine designs are made to generate a pre-combustion mixture of the appropriate strength and location, and neglect late-cycle effects.

Computational fluid dynamics (CFD) simulations by Kleemann et al. [25] were performed using FLUENT to provide knock sensitivity study for a multi-cylinder SI engine. The study was done to predict wall temperature and in-cylinder conditions. Thermal coupling of combustion calculations were done with the cooling circuit simulations. Regions that utilized thermal coupling included the exhaust manifolds, valves, valve seats and the cylinder head. The appropriateness of thermal boundary conditions and combustion conditions were gauged by considering several engine operating parameters. Thermal coupling provided improved agreement between the numerical simulations and the experiments. The study showed the need for better mesh around the valve and its seat. Also, there was a lack of experimental data present for the study that required additional experimental data to better validate the results.

In-cylinder pressure is one of the most important parameters that affect the engine performance of a spark-ignition engine while heat release analysis is another important tool for IC engine development [26].

Mixtures of n-heptane/air, gasoline/air, surrogate fuel A (63% iso-octane, 20% toluene, 17% n-heptane) and, surrogate fuel B (69% iso-octane, 14% toluene, 17% n-heptane) were tested behind a reflected shock wave for homogeneous charge compressions ignition (HCCI) engine conditions [27]. The purpose of the study
was to determine the auto-ignition characteristics of the above-mentioned mixtures. Lean, stoichiometric and rich mixtures were tested with $\phi=0.5$, 1.0 and 2.0. The results for n-heptane showed better agreement with the existing shock tube data. Gasoline and surrogate A showed strong agreement amongst each other for the experimental conditions. The ignition delay time for fuel lean mixture was longer than the stoichiometric mixture for both gasoline and surrogate A at low and high pressure conditions. It was noted that the surrogates might now replicate the gasoline mixture results for other engine experiments. It was also observed that in-cylinder pressure, species concentrations and heat release rates are important parameters that provide information on the radical formation during the reactions.

Regulations regarding controlling the CO$_2$ emissions have forced scientists to develop and try various alternative fuel blends such as crop produced alcohols. An experimental study was performed with ethanol, butanol, iso-octane and gasoline fuels [28]. Calculations of projected spray areas were performed to extract information of atomization and evaporation of each of the testing fuels. In-cylinder pressure histories were also measured for all the testing fuels. It was observed that the coolant temperature has a profound effect on spray formation. This was found true for fuels having boiling points less than or close to coolant temperature. Gasoline and ethanol are made up of high volatility components hence; the sprays formed a spray cloud at extreme temperatures (at 90$^\circ$C) and causing the spray to collapse. Iso-octane spray did not collapse even at extreme temperatures and retained good directionality.
A continuous multi-component (CMC) fuel model was used along with an improved mathematical combustion model along with the detailed chemical kinetics [29]. Multi-component fuels have different vaporization characteristics than the single component fuels. The vapor fuel distributions of their sprays are very different. This is the reason to use a multi-component fuel for accurate predictions of combustion and engine performance parameters. The study included the research on flame speeds. The model was used to study flame propagation and fuel distribution in a gasoline direct injection (GDI) engine. In-cylinder pressure showed complete agreement for some cases but not for all and showed some deviation at peak pressures. Heat release rate did not show a complete agreement between the numerical simulations and experiments. There was a lag between the curves obtained from experiment and the numerical simulations for in-cylinder pressure and heat release rate. Effect of laminar flame speed was also implemented in the multi-component combustion model which could have led to the inaccuracies.

Experimental work was done on a DISI engine to check the effect of fuel temperature on nano-scale particulate matter (PM) by injection of chilled fuel in the combustion chamber [30]. Higher in-cylinder pressure, a longer combustion duration and lower particulate number was observed by injection of chilled fuel as compared to the fuel injected at ambient temperature.

Dahms et al. [31] performed modeling and experimental validation in a spray-guided gasoline engine. The concept of spray-guided engines is to inject the fuel
directly into the spark plug with all the vaporization occurring at the spot. The results showed agreement of in-cylinder pressure and heat release rate with the experimental data.

An impact of cycle-to-cycle velocity variations and issues of misfires were tested on engine performance in DISI engine by Goryntsev et al. [32]. The study showed the effects of cycle-to-cycle velocity variations on combustion, specific fuel consumption, work output and the emissions. The results also showed a strong dependence of the cyclic velocity variation and the temperature behavior.

Experiments were performed on the fuel blends of 30% and 50% n-butanol in gasoline to determine the effects on emissions and engine performance by Pechout et al. [33]. Results showed that the early combustion for both mixtures was shorter as compared to gasoline. This resulted in shifting of combustion further from top-dead-center (TDC). Emissions of CO and HC decreased as compared to gasoline but NOx increased.

An injection timing retard was used in a DISI engine with gasoline and E85 to reduce the NOx emissions and check the engine performance by Sjoberg et al. [34]. Results showed that the injection-timing retard reduced the engine-out NO emissions for both fuels.

Experiments were performed in an optical access DISI engine to investigate the effects of using gasoline, E50 and E85 fuels on engine performance [35]. Direct fuel injectors for fuel pressures of 5-10 MPa and 3 MPa were used to investigate
the effects of fuel injection pressure. Results showed that the burn duration was shorter and flame growth was faster for higher fuel injection pressure. It was also observed during the experiments that as the ethanol content increased in the ethanol-gasoline fuel, the flame growth became faster. Therefore, it was found that the ethanol-gasoline blended fuel had a faster flame growth than gasoline.

Experiments were performed to investigate the engine performance during cold start [36]. In-cylinder pressure, HRR and emissions were used as engine performance parameters. Results showed existence of optimal ignition timing for engines to obtain a better cold start performance. Increasing injection pressure and second fuel injection amount also improved the first cycle firing performance. When the air-fuel ratio was 14.7, an increase in the second fuel injection amount was found favorable to improve the first cycle firing performance.

Fontanesi et al. [37] investigated multi-cycle analysis of a turbo charged DISI engine using large eddy simulations (LES). LES is a mathematical model for turbulence which is used in computational fluid dynamics (CFD) solutions. LES reduces the computational time by ignoring smallest length scales. Engine performance was studied including the engine performance parameter of in-cylinder pressure. The results showed an overestimation of pressure curves due to ignition phase overestimation.

Experiments were performed in a single cylinder optical DISI engine with gasoline, ethanol and butanol fuels to investigate engine performance and flame
characteristics [38]. In-cylinder pressure was measured and flame images were recorded at early stage of flame development to visualize flame characteristics. Heat release was derived from in-cylinder pressure measurements. At low temperature and low swirl ratio, results showed slightly better combustion of gasoline than ethanol and butanol. It was observed that once the temperature and swirl ratio increased, the combustion results became identical for all fuels.

In-cylinder combustion and heat release characteristics impacted by the exhaust valve timing were investigated by Kang et al. [39]. The results based on the in-cylinder pressure showed formation of a faster flame kernel by initial advance of exhaust valve timing but severe deterioration in combustion was observed when the exhaust valve timing was further advanced to 32° before top dead center (BTDC). This was caused by higher dilution level and lower fluctuation kinetic energy.

Single cylinder with optical access DISI engine was used by Mittal et al. [40] to investigate the combustion and spray characteristics. In-cylinder pressure was recorded during the experiments. The results also showed the faster flame growth and shorter burnt time with increase in fuel injection pressure. Spray area increased with increase in fuel pressure.

Engine performance was studied under knock conditions [41, 42]. An experimental and numerical investigation was carried out by Catapano et al. [41] to study engine performance of a GDI engine under knock conditions. Results showed
good agreement with experiments for the flame propagation. In-cylinder and heat release rate were also measured and validated which showed a good agreement.

Wang et al. [42] studied the gasoline direct injection (GDI) engine performance under knock behavior. The correlation between the soot emissions and knock behavior was studied and it was found that higher in-cylinder soot emission correlated with knock cycles. It was also shown in the test results that under similar temperature and pressure near firing TDC, higher temperature and larger diameter carbon particles could lead to knock.

Downsizing of engine design has led to rise in thermal loads [43, 44, and 45]. To predict the engine thermal field, in-cylinder combustion analysis along with the conjugate heat transfer (CHT) analysis was performed to predict engine performance [43]. CHT has the capability to accurately predict the wall heat flux due to combustion. This resulted in the improved accuracy in estimation of combustion heat flux. In-cylinder pressure and heat release rate were measured and validated.

Nora et al. [44] performed a study and modified a four valve GDI engine into a two stroke engine. Several loads at 800 rpm and 1600 rpm were tested and engine performance and emissions were measured. This resulted in obtaining very high torque at low engine speeds and low in-cylinder pressure.

Jo et al. [45] proposed a solution to inject dual fuel in a downsized engine. Engine performance and emission analysis was performed. Dual fuel was injected
only when the engine was about to knock. Effects of downsizing, retarding spark timing and increased compression ratio on dual fuel were also investigated. This resulted in increased fuel economy. Increasing compression ratio above 11.5 increased the fuel economy marginally.

Experimental and numerical study was performed by Verma et al. [46] to study the spray properties in gasoline direct-injection (GDI) engine and to investigate the engine performance. A multi-component surrogate blend (230 species, 1740 reactions) was used to represent the physical and chemical properties of gasoline. The results showed better agreement of in-cylinder pressure and heat release rate with the experimental results.

Methane was direct injected and engine performance was investigated in an optical SI engine [47]. Melaika et al. [47] performed a study in SI engine to study methane to determine the advantages and disadvantages. The results showed that stratified combustion with methane was possible. The results obtained by in-cylinder pressure and heat release analysis showed the difficulty of proper mixing methane and air causing the high cycle to cycle variations. This resulted in the formation of soot.

### 2.1.2. Premixed or Port Injection

Experiments were performed [6, 7] by fully premixing the air-fuel mixture upstream of the intake port that created a fully premixed and pre-vaporized (PMPV) fuel-air charge and eliminated liquid fuel in-cylinder. A baseline particle
size distribution (PSD) was demonstrated using multiple fuels including gasoline, methanol, and E100. Particulate formation studies were conducted for new experimental operation that ensured a fully premixed flame inside the cylinder. The air and fuel were premixed well ahead of the intake port. This ensured a premixed and fully pre-vaporized (PMPV) air-fuel mixture in the cylinder. Using the PMPV technique, the effects of fuel chemistry, mixture enrichment, pressure, temperature, and residence time were characterized for in-cylinder premixed flames [7].

Experiments were performed on the same engine geometry for both premixed as well as direct injection case [48, 49]. Response of premixed flame with respect to the particle formation was determined in an experimental sensitivity analysis performed on a spark-ignition engine. Variable parameters included intake pressure, intake temperature, and equivalence ratio. Gasoline fuel was used for all experiments. Fuel was injected at high pressure well ahead of intake port to achieve a fully premixed air-fuel mixture. Experiments were also performed to study the effects of equivalence ratio on particulate formation for premixed conditions. The equivalence ratio was swept from $\Phi = 0.8$ to $\Phi = 1.2$. Results showed existence of significant number of small particulate formation under stoichiometric and lean conditions while large particles exist with increasing equivalence ratio.

In-cylinder pressure is one of the most important parameters that affect the engine performance of a spark-ignition engine while heat release analysis is another important tool for IC engine development [26].
Wiles et al. [50] performed a numerical and experimental study for the premixed case. The purpose of the study was to remove the intake-generated turbulence from the bulk gas. This resulted in a nearly quiescent flow field. This flow field retained the same time-varying geometry and thermodynamic conditions. Results showed that mass and temperature reduction due to heat loss to the chamber walls contributed towards decrease in the peak in-cylinder pressure.

Rothe et al. [51] studied knock behavior under full load conditions. Knock behavior at these conditions are of utmost importance because of the effect on in-cylinder pressure. Results showed that the knock behavior is strongly affected by combustion, mixture formation, and in-cylinder flow field. The amplitude of the knock was found to be dependent on the volume of the hot spot at the time of auto-ignition. The air-fuel ratio at the hot spot was found to be another contributing factor in the knock.

Numerical simulations were performed with the help of a multidimensional model developed for premixed case analysis for a gasoline direct injection (GDI) engine [52]. The model was used to investigate various combustion chamber designs to determine the influence on air fuel mixing, stratified combustion and NOx emissions. Combustion chamber bowl offsets in the range of 0-1.7 cm with increments of 0.25 cm caused the air fuel mixing to become more uniform but resulted in shorter ignition delay and slower combustion that resulted in lower in-cylinder peak temperature.
Regulations regarding controlling the CO₂ emissions have forced scientists to develop and try various alternative fuel blends such as crop produced alcohols. Spray development and combustion of various blends of ethanol with gasoline and iso-octane were used to study in-cylinder pressure [53]. The engine used was an optical Direct Injection Spark Ignition (DISI) engine. Various mixtures of gasoline/ethanol and iso-octane/ethanol were tested to determine the emissions from each mixture. The study was conducted using both port-injection and direct injection techniques. Results showed better flame development using direct injection. Direct injection produced similar in-cylinder pressures with all the blends while port injection produced high peak pressure values.

Iso-octane, gasoline and toluene were experimentally tested for the instantaneous in-cylinder heat flux [54]. Similarly, the study used both port injection and direct injection modes. An engine thermodynamic simulation code was used to calculate the gas to wall heat transfer. The paper used a modified Woschni correlation [55] to model the in-cylinder heat transfer. A constant scaling factor to match the engine geometry was used to get a reasonable agreement with the experimental results.

A comparative analysis was performed between CFD simulations utilizing turbulent chemistry combustion model results and experimental studies in internal combustion engines. The study was performed for premixed charge compression ignition (PCCI) and diesel engines [56]. Better agreement in results was found for the computed pressure and heat release profiles because of inclusion of detailed
chemistry. Large deviations were found between computed and experimental results for CO and HC emissions which require further work in numerical modeling for emissions.

Mittal et al. [57] used the measured in-cylinder pressure to calculate the mass fraction burned (MFB) in an SI engine. Analysis of measured in-cylinder pressure data was used to extract MFB data. MFB curves were evaluated at various load conditions using a net pressure method. Results showed good agreement of MFB curves at part-load and high-load conditions against Rassweiler-Withrow method [58]. This method is based on the assumption that during combustion in an engine, the total pressure rise is addition of pressure rise due to combustion and pressure rise due to volume change.

A study was performed to determine a novel method to measure the wall heat transfer during engine start-up and compare it with the existing models [59]. A novel heat flux sensor was used to measure the time resolved heat flux density measurements. Results of the measurements obtained during the experiments were compared with the existing wall heat transfer numerical models. There are two existing methods for measuring wall heat flux. The first method is an indirect measurement method that provides a temperature equivalent signal of wall surface. The indirect method requires an offset correction of calculated heat flux that is calculated during compression stroke by assuming adiabatic state. For this assumption to be applicable, the wall temperature needs to be higher than the intake air. This assumption and hence the method cannot be apply to cold start of engines.
The second type of method is direct method that provides signal to the wall heat flux. It was observed that the current wall heat transfer models were inadequate to correctly model the heat transfer at start-up and needed a novel method to be applied. The novel technique is called Atomic-Layer-Thermopile (ATPL). The ATPL sensor thermopile is constructed from copper peroxide (CuO$_2$).

Port fuel injection (PFI) of gasoline and direct injection (DI) of diesel fuel were used to test a premixed charge compression ignition (PCCI) and homogeneous charge compression ignition (HCCI) engine [5]. The study used a KIVA-CHEMKIN code and reduced primary reference fuel (PRF) (45 species, 142 reactions) for HCCI operation to determine the best fuel blend. Neat diesel and neat gasoline was used in the HCCI engine to control the combustion phasing by utilizing in-cylinder fuel blending using port-fuel injection of gasoline and early cycle direct injection of diesel fuel. Results showed that stratification of fuel reactivity was required to control the heat release rate with increasing load. The engine was also subjected to dual fuel engine experiments. Port fuel injection (PFI) of gasoline and direct injection (DI) of diesel fuel in the engine was performed. Dual fuel blends of gasoline (iso-octane) and diesel (n-heptane) were used. Due to presence of diesel fuel (n-heptane), formaldehyde was formed for low temperature reactions. It was later consumed as the reactions progressed. The experiment also showed that gasoline (iso-octane) did not consume or burn until the thermal ignition of diesel fuel (n-heptane) occurred. This allowed controlled PCCI
operation and extended combustion duration. Dual-fuel operation of the PCCI engine reduced the emissions as well.

