

A Numerical Investigation on Ignition Characteristics of n-Heptane/Methane in Homogenous Systems and HCCI

BY

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THESIS

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Abbreviation

The following are the full meaning of the abbreviation used in the thesis

BMEP	Break Mean Effective Pressure
NTC	Negative Temperature Coefficient
HCCI	Homogenous Charge Compression Ignition
ROP	Rate of Production
PAH	Polycyclic Aromatic Hydrocarbon
ϕ	Equivalence Ratio
CR	Compression Ratio
ATDC	After Top Dead Center

Abstract:

A promising solution for improving combustion performance and reducing emissions is to control the ignition behavior, such as ignition delay in internal combustion engines. The purpose of this study is to numerically investigate the effect of natural gas on the ignition characteristics of diesel fuel in a homogeneous system and an HCCI engine. Methane is considered as the main component of natural gas and n-heptane is considered as the surrogate for diesel fuel. Simulations are performed using Chemkin software for a constant-pressure reactor, a constant-volume reactor and an HCCI engine. Parameters considered in this study include n-heptane/methane blend composition, initial temperature and equivalence ratio for homogenous systems with constant pressure or constant volume. In addition, effects of the start of injection, equivalence ratio and blend composition in an HCCI engine are examined. The three different mechanisms used are the CRECK mechanism (435 species and 13532 reactions) developed at Polytechnic University of Milan, LLNL mechanism (874 species and 3796 reactions) developed at Lawrence Livermore National Laboratory and Chalmers mechanism (73 species and 417 reactions) developed at the Chalmers University of Technology in Sweden. These mechanisms are validated using ignition delay data for n-heptane and methane. Numerical results are found to be in good agreement with experiments. CRECK and LLNL mechanisms predict a continuous increase in ignition delay as the amount of methane is increased in the blend. However, Chalmers mechanism shows that the ignition delay first decreases and then increases. In order to identify the important reactions, a sensitivity analysis is performed using the CRECK and Chalmers mechanisms. Simulations are also performed using the engine simulator of Chemkin and 3D CFD software Converge.

An additional comparison using homogenous constant volume reactor and closed internal combustion engine simulator has been performed under comparable conditions. The effect of blend composition on two-stage ignition process has been analyzed. As more methane is added, the first stage ignition delay remains nearly constant, while the second stage ignition delay increases dramatically. It is shown that the first- and second-stages ignition delays for HCCI engine and constant-volume system show quantitatively good agreement with each other. Finally, the effect of adding methane on BMEP and the production of important species, NO_x and PAH are discussed.

Keywords:

Methane, n-heptane, ignition characteristics, HCCI engine

Chapter 1

Introduction

Energy is one of the most important aspects of our day-to-day lives. Without energy, it would be impossible to live in our current world. The fuels burned to generate this necessary energy are limited and therefore serious efforts should be initiated to enhance the fuel consumption. This limited amount of fuel must be properly consumed to ensure the next generation has access to this finite energy source. One of the main consumers of these fuel sources are engines, which burn the fuel to produce energy, but seldom do we think about the source of this energy.

Approximately 86% of the total energy used in the United States is derived from fossil fuels. On a daily basis 70% of the 86 million barrels of unpolished oil is used in Internal Combustion engines. Particularly in the United States, everyday more than 10 million barrels are being used in cars and light-duty trucks, in addition another 4 million barrels is being used in heavy-duty vehicles. Given the amount used this roughly equals 2.5 gallons per person every day. When taking into consideration how much crude oil is used each day one must not exclude issues concerning pollution, greenhouse gas emission, and threat to the ozone layer. Attention must be paid to how these fuels are being consumed including the impacts, both positive and negative, that this usage is having on the environment [1].