Similarly, research work was performed by using experimental work from shock wave and rapid compression machine to validate the newly developed Lawrence Livermore National Laboratory reaction mechanism (1250 species and 5300 reactions) [60]. The results showed improvement in the prediction of heat release rate and combustion when compared to the previous primary reference fuel (PRF) mechanism. The combustion phase still shows a small difference at very lean conditions when the new PRF mechanism is compared with the experimental results.

Heat release rate was derived from in-cylinder pressure measurements. The results correlated with the Photo-Multiplier Tube (PMT) signals [61]. High speed video photography of soot thermal radiation as well as the in-cylinder spray imaging was performed. OH, C$_2$ and CH radical emissions were also confirmed by spectroscopic measurements. The results obtained from the high speed photographic images of fuel spray analyzed the fuel droplets existence in the spark plug gap at two different spark plug orientations.

Since large chemical reactions are time-expensive to use in the simulations, Shi et al. showed the decrease in computational time and validation of numerical results in a HCCI engine by using different processors from Tesla and Intel [62]. The results showed that Tesla C2050 processor was 1.5 times faster than Intel GTX
The results showed the validation of in-cylinder pressure which was in better agreement against the experimental results.

Coble et al. [63] used the Probability Density Function (PDF) along with the Stochastic Reactor Model (SRM). The model accounts for detailed chemical kinetics, fuel injection, turbulent mixing and heat transfer while retaining cylinder stratification of fuel mixture. Validation was performed for modeling in a premixed charge compression ignition (PCCI) engine. The purpose was to reduce the detailed mechanism. Detailed chemistry is necessary to predict the engine parameters correctly but it comes at a computational cost. Instead the technique used in this paper required to reduce the mechanism along with using the PDF and SRM models to predict the engine parameters. The results had better agreement but the in-cylinder pressure curve for numerical and experimental results still did not completely superimpose each other and experimental and numerical results did not show complete agreement.

A single cylinder spark ignition engine was used by Wigg et al. [64] to study the engine performance using neat n-butanol, gasoline and ethanol fuels and to compare the emissions. Torque, in-cylinder pressure, and exhaust gas temperature were compared. Gasoline and n-butanol were found closest in engine performance. On the other hand, measurements of hydrocarbons showed that butanol produced unburned hydrocarbons (UHC) three times more than the gasoline. This led to the conclusion that atomization of gasoline and ethanol was better as compared to butanol.
Zeng et al. performed [65] a study that used the high speed imaging and combustion luminosity in an optical engine to determine the heat release rates (HRR) and mass fraction burned (MFB) of the fuel in a direct injection spark ignition (DISI) engine. Since ignition at low loads and low speeds is difficult in DISI engines, this study utilized high speed imaging to analyze the flame growth which showed fast early flame kernel growth and spherical flame propagation for good burn cycles. A good agreement was found between HRR and MFB obtained from cylinder pressure analysis.

Similar to the studies performed reviewed earlier in this chapter on various fuel blends, Sjoberg et al. [66] also considered the fuels of ethanol and ethanol/gasoline blends. The purpose of the study was to investigate heat release rate (HRR) in HCCI engines. Since HCCI can only run at low or moderate loads due to high heat release rates (HRR) at higher fueling rates, the study aimed at utilizing partial fuel stratification to reduce the heat release rate (HRR) at high loads. This resulted in smoothing HRR. Also, with CA50 (crank angle for 50% heat release ATDC) held fixed, the maximum pressure rise was reduced as well.

Engine performance of a spark ignition (SI) engine was evaluated to check the sensitivity and effect of at various ignition timings [67]. The effect of ignition timing was analyzed to maximize engine performance parameters of power, torque and thermal efficiency. In-cylinder pressure and heat release rate curves were determined at various ignition timings. It was determined that the engine performance highly depends on the ignition timing. It was suggested to determine
the optimum ignition timing for each engine by the same analysis performed in this study.

Numerous studies have been performed on diesel engines and HCCI engines. In a study by Aronsson et al. [68], an investigation was performed to find the errors in heat release calculations in the optical diesel engines. The errors were eliminated by subtraction of motored heat release traces from a fired pressure trace.

Experiments were performed in a diesel engine utilizing the chemiluminescence measurements [69]. Chemiluminescence is emission of light during a chemical reaction. Experimental results were also validated against numerical simulations. The chemiluminescence allowed a direct comparison and validation of simulation results with the experimentally measure chemiluminescence. The results showed the existence of excited-state species by recording the emissions spectra. The cylinder pressure was measured by a piezo-electric pressure transducer mounted in cylinder head and validated against experimental data.

Ignition timing is one of the important parameters that play a vital role in determining the SI engine performance [70]. The effect of advanced and retarded spark timing on the engine performance was investigated using a numerical model. Optimum spark timing was determined at maximum thermal efficiency. The results showed that if the spark timing was over advanced, the combustion process started while the piston was moving towards TDC. On the other hand, if the spark timing
was retarded, the combustion process was delayed, and the peak pressure occurred too late into the expansion stroke.

Numerical simulations using large eddy simulations (LES) were performed on four valve port injected SI engine [71]. The results showed considerable cyclic variations in terms of in-cylinder pressure at full load. In-cylinder pressure and heat release rate were validated and in general, better agreement with the experiments had been found with some over predicted results as well due to grid resolution in LES.

Nithyanandan et al. [72, 73] investigated the effect of various fuel blends on engine performance. Acetone-Butanol-Ethanol blend was used along with gasoline. These blends were tested in a port injected SI engine. The performance evaluation of the fuel blends was determined by measuring in-cylinder pressure and emissions. The results showed that the peak in-cylinder pressure for the fuel blends was higher than that of gasoline.

Numerical simulations were performed by Jiao et al. [74] to investigate particulate formation in SI engine. The chemical kinetic model used 379 reactions and 79 species. A large chemical kinetic model was used for the study that is more computational expensive and needed more reduction. Also the heat release rate was not investigated as part of the study which demanded investigation. Analysis of the results show that although with better predictions, the in-cylinder pressure curves
for experimental data and numerical simulations had a very visible and significant initial lag.

SI engine with port injection was tested for engine performance with fuel blends of gasoline, n-butanol, iso-butanol and ethanol by Pechout et al. [75]. The results showed small changes in heat release among the fuels. Also, the emissions did not increase excessively. Results showed that by using either butanol isomer exceeding 30%, the engine storability worsened.

Experimental studies were performed by Moxey et al. [76] on various ethanol content fuels for investigating the turbulent flame process. The fuels used were gasoline, iso-octane, ethanol and E10. High speed chemical light or chemiluminescence was used to study the effect of low and high ethanol content on the turbulent flame. In-cylinder pressure was also measured during the experiment. The experiments concluded that the faster burning of ethanol was due the marginally high flame speed which produced high in-cylinder pressure.

Augoye et al. [77] performed a study for investigating the port injected (PI) and direct injected (DI) SI engine with hydrous and anhydrous ethanol in comparison with gasoline and iso-octane fuels. All tests were conducted at stoichiometric conditions. The investigation revealed that all of the alcohol fuels, hydrous and anhydrous, burn faster than gasoline and iso-octane (iC₈H₁₈) for both PI and DI. The results also showed a reduction in peak in-cylinder pressure as water content in
hydrous ethanol was increased. For all fuels that were tested in the study, the peak
in-cylinder pressure for PI was higher than DI.

Experimental studies were performed by Steurs et al. [78] to study knock in
premixed ethanol fueled SI engine at stoichiometric conditions. Heat release rate
(HRR) was computed and in-cylinder pressure was measured under knock
conditions. It was found that the factors in determining knock are the heat release
rate and amplitude of pressure oscillations. It was also concluded that the operating
points with high cycle-to-cycle variations are more prone to knock.

Particulate emissions independent of fuel particle was studied by Maier et al.
[79] in a gasoline direct injection engine. The engine was run with gasoline at four
different loads. The operation was then switched to hydrogen or methanol port
injected fuel and comparison was made for the particulate emissions and engine
performance. Results showed that at higher engine loads, the fuel combustion is a
dominant contributing factor in the particulate emissions.

Xu et al. [80] performed the study on lean burn gas engine. Methane was used
for validation and benchmarking. The results showed overestimations at lean and
rich conditions due to over-predicted laminar flame speed and Damkohler
correlation.
2.2. Combustion Physics and Phenomenon

2.2.1. Reaction Mechanisms/Models, Surrogates, Reduction and Sensitivity Analysis

Oxidation of hydrocarbons is shown by detailed chemical kinetic mechanisms. These detailed mechanisms are very large and comprised of a large number of species and reactions. As the size of the hydrocarbon increases, the length (number of species and reactions) of the mechanism increases along with it. Due to the construction from smaller hydrocarbons (HC) progressing to larger HC and intermediate radicals, detailed mechanisms of large hydrocarbons contain many species and reactions that are not needed for simulating ignition phenomenon. These redundant species and reactions needlessly raise the computational time and can be eliminated from the detailed reaction mechanism without compromising the accuracy and integrity of the detailed reaction mechanism. Reaction mechanisms are tested for laminar flame speeds, adiabatic flame temperatures, and species profiles etc. to make sure that the skeletal mechanism obtained by reducing the detailed mechanism reproduces the same properties. The detailed and large mechanisms cannot be employed in present solvers because they are time expensive. For example, gasoline and diesel fuels consist of thousands of reactions and hundreds of hydrocarbons [81].

Fuels, such has gasoline and diesel, are composed of hundreds of hydrocarbons. These hydrocarbons include alkanes, alkenes, aromatics and napthenes. Surrogate fuel mechanisms that contain limited number of hydrocarbons from all of the above
hydrocarbons types are important in this regard. There is a necessity to use reduction techniques to produce reduced order mechanisms that can replicate the predictions of detailed mechanisms. The reduction techniques decrease the number of reactions and number of species.

Saylam et al. [81] recognizes the redundant reactions by two methods/techniques:

a. reaction rates analysis and,

b. sensitivity analysis

The reaction rates analysis divides the entire reaction set into groups of slow and fast reactions. The sensitivity analysis also divides the reaction set into groups of rate limiting and non rate limiting reactions. These analyses are combined to identify the redundant reactions. By this method, the redundant reactions identified are non rate limiting slow reactions. As the redundant reactions are eliminated, the species taking part in those reactions gets automatically eliminated, hence, a reduced mechanism is obtained [81].

Detailed and global chemical kinetic computations for hydrogen-air mixtures were performed [82] to determine flame properties such as flame propagation, flame structure and ignition phenomena. Simulations of laminar flame speeds, flame compositions and shock tube ignition delay times were successfully performed. A sensitivity analysis was applied to determine the governing rate-controlling reactions for the experimental data sets examined. The reactions, OH +
H₂ = H₂O + H, O + H₂ = OH + H, and, O + OH = O₂ + H were found to be very important for the flame structure study. Global reaction for hydrogen, H₂ + ½ O₂ = H₂O was validated against the laminar flame speed of hydrogen-air.

Battin-Leclerc performed a study [83] to review gas-phase detailed kinetic models developed to simulate the low-temperature oxidation and auto-ignition of gasoline and diesel fuel and of mixtures of several of them, which were proposed as surrogates. The recent proposed models were summarized, as well as the experimental results available for their validation. A comparison between the major models in terms of considered elementary steps and associated rate constants were also proposed in the study. The review concluded that there were important problems that remain to model oxidation of aromatic compounds at low temperatures, especially in case of toluene. The study also reviewed various reduction techniques. Using the computational singular perturbation (CSP) technique, reduction of iso-octane/n-heptane reaction mechanism by Sohan et. al [84] and Valorani [12] has been performed that has resulted in reduced and skeletal mechanisms.

Soyhan et al. [84] performed a validation of experimental results with the numerical simulations for spark ignition engines. A reaction mechanism was developed to replicate the experimental results. A method for automatic reduction of detailed kinetic mechanisms of a mixture of iso-octane and n-heptane was developed for the conditions of knock in spark ignition (SI) engines. The reduction method simultaneous utilizes sensitivity, reaction-flow, and extended lifetime.
analyses. Species that were sensitive to the combustion process were identified by
the sensitivity analysis performed by the method. After identification of the
sensitive species, the reduction of the detailed mechanism (74 species and 510
reactions) resulted in a skeletal mechanism (63 species and 386 reactions) by
elimination of redundant species from the detailed mechanism. The research also
found that the skeletal and reduced mechanisms were only valid for the initial and
boundary conditions for which they were reduced.

Herbinet et. al [85] developed a detailed chemical kinetic mechanism and used
it to study the oxidation of methyl decanoate, a surrogate for biodiesel fuels. The
detailed mechanism includes all the reactions known to be pertinent to both low
and high temperatures. Computed results were compared with methyl decanoate
experiments in an engine. A feature of the reaction mechanism was the ability to
predict early formation of carbon monoxide (CO) and carbon dioxide (CO$_2$). The
reaction mechanism included low temperature pathways which enabled it to study
in diesel ignition and sooting problems as well as combustion in homogeneous
charge compression ignition (HCCI) engines. A similar research was performed in
[86].

A study was performed by Wang et al. [87] to optimize global mechanism
selection for predicting the major species concentration of methane (CH$_4$)
combustion. For this purpose, six different global combustion mechanisms,
including the four-step mechanism for premixed and non-premixed flames of
hydrocarbons with the water-shift reaction (to form carbon dioxide (CO$_2$))
developed by Jones and Lindstedt (JL) [88], the two-step mechanism of Westbrook and Dryer (WD) [89] of oxidation of carbon monoxide (CO) to carbon dioxide (CO₂) for modeling in hydrocarbon combustion, and several modified versions of them, were investigated. The results showed that the peak and exit concentrations of CO were better predicted by WD. Also, JL over predicted CH₄ concentrations, WD better predicted the results.

Jazbec et al. [90] performed sensitivity analysis of methane reaction mechanism to reduce the mechanism to 16 species and 28 reactions, and study combustion ignition. The problem of reduced chemistry and reaction mechanism was applied to an industrial problem for prediction of ignition in methane mixtures. The results showed the reduction of the chemical mechanism provided promising data including species profiles and adiabatic flame temperature which assisted in the design of a pressurized combustor.

A new combustion model was developed by Fan et al. [91] and tested for premixed spark-ignition engines. The model investigated the flame-front growth and flame properties. The study was performed by using homogeneous charge Caterpillar SI engine. Iso-octane was used as a gasoline surrogate. Results showed the modeled predictions to be in good agreement with the experiments for the flame properties as well as the in-cylinder pressure.

Detailed chemical model of iso-octane was developed and experimentally tested in a jet stirred reactor, flow reactor, shock tube and a motored engine by Curran et al. [92]. The mechanism was based on the early research in the modeling
of n-heptane mechanism. The initial pressure tested was from 1-45 atm and at temperature range of 550-1700 K. The experimental results were utilized to validate and develop the predictive capability of the reaction mechanism at low and high temperatures. The results also reproduced the experimental species profiles with the modeling having better agreement in the shock tube experiments.

Su et al. [93] achieved the reduction of n-heptane fuel reaction mechanism by a sensitivity analysis. The reaction mechanism was reduced to be used in HCCI engines. The final reaction mechanism had 40 species and 62 reactions. The mechanism was reduced from the detailed mechanism having 544 species and 2446 reactions. The reduced model agreed well with the in-cylinder temperature and pressure histories as of detailed mechanism and showed a reduction of computational time by 1/1000.

Babajimopoulos et al. [94] performed numerical simulations for a premixed charge compression ignition (PCCI) engine using KIVA-3V [2] by coupling it with a multi-zone model with detailed reaction mechanism. Results showed good agreement with ignition timing, burn duration and emissions when full chemistry in each cell is compared with 100 zones. The research did show that at the ignition point, the pressure curves had a small lag or difference but it was a very small difference. The data was not compared with experimental results and was purely a computational effort.

Numerous studies have also been performed for n-heptane and HCCI engines. A sensitivity analysis was performed by Maroteaux et al. [95] to reduce n-heptane
detailed mechanism for a HCCI engine. Two reduced reaction mechanisms with 61 reactions, 37 species and 26 reactions, 25 species were produced. The reduced reaction mechanism ignition delay was validated against shock tube experiment results already present in the literature. Comparison of in-cylinder pressure amongst the reduced mechanisms and detailed mechanism showed that with 61 reactions, 37 species produced better agreement of in-cylinder pressure but the results for the heat release were off and the curves had a lag for both reduced mechanisms. In-cylinder pressure and heat release rates obtained from detailed and reduced mechanisms were not compared with experimental data.

Similarly, a computational study was also performed for HCCI engines using n-heptane fuel by Zheng et al. [96]. In-cylinder pressure and heat release rate was shown but not compared with the experimental data. The results showed that the reaction path was converted to the low temperature branching for alkyl decomposition. This showed that CH$_2$O and H$_2$O$_2$ are important products at low temperature reactions.

To better model the fuel combustion and pollutant formation, Liang et al. [97] used detailed chemical kinetics of propane (100 species, 539 reactions) to model combustion. The model was then used with KIVA-3V to model the homogeneous charge and stratified charge combustion in the SI engines. The results showed a better agreement of in-cylinder pressure with the experimental results, as a function of spark timing.
Petroleum based fuels are a complex mixture of hundreds of hydrocarbons. Gasoline is petroleum based complex fuel with hundreds of hydrocarbons [98]. Pitz et al. [98] performed a study to review the development of surrogate fuel mixtures for gasoline. Homogenous charge compression ignition (HCCI) engines were studied at conditions of pressure, temperature and reactant concentrations. The research recommended use of a mixture of iso-octane, n-heptane and toluene as gasoline surrogate fuel especially in HCCI and SI engines. Further addition of di-isobutylene and methylcyclohexane was also recommended.

Surrogate fuels are defined as mixture of few hydrocarbon compounds. The relative concentrations of surrogate fuels can be adjusted so that the physical and chemical properties of the surrogate fuels are similar to the commercial fuels. The physical and chemical properties of fuels effect combustion and therefore, should be similar to commercial fuels [99].

There are two different types of surrogates: physical surrogates and chemical surrogates. Physical surrogates are constructed to reproduce the physical properties of commercial fuels. These properties include density, thermal conductivity, heat capacity, viscosity, surface tension and volatility. Chemical surrogate generally have the same chemical class composition of commercial fuels. They have the similar hydrocarbon types and distribution and can reproduce chemical properties. These properties are oxidation stability, ignition temperature, rates of reaction, and sooting behavior. Three key steps in developing chemical surrogates are:
1. The aspects of combustion that the surrogate is expected to reproduce must be clearly defined.

2. The chemical kinetic mechanism for components in the surrogate must be developed, and,

3. The last step is to assemble the chemical kinetic mechanism for the surrogate by using the individual mechanism of its components.

   A kinetic scheme was presented to take into account the chemistry of the compounds included in the surrogate mixture [100]. The kinetic model was validated through comparisons with experimental data of laminar flame speeds, structure and species profiles. Four elements were provided for the formulation strategy:

   1. Feasibility: The surrogates in this category should have a known chemical reaction mechanism.

   2. Simplicity: This criteria requires the surrogates for the paraffins to have less than 12 carbon atoms. Paraffins or alkanes have a general formula \( C_nH_{2n+2} \)

   3. Similarity: This criteria requires the surrogate to match both physical and chemical properties, such as volatility, sooting, and heat of formation.


   The process of selecting individual hydrocarbon species is an iterative process. The blending and testing of the surrogate fuel should satisfy the above four criteria.

   Knock was investigated by Liang et al. [101] using KIVA-3V code and detailed chemistry and validated against experimental data from shock tube and HCCI
engine. Validation was also done at stratified charge lean-burn conditions in a DISI engine. Iso-octane was used as a gasoline surrogate and an existing primary reference fuel (PRF) reaction mechanism was adopted in the study. The results showed good agreement at lean-burn conditions for in-cylinder pressure and heat release rate.

A reduced chemical kinetic mechanism of iso-octane combined with n-heptane to form 130 reactions and 41 species by performing sensitivity analysis [102]. Validation of the reaction mechanism was performed with the existing experimental data for shock tubes, HCCI and direct injection diesel engines. The results showed a good agreement of in-cylinder pressure, and heat release rate with the experimental data. The engine-out emissions were also checked against experimental data but were found to have discrepancies.

A chemistry-guided reduction (CGR) technique was applied to the n-heptane mechanism [103]. The technique was based on necessity analysis, combination of reaction flow and sensitivity analysis, which identified redundant species. Necessity analysis can only be applied to comprehensive detailed mechanism that has been thoroughly tested for combustion parameters. The research achieved a 47 species, 468 reaction mechanism for n-heptane. The mechanism was tested and validated for flame speed, flame structure and species profiles which showed better agreement with the detailed mechanism.

The paper reviewed the need for realistic based chemistry in large scale models [104]. It also compared the detailed and reduced chemistry. The study also
reviewed various reduction techniques including directed relation graph (DRG) and computational singular perturbation (CSP). DRG method identifies the species closely coupled with major species, such as fuel and oxidizer. This is achieved from sensitivity analysis that uses Jacobian matrix (first order differentials of the vector G) or sensitivity matrix that can be normalized. CSP uses the concept of vector G that represents the rate of change of species mass fractions and temperature. CSP decouples the fast and slow subspace with Jacobian analysis.

A reduced chemical kinetic model consisting of 67 reactions and 48 species was developed by Lee et al. [105]. The fuel mixture blend included iso-octane, n-heptane and toluene. The results were validated as a gasoline surrogate fuel for gasoline HCCI engine. From the experiments conducted, a gasoline surrogate with mixture ratio of iso-octane: 54%, n-heptane: 22% and toluene: 24% by liquid volume, proved much more similar to gasoline. The results showed better agreement of pressure histories in a rapid compression machine (RCM).

Soyhan et al. [106] performed a study to use an automatic reduction model for fuels. The model performed a sensitivity analysis using a quasi-steady state assumption (QSSA) method eliminating the redundant species. QSSA is a time scale method that assumes that the fast depleting species remain in low concentrations due to quick depletion. The skeletal and reduced mechanisms generated were only valid for pre-determined specific boundary and initial conditions. The initial temperature was 1200K, with the wall boundary condition
temperature of 300K. The results showed the error calculation for auto-ignition
time due to elimination of species increased with the auto-ignition time.

Similarly, a study performed by Sun et al. [107] used path flux analysis (PFA)
technique to reduce the mechanisms applied to n-heptane and n-decane/air
mixtures. To identify the reaction pathways, PFA uses production and consumption
fluxes instead of using absolute reaction rate. The results were compared with the
DRG reduction method described previously. The results showed PFA producing
better accuracy than DRG in reproducing ignition and extinction of n-decane and n-
heptane, although temperature profile and species profiles for n-decane combustion
and its products, CO$_2$ and CO showed better agreement.

A gasoline detailed mechanism with 5935 reactions and 1389 species was
reduced by Niemeyer et al. [108] to various reaction mechanisms with different
complexity level. Results were validated against experimental results from HCCI
combustion engine. Species profiles for fuel and CO were found to be in good
agreement but noticeable error was found in exit CO for very lean low load case
which was outside the range of conditions used in skeletal reduction.

A reduced reaction mechanism was automatically developed with 155 reactions
and 33 species for ethanol ignition by Perini et al. [109]. Simulation results were
validated against experimental results from HCCI engine. Predictions for in-
cylinder pressure and species profiles achieved showed a big lag in the in-cylinder
curves and heat release.
A reduced PRF mechanism of 296 reactions and 73 species was proposed by Wang et al. [13] for diesel/gasoline combustion simulations. Experiments were performed to validate the HCCI, PPCI combustion data as well as the diesel/gasoline combustion data for direction injection spray. In-cylinder pressure and heat release rate showed better agreement with the experimental results, although species profiles showed lag between the experimental and simulation curves.

A study by Wolk et al. [110] developed a 96 species reduced chemical kinetic reaction mechanism for HCCI engine. KIVA-3V coupled with CHEMKIN was used to perform the numerical simulations. SENKIN was also used to perform the sensitivity analysis. Numerical data was validated against the experimental data. The study was performed for fuel stratification in HCCI engine to reduce the pressure rise. The results showed better agreement of heat release rate and in-cylinder pressure although some lag in the curves was observed.

Detailed mechanism for gasoline developed by Lawrence Livermore National Laboratory (LLNL) has 5935 reactions and 1389 species [111]. The detailed mechanism was found to be computationally expensive and could not be used for engine simulations. Instead reduced mechanisms could be developed to be used for engine simulations. Reduced mechanisms were developed for error constraints of 10% and 30% by using the directed relation graph with error propagation (DRGEP). The reduced mechanisms consisted of four component gasoline surrogates with 245 and 178 species. The mechanisms were reduced using
reduction technique of quasi-steady state (QSS) approximation using computational singular perturbation (CSP) method, which are previously discussed. Results were validated using homogenous auto-ignition conditions. The results showed better agreement in predicting the auto-ignition but the research did not provide analysis of in-cylinder pressure and heat release rate. The study also mentioned that it requires The research also recommended using CSP reduction technique for further reduction instead of using other techniques, as CSP technique provides better reduced mechanisms which can validate the chemical and physical properties of a detailed mechanism.

Similarly, n-heptane mechanism by Lawrence Livermore National Laboratories (LLNL) was reduced by Tsai et al. [112]. Skeletal mechanism of 144 species and a reduced mechanism of 62 species were developed. Validation was done for the shock tube data. KIVA-3V was used to perform engine simulations. The simulation results were found satisfactory for diesel conditions but inaccurate for HCCI conditions. In-cylinder pressure and ignition delay were validated against experimental results.

Similar study for reduction of LLNL mechanism to skeletal mechanism of 213 species and a reduced mechanism of 148 species was conducted for gasoline surrogate by Niemeyer et al. [113]. The study used the reduction technique of DRGEP with error limit of 10%. The study is similar to the research performed in [111]. The validation study showed the results of temperature profiles and laminar flame speeds to be within the 10% error limit.
In addition to reducing the gasoline surrogate mechanism, ethanol was added to the gasoline surrogate of iso-octane and n-heptane to simulate the results for gasoline/ethanol fuel blend in a study performed by Cai et al. [114]. The numerical data was validated against experimental data. The results showed better agreement for the flame speed, and flame structure but showed some difference and lag in the species profile curves.

Gasoline surrogate models for HCCI and SI engines as well as gasoline/ethanol blends and to use reduced mechanisms was discussed by Pitz et al. [115]. The research discussed the need to develop predictive chemical kinetic models for the surrogate fuels and their components and using the models in the computational fluid dynamics (CFD) study for advanced engine combustion. The research also stressed the need to improve the accuracy of CFD simulations by using detailed fuel chemistry. This will increase the predictability for the engine designers. The results showed pressure histories, flame speeds, temperature profiles and heat release rate as the means of validation of surrogate fuels.

The study performed by Liu et al. [116] gave a detailed overview for using CSP method to reduce the detailed chemical mechanisms. Skeletal mechanism and reduced mechanism were developed from a detailed n-butane mechanism. The unimportant reactions in the reduced mechanism were eliminated using the importance index defined in computational singular perturbation (CSP). Finally, global quasi-steady-state species were identified using a CSP-based time-scale analysis, leading to a reduced mechanism. Validation of the reduced mechanisms
showed good agreement with the detailed mechanism for both the ignition delay time and the distribution of species concentration over a wide range of simulation conditions.

2.3. Integration of Detailed Chemical Kinetics into CFD

As the engine computational fluid dynamics (CFD) codes have evolved, so has the detailed chemistry integration with CFD. The evolution process began from simplified, single-zone, zero-dimensional models and moved towards physical and chemical three-dimensional sub-models that are more realistic. With the evolution of modeling, one fact remained unchanged. The coupled study of CFD with detailed chemical kinetics is computationally and memory intensive. The reason for the time expensive attribute is the large size of the reaction mechanisms. The answer to this problem lies in the optimization techniques that, while maintaining accuracy, they should be implemented to reduce the computational time [1]. This optimization can occur by using reduced mechanisms that carry detailed chemistry to accurately model the CFD solution. KIVA and CHEMKIN were coupled to enhance the combustion model of KIVA. The process of coupling of detailed chemical kinetics using the chemistry solver CHEMKIN with CFD code KIVA was discussed in detail [1]. The advantage to coupling CHEMKIN with KIVA would use the reaction properties and library of CHEMKIN, easiness of importing CHEMKIN reaction and species data into KIVA input file, and avoidance of manual input of large mechanism reaction and species data into KIVA input file. KIVA-4 code was used to couple with the chemistry solver, CHEMKIN. The
research model was applied to direct injection (DI) diesel and homogeneous charge compression ignition (HCCI) models. The research showed successful simulation and validation of premixed HCCI model while the DI case did not model accurately. Emissions study was also not performed. The DI case could not model the results accurately due to lack of turbulent mixing model, presence of sensitivity of intake conditions and experimental uncertainties.

Researchers have used various coding methods to couple detailed chemistry with the CFD codes. Golovitchev et al. [117] presented coupling KIVA-3V with CHEMKIN solver for diesel engine modeling to achieve the objective. Predicted in-cylinder pressure curve showed a lag with the experimental data.

Aceves et al. [118] performed a study where the solutions were mapped back and forth between KIVA and CHEMKIN. HCCI engine performance results were determined and validated by complete integration of KIVA and CHEMKIN. The results showed accurate prediction of in-cylinder pressure but the heat release rate (HRR) curves had a lag.

Research was conducted for diesel engines with n-heptane fuel using KIVA-CHEMKIN coupling by Reitz et al. [119]. The results showed better agreement of in-cylinder pressure and species profile for CO and NO.

Similarly, Kokjohn et al. [120] performed a study on diesel engines and used KIVA-CHEMKIN code to optimize light duty diesel engine using n-heptane reduced reaction mechanism. Emission trends showed a difference in predicted and experimental results. The in-cylinder pressure and heat release rate had better
prediction although the heat release curve had a small lag with the experimental results.

The performance and emission of a spark ignition (SI) engine by using increased ethanol was evaluated by Motlagh et al. [121]. Only in-cylinder pressure was validated against the experimental data that showed a good agreement with the experimental results.
3. KIVA-CHEMKIN Interface

The present study used coupling of CFD solution with detailed chemistry. This is achieved through integration of CFD solver, KIVA, with a chemistry solver, CHEMKIN. It is done by writing down the code inside KIVA. The current code is written inside KIVA that gelled up KIVA and CHEMKIN in one executable making the CHEMKIN library part of KIVA. Since KIVA library lacks the thermodynamics and reaction data for the intermediate species, the purpose of the code developed in this research is to read the reaction properties, such as reaction rates and reaction constants from CHEMKIN and use the information to input in the input file used by KIVA. Since CHEMKIN library code became part of KIVA executable, the reactions and species data is directly read from the CHEMKIN binary file and it is input into the output file in KIVA. It also uses the species and their properties from CHEMKIN and updates in the KIVA output file. To achieve this research objective, a code is developed in KIVA that is used to interact between CHEMKIN and KIVA. At this point, both the CFD and chemistry softwares need to be introduced.

3.1. Introduction to KIVA

To better model the chemistry and physics inside an internal combustion engine, this chapter aims to integrate detailed chemical kinetics into fluid dynamics software. The computational fluid dynamics (CFD) code used for this study is KIVA-3V. KIVA [2] is developed by Los Alamos National Laboratory (LANL)
and has been in use since 1985. It is an unsteady compressible turbulent Navier-Stokes solver with finite rate chemistry and liquid spray injection. After its first release, it has been continually improved upon with various improved versions coming out such as KIAV-II, KIVA-3, KIVA-3V and the latest version as KIVA-4. This chapter is dedicated to a brief introduction of KIVA and CHEMKIN and is followed by the development of a shared executable for KIVA and CHEMKIN.

The various versions of KIVA codes were first developed in early 1980s. The code is under constant improvement and development to this day as more research and experimental data becomes available. The code has been adopted as a design and research tool for complex transient reactive flow problems. The code is an open-source structure and allows the user to improve the code based on new insights and research. KIVA can model a wide range of applications but specializes in the internal combustion engine applications.

KIVA is a Navier-Stokes solver that performs numerical simulations, calculations and solutions for the transient thermal problems with physical process inside a reactive domain [1]. It can model various problems including premixed combustion, liquid spray injection, droplet breakup and evaporation, gas-liquid charge mixing, various ignition and combustion processes, and heat transfer. An arbitrary Lagrangian-Eularian (ALE) method is used to solve the governing equations. The solution of sub-models is coupled using the operator splitting approach. Due to piston movement, and phase change during combustion, various properties of the reactants change inside the engine. The change in species densities
is a perfect example. This approach makes it possible to incrementally add the changes and the contributions due to all those factors of combustion and compression. The KIVA code is organized and coded in a way which makes it a centralized program. It uses the main program to call other sub-models. These sub-models define various processes that are occurring in the computational domain with respect to time.