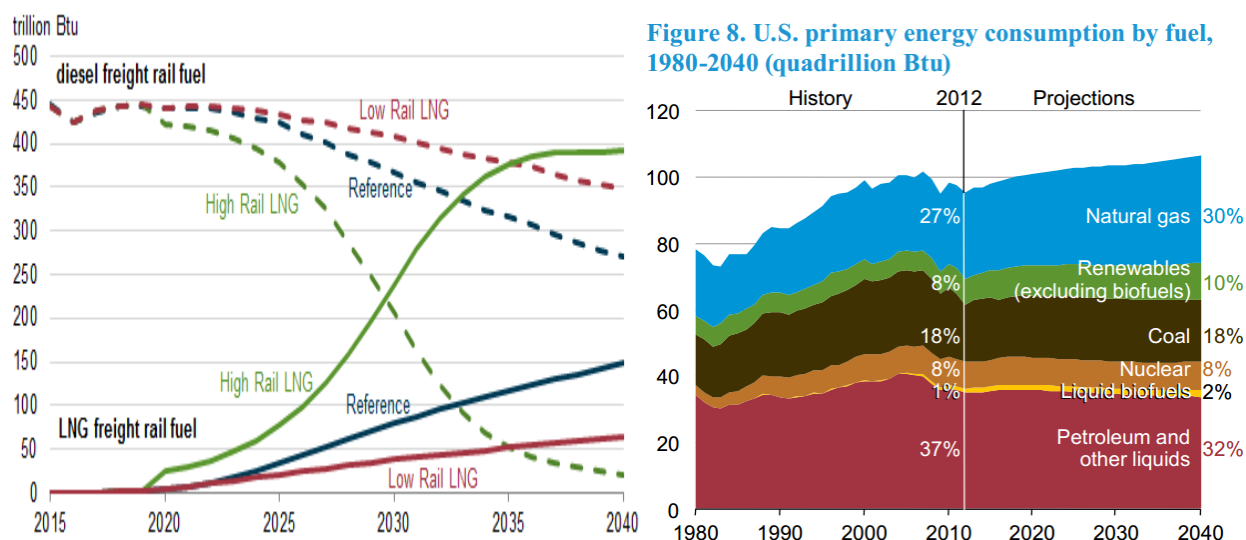


Figure 1 Comparison of energy consumption for freight rail using diesel and LNG (2015-40) [2]

In this study the main surrogate of diesel fuel, n-heptane, is examined. After the initial analysis of n-heptane attention is given to methane and the mixture of the two to see how they affect the ignition characteristics in HCCI engines. Actual diesel fuel has too many species, which are difficult to predict and it also has a very complicated structure making it impractical to analyze with software. Researchers often analyze the surrogate fuels (compound of similar chemical attributes to the analyte of interest) to simplify the calculations and save time.

Fuel surrogates are mixtures of one or more simple fuels, designed to emulate combustion properties (ignition delay, NO_x and soot formation, etc.) of a more complex fuel. Although surrogate fuels have shown many different behaviors, it is not necessary for the surrogate fuel to have all those components to be analyzed, i.e. it only needs to have specific properties which are of our interest. Diesel is an example of a fuel requiring a surrogate for experimental research and numerical modeling due to its complexity and high content variability from one batch to the next. The common diesel surrogates are iso-octane and n-heptane. In this study pure n-heptane fuel was used as a main component of surrogate fuel in closed homogenous reactor and simulations have been performed in engine-like initial conditions.

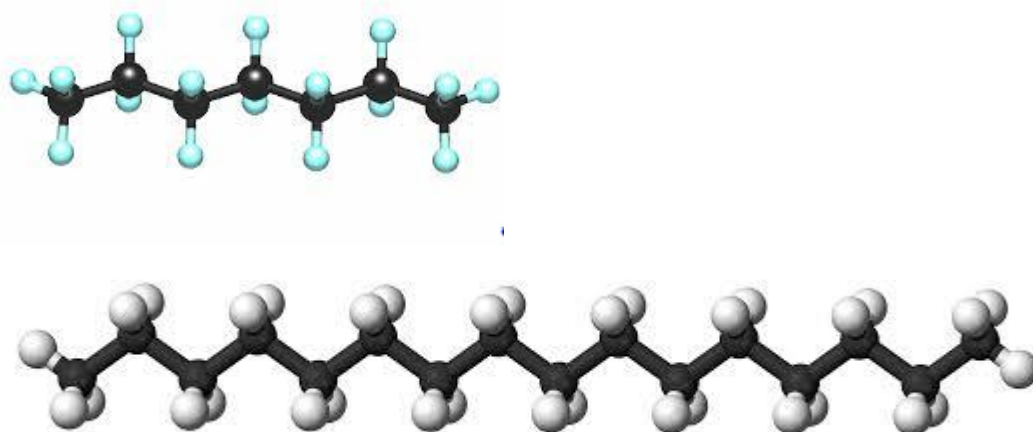


Figure 2 The structures of diesel surrogates.