KIVA applies the ALE method to the computational domain. The computational domain, or the grid or mesh, is comprised of many cells, or finite volumes. Governing equations are solved by KIVA for any problem with respect to time for all of the cells in the computational domain. As the grid, or the computational domain gets bigger with increased number of cells, the computational complexity and time increases.

KIVA has a built in library of fuels which includes paraffins, olefins, and aromatics. The library contains information such as molecular weights, heating values, and enthalpies. The library can further be extended as more fuel data becomes available.

3.2. Introduction to CHEMKIN

CHEMKIN [3] is a FORTRAN-based code and is a standard for chemistry applications for chemistry based solvers. It was developed by Sandia National Laboratories. It analyses and solves the gas phase chemical and plasma kinetics.
Unlike KIVA, it requires the executables to be generated for every utility but extracts the relevant information and data from the CHEMKIN binary file as all of the reaction and species information is dumped into the binary file after the first CHEMKIN executable run. It contains a wide ranging powerful set of utilities, which helps in solving for the chemistry source terms in reactive flow applications.

CHEMKIN requires two types of inputs; reaction mechanisms and thermodynamic database. The reaction mechanism declares elements, species and the reactions. The reactions include all the information regarding Arrhenius coefficients. The coefficients include pre-exponential factor, temperature exponent and activation energy. Following is the Arrhenius equation that utilizes the Arrhenius coefficients in determining the reaction rates.

\[ k(T) = A T^b \exp \left( -E_A / R_u T \right) \]  

(1)

where A, b, and E_A are three empirical parameters. A is a constant termed as pre-exponential factor, and E_A is the activation energy. These parameters are shown in Appendix A for the reduced mechanism used in this study.

\section*{3.3 KIVA-CHEMKIN Model}

The work in this chapter focuses on the development of a combustion sub-model which directly couples the CFD solution obtained from KIVA with the detailed chemistry solved by the chemistry solver, CHEMKIN. In this study, KIVA-3V is used to couple with CHEMKIN.
3.3.1. Detailed Instructions for the new code and interaction with KIVA

KIVA-CHEMKIN model is developed for KIVA-3V, which is written in FORTRAN. The new combustion model, require coding in two files; cklib.f which is a CHEMKIN library and rinput.f which is KIVA file. An override flag chemk is introduced in the simulation input file. As soon as the new rinput.f is called, it gathers the species and reaction data from the chem.bin file and inputs it in the KIVA output file. A partial input file is also generated in case the user wants to use KIVA executable for the simulations.

The following KIVA-3V default input files are needed by the KIVA-CHEMKIN interface:

1. Simulation input file, itape5,

2. Computational grid file, itape17, and

3. Update to species enthalpy data file, bdcomd.f.

A fourth input file is needed as the detailed chemistry subroutine is called by activating the chemk override flag in the input file. The additional file is a binary file, chem.bin. This file is generated by using the CHEMKIN pre-processor. The grid file remains unchanged for a specified geometry, but specific instructions must be followed for the preparation of the remaining input files. Required steps to create or update the remaining input files are discussed below. The final executable created in KIVA has the CHEMKIN library in-built into it.
The first step in using the KIVA-CHEMKIN interface is to create the binary file, chem.bin, by using CHEMKIN. The input files needed to create the binary file are the reaction mechanism (chem.inp) and thermodynamic database (therm.dat). These input files must be pre-processed to generate a binary linking file (chem.bin). KIVA-CHEMKIN interface requires it to be an additional input file as the reactions and species are extracted from the binary file by rinput.f to fill in the place for reactions and species data input into the output file. It is utmost important to make sure that the order of species in the chem.inp file is same as the order of species defined in the enthalpy file bdcomd.f as KIVA relies on the array indices and not on the chemical formulas to update any variables. Therefore, listing of species in the CHEMKIN mechanism file (chem.inp) must be consistent with KIVA. If there are any changes or rearrangement of species made in the chem.inp or therm.dat files, chem.bin must be regenerated after any change made to those files. Two output files are created while pre-processing the input files. Those output files are the binary file, chem.bin, and a user-friendly readable file, chem.out. Always check the partial input file for KIVA to make sure that all of the extracted data corresponds to the chem.out file.

The first step towards integrating KIVA with CHEMKIN is that both codes must be able to use the shared set of reactions and species data including the thermodynamic database. The thermodynamic database or the therm.dat file helps
in constructing the enthalpy file bdcomd.f. The user must make sure to update bdcomd.f file concurrent with the reaction mechanism and species being used.

KIVA requires data containing species information, such as species formulas, molecular weights and heats of formation, to be used as an input in the input file. It also requires specifying the mass fractions of the participating species to be entered in the input file. The KIVA-CHEMKIN interface developed in this study does not require user to input any species formulas, molecular weights and heats of formation and automatically inputs it in the output file. But it does require the user to input the mass fractions of the participating species in the input file. For the reactions, the code does not require the user to input any reaction data as it is automatically extracted from the binary file and input into the output file and the partial input is generated. The KIVA-CHEMKIN code gathers that data automatically and inputs it directly into the output file. The partial input file generated by the code contains all the reactions written in the KIVA format in case the user wants to use it directly into a complete input file for KIVA runs.

The enthalpy data file, bdcomd.f, contains enthalpy data for all gaseous species. For fuels, the enthalpy data is already present in the KIVA fuel library. The bdcomd.f file constructed for the reduced mechanism in this study is shown in Appendix B. The file shows all the fifty-one enthalpy points, corresponding to the enthalpies in the units of kcal/mol, from 0 to 5,000 K in 100 K intervals.
4. Chemical Kinetics Modeling and Mechanism Reduction

4.1. Global VS Quasi-Global Mechanism

The program to be used in the current study is the KIVA-3V code developed by Los Alamos National Laboratory for numerical calculation of transient, two- and three-dimensional chemically reactive fluid flows with sprays.

The study investigates the variation between the experimental results and simulations performed in KIVA-3V for premixed case. To perform the studies, iso-octane is used as a gasoline surrogate with global and quasi-global reaction mechanisms.

Global mechanism [122] uses the one-step fuel reaction mechanism which burns with air along with the three reactions from the extended Zeldovich mechanism for prediction of NO\textsubscript{x} formation. The chemical reaction equation for the global mechanism is:

\[ iC_8H_{18} + 12.5 O_2 + 47 N_2 \rightarrow 8CO_2 + 9H_2O + 47 N_2 \] (2)

Quasi-global mechanism [122] uses a four-step reaction mechanism for the fuel that burns with air along with three reactions from the extended Zeldovich mechanism. The chemical reaction equations for the quasi-global mechanism are:
\[ iC_{8}H_{18} \rightarrow 4C_{2}H_{4} + H_{2} \]  \hspace{1cm} (3)

\[ C_{2}H_{4} + O_{2} \rightarrow 2CO + 2H_{2} \]  \hspace{1cm} (4)

\[ 2CO + O_{2} \rightarrow 2CO_{2} \]  \hspace{1cm} (5)

\[ 2H_{2} + O_{2} \rightarrow 2H_{2}O \]  \hspace{1cm} (6)

The chemical reaction equations for the Zeldovich mechanism are:

\[ 2N_{2} + O_{2} \rightarrow 2N + 2NO \]  \hspace{1cm} (7)

\[ N_{2} + 2O_{2} \rightarrow 2O + 2NO \]  \hspace{1cm} (8)

\[ N_{2} + 2OH \rightarrow 2H + 2NO \]  \hspace{1cm} (9)

The analysis and comparison helped in determining the correct reaction mechanism to mitigate experimental results as well as understanding the chemical kinetics. Experimental results were obtained from [6, 7] for premixed case, at equivalence ratio of 0.98 and 1.3. The engine geometry used 85.96 mm bore, 94.6 mm stroke, compression ratio of 11.97 and running at 2100 rpm. The analysis was performed at equivalence ratios of 0.98 and 1.3. Comparison analysis was performed for engine parameters; in-cylinder pressure and heat release rate.

4.2. Reduced Mechanism with Detailed Chemistry

Computations based on detailed reaction mechanisms are complex because of chemical stiffness and large size of reaction mechanism. Reduction of chemical mechanism is needed to be performed and can be performed at two levels. The reduced mechanism is a subset of a larger detailed mechanism.
Level I: The first level requires skeletal reduction. It is done using methods such as directed relation graph (DRG), DRG with error propagation (DRGEP), path flux analysis (PFA), revised DRG (DRGMAX), or computational singular perturbation (CSP). These methods eliminate the unimportant reactions and species.

Level II: The second level of reduction is performed using global reduction methods. The methods used in this level are computational singular perturbation (CSP), and quasi-steady-state approximation (QSSA). These methods analyze the impact of the timescales on the reaction mechanism [116].

The first step to reduce the detailed reaction mechanism to a skeletal reaction mechanism is the elimination of unimportant species [8]. This step is achieved by DRG method. This method identifies the species closely coupled with major species, such as fuel and oxidizer. This is achieved from a sensitivity analysis that uses Jacobian matrix or sensitivity matrix that can be normalized. Jacobian matrix is the matrix of all first-order partial derivatives of a vector valued function. This method is important for reduction of large reaction mechanism. The reduced skeletal mechanisms obtained from DRG are not minimal due to assumption of the upper-bound error propagation. A more straightforward definition of DRG is,

\[
\mathbf{r}_{A,B} = \frac{\sum_{j=1}^{J} |\nu_{Aj} \omega_{ij} \delta_{Bj}|}{\sum_{j=1}^{J} |\nu_{Aj} \omega_{ij}|} \tag{10}
\]

where, \(\delta_{Bj} = 1\), if the ith elementary reaction involves species B, otherwise, 0; \(\mathbf{r}_{AB}\) is the relative error induced to species A by elimination of B, subscript i represents
the ith elementary reaction and j represents the jth species, \( \nu_A \) is the net stoichiometric coefficient of species A, \( \omega_i = \omega_{f,i} - \omega_{b,i} \) where \( \omega_{f,i} \), \( \omega_{b,i} \) and \( \omega_i \) is the forward, backward and net reaction rates respectively, that can be calculated from the already given coefficients and activation energy in the CHEMKIN input file. If \( r_{A,B} < \epsilon \) for all species, then the relation between B and A is considered to be negligible. Species B is selected when \( r_{A,B} \geq \epsilon \). Here \( \epsilon \) is a user-defined small threshold value. In most cases, \( \epsilon = 0.1 \) is used [104, 107].

Therefore, the second step is to further reduce the skeletal mechanism by using the technique called directed relation graph-aided sensitivity analysis (DRGASA). This method further reduces the species set by performing the sensitivity analysis on the already obtained species data from the previous method, DRG. The parameters that are focused for the DRGASA method are ignition delays, extinction times, and laminar flame speeds. The reduction with this method is carried out using for a range of pressure, temperature and equivalence ratio. These two steps provide the researchers with a skeletal mechanism.

Skeletal mechanisms are still large to be used in the computational work and it is important to reduce the skeletal mechanism into a reduced mechanism. For the formulation of a reduced mechanism, a complex system of elementary reactions is simplified by neglecting unimportant reactions based on DRGASA. A major advancement in the CSP technique has been introduction of a new concept of using a vector \( G \) that represents the rate of change of species mass fraction (Y) and temperature (T). Numerical computations are used to monitor any contributions to
vector $G$. Identification of various terms becomes very easy with this method as it can help identify the reactions that are controlling the reaction, constant terms and chemical species that have depleted \([9]\). The ODEs given for a reactive system,

$$G = \frac{dy}{dt} = S_r F_r, \text{ where } y = y_1 \text{ and } y_1 = Y_1 \text{ or } T$$

where, $S_r$ is the stoichiometric vector and $F_r$ is the reaction rate of $r$th reaction.

$$G = \frac{dy}{dt} = S_r F_r = \nu_r q_r$$  \hspace{0.5cm} (12)

$$\nu_r = [\nu_1 \nu_2 \ldots \ldots \nu_n]^T$$  \hspace{0.5cm} (13)

where, $r = 1,\ldots,N$ and $n = 1,\ldots,s$. Here ‘$r$’ is number of reactions and ‘$n$’ is number of species.

All the reactions in the reactive system form the vector $G$.

$$\frac{dG}{dt} = J.G \text{ , } J = \frac{dG}{dy}$$  \hspace{0.5cm} (14)

where, $J$ is a Jacobian. $G$ is divided into fast and slow subspace. The following steps are performed to solve a CSP problem \([9]\):

1. Identify $S_r$ and $F_r$ (or alternatively $\nu_r$ and $q_r$ respectively, both symbols are synonymous here) from a given $G(y)$
2. Find Jacobian
3. Find eigenvalues, $\lambda$
4. An eigenvalue is considered large if, $|\lambda \Delta t| > 1.0$, where $\Delta t$ is the time step.
5. Determine the total number of large eigenvalues ($m$) from step 4.
6. Since, reaction mechanism is composed of fast and slow reactions, therefore, \( G(y) = G_{\text{fast}} + G_{\text{slow}} \). To determine \( G_{\text{fast}} \) and \( G_{\text{slow}} \), we first find the characteristic chemical timescale of each reaction by taking the negative reciprocal of the eigenvalues determined in Step 3, i.e. \(-1/\lambda = \tau\). This timescale calculation will show the magnitude of fast and slow reactions.

7. Eliminate fast reactions. As long as step 4 satisfies, fast reactions can be eliminated.

Using CSP method, a term is only discarded or eliminated when it becomes numerically too small that it does not make any difference. This is determined by the importance index equation (15). CSP, as a reduction method, has won approval among experts [8, 10, and 11].

Lu and Law [8] developed the CSP method to remove the unimportant reactions through an importance index after eliminating the unimportant species. For this method, the importance index of the reaction is defined as

\[
I_{A,i} = \frac{|v_{A,i} q_i|}{\sum_{j=1}^{N_R} |v_{A,j} q_j|}
\]

where, ‘A’ is species, ‘i’ is reaction and ‘q’ is overall reaction rate of the ith reaction. Also, \( v_{A,j} \) is the stoichiometric coefficient of species A in the jth reaction. It must be noted that a reversible reaction must be treated as a single reaction.

If \( I_{A,i} < \epsilon_{\text{Reac}} \) for all species, then the reaction is an unimportant reaction where \( \epsilon_{\text{Reac}} \) is a user-defined small threshold.
The parameter $\epsilon_{Reac}$ is a dimensionless parameter and can be defined as [10]:

$$
\epsilon_{Reac} = \left| \frac{\tau_{\text{fast}}}{\tau_{\text{slow}}} \right| \quad (16)
$$

$|\tau_{\text{fast}}|$ is the slowest relevant time scale for the fast reaction group and $|\tau_{\text{slow}}|$ is the fastest relevant time scale for the slow reaction group. $\tau$ is defined as the characteristic chemical time scale. The characteristic time scales are negative reciprocals of the diagonal elements of the problem’s Jacobian [11].

Simplification of detailed model is achieved by eliminating the following [12]:

(i) the species whose kinetics are not tightly coupled with the species that are of interest and,

(ii) the reactions deemed unimportant to the species that are retained.

The above procedure results in a smaller kinetic mechanism. This smaller mechanism is formed from the detailed mechanism and is a subset of the detailed mechanism. The accuracy of this “skeletal” mechanism is defined with respect to the species that are declared of interest for the problem and the domain of applicability defined for the problem. The domain of applicability is defined on the following criterion:

(i) the reference problem defined for example, ignition, flames, PSR, plug flow reactor, etc., and
(ii) the defined range of pressure, initial temperature, and equivalence ratio.

The reference problems would be investigated for the specific range of pressure, initial temperature and equivalence ratio.

Reaction flow analysis can prove to be very helpful with complex reactions. If the reaction rate satisfies the following condition for all times \( t \), then the reaction rate is unimportant [9]:

\[
|RR_{t,r,s}| < \varepsilon \max_{r=1,2,...,M} |RR_{t,r,s}| \quad s = 1, 2, ... N \quad t = 0, ..., t_{total} \tag{17}
\]

where \( \varepsilon \) is a very small value which is arbitrarily specified, \( 'r' \) is elementary reaction number, and \( 's' \) is number of species.