N-heptane is a volatile, colorless, highly flammable liquid hydrocarbon with the chemical formula of $\text{H}_3\text{C}(\text{CH}_2)_5\text{CH}_3$ or C_7H_{16} . Since it has an analogous cetane number as regular diesel fuels, it is usually used as a component of surrogate diesel fuel. Heptane (and its many isomers) is being used as a totally non-polar solvent in many laboratories. Heptane as a liquid is ideal for transportation and storage. Heptane has nine isomers, or eleven if enantiomers are counted, the one that is used in this study is n-heptane. This isomer was chosen because it has better compatibility with the actual diesel fuel, and also n-heptane is cheaper than other isomers and it is much more accessible than other fuels. N-heptane has the following structure: $\text{H}_3\text{C}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$

Methane is a colorless, odorless gas with a wide distribution in nature. It is the simplest alkane and the principal component of natural gas with the chemical formula CH_4 . The relative wealth of methane makes it an attractive fuel to study. Methane is difficult to store since it is a low dense gas at room temperature. Burning methane produces less carbon dioxide for each unit of heat released compared to other hydrocarbon fuels. Given the ratio of heat combustion to molecular mass, methane is shown to have the highest heat per mass unit (55.6 kJ/g) when compared to other complex hydrocarbons. The energy content of methane (natural gas) is 39 MJ/m^3 , or $1,000 \text{ BTU/ft}^3$ [3].

In the first chapter of this research, the ignition behavior of the diesel fuel surrogate (n-heptane) is examined in a diesel engine. Next, methane is added to see how it affects the ignition, combustion and emission behavior. The main property examined is the effect of methane on the ignition delay. The effect of adding methane to n-heptane can be very diverse but the most

important influence is the ability to control the ignition timing. The NO_x formation and soot formation are studied as well.

The reasons for using methane in diesel engines are varied. The low cost, superior emissions results, a cleaner fuel with superior emission characteristics, accessibility of procuring, and the fact that methane provides higher engine performance than such additives as iso-octane and hydrogen make it a valued resource.

The software used is Chemkin 15113, which is a reliable and accurate software to calculate the properties of substances in different modules. The module used is a closed homogenous batch reactor with constant pressure/volume and a constant mass. For the purpose of this study, a closed homogenous batch reactor is used to investigate how various fuel compositions affect the ignition behavior with given operating conditions. It solves the species, energy, and momentum equations. Here one of our interests are determining the ignition time under a specified set of initial pressure and temperature conditions assuming no heat loss to the environment (adiabatic conditions). Sensitivity Analysis has been conducted in order to identify important reactions having an influence on ignition delay timing.

1.1 Background:

Internal combustion (IC) engines have many various applications. In order to reduce the emissions levels from these engines a new mode of combustion is required: homogeneous charge compression ignition (HCCI) engine technology is a potential candidate. “The HCCI technique is the process by which a homogeneous mixture of air and fuel is compressed until auto-ignition occurs near the end of the compression stroke, followed by a combustion process that is significantly faster than either Compression Ignition (CI) or Spark Ignition (SI) combustion.”[36] HCCI technology claimed to improve the thermal efficiency of engines while maintaining low emissions. Modifying either SI or CI engines using any combination of fuels might be the best way to decrease harmful particulates. In HCCI engines, the quality of air/fuel mixture is usually lean, thus auto-ignition takes place in multiple locations all around the cylinder. As a result of

this auto-ignition, the fuel is burned volumetrically and it does not include any visible flame propagation. When the homogeneous mixture of air and the fuel has sufficient chemical activation energy, combustion takes place. Chemical kinetics is the only factor controlling this chemical kinetics, it is not depended on spark or injection timing.

1.2 HCCI

1.2.2 Terminology:

HCCI belongs to internal combustion engines group in which well-mixed fuel and air are compressed till auto ignition takes place. HCCI engines can be considered as next generation of engines even though the very first research was conducted by Onishi et al. in 1979 [17]. Scientists worldwide are studying HCCI engines as this technology has not yet been sufficiently studied and advanced and commercially available to public.

Since this ignition contains exothermic reactions, it releases chemical energy which can be transformed in the engine into work and unwanted heat. They can be used in engine configurations with a high CR. HCCI engines function without using diesel injectors or spark plugs and their high efficiency can be attained with low NO_x and soot emissions. “General Motors (GM) corporation has unveiled a prototype car with a gasoline HCCI engine, which could cut fuel consumption by 15%” [18]. The engine is capable of eliminating NO_x emissions virtually and lowering throttling losses, which improves fuel economy.

HCCI engines practically combines characteristics of gasoline and diesel engine. HCCI stands for homogenous charge spark ignition and is a combination of homogenous charge (HC) and spark ignition (SI). SCCI stands for stratified charge compression ignition and is a combination of stratified charge (SC) and compression ignition (CI). Controlling HCCI requires having the control on the ignition process. The best design includes achieving gasoline engine-like emissions with diesel engine-like efficiency. Emissions regulations are becoming more stringent and HCCI engines produce low levels of Nitrogen Oxide (NO_x) and soot emissions without sacrificing thermal efficiency, which is close to that of CI engines [19].

In HCCI engines when the concentration and temperature of reactants is sufficiently high, the mixture of fuel and air starts to ignite. There are several techniques to modify the concentration and/or temperature. “These techniques are as follows:

- i. Increasing Compression Ratio (CR)
- ii. Pre-heating of induction gases
- iii. Forced induction
- iv. Retained or re-inducted exhaust gases”[37]

After the fuel ignites the combustion takes place in a very small fraction of a second and when Auto-ignition occurs in not a desire time i.e. when the mixture of fuel/air auto-ignites too early or with excessive chemical energy, combustion speed becomes too fast and the engine components might malfunction due to high in-cylinder pressures. Because of this reason, HCCI engines are typically functioned with overall lean mixtures. Since the fuel is fully handled by chemical kinetics and fuel/air mixture quality is lean, there are some challenges in advancing HCCI engines industry as controlling the auto-ignition of air/fuel mixture is not easy and the heat Release Rate (HRR) at high load task, meet allowed emission standards [15], achieve cold start and control knock [16].

1.2.3 Advantages and disadvantages:

Table 1 Advantages and disadvantages of HCCI engines.

Advantages	Disadvantages
Since lean fuels are used in HCCI engines they can operate at very high compression ratios similar to diesel, thus it leads to 35% higher efficiencies than regular SI gasoline engines.	Auto ignition is difficult to control in HCCI engines, In SI engines it can be controlled by spark plugs and in CI engines it is controlled by in-cylinder fuel injectors.
HCCI avoids throttle losses, which further improves efficiency.	High in-cylinder pressure during the compression stroke may damage the engine.
Since the mixture of fuel and air is homogenous, combustion will be cleaner and less emissions will be produced.	Compared to a typical SI engine, HCCI produces higher amount of Carbon monoxide (CO) and hydrocarbon (HC) due to incomplete oxidation and trapped crevice gases, respectively.
Since the temperatures are significantly lower than a typical SI engines, less NO _x will be formed	“HCCI engines usually have a small power range, controlled at low loads by lean flammability bounds and high loads by in-cylinder pressure limitations”[38]

HCCI engines are very flexible in choosing the fuel, they can operate with diesel fuel, gasoline and most alternative fuels.	High heat release and pressure rise rates contribute to engine wear.
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1.3 Control:

Due to lower in-cylinder temperature and higher in-cylinder pressure, HCCI engines are more challenging to control, whereas other regular combustion engines such as spark ignition and compression ignition engine are easier to control. In gasoline engines, a spark is employed to ignite the pre-mixed air and fuel, whereas in diesel engines, the fuel is injected into pre-compressed air and then the combustion initiates. Thus in both cases, combustion timing is controlled. “In an HCCI engine, however, fuel/air homogeneous mixture is compressed and combustion begins whenever sufficient pressure and temperature are reached. This means that no well-defined combustion initiator offers direct control. Engines must be designed so that ignition conditions take place at the desired timing. To achieve dynamic operation goal, the control system must manage the conditions that induce combustion. Available options include:

- ✓ Compression ratio
- ✓ Inducted gas temperature
- ✓ Inducted gas pressure
- ✓ Fuel-air ratio
- ✓ Quantity of retained or re-inducted exhaust”[38]

Several control methods are explained in the following.

1.3.1 Compression ratio:

Compression Ratio (CR) is one of the crucial factors in controlling the HCCI engines, CR is dependent on geometric shape of engines. Two most important compression ratios are

1. Geometric Compression Ratio (GCR)

2. Effective Compression Ratio (ECR)

Geometric compression ratio (GCR) is very easy to change, it can be changed by moving the movable plunger located at the top of the cylinder head. By closing the intake valve either very late or very early with Variable Valve Actuation (VVA), the effective compression ratio (ECR)

can be reduced from the geometric ratio. Both of these approaches are in need of energy for a fast response. In addition, operation is not cheap, but is effective. Later on this study some important effects of compression ratio (CR) on HCCI combustion have been discussed broadly.