The physics of the process of reaction of complex hydrocarbons follows the three basic reaction steps: chain-initiating reactions, chain-branching/carrying reactions and chain-terminating reactions. Chain-initiating reactions are those elementary reactions that produce free radicals. Similarly, free radicals are destroyed in chain-terminating reactions. Chain-propagating reactions or chain-carrying reactions are defined as the elementary reactions where the ratio of free radicals in products to the free radicals in reactants is equal to 1. If this ratio is greater than 1, then the reactions are called chain-branching reactions [123]. Concentrations of free radicals are treated as constant as they remain essentially constant throughout the reaction, except for the short initial and final periods which is minimal as compared to the entire reaction period.

High temperature oxidation of paraffins \((C_nH_{2n+2})\) that are larger and more complex than the methane is a complicated subject as they include many complex
hydrocarbons in the mixture. Since the combustion science has evolved much and detailed combustion mechanisms for those smaller hydrocarbons are now part of various combustion libraries, it is possible to develop a general framework of the complex combustion process [123].

The first step in the combustion of larger paraffin \((C_nH_{2n+2})\) is that instead of directly breaking into \(CH_3\), it first breaks down into hydrocarbon radicals of lower order, \(C_nH_{2n+1}\). The hydrocarbon radicals of higher order are highly unstable and are further broken down to \(CH_3\) and a lower order olefinic compound, \(C_{n-1}H_{2n-2}\). For hydrocarbons larger than \(C_3H_8\), the process of fission takes place between the olefinic compound and a lower order radical. Further reactions of those radicals include intermediate steps that eventually form methyl (\(CH_3\)) radical. Also, formaldehyde formed during the reactions is rapidly attacked in flames by the O, H, and OH atoms. Therefore, formaldehyde is found only in trace amounts in flames. The situation is more complex for fuel rich hydrocarbon flames.
Figure 1: Reaction Pathway Analysis; High temperature pathway shown by hollow arrows, low temperature pathway shown by solid arrows
Hydrocarbons follow a same set of steps for combustion and oxidation. The difference between various hydrocarbons requires further intermediate steps but they go through the same oxidation procedure. The process of complex hydrocarbon oxidation occurs in the following manner [122]:

1. Carbon-carbon (C-C) bond is broken: The C-C bonds are primarily broken over H-C bond because C-C bonds are much weaker than H-C bonds.
2. H-atom abstraction: Resulting hydrocarbon radicals further break down into olefins (hydrocarbons with double carbon bonds, C=C) and H-atoms.
3. Radical formation: Creation of H-atoms forms a pool of radicals.
4. Formation of radicals gives pathways for fuel molecules to attack O, OH and H atoms.
5. Hydrocarbon radicals again decay via H-atom abstraction.
6. Formyl radical (HCO) and Formaldehyde (CH\textsubscript{2}O) are formed.
7. Radical reacts with O-atoms that result in the formation of carbon monoxide (CO).
8. Carbon monoxide (CO) oxidation occurs and results in the formation of carbon dioxide (CO\textsubscript{2}).

Figure 1 shows the above-mentioned generic steps of reaction pathway analysis. Hollow arrows show the high temperature reaction pathway while solid arrows show the low temperature reaction pathway.
Figure 2: High & low temperature reaction pathway diagram for combustion of iso-octane for skeletal mechanism
Figure 3: High & low temperature reaction pathway diagram for combustion of iso-octane for reduced mechanism
Figure 2 shows the reaction pathway analysis for the skeletal mechanism [13]. Figure 3 shows the reaction path for the reduced mechanism obtained through this study. The pathway for the reduced mechanism is due to the inclusion of slow reactions as slow reactions are the rate-controlling reactions in a mechanism.

A skeletal mechanism [13] was selected and used for further reduction. The skeletal mechanism was enhanced with extended Zeldovich mechanism to cover for the NO\textsubscript{x} emissions which resulted in 299 reactions and 75 species. Reduction was performed using the CSP technique to achieve 53 reactions and 44 species in the reduced mechanism. The species that were dropped subsequent to the elimination of reactions are: CH\textsubscript{4}, CH\textsubscript{2}, CH\textsubscript{3}CO, iC\textsubscript{3}H\textsubscript{7}, nC\textsubscript{3}H\textsubscript{7}, CH\textsubscript{3}O\textsubscript{2}, CH\textsubscript{3}O\textsubscript{2}H, C\textsubscript{4}H\textsubscript{8}, CH\textsubscript{3}COCH\textsubscript{2}, C\textsubscript{3}KET\textsubscript{21}, nC\textsubscript{3}H\textsubscript{5}CHO, iC\textsubscript{3}H\textsubscript{7}CHO, tC\textsubscript{3}H\textsubscript{6}CHO, tC\textsubscript{3}H\textsubscript{6}O\textsubscript{2}CHO, tC\textsubscript{3}H\textsubscript{6}O\textsubscript{2}HCO, iC\textsubscript{3}H\textsubscript{7}CO, CH\textsubscript{3}COCH\textsubscript{3}, CH\textsubscript{2}CCH\textsubscript{2}OH, CH\textsubscript{3}COCH\textsubscript{2}O\textsubscript{2}, iC\textsubscript{4}H\textsubscript{6}OH, C\textsubscript{7}H\textsubscript{15}O\textsubscript{2}, C\textsubscript{7}H\textsubscript{14}OOH\textsubscript{2}, nC\textsubscript{7}KET\textsubscript{24}, aC\textsubscript{8}H\textsubscript{17}, aC\textsubscript{8}H\textsubscript{17}O\textsubscript{2}, aC\textsubscript{8}H\textsubscript{16}OOH-b, iC\textsubscript{8}ETERAB, aC\textsubscript{8}H\textsubscript{16}OOH-bO\textsubscript{2}, and iC\textsubscript{8}KETAB. The reduced mechanism was used in the KIVA-CHEMKIN interface to make it part of the KIVA input file. Simulations were performed for the same conditions performed in the engine study for premixed engine [6, 7]. This reaction mechanism has proved to predict and validate the results for both stoichiometric and fuel-rich conditions.

The present mechanism reduced and used for this study was reduced using the computational singular perturbation (CSP) method. The reduced mechanism used for this study is mentioned in Appendix A.
Sensitivity analysis using SENKIN [4] was performed for both compression and power stroke as the combustion takes place during some part of both strokes. The criterion of CSP analysis is set by the investigator [8]. The smallness of the time criterion for the characteristic chemical reaction times is set to discard the fast reactions and include the rate limiting reactions as the slower reactions are the rate-controlling reactions. The fast reactions on the other hand make the numerical methods unstable as they magnify the inaccuracies. In the present study, the time criterion for CSP is set that it covers the combustion to the end of power stroke.

The reduced mechanism covers for the combustion duration so the reactions selected are sensitive to the combustion in the engine. The reactions selected were all of the reactions important during the combustion.

An excel file was developed for the calculations of mass fractions of species involved at the required equivalence ratios.
5. Numerical Simulations and Validation

5.1. Overall Goals and Progress

The overall goal of using KIVA-CHEMKIN in the numerical modeling is to use the detailed chemistry. Numerical modeling is performed for pentroof engine geometry. The skeletal gasoline mechanism [13] is reduced and analyzed. Reduced model was constructed and then validated for the values of $\phi = 0.98 \& 1.3$.

5.2. Premixed Case

5.2.1 Engine Geometry

Experimental results were obtained from [6, 7] for premixed case, at equivalence ratio of 0.98 and 1.3. The engine geometry used 85.96 mm bore, 94.6 mm stroke, compression ratio of 11.97 and running at 2100 rpm. The analysis was performed at equivalence ratios of 0.98 and 1.3. Comparison analysis was performed for engine parameters; in-cylinder pressure and heat release rate. Results showed improvement in prediction of in-cylinder pressure with increase in number of reactions and species. This provides reliable data for the engine performance parameters. Figure 4, Figure 5 and Table 1 show the pentroof engine geometry.
Figure 4: Pentroof Engine Geometry [6, 7] – Isometric View

Figure 5: Pentroof Engine Geometry [6, 7] – Side View
There are no moving valves in the geometry. The red color of the mesh and geometry is chosen for greater visibility and detail. A mesh independent study is performed for the reduced mechanisms. Three meshes are constructed for this study; Mesh # 1: 100,000 cells, Mesh # 2: 178,000 cells and, Mesh # 3: 230,000 cells. Studies are performed to verify the general trend of the engine performance parameters for in-cylinder pressure and heat release rate (HRR). With all the above three meshes, the general trend of the both of the engine performance parameters remains same. Figure 6, Figure 7 and Figure 8 shows the side, isometric and top view of mesh # 1; Figure 9, Figure 10 and Figure 11 shows the side, isometric and
top view of mesh # 2; Figure 12, Figure 13 and Figure 14 shows the side, isometric and top view of mesh # 3.

**Table 2: Mesh Independent Study**

<table>
<thead>
<tr>
<th>Number of cells</th>
<th>Mesh # 1</th>
<th>Mesh #2</th>
<th>Mesh # 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of cells</td>
<td>100,000</td>
<td>178,000</td>
<td>230,000</td>
</tr>
</tbody>
</table>

**Figure 6: Mesh # 1 – Side View**
Figure 7: Mesh # 1 – Isometric View
Figure 8: Mesh # 1 – Top View
Figure 9: Mesh # 2 – Side View
Figure 10: Mesh # 2 – Isometric View
Figure 11: Mesh # 2 – Top View
Figure 12: Mesh # 3 – Side View
Figure 13: Mesh # 3 – Isometric View
5.2.2 Proof of Concept: Global and Quasi-Global Mechanisms

Global reactions are used very commonly for solving combustion problems but they are inadequate to model the detailed chemistry of the problem. Quasi-global reaction mechanism has also been used in the combustion research but it also does not model the correct chemistry of the problem.

In this chapter, numerical simulations are conducted to compare engine performance parameters against the experimental data. The engine performance parameters are in-cylinder pressure and heat release rate (HRR). To benchmark, the
first comparison is done for global and quasi-global reaction mechanisms. This will establish the need to use detailed chemistry for validation and correct prediction of engine performance parameters.

Numerical simulations for global and quasi-global reaction mechanisms is conducted at $\phi = 0.98$ and 1.3. The results obtained through these simulations are compared and discussed to understand the need for detailed chemistry.

The fuel used for the global and quasi-global reaction mechanisms is iso-octane ($\text{iC}_8\text{H}_{18}$). The reaction equations are already discussed in chapter 4. For global mechanism, equation 2 is used to model the chemistry of the problem. For quasi-global mechanism, equations 3 to equation 6 are used to model the chemistry. Extended Zeldovich mechanism is employed for NO$_x$ formation in Equations 7, 8 and 9.

Mesh # 3 is used to perform the proof of concept. The numbers of cells used in the grid are 230,000. The initial temperature is 333 K and the pressure is $34.6 \pm 1$ kPa [6, 7]. The cylinder wall temperature, cylinder firedeck temperature, and the piston temperature are set at 400K.

The computational problem is solved by using the RNG k-epsilon turbulence model which is recommended for engine applications in KIVA. The model also utilizes the turbulent mixing-controlled chemistry for fuel oxidation. The model is set for fired simulations. The wall heat transfer is determined by the variable LWALL. It is set to +1 for engine simulations and applications, which lets KIVA calculate the heat transfer at the wall. The initial swirl ratio is clockwise. Turbulent
velocities and breakup model for the fuel droplet is turned on which by experience is used for spark ignition engines. The way the fuel is injected in the cylinder is determined by the fact if it is a premixed or direct injection case. The parameter PULSE is used to define and specify it. It ranges from 0.0 (for continuous spray applications) to 4.0 (for real reciprocating engine applications). For premixed applications, it is set at 1.0. The relative error defined in the input file for mass diffusion, momentum diffusion, heat diffusion, turbulent kinetic energy diffusion is used as 1.0e-03 which is an allowed relative error (epsilon) value used in the modeling. The allowed relative error in pressure iteration is 1.0e-05.

The mixture is ignited at 20° BTDC. Two important variables in the study are ignition duration and ignition energy which were not recorded in the experimental studies [6, 7]. Instead, the experimental study focused at obtaining CA50 at 8°ATDC. Mass fractions for fuel and oxidizer are calculated. The fuel used for reduced mechanism is 90% iso-octane and 10% n-heptane [5] given the complexity of a multi-component detailed chemistry model.

**Equivalence Ratio, \( \Phi = 0.98 \):**

Numerical simulations and comparison is performed for iso-octane (iC\(_8\)H\(_{18}\)) at \( \phi = 0.98 \). The ignition timing is 20° BTDC.
Figure 15: In-cylinder Pressure at equivalence ratio 0.98

Figure 15 shows the in-cylinder pressure inside the SI engine. Experimental data [6, 7] is compared with the numerical results for global and quasi-global reactions. The plot shows that the in-cylinder pressure curves for the global and quasi-global reaction mechanisms do not match the experimental data. This shows that although the CFD model is correct, the chemistry needs better modeling to predict the in-cylinder pressure correctly.
Figure 16: Heat Release Rate (HRR) at equivalence ratio 0.98

Figure 16 shows the plot for heat release rate (HRR). The HRR plot shows again that global and quasi-global reactions did not model and predict the HRR correctly.

**Equivalence Ratio, \( \Phi = 1.3 \):**

Numerical simulations and comparison is performed for iso-octane (iC\(_8\)H\(_{18}\)) at \( \phi = 1.3 \).
Figure 17: In-cylinder Pressure at equivalence ratio 1.3

Figure 17 shows the in-cylinder pressure plot at equivalence ratio of 1.3. The plot again shows the inability of global and quasi-global reaction mechanism to correctly predict the experimental results.
Figure 18: Heat Release Rate (HRR) at equivalence ratio 1.3

The above plot in Figure 18 shows the heat release rate (HRR) curve at $\phi = 1.3$. It also did not predict the experimental results correctly.

Figure 16 and Figure 18 shows the haphazard trend of the HRR. The reason for such a trend is that global and quasi-global reaction mechanisms do not embody the detailed chemistry and the intermediate species to control the trend of the HRR. Quasi-global mechanism breaks the paraffin (iso-octane) directly into ethylene ($\text{C}_2\text{H}_4$) without any oxidation reaction, by assuming that ethylene is the intermediate hydrocarbon. Moreover, instead four species that are used for global reactions, quasi-global uses three species. This may release massive amounts of heat. By definition, global models do not capture the complete details of hydrocarbon oxidation [122]. Another reason for the HRR value to be higher for
quasi-global mechanism in Figure 18 is because it is a fuel rich case; therefore, the higher concentration of fuel released more energy for the quasi-global mechanism.

### 5.2.3 Reduced Mechanism

To better predict the engine performance parameters of in-cylinder pressure and heat release rate (HRR), detailed chemistry is incorporated into the CFD model. To achieve this, KIVA-CHEMKIN interface is used to extract reaction rates and reaction constants for the reaction data and, heat of formation and molecular weights for the species data, that is used for input into KIVA simulations. The reduced reaction mechanism has 53 reactions and 44 species.

### 5.2.4 In-cylinder Pressure and Heat Release Rate, $\Phi = 0.98$

Numerical simulations and comparison is performed for a mixture of 90% iso-octane ($iC_8H_{18}$) and 10% n-heptane ($nC_7H_{16}$) at $\phi = 0.98$. The ignition timing is 20° BTDC. Figure 19 shows the validation of in-cylinder pressure against the experimental data from Mesh # 1, Figure 20 shows the validation of in-cylinder pressure against the experimental data from Mesh # 2, and, Figure 21 shows the validation of in-cylinder pressure against the experimental data from Mesh # 3. The results obtained by all of the meshes show the same general trend for the curves of in-cylinder pressure at $\phi = 0.98$. The results also show a good agreement and prediction of the numerical simulations against the experimental data. When the in-cylinder pressure results obtained by the reduced mechanism are compared against the results obtained by global and quasi-global mechanisms in Figure 15 and Figure
17, it shows a clear improvement and agreement due to inclusion of detailed chemistry.