1.3.2 Induction temperature:

HCCI's auto ignition event is extremely sensitive to and dependent on temperature. The easiest way to having a control on the temperature is by installing resistance heaters to differ the inlet temperature. This approach on a cycle-to-cycle frequency might be relatively slow. There is an alternative technique called "*fast thermal management (FTM)*". It can be pursued by mixing cold and hot air streams, thus changing the intake charge temperature. This approach is fast enough and it allows us to have a control on cycle-to-cycle. It is also relatively expensive to implement and has some limitation.

1.3.3 Exhaust gas percentage:

Exhaust gas is extremely cool if it is recirculated through the intake such as in conventional EGR systems or hot if it is taken or re-inducted from the prior combustion cycle. The exhaust system has dual influences on HCCI combustion performance. By diluting the fresh charge, it causes ignition delay and decreases the air/fuel mixture chemical energy and engine output. On the other hand hot combustion products increase gas temperature in the cylinder and advance ignition.

1.3.4 Valve actuation:

Increasing or decreasing the engine working region may be an option to control the temperature and pressure in cylinder. "*Variable valve actuation (VVA)* extends the HCCI working region by providing better control over the temperature-pressure-time envelope within the combustion chamber"[39]. There are two different options to extend HCCI working region:

- ✓ modifying the effective compression ratio (CR)
- ✓ Controlling the amount of hot exhaust gas retained in the combustion chamber

1.3.5 Fuel mixture:

Extending the functioning range can also be achieved by controlling the beginning of ignition and the Heat Release Rate (HRR). They can be controlled by modifying the air/fuel mixture itself. By blending multiple fuels "on the fly" for the same engine condition, they can be controlled. Examples include adopting natural gas (methane), blending of diesel fuels. This can be attained in a number of different ways, including:"

Upstream blending: Fuels are mixed in the liquid phase, one with low ignition resistance (such as diesel) and a second with greater resistance (gasoline). Ignition timing varies with the ratio of these fuels blending together.

In-chamber blending: One fuel can be injected in the intake duct (port injection) and the other directly into the cylinder.”[40]

1.4 Fuel selection:

1.4.1 A short summary on fuel used in HCCI engines:

A wide variety of fuels can be used in HCCI engines. The only characteristics they should have is, the ability to be vaporized and mixed with air in advance of ignition. In order to have smoother engine operation, the fuels auto-ignition point should be assessed. Auto-ignition point is influenced by chemical kinetics of the fuel.

The compositions of natural gas show a discrepancy for different countries as shown in Table 2. The reasons for using methane in diesel engines are varied. It is easily adapted for use as a fuel due its wide-ranging availability, is cost-effective and has environmental benefits because it produces fewer emissions than crude oil and coal, as demonstrated in Figure 3 [27] and [28]. It can be understood that crude oil and coal produced carbon dioxide 1.4 to 1.75 more than natural gas. Natural gas is also more freely available than crude oil, while it always has been cheaper than crude oil [29]. Natural gas has the ability to function as a single fuel in an IC engine while having low levels of HC and CO emissions, however it undergoes less power output in HCCI engines [30], [31] and [32]. “Its high auto-ignition point (about 810 K) gives it a significant advantage over diesel–natural gas operation by maintaining the high CR of a diesel engine and lowering emissions at the same time” [22]. Duc and Watta navichien [33] claimed that the high octane number of methane (about 120) allows engines to operate at a high CR.

Table 2 The difference in natural gas components between some random countries.

Components	Volume fraction				
	US	Sweden	Malaysia	Greece	Australia
Methane (CH ₄)	91.1	87.58	92.74	98.0	90.0
Ethane (C ₂ H ₆)	4.7	6.54	4.07	0.6	4.0
Propane (C ₃ H ₈)	1.7	3.12	0.77	0.2	1.7

Butane (C ₄ H ₁₀)	1.4	1.04	0.14	0.2	0.4
Pentane (C ₅ H ₁₂)	-	0.17	-	0.1	0.11
Hexane (C ₆ H ₁₄)	-	0.02	-	-	0.08
Heptane (C ₇ H ₁₆)	-	-	-	-	0.01
Carbon dioxide (CO ₂)	0.5	0.31	1.83	0.1	2.7
Nitrogen (N ₂)	0.6	1.22	0.45	0.8	1.0

CO = Carbon dioxide. No = Nitrogen oxides. SO = Sulfur dioxide. CO = Carbon monoxide. HC = Hydrocarbon.

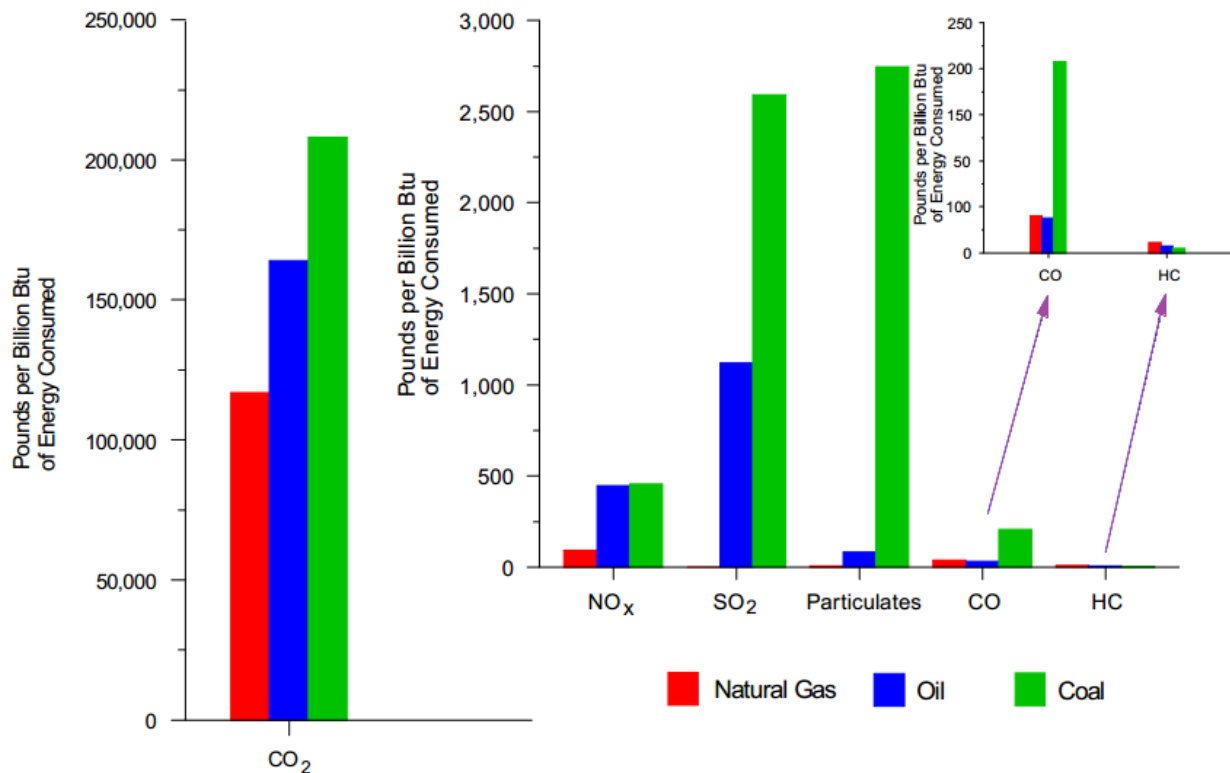


Figure 3 Air Pollutant Emissions by Fuel Type

Source: Energy Information Administration (EIA) Office of Oil and Gas. Carbon Monoxide: derived from EIA, Emissions of Greenhouse Gases in the United States 1997, Table B1, p. 106. Other Pollutants: derived from Environmental Protection Agency, Compilation of Air Pollutant Emission Factors, Vol. 1 (1998). Based on conversion factors derived from EIA, Cost and Quality of Fuels for Electric Utility Plants (1996).

1.5 Objective:

Based on the above considerations, the major objective of this work is to examine the effects of methane addition on the ignition behavior of n-heptane/air mixtures under HCCI relevant conditions. Simulations are performed for homogenous constant-volume and constant-pressure systems, and for a compression ignition engine using both Chemkin and 3-D CFD Converge software.

For the homogenous systems, predictions using the two detailed mechanisms, i.e. CRECK and LLNL, and a reduced mechanism, i.e. Chalmers, are compared with ignition delay data for n-heptane/air and methane/air mixtures at engine-like conditions. These three mechanisms are then used to examine the effect of methane addition on the ignition behavior of n-heptane/air mixtures for a range of pressures, temperatures and equivalence ratios. Results are also presented for the first-stage and second-stage ignition delays for n-heptane/methane blends. Some discrepancy with the Chalmers mechanism for the ignition of blends with relatively low methane fractions is highlighted. A sensitivity analysis is performed to identify the important reactions during ignition, and to further examine the above discrepancy. Finally simulation results are presented for the ignition, combustion and emission characteristics of a dual-fuel CI engine using 3D CFD Converge software and Chemkin with the engine simulator option.