Figure 19: In-cylinder Pressure; 100,000 cells
Figure 20: In-cylinder Pressure; 178,000 cells

Figure 21: In-cylinder Pressure; 230,000 cells
Figure 22: Heat Release Rate (HRR); 100,000 cells

Figure 23: Heat Release Rate (HRR); 178,000 cells
Figure 24: Heat Release Rate (HRR); 230,000 cells

Figure 22, Figure 23 and Figure 24 shows a good agreement of predicted heat release rate (HRR) obtained from the numerical solution from the reduced mechanism using KIVA-CHEMKIN interface against the experimental data. HRR is the ratio of difference in heat release values and corresponding crank angle values. These values are obtained from KIVA output file. This also shows that detailed chemistry is very important to capture the correct trend of engine performance parameters. The reduced mechanism achieved from this research has given a confident deduction that the numerical simulations for $\phi = 0.98$ has successfully modeled the engine performance parameters of in-cylinder pressure and heat release rate (HRR). It is recommended to build a library of reduced
mechanisms for all the fuels that are used in the internal combustion engines so that the correct prediction of experimental results can be recorded and achieved.

5.2.5 Detailed in-cylinder flow parameter plots

Utilizing GMV (General Mesh Viewer) [124] software for post processing of various 3D plots including temperature and mass fractions. The plots shown in Figure 25 to Figure 42 were constructed at $\phi = 0.98$ to compare the temperature distribution, and fuel burn out using global, quasi-global and reduced mechanisms. The plots show a faster burn out of fuel using global and quasi-global mechanisms whereas the reduced mechanism shows a controlled burn.

![Temperature plot for global mechanism at 5° BTDC at $\phi = 0.98$](image)

Figure 25: Temperature plot for global mechanism at 5° BTDC at $\phi = 0.98$
Figure 26: Temperature plot for quasi-global mechanism at 5° BTDC at $\phi = 0.98$

Figure 27: Temperature plot for reduced mechanism at 5° BTDC at $\phi = 0.98$
Figure 28: Temperature plot for global mechanism at $10^\circ$ ATDC at $\phi = 0.98$

Figure 29: Temperature plot for quasi-global mechanism at $10^\circ$ ATDC at $\phi = 0.98$
Figure 30: Temperature plot for reduced mechanism at 10° ATDC at $\phi = 0.98$

Figure 31: Temperature plot for global mechanism at 20° ATDC at $\phi = 0.98$
Figure 32: Temperature plot for quasi-global mechanism at 20° ATDC at $\phi = 0.98$

Figure 33: Temperature plot for reduced mechanism at 20° ATDC at $\phi = 0.98$
Figure 34: Fuel mass fraction plot for global mechanism at 5° BTDC at $\phi = 0.98$

Figure 35: Fuel mass fraction plot for quasi-global mechanism at 5° BTDC at $\phi = 0.98$
Figure 36: Fuel mass fraction plot for reduced mechanism at 5° BTDC at $\phi = 0.98$

Figure 37: Fuel mass fraction plot for global mechanism at 10° ATDC at $\phi = 0.98$
Figure 38: Fuel mass fraction plot for quasi-global mechanism at $10^\circ$ ATDC at $\phi = 0.98$

Figure 39: Fuel mass fraction plot for reduced mechanism at $10^\circ$ ATDC at $\phi = 0.98$
Figure 40: Fuel mass fraction plot for global mechanism at 20° ATDC at $\phi = 0.98$

Figure 41: Fuel mass fraction plot for quasi-global mechanism at 20° ATDC at $\phi = 0.98$
5.2.6 In-cylinder Pressure and Heat Release Rate, $\Phi = 1.3$

Numerical simulations and comparison is performed below for a mixture of 90% iso-octane (iC$_8$H$_{18}$) and 10% n-heptane (nC$_7$H$_{16}$) at $\phi = 1.3$ using the reduced mechanism.
Figure 43: In-cylinder Pressure; 100,000 cells

Figure 44: In-cylinder Pressure; 178,000 cells
Figure 45: In-cylinder Pressure; 230,000 cells

Good prediction of in-cylinder pressure for $\phi = 1.3$ is achieved using the reduced mechanism and is shown in Figure 43, Figure 44 and Figure 45.
Figure 46: Heat Release Rate (HRR); 100,000 cells

Figure 47: Heat Release Rate (HRR); 178,000 cells
Figure 48: Heat Release Rate (HRR); 230,000 cells

Figure 46, Figure 47 and Figure 48 shows the heat release rate (HRR) for $\phi = 1.3$. The results for Heat release rate (HRR) obtained from the numerical solution from the reduced mechanism using KIVA-CHEMKIN interface again shows a good prediction. This also shows that detailed chemistry is very important to capture the correct trend of engine performance parameters.
5.2.7 Detailed in-cylinder flow parameter plots

The plots shown in Figure 49 to Figure 66 were constructed for $\phi = 1.3$ to compare the temperature distribution, and fuel burn out using global, quasi-global and reduced mechanisms. The plots show a faster burn out of fuel using global and quasi-global mechanisms whereas the reduced mechanism shows a controlled burn.

Figure 49: Temperature plot for global mechanism at $5^\circ$ BTDC at $\phi = 1.3$
Figure 50: Temperature plot for quasi-global mechanism at 5° BTDC at $\phi = 1.3$

Figure 51: Temperature plot for reduced mechanism at 5° BTDC at $\phi = 1.3$
Figure 52: Temperature plot for global mechanism at 10° ATDC at $\phi = 1.3$

Figure 53: Temperature plot for quasi-global mechanism at 10° ATDC at $\phi = 1.3$
Figure 54: Temperature plot for reduced mechanism at 10° ATDC at $\phi = 1.3$

Figure 55: Temperature plot for global mechanism at 20° ATDC at $\phi = 1.3$
Figure 56: Temperature plot for quasi-global mechanism at 20° ATDC at $\phi = 1.3$

Figure 57: Temperature plot for reduced mechanism at 20° ATDC at $\phi = 1.3$
Figure 58: Fuel mass fraction plot for global mechanism at 5° BTDC at $\phi = 1.3$

Figure 59: Fuel mass fraction plot for quasi-global mechanism at 5° BTDC at $\phi = 1.3$
Figure 60: Fuel mass fraction plot for reduced mechanism at 5° BTDC at $\phi = 1.3$

Figure 61: Fuel mass fraction plot for global mechanism at 10° ATDC at $\phi = 1.3$
Figure 62: Fuel mass fraction plot for quasi-global mechanism at 10° ATDC at $\phi = 1.3$

Figure 63: Fuel mass fraction plot for reduced mechanism at 10° ATDC at $\phi = 1.3$
Figure 64: Fuel mass fraction plot for global mechanism at 20° ATDC at $\phi = 1.3$

Figure 65: Fuel mass fraction plot for quasi-global mechanism at 20° ATDC at $\phi = 1.3$
Figure 66: Fuel mass fraction plot for reduced mechanism at 20° ATDC at $\phi = 1.3$

5.3. Emissions

Apart from validating the engine performance parameters of in-cylinder pressure and heat release rate (HRR), this study also validated the emission results with the experimental data [7]. The engine-out exhaust emission data is shown in Figure 67 for the exhaust species of H$_2$, CO$_2$ and CO. The results show a good agreement between the numerical and experimental results for the equivalence ratio of $\phi = 0.98$ and $\phi = 1.3$. 
Apart from the validation of above-mentioned emissions data, GMV plots were also constructed. The mass fractions of carbon dioxide (CO$_2$), carbon monoxide (CO), and nitrous oxides (NO$_x$) were constructed to compare the pollutant formation using global, quasi-global and reduced mechanisms.

**Equivalence Ratio, $\Phi = 0.98$:**

The following plots show in detail the pollutant formation. The plots from Figure 68 to Figure 94 show CO$_2$, CO and NO$_x$ formation. The plots further show a lesser
pollutant formation with reduced mechanism as compared to global and quasi-global mechanisms.

Figure 68: CO$_2$ mass fraction plot for global mechanism at 5° BTDC at $\phi = 0.98$

Figure 69: CO$_2$ mass fraction plot for quasi-global mechanism at 5° BTDC at $\phi = 0.98$
Figure 70: CO₂ mass fraction plot for reduced mechanism at 5° BTDC at $\phi = 0.98$

Figure 71: CO₂ mass fraction plot for global mechanism at 10° ATDC at $\phi = 0.98$
Figure 72: CO₂ mass fraction plot for quasi-global mechanism at 10° ATDC at $\phi = 0.98$

Figure 73: CO₂ mass fraction plot for reduced mechanism at 10° ATDC at $\phi = 0.98$
Figure 74: CO$_2$ mass fraction plot for global mechanism at 20° ATDC at $\phi = 0.98$

Figure 75: CO$_2$ mass fraction plot for quasi-global mechanism at 20° ATDC at $\phi = 0.98$
Figure 76: CO$_2$ mass fraction plot for reduced mechanism at 20° ATDC at $\phi = 0.98$

Figure 77: CO mass fraction plot for global mechanism at 5° BTDC at $\phi = 0.98$
Figure 78: CO mass fraction plot for quasi-global mechanism at 5° BTDC at $\phi = 0.98$

Figure 79: CO mass fraction plot for reduced mechanism at 5° BTDC at $\phi = 0.98$
Figure 80: CO mass fraction plot for global mechanism at 10° ATDC at $\phi = 0.98$

Figure 81: CO mass fraction plot for quasi-global mechanism at 10° ATDC at $\phi = 0.98$
Figure 82: CO mass fraction plot for reduced mechanism at 10° ATDC at $\phi = 0.98$

Figure 83: CO mass fraction plot for global mechanism at 20° ATDC at $\phi = 0.98$
Figure 84: CO mass fraction plot for quasi-global mechanism at 20° ATDC at $\phi = 0.98$

Figure 85: CO mass fraction plot for reduced mechanism at 20° ATDC at $\phi = 0.98$
Figure 86: NO mass fraction plot for global mechanism at 5° BTDC at $\phi = 0.98$

Figure 87: NO mass fraction plot for quasi-global mechanism at 5° BTDC at $\phi = 0.98$
Figure 88: NO mass fraction plot for reduced mechanism at 5° BTDC at $\phi = 0.98$.

Figure 89: NO mass fraction plot for global mechanism at 10° ATDC at $\phi = 0.98$. 
Figure 90: NO mass fraction plot for quasi-global mechanism at 10° ATDC at $\phi = 0.98$

Figure 91: NO mass fraction plot for reduced mechanism at 10° ATDC at $\phi = 0.98$
Figure 92: NO mass fraction plot for global mechanism at 20° ATDC at $\phi = 0.98$

Figure 93: NO mass fraction plot for quasi-global mechanism at 20° ATDC at $\phi = 0.98$
Equivalence Ratio, $\Phi = 1.3$: 

The following plots show in detail the pollutant formation. The plots from Figure 95 to Figure 121 show CO$_2$, CO and NO$_x$ formation. The plots further show lesser pollutant formation with reduced mechanism as compared to global and quasiglobal mechanisms.
Figure 95: CO₂ mass fraction plot for global mechanism at 5° BTDC at $\phi = 1.3$

Figure 96: CO₂ mass fraction plot for quasi-global mechanism at 5° BTDC at $\phi = 1.3$
Figure 97: CO$_2$ mass fraction plot for reduced mechanism at 5° BTDC at $\phi = 1.3$

Figure 98: CO$_2$ mass fraction plot for global mechanism at 10° ATDC at $\phi = 1.3$
Figure 99: CO₂ mass fraction plot for quasi-global mechanism at 10° ATDC at \( \phi = 1.3 \)

Figure 100: CO₂ mass fraction plot for reduced mechanism at 10° ATDC at \( \phi = 1.3 \)
Figure 101: CO$_2$ mass fraction plot for global mechanism at 20º ATDC at $\phi = 1.3$

Figure 102: CO$_2$ mass fraction plot for quasi-global mechanism at 20º ATDC at $\phi = 1.3$
Figure 103: CO$_2$ mass fraction plot for reduced mechanism at 20° ATDC at $\phi = 1.3$

Figure 104: CO mass fraction plot for global mechanism at 5° BTDC at $\phi = 1.3$
Figure 105: CO mass fraction plot for quasi-global mechanism at 5° BTDC at $\phi = 1.3$

Figure 106: CO mass fraction plot for reduced mechanism at 5° BTDC at $\phi = 1.3$
Figure 107: CO mass fraction plot for global mechanism at 10° ATDC at $\phi = 1.3$

Figure 108: CO mass fraction plot for quasi-global mechanism at 10° ATDC at $\phi = 1.3$
Figure 109: CO mass fraction plot for reduced mechanism at $10^\circ$ ATDC at $\phi = 1.3$

Figure 110: CO mass fraction plot for global mechanism at $20^\circ$ ATDC at $\phi = 1.3$
Figure 111: CO mass fraction plot for quasi-global mechanism at 20° ATDC at $\phi = 1.3$

Figure 112: CO mass fraction plot for reduced mechanism at 20° ATDC at $\phi = 1.3$
Figure 113: NO mass fraction plot for global mechanism at 5° BTDC at $\phi = 1.3$

Figure 114: NO mass fraction plot for quasi-global mechanism at 5° BTDC at $\phi = 1.3$
Figure 115: NO mass fraction plot for reduced mechanism at 5° BTDC at $\phi = 1.3$

Figure 116: NO mass fraction plot for global mechanism at 10° ATDC at $\phi = 1.3$
Figure 117: NO mass fraction plot for quasi-global mechanism at $10^\circ$ ATDC at $\phi = 1.3$

Figure 118: NO mass fraction plot for reduced mechanism at $10^\circ$ ATDC at $\phi = 1.3$
Figure 119: NO mass fraction plot for global mechanism at $20^\circ$ ATDC at $\phi = 1.3$

Figure 120: NO mass fraction plot for quasi-global mechanism at $20^\circ$ ATDC at $\phi = 1.3$
Figure 121: NO mass fraction plot for reduced mechanism at 20° ATDC at $\phi = 1.3$

5.4 Conclusions

A novel reduced mechanism was developed for this study. The second aspect of the novelty of this research has been application of the single reduced mechanism to SI engine geometries, application of low temperature reaction pathway analysis, validation of engine performance parameters (in-cylinder pressure and heat release rate) and combustion parameters (emissions). Work on the reduced mechanism has provided a good prediction of engine performance and combustion parameters. This project has provided understanding of the reduction techniques, and a practical reduced reaction mechanism for spark-ignition engines and combustion.

In the present study, detailed chemistry has helped in good prediction of engine performance parameters and also increased the confidence in the CFD solutions.
Numerical solutions obtained using KIVA-CHEMKIN interface has provided good agreement between the numerical and experimental work for the engine performance parameters of in-cylinder pressure, heat release rate (HRR) and emissions. This study has shown the need for using detailed chemistry in reactive flow problems which can help predict the combustion and engine performance parameters more accurately.

The results depicted in the GMV plots also show the controlled burn and lesser emissions while using the reduced mechanism as compared to global and quasi-global mechanisms.
6. Conclusions & Future Work

A novel reduced mechanism was developed for this study. The second aspect of the novelty of this research has been application of the single reduced mechanism to spark ignition (SI) engine geometries, application of low temperature reaction pathway analysis, validation of engine performance parameters (in-cylinder pressure and heat release rate) and combustion parameters (emissions). Work on the reduced mechanism has provided a good prediction of engine performance and combustion parameters. This project has provided understanding of the reduction techniques, and a practical reduced reaction mechanism for spark-ignition engines and combustion. The reduced mechanism obtained through this study is validated for $\Phi = 0.98$ and, $\Phi = 1.3$, and is applicable to intake temperature and intake pressure conditions suitable for spark ignition engines.

The results showed that the premixed combustion model did not predict the results correctly using global and quasi-global mechanisms. The results showed a good agreement while using the reduced mechanism constructed in this research. The reason for the good agreement using detailed chemistry is that the global and quasi-global mechanism lacks detailed chemistry and intermediate species. They rely on a single or four step mechanisms using only 12 and 13 species respectively. The single droplet of fuel does not contain the mixture of complex hydrocarbons and does not follow the detailed reaction path as depicted in Figure 2 and Figure 3. This produces a faster high temperature burn that overpredicts the engine performance parameters. With the reduced mechanism, premixed combustion
model was able to utilize the detailed chemistry. With the intermediate species and reactions incorporated in the reduced mechanism and by taking the low temperature pathway analysis, the results produced good agreement against the experimental results. By looking at Figure 15 and Figure 17, it is evident that the pressure curve kept increasing due to the fact that it merely showed the properties of a single component or two-component hydrocarbon with only one step to model carbon dioxide formation and one step to model water formation. The actual gasoline properties are not modeled by the global and quasi-global mechanism. On the other hand, the controlled rise of in-cylinder pressure by using the reduced mechanism shows that not only most of the complex hydrocarbons were modeled but also the detailed reactions leading to the formation of carbon dioxide and water were included. It actually shows the complete process of combustion and formation of radicals and intermediate species as mentioned in Chapter 4. The premixed study also validated the emissions.

Future work should entail establishment of library of reaction mechanisms for all fuels used in internal combustion engines. This will help to predict the engine performance parameters correctly and will increase the confidence in CFD solutions. KIVA combustion model and intermediate species library can also be amended to utilize a detailed library of reduced mechanisms for its fuel and reaction library. This will not only predict correct results for premixed combustion, it will also model the correct and detailed chemistry. Application of the reduced mechanism generated in this study can be extended to the direct injection studies as
well for the validation of engine performance parameters against the experimental results.
References


Appendix A: Reduced Mechanism

Reduced mechanism for iso-octane is included in appendix A.

A.1. Reduced Reaction Mechanism

SPECIES
ic8h18
o2 n2 co2 h2o h h2
o n oh co no ho2
h2o2 hco hcco ch2o ch3
ch3o ch2co ch3oh ch2oh ch3cho
c2h6 c2h5 c2h4 c2h3 c2h2
c3h6 c3h5 c3h4 ic4h7 c5h10
ic4h8 ic4h9 pc4h9 tc4h9
c7h15-2 ch2cho c3h3
ic3h5cho
ic3h5co
ic4h7o
nc7h16
END

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<th>S. No.</th>
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<th>k = A T**b exp(-E/RT)</th>
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<td>ic8h18&lt;=tc4h9+ic4h9</td>
<td>7.83E+29 -3.9 84150.0</td>
</tr>
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<td>2.</td>
<td>nc7h16+oh&lt;=c7h15-2+h2o</td>
<td>1.90E+06 2.0 -596.0</td>
</tr>
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<td>Forward Reaction</td>
<td>Reverse Arrhenius coefficients:</td>
</tr>
<tr>
<td>---</td>
<td>------------------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>3.</td>
<td>nc7h16+ho2&lt;=&gt;c7h15-2+h2o2</td>
<td>3.62E+02 2.9 19140.0</td>
</tr>
<tr>
<td>4.</td>
<td>nc7h16+o2&lt;=&gt;c7h15-2+ho2</td>
<td>4.98E-01 3.7 2562.0</td>
</tr>
<tr>
<td>5.</td>
<td>c7h15-2&lt;=&gt;pc4h9+c3h6</td>
<td>1.00E+09 0.6 309.0</td>
</tr>
<tr>
<td>6.</td>
<td>c5h10=c2h5+c3h5</td>
<td>3.15E+19 -1.8 31360.0</td>
</tr>
<tr>
<td>7.</td>
<td>pc4h9=c2h5+c2h4</td>
<td>4.00E+12 0.0 -596.0</td>
</tr>
<tr>
<td>8.</td>
<td>ic4h8+oh=ic4h7+h2o</td>
<td>7.50E+17 -1.4 29580.0</td>
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<tr>
<td>9.</td>
<td>ic4h8+h2o2=ic4h7+h2o2</td>
<td>3.30E+11 0.0 7200.0</td>
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<tr>
<td>10.</td>
<td>ic4h8=ic4h7+h</td>
<td>5.20E+06 2.0 -298.0</td>
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<tr>
<td>11.</td>
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<td>4.56E+08 1.4 32470.0</td>
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<tr>
<td>12.</td>
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<td></td>
<td>ic4h8</td>
<td>3.07E+55 -11.5 114300.0</td>
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<tr>
<td></td>
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<td>7.00E+12 0.0 -1000.0</td>
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<td>Preexponential Factor ($A$)</td>
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<td>------------------</td>
<td>-----------------------------</td>
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<td>14.</td>
<td>$\text{ic3h5cho}+\text{oh}=\text{ic3h5co}+\text{h2o}$</td>
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<td>15.</td>
<td>$\text{ic3h5cho}+\text{ho}_2=\text{ic3h5co}+\text{h2o}_2$</td>
<td>1.00E+12</td>
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<td>17.</td>
<td>$\text{c3h6}+\text{oh}&lt;&gt;\text{c3h5}+\text{h2o}$</td>
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<td>18.</td>
<td>$\text{c3h5}+\text{ho}_2&lt;&gt;\text{c3h6}+\text{o}_2$</td>
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<td>19.</td>
<td>$\text{c3h5}+\text{ho}_2&lt;&gt;\text{oh}+\text{c2h3}+\text{ch}_2\text{o}$</td>
<td>3.00E+12</td>
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<td>20.</td>
<td>$\text{c3h4}+\text{oh}&lt;&gt;\text{c3h3}+\text{h2o}$</td>
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<td>21.</td>
<td>$\text{c3h4}+\text{o}_2&lt;&gt;\text{ch}_3+\text{hco}+\text{co}$</td>
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<td>22.</td>
<td>$\text{c3h3}+\text{o}_2&lt;&gt;\text{ch}_2\text{co}+\text{hco}$</td>
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<td>23.</td>
<td>$\text{c2h6}+\text{oh}=\text{c2h5}+\text{h2o}$</td>
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<td>24.</td>
<td>$\text{c2h5}+\text{o}_2=\text{c2h4}+\text{ho}_2$</td>
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Declared duplicate reaction...
<p>| Reaction | Equation | $k$ | Preexponential | Temperature |
|----------|----------|-----|----------------|-------------|-----------|
| 25.      | $\text{C}_2\text{H}_5 + \text{O}_2 = \text{C}_2\text{H}_4 + \text{HO}_2$ | $4.00 \times 10^{-1}$ | 3.9 | 13620.0 | Declared duplicate reaction... |
| 26.      | $\text{C}_2\text{H}_5 + \text{O}_2 = \text{CH}_3\text{CHO} + \text{OH}$ | $8.26 \times 10^{2}$ | 2.4 | 5285.0 |
| 27.      | $\text{C}_2\text{H}_4 + \text{H}_2\text{O} = \text{C}_2\text{H}_2 + \text{H}_2 + \text{H}_2\text{O}$ | $8.00 \times 10^{12}$ | 6.0 | 88770.0 |
| 28.      | $\text{C}_2\text{H}_4 + \text{OH} = \text{C}_2\text{H}_3 + \text{H}_2\text{O}$ | $1.80 \times 10^{6}$ | 2.0 | 2500.0 |
| 29.      | $\text{C}_2\text{H}_3 + \text{O}_2 = \text{C}_2\text{H}_2 + \text{HO}_2$ | $2.12 \times 10^{-6}$ | 6.0 | 9484.0 |
| 30.      | $\text{C}_2\text{H}_3 + \text{O}_2 = \text{CH}_2\text{O} + \text{HCO}$ | $8.50 \times 10^{28}$ | -0.6 | 5260.0 |
| 31.      | $\text{CH}_2\text{CHO} = \text{CH}_2\text{CO} + \text{H}$ | $4.07 \times 10^{15}$ | -0.3 | 50600.0 |
| 32.      | $\text{C}_2\text{H}_2 + \text{O}_2 = \text{HCO} + \text{OH}$ | $2.00 \times 10^{8}$ | 1.5 | 30100.0 |
| 33.      | $\text{CH}_2\text{CHO} = \text{CH}_2\text{CO} + \text{H}$ | $4.07 \times 10^{15}$ | -0.3 | 50600.0 |
| 34.      | $\text{HCO} + \text{O}_2 = \text{OH} + \text{2CO}$ | $4.20 \times 10^{10}$ | 0.0 | 850.0 |
| 35.      | $\text{OH} + \text{CH}_3 + \text{H}_2\text{O} = \text{CH}_3\text{OH} + \text{H}_2\text{O}$ | $2.79 \times 10^{18}$ | 6.0 | 1330.0 |
|          | Reverse Arrhenius coefficients: | | | | 0.0 |
|          |          | | | | 0.0 |
|          |          | | | | 0.0 |</p>
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<td>H$_2$O$_2$ + H$_2$O = 2OH + H$_2$O</td>
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<td>HCO + H$_2$O = H + CO + H$_2$O</td>
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178
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<td>ch₂O = CO+H₂</td>
<td>Value</td>
<td>1.83E+32</td>
</tr>
<tr>
<td></td>
<td>Reverse Arrhenius Coefficients:</td>
<td>Value</td>
<td>5.07E+27</td>
</tr>
<tr>
<td>51.</td>
<td>N₂+O &lt;=&gt; N+NO</td>
<td>Value</td>
<td>7.60E+13</td>
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<tr>
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<td>Reverse Arrhenius Coefficients:</td>
<td>Value</td>
<td>1.60E+13</td>
</tr>
<tr>
<td>52.</td>
<td>N+O₂ &lt;=&gt; O+NO</td>
<td>Value</td>
<td>6.40E+09</td>
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<tr>
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<td>Reverse Arrhenius Coefficients:</td>
<td>Value</td>
<td>1.50E+09</td>
</tr>
<tr>
<td>53.</td>
<td>N+OH &lt;=&gt; H+NO</td>
<td>Value</td>
<td>4.10E+13</td>
</tr>
<tr>
<td></td>
<td>Reverse Arrhenius Coefficients:</td>
<td>Value</td>
<td>2.00E+14</td>
</tr>
</tbody>
</table>
Appendix B : bdcomd.f

Enthalpy data for bdcomd.f file is mentioned in Appendix B.

B.1. bdcomd.f

block data bdcomd

include 'comkiva.i'

data jnm / ' 060198' /
data pi /3.14159 26535 89793 23846/
data minus1,zero,one,two,three / -1.0, 0.0, 1.0, 2.0, 3.0 /
data rgas /8.3143e+7/
data t,dtgrof,grind,tchem,tevap /0.0,1.10,0.0,1.0e-10,1.0e-10/
data pgsrat /0.04/
data dtfc,dtfa,dtfst /0.2,0.5,0.6/
data moving,solid,axis,fluid,periodf,periodd,inflow,outflow,
& presin,presout / 1.0,2.0,3.0,4.0,5.0,6.0,7.0,8.0,9.0,10.0 /
data flfluid,flface,flbowl,flsqsh,fldome,flhead
& / 1.0 , 2.0 , 3.0 , 4.0 , 5.0 , 6.0 /
data tkelow,epslow / 1.0e-8,1.0e-12 /
data wchem,wpdv / 2*0.0 /
data csubmu,csubk,cfocb / 10.0,8.0,0.666666666666667 /
data t2inj,tm2inj,tcrit,reedin,reedout,snapflg,sortflg /7*0.0/
data anc4 / 0.0 /
data fluxin , fluxout , wheat / 3*0.0 /
data pmentral,pmentrar,pmfilm1,pmfilmr,vapoutl,vapoutr / 6*0.0 /
data snapper / 1.0 /
data ncyc,ndump,np,icount,irecycle,ngmv,lastful / 6*0,-1 /
data ranb,rans /2396745.,2396745./
data time,timetotal / 2*0.0 /
data nsnapsfce,nsnapstop / nmovemx*0 , nmovemx*0 /
data idvport / nmovemx*0 /
data maxpit /75/
data rhop / 1.0 /
data zpistnt , wmove(1) / +1.0e+10 , 0.0 /
data datestr" time: "/
c +++
c +++ correlate names used in subroutine soot with species numbers:
c +++ krn=r-n (radical nuclei), kpn=p-n (particle nuclei (soot)),
c +++ kfict=fictitious (soot forming) species

c +++
data kfuel/1/ , ko2/2/ , koh/10/ , kno/12/ , krn/45/ , kpn/46/ ,
& kfict/47/
data avogad,amum,sigsb /6.02252e+23,1.657e-24,5.6697e-5/
data drni,dnuci /2*0.0/
data (cho(n),n=1,44) / 3*0.0,5*1.0,0.0,2*1.0,0.0,32*1.0 /
data (hk(n,1),n=1,51) / 51*0. /  
data (hlat0(n),n=1,51) / 51*0. /  
data (pvap(n),n=1,lvap) / lvap*0. /  
data (visliq(n),n=1,lvap) / lvap*0. /  
data (surften(n),n=1,lvap) / lvap*0.0 /  
data (thcon(n),n=1,lvap) / lvap*0.0 /  

hk arrays are the enthalpies of the species, taken from the  
janaf thermochemical tables, which have the zero point at t=298k.  
intervals are t=100(n-1), and units are kcal/mole (all enthalpy  
data is converted to sie in ergs/gm in subroutine rinput).  
species #1 is assumed to be the fuel, and its hk is loaded by  
subroutine fuel. species #2-13 below are as follows:  
2=o2, 3=n2, 4=co2, 5=h20, 6=h, 7=h2, 8=o, 9=n, 10=oh,  
11=co, 12=no, 13=ho2. note: for h2 combustion, select h2 as the  
fuel (species #1), and do --not-- refer to species #7 in any  
chemical reactions. species 13 enthalpy data below will need to  
be activated, and parameter lnsp must be increased to 13.  

data (hk(n,2),n=1,51) / -2.075,-1.381,-.685,.013,.724,1.455,2.21,2.  
1 988,3.786,4.6,5.427,6.266,7.114,7.971,8.835,9.706,10.583,11.465,1  
4 4,30.236,31.221,32.209,33.201,34.196,35.193,36.193,37.196,38.201,  

182
data (hk(n,3),n=1,51) /-2.072,-1.379,-0.683,0.013,1.413,2.125,2.
1 853,3.596,4.355,5.129,5.917,6.718,7.529,8.35,9.179,10.015,10.858,
4 28.399,29.295,30.191,31.089,32.888,33.788,34.690,35.593,36
5 .496,37.4,38.306,39.212,40.119/

data (hk(n,4),n=1,51) /-2.238,-1.543,-0.816,0.016,0.958,1.987,3.087,4
3 13,32.088,33.567,35.049,36.535,38.024,39.515,41.017,42.507,44.006,
4 45.508,47.012,48.518,50.027,51.538,53.051,54.566,56.082,57.601,59
5 .122,60.644,62.169,63.695,65.223,66.753/

data (hk(n,5),n=1,51) /-2.367,-1.581,-0.784,0.015,0.825,1.654,2.509,3
4 469,41.043,42.422,43.805,45.192,46.583,47.977,49.375,50.777,52.18
5 1,53.589,55.,56.413,57.829/

data (hk(n,6),n=1,51) /-1.481,-0.984,-0.488,0.009,0.506,1.003,1.5,1.99
1 6,2.493,2.99,3.487,3.984,4.481,4.977,5.474,5.971,6.468,6.965,7.46
2 1,7,958,8.455,8.952,9.449,9.945,10.442,10.939,11.436,11.933,12.43
183
\[ 9.22.366, 22.863, 23.359 \]

\[
\]