Chapter 2

Theory

2.1 General Equations

There are several equations governed in a closed homogeneous reactor, such as: conservation of mass, energy, and species. These equations employ the net generation of species within the chamber, mass to surface and net loss of species in the reactor. In closed homogeneous reactors there is no inlet or outlet flow during the given time, although there may or may not be heat transfer to or from the external environment. The chemical state changes as species are produced or destroyed, thus the closed homogeneous reactor is transient.



Figure 4 A perfectly mixed closed homogeneous reactor

Figure 4 illustrates a closed homogeneous reactor with stirrer. Figure 4 illustrates a very simple view of typical reactor, this reactor has a single surface. An actual reactor might contain many different material surfaces, such as silicon wafer, reactor walls, a substrate holder, etc. “Each one of these materials used in the reactor may have a different set of reaction kinetics associated with it. Because of this reason, the ability of defining multiple surface materials that represent different fractions of the total surface area, with corresponding surface chemistry mechanisms is included in this function.”[39]

2.2 Constant-Pressure Fixed Mass Reactor:

2.2.1 Application of Conservation Laws:

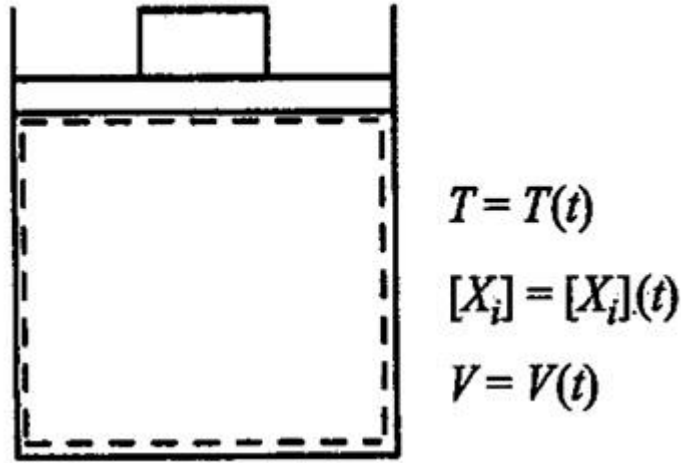


Figure 5 Perfectly mixed homogenous reactor constant-pressure fixed mass reactor.

In the constant pressure chamber the reactants react at each and every possible location within the volume at the same time. In the constant-pressure all the properties including temperature and composition gradients are the same everywhere. In order to describe the evolution of the system, temperature and a set of species concentration will be assessed. Both temperature and volume increases during the given time. There may be heat transfer through the reaction vessel walls, but in most cases it has been assumed to be zero for simplifying the calculations. Conservation of energy for fixed-mass system is as follows

$$\dot{Q} - \dot{W} = m \frac{du}{dt} \quad (1)$$

$\dot{Q}$ = heat transfer rate

$\dot{W}$ = work done

By definition of enthalpy we have: $h \equiv u + P v$

Differentiating from equation (1) leads to,

$$\frac{du}{dt} = \frac{dh}{dt} - P \frac{dv}{dt} \quad (2)$$

Work of the piston is defined as Pdv thus,

$$\frac{\dot{W}}{m} = P \frac{dv}{dt} \quad (3)$$

Substituting (2) and (3) into (1),

$$\frac{\dot{Q}}{m} = \frac{dh}{dt} \quad (4)$$

The enthalpy of system in term of composition is:

$$h = \frac{H}{m} = [\sum_{i=1}^N N_i \bar{h}_i] / m \quad (5)$$

by differentiating from the above equation,

$$\frac{dh}{dt} = \frac{1}{m} \left[\sum_{i=1}^N \left(\bar{h}_i \frac{dN_i}{dt} \right) + \sum_{i=1}^N \left(N_i \frac{d\bar{h}_i}{dt} \right) \right] \quad (6)$$

For an Ideal Gas, $\bar{h}_i = f(T)$ only,

$$\frac{d\bar{h}_i}{dt} = \frac{\partial \bar{h}_i}{\partial T} \frac{dT}{dt} = \bar{C}_{p,i} \frac{dT}{dt} \quad (7)$$

$\bar{C}_{p,i}$ = Average molar specific heat at constant pressure

By solving (7), the temperature can be found.