\[
\text{data (hk(n,8), n=1,51)} / -1.608, -1.08, -0.523, 0.01, 0.528, 1.038, 1.544, 2.05, 2.59, 3.13, 3.67, 4.22, 4.77, 5.33, 5.88, 6.44, 7.10, 7.66, 8.23, 8.80, 9.37, 10.05, 10.72, 11.40, 12.10, 12.80, 13.51, 14.23, 14.96, 15.70, 16.45, 17.22, 18.01, 18.82, 19.65, 20.49, 21.34, 22.21, 23.10, 24.01, 24.94, 25.89, 26.86, 27.85, 28.87, 29.91, 31.03, 32.18, 33.34, 34.53, 35.75, 37.00, 38.28, 39.60, 41.00, 42.44, 43.99, 45.66, 47.45, 49.36, 51.39, 53.56, 55.86, 58.29, 60.87, 63.59, 66.47, 69.50, 72.68, 76.01, 79.48, 83.09, 87.85, 92.77, 98.02, 103.42, 109.03, 114.88, 120.96, 127.28, 133.83, 140.75, 147.98, 155.56, 163.49, 171.79, 180.47, 189.54, 198.99, 208.88, 219.23, 230.05, 241.34, 253.03, 265.14, 277.69, 290.78, 304.41, 318.60, 333.36, 348.69, 364.59, 381.09, 398.31, 416.29, 434.98, 454.46, 474.76, 495.89, 518.02, 540.07, 562.13, 584.21, 606.33, 628.50, 650.71, 673.07, 695.57, 718.23, 741.04, 764.00, 787.10, 810.36, 833.80, 857.41, 881.21, 905.20, 929.48, 953.96, 978.74, 1003.76, 1029.02, 1054.53, 1080.31, 1106.35, 1132.66, 1159.25, 1186.14, 1213.33, 1240.83, 1268.65, 1296.79, 1325.26, 1354.08, 1383.25, 1412.77, 1442.65, 1472.91, 1503.56, 1534.59, 1566.02, 1597.87, 1629.15, 1660.88, 1692.11, 1723.83, 1755.33, 1787.45, 1819.33, 1851.93, 1884.37, 1917.68, 1951.87, 1986.94, 2022.90, 2059.87, 2097.90, 2136.17, 2175.79, 2216.88, 2258.56, 2301.99, 2347.31, 2394.55, 2443.87, 2495.38, 2548.13, 2602.37, 2658.27, 2716.85, 2777.25, 2840.59, 2906.94, 2975.45, 3047.29, 3122.61, 3201.57, 3284.38, 3371.25, 3462.35, 3557.93, 3657.93, 3763.59, 3875.83, 3994.89, 4111.88, 4236.96, 4369.49, 4509.59, 4657.69, 4814.25, 4980.47, 5156.54, 5343.72, 5542.56, 5754.89, 5979.88, 6218.92, 6474.88, 6750.55, 7047.78, 7368.56, 7715.22, 8093.36, 8498.40, 8935.16, 9408.33, 9920.34, 10484.65, 11097.57, 11764.37, 12489.38, 13276.83, 14133.55, 15065.31, 16079.74, 17182.34, 18399.97, 19746.38, 21256.52, 22957.47, 24879.30, 27051.34, 29493.26, 32245.12, 35337.47, 38790.01, 42544.24, 46620.20, 51057.93, 55902.90, 61217.93, 67015.50, 73346.44, 80152.25, 87553.18, 95685.65, 104680.74, 114686.77, 126159.35, 139277.77, 153502.13, 169419.03, 186472.55, 204969.84, 225336.26, 248918.87, 275573.56, 305747.73, 340510.80, 380196.08, 425132.20, 476997.50, 536253.54, 605687.72, 687740.77, 786591.26, 905208.72, 1042516.12, 1204660.21, 1408575.42, 1658904.84, 2000000.00.}
data (hk(n,11), n=1,51) /-2.072,-1.379,-.683,.013,.711,1.417,2.137,
1 2.873,3.627,4.397,5.183,5.983,6.794,7.616,8.446,9.285,10.13,10.98
2 ,11.836,12.697,13.561,14.43,15.301,16.175,17.052,17.931,18.813,19
4 19,28.617,29.516,30.416,31.316,32.218,33.121,34.025,34.93,35.835,
5 36.741,37.649,38.557,39.465,40.375/
data (hk(n,12), n=1,51) /-2.197,-1.451,-.705,.013,.727,1.448,2.186,
1 2.942,3.716,4.507,5.313,6.131,6.96,7.798,8.644,9.496,10.354,11.21
4 4,28.997,29.9,30.805,31.71,32.616,33.523,34.431,35.34,36.249,37.1
5 59,38.07,38.982,39.894,40.807/
data (hk(n,13), n=1,51) /-2.390,-1.596,-.799,.015,.877,1.797,2.771
1 ,3.791,4.850,5.943,7.066,8.215,9.387,10.580,11.791,13.019,14.261,
3 27.200,28.528,29.859,31.195,32.534,33.875,35.220,36.567,37.917,
4 39.268,40.622,41.978,43.335,44.694,46.055,47.417,48.780,50.144,
5 51.510,52.876,54.244,55.613,56.982,58.353,59.724/
data (hk(n,14), n=1,51) /-.256,-1.831,-.965,.019,1.113,2.304,3.57
2 06,20.927,22.67,24.432,26.212,28.007,29.817,31.64,33.474,35.319,3
3 7.173,39.036,40.906,42.783,44.666,46.555,48.449,50.348,52.251,54.
4 158,56.07,57.984,59.902,61.823,63.747,65.675,67.605,69.537,71.47

185
data (hk(n,15),n=1,51) /-2.133,-1.502,-.778,.015,.867,1.77,2.722,
1 3.723,4.773,5.87,7.006,8.409,9.598,10.809,12.039,13.287,14.55,
3 7.29,078,30.433,31.792,33.154,34.519,35.887,37.258,38.631,40.008,
4 41.387,42.769,44.154,45.542,46.932,48.325,49.721,51.119,52.52,53.
5 923.5327,56.733,58.14,59.548,60.955/

data (hk(n,16),n=1,51) /-3.381,-2.335,-1.199,.023,1.329,2.714,4.17
2 591,23.416,25.257,27.113,28.981,30.86,32.749,34.647,36.552,38.46
3 3.40,38,42.301,44.225,46.153,48.082,50.014,51.947,53.882,55.818,
4 57.757,59.698,61.642,63.59,65.544,67.504,69.473,71.451,73.442,75.
5 447,77.469,79.512,81.578,83.671,85.794,87.953/

data (hk(n,17),n=1,51) /-1.835,-1.393,-.761,.015,0.911,1.912,3.01
1 1.4.206,5.496,6.875,8.332,10.266,11.829,13.436,15.082,16.762,18.4
3 9.36.664,38.546,40.434,42.328,44.227,46.13,48.038,49.949,51.864,
4 53.783,55.706,57.632,59.561,61.494,63.43,65.37,67.312,69.258,71.2
5 06,73.156,75.108,77.061,79.015,80.968,82.92/

data (hk(n,18),n=1,51) /-2.185,-1.602,-.854,.017,0.984,2.031,3.15,
3 5.201,37.045,38.898,40.76,42.628,44.503,46.384,48.27,50.161,52.05
4 8.53.959,55.864,57.773,59.687,61.604,63.525,65.45,67.378,69.309,7
data (hk(n,19),n=1,51) /
2 16.25,33.27.58,29.864,32.177,34.515,36.877,39.258,41.658,44.072,
3 46.5,48.939,51.388,53.845,56.309,58.78,61.255,63.735,66.218,68.7
4 05.71,195,73.687,76.183,78.68,81.181,83.685,86.191,88.701,91.215,
5 93.733,96.255,98.783,101.315,103.854,106.398/
data (hk(n,20),n=1,51) /
2 5,27.837,30.157,32.502,34.869,37.257,39.663,42.084,44.519,46.966,
3 49.423,51.89,54.364,56.846,59.333,61.825,64.321,66.821,69.324,
4 71.829,74.338,76.848,79.361,81.876,84.394,86.913,89.435,91.96,
5 94.487,97.018,99.552,102.091,104.633,107.179,109.731/
data (hk(n,21),n=1,51) /
2 48.29,129,31.756,34.426,37.134,39.875,42.646,45.444,48.265,51.10
3 75.967,56.842,59.731,62.632,65.544,68.464,71.391,74.326,77.266,
4 80.211,83.16,86.114,89.071,92.033,94.998,97.968,100.941,103.92,10
5 6.903,109.891,112.886,115.886,118.894,121.909,124.933/
data (hk(n,22),n=1,51) /
1 5.742,7.449,9.238,11.096,13.014,14.983,16.999,19.054,22.034,24.15
2 6,26.308,28.486,30.688,32.911,35.155,37.417,39.695,41.987,44.293,
3 46.611,48.939,51.277,53.623,55.977,58.339,60.706,63.079,65.458,
4 67.841,70.229,72.621,75.017,77.416,79.819,82.226,84.636,87.049,
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<th>Data (hk(n,23), n=1, 51)</th>
<th>89.465, 91.884, 94.306, 96.731, 99.16, 101.591, 104.024</th>
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<tr>
<td>Data (hk(n,24), n=1, 51)</td>
<td>-2.706, -2.073, -1.163, 0.024, 1.481, 3.193, 5.13</td>
</tr>
<tr>
<td>Data (hk(n,25), n=1, 51)</td>
<td>-2.291, -1.843, -1.073, 0.023, 1.438, 3.155, 5.15</td>
</tr>
<tr>
<td>Data (hk(n,26), n=1, 51)</td>
<td>1.464, -1.379, -1.250, 1.173, 2.563, 4.15</td>
</tr>
</tbody>
</table>

188
5 91,110.99,114.093,117.2,120.309,123.42,126.53,129.639/ 
   data (hk(n,27),n=1,51) /-2.271,-1.656,-.894,.018,1.081,2.291,3.64 
2 49,25.784,28.05,30.347,32.67,35.018,37.386,39.773,42.176,44.592, 
3 47.021,49.46,51.908,54.364,56.826,59.294,61.767,64.245,66.726, 
4 69.212,71.7,74.192,76.687,79.186,81.687,84.192,86.701,89.213,91.7 
5 29.94,248,96.772,99.299,101.831,104.367,106.906/ 
   data (hk(n,28),n=1,51) /-2.284,-1.743,-.959,.019,1.153,2.409,3.76 
1 2,5,194,6.692,8.247,9.853,11.629,13.328,15.068,16.846,18.657, 
2 20.5,22.371,24.268,26.188,28.13,30.091,32.07,34.065,36.075,38.09 
3 9,40.134,42.182,44.24,46.308,48.385,50.471,52.566,54.668,56.778, 
4 58.896,61.021,63.153,65.292,67.437,69.59,71.749,73.914,76.085, 
5 78.262,80.445,82.633,84.826,87.023,89.224,91.428/ 
   data (hk(n,29),n=1,51) /-2.752,-2.246,-1.316,0.028,1.767,3.87,6.30 
1 1,9.018,11.985,15.165,18.531,23.554,27.203,30.968,34.84,38.809,42 
2 .866,47.002,51.21,55.481,59.81,64.19,68.615,73.079,77.578,82.108, 
3 86.664,91.243,95.842,100.457,105.087,109.729,114.381,119.042,123. 
4 711,128.387,133.069,137.756,142.449,147.147,151.851,156.56,161.27 
5 5,165.997,170.726,175.464,180.21,184.965,189.732,194.51,199.3/ 
   data (hk(n,30),n=1,51) /-2.682,-2.193,-1.291,.028,1.742,3.81,6.181 
1 ,8.8,11.619,14.603,17.738,22.258,25.633,29.104,32.663,36.3,40.009 
2 ,43.781,47.611,51.492,55.417,59.383,63.385,67.417,71.477,75.56,79 
3 ,665,83.787,87.924,92.0760,96.239,100.412,104.594,108.784,112.982 
4 ,117.186,121.396,125.613,129.835,134.062,138.296,142.535,146.78,1

189
5 51.032,155.289,159.554,163.824,168.101,172.385,176.675,180.971/
data (hk(n,31),n=1,51) /-2.822,-2.172,-1.23,0.261,1.59,3.437,5.352,
2 905.38,178.4,41.5,44.864,48.267,51.704,55.175,58.662,62.178,65.713,6
3 9.265,72.833,76.413,80.005,83.607,87.217,90.834,94.458,98.089,101
5 986,134.666,138.352,142.043,145.74,149.442,153.15,156.862/
data (hk(n,32),n=1,51) /-3.346,-2.933,-1.769,0.38,2.49,5.235,8.47
2 .821,62.064,67.382,72.767,78.212,83.71,89.257,94.846,100.472,106.
3 132,111.821,117.536,123.274,129.032,134.807,140.598,146.402,152.2
4 19,158.046,163.884,169.73,175.585,181.449,187.32,193.198,199.085,
5 204.978,210.88,216.789,222.705,228.63,234.562,240.5,246.4,252.4/
data (hk(n,33),n=1,51) /-4.475,-3.736,-2.220,0.48,3.025,6.645,10.8
1 37,15.523,20.631,26.096,31.872,40.731,46.975,53.414,60.031,66.81,
2 73.738,80.801,87.985,95.28,102.675,110.159,117.723,125.359,133.05
3 8,140.814,148.621,156.471,164.36,172.284,180.237,188.218,196.222,
4 204.247,212.291,220.352,228.429,236.521,244.627,252.746,260.88,26
5 9.02,277.1,285.3,2.5,301.7,309.9,318.242,326.508,334.796,343.106/
data (hk(n,34),n=1,51) /-3.647,-3.087,-1.832,0.39,2.461,5.368,8.70
2 9.85,65.461,71.159,76.933,82.778,88.684,94.646,100.656,106.711,11
3 2.804,118.93,125.087,131.27,137.476,143.703,149.947,156.208,162.4
4 82,168.769,175.068,181.377,187.697,194.026,200.363,206.71,213.065
data (hk(n,35),n=1,51) / -3.275,-3.000,-1.856,.041,2.591,5.704,9.30
1 3,13.32,17.696,22.381,27.334,32.518,37.904,43.465,52.976,58.821,6
2 4.778,70.838,76.988,83.222,89.528,95.901,102.332,108.815,115.344,
3 121.914,128.519,135.156,141.82,148.509,155.219,161.947,168.692,17
4 5.451,182.224,189.008,195.804,202.61,209.425,216.25,223.084,229.9
5 28,236.78,243.6,250.5,257.3,264.2,271.181,278.09,285.007,291.934/
data (hk(n,36),n=1,51) / -3.461,-3.092,-1.889,.041,2.606,5.721,9.31
1 3,13.315,17.673,22.338,27.268,32.429,37.789,43.323,52.645,58.462,
2 64.393,70.425,76.551,82.759,89.042,95.392,101.802,108.264,114.773
3 ,121.324,127.912,134.532,141.18,147.854,154.549,161.264,167.997,1
4 74.744,181.506,188.28,195.066,201.862,208.669,215.485,222.311,229
5 .147,235.9,242.8,249.71,256.5,263.4,270.36,277.2,284.174,291.095/
data (hk(n,37),n=1,51) / -2.021,-2.127,-1.415,.033,2.140,4.836,8.05
1 4,11.733,15.817,20.255,24.999,30.009,35.249,40.684,50.688,56.433,
2 62.301,68.281,74.362,80.532,86.783,93.105,99.492,105.934,112.427,
3 118.963,125.538,132.147,138.785,145.449,152.135,158.842,165.565,1
5 6,233.4,240.3,247.1,254.05,260.9,267.8,274.7,281.6,288.5/
data (hk(n,38),n=1,51) / -5.982,-5.264,-3.198,.07,4.407,9.687,15.79
1 5,22.629,30.092,38.101,46.578,55.457,64.679,74.196,90.815,100.8,1
2 10.975,121.323,131.828,142.474,153.247,164.133,175.121,186.199,19
4 626,300.201,311.801,323.424,335.067,346.73,358.411,370.11,381.826
191
5 ,393.559,405.3,417.07,428.8,440.6,452.4,464.3,476.1,488.0,499.9/
data (hk(n,39),n=1,51) /-2.975,-2.191,-1.189,.024,1.441,3.048,4.82
2 9,31.959,34.697,37.469,40.271,43.1,45.953,48.826,51.717,54.624,57
3 .544,60.477,63.419,66.37,69.328,72.292,75.262,78.236,81.214,84.19
4 5,87.179,90.166,93.155,96.148,99.143,102.141,105.142,108.147,111.
5 156,114.169,117.186,120.209,123.237,126.271,129.311/
data (hk(n,40),n=1,51) /-2.996,-2.432,-1.381,.028,1.703,3.576,5.60
1 2,7.754,10.015,12.373,14.816,17.848,20.425,23.059,25.744,28.476,3
2 1.251,34.064,36.91,39.788,42.692,45.621,48.571,51.54,54.525,57.52
3 5,60.538,63.562,66.596,69.638,72.688,75.744,78.806,81.873,84.945,
4 88.021,91.101,94.185,97.272,100.363,103.458,106.556,109.658,112.7
5 63,115.873,118.986,122.103,125.224,128.348,131.477,134.609/
data (hk(n,41),n=1,51) /-31.239,-30.675,-29.321,-27.3,-24.717,-21.
1 164,-18.217,-14.442,-10.393,-6.113,-1.639,2.94,7.762,12.69,17.714
2 22.826,28.018,33.281,38.609,43.995,49.434,54.919,60.447,66.011,7
3 1.608,77.235,82.888,88.564,94.261,99.976,105.707,111.453,117.212,
4 122.984,128.767,134.562,140.366,146.181,152.006,157.84,163.685,16
6 808,222.776/
data (hk(n,42),n=1,51) /0.338,1.099,2.559,4.602,7.13,10.056,13.312
1 16.84,20.593,24.534,28.634,32.815,37.204,41.683,46.244,50.88,55.
2 582,60.346,65.165,70.033,74.946,79.898,84.886,89.904,94.951,100.
3 22,105.114,110.226,115.354,120.497,125.653,130.82,135.997,141.183
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