$$x_i = \frac{V_i}{V} = \frac{n_i}{n}$$

$$N_i = V [X_i] \quad (8)$$

$$\frac{dN_i}{dt} = V \dot{\omega}_i \quad (9)$$

$\dot{\omega}_i$ = net production rate of species i

By Substitute Eqns (7)-(9) into (6), we get

$$\frac{dT}{dt} = \frac{\left(\frac{\dot{Q}}{V} \right) - \sum_i (\bar{h}_i \dot{\omega}_i)}{\sum_i ([X_i] \bar{C}_{p,i})} \quad (10)$$

Calorific equation of state:

$$\bar{h}_i = h_{f,i}^0 + \int_{T_{ref}}^T C_{p,i} dT \quad (11)$$

Volume is obtained by

$$V = \frac{m}{\sum_i ([X_i] MW_i)} \quad (12)$$

$[X_i]$ Changes with time as a result of both chemical reactions and changing volume

$$\frac{d[X_i]}{dt} = \frac{d\left(\frac{N_i}{V}\right)}{dt} = \frac{1}{V} \frac{dN_i}{dt} - N_i \frac{1}{V^2} \frac{dV}{dt} \quad (13)$$

Or

$$\frac{d[X_i]}{dt} = \dot{\omega}_i - [X_i] \frac{1}{V} \frac{dV}{dt} \quad (14)$$

The Ideal Gas law,

$$PV = \sum_i N_i R_u T \quad (15)$$

Differentiating for P=constant, and rearranging

$$\frac{1}{V} \frac{dV}{dt} = \frac{1}{\sum_i N_i} \sum_i \frac{dN_i}{dt} + \frac{1}{T} \frac{dT}{dt} \quad (16)$$

Substitute Eqn. 9 into 15, and then substitute the result into Eqn. (14):

The rate of change for the species concentrations:

$$\frac{d[X_i]}{dt} = \dot{\omega}_i - [X_i] \left[\frac{\sum_i \dot{\omega}_i}{\sum_j [X_j]} + \frac{1}{T} \frac{dT}{dt} \right] \quad (17)$$

There are two sets of differential equations that need to be solved in order to find the outputs of a constant pressure homogenous reactor

$$\frac{dT}{dt} = f([X_i], T) \quad (18)$$

$$\frac{d[X_i]}{dt} = f([X_i], T) \quad i = 1, 2, \dots, N \quad (19)$$

Applying the given boundary conditions

$$T(t = 0) = T_0 \quad (20)$$

$$[X_i](t = 0) = [X_i]_0 \quad (21)$$

Functional forms of Eqns. (20) and (21) are obtained from Eqns. (10) and (17).

Eqn.(11) gives enthalpy and Eqn. (12) gives volume. Most of the time there is no analytical solution. Numerical integration can be done using an integration routine capable of handling stiff equations.

2.3 Constant-Volume Fixed Mass Reactor:

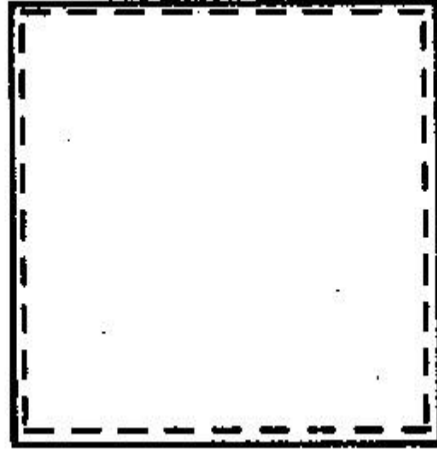


Figure 6 Homogenous reactor, constant volume fixed mass reactor

2.3.1 Application of Conservation Laws:

Application of energy conservation to constant-volume fixed mass reactor is very similar to constant-pressure fixed mass reactor. The only exception is, since $V = \text{constant}$ thus $\dot{W} = 0$.

Hence

$$\frac{du}{dt} = \frac{\dot{Q}}{m} \quad (22)$$

Noting that u now plays the same role as h in analysis for constant pressure. eqns. (5) and (7) can be developed and substituted in equation (22). By rearranging,

$$\frac{dT}{dt} = \frac{\left(\dot{Q}/V\right) - \sum_i(\bar{u}_i \dot{\omega}_i)}{\sum_i([X_i] \bar{C}_{v,i})}$$

Since $\bar{u}_i = \bar{h}_i - R_u T$ and $\bar{C}_{v,i} = \bar{C}_{p,i} - R_u$

$$\frac{dT}{dt} = \frac{\left(\dot{Q}/V\right) + R_u T \sum_i \dot{\omega}_i - \sum_i(\bar{h}_i \dot{\omega}_i)}{\sum_i([X_i] \bar{C}_{p,i} - R_u)} \quad (23)$$

In constant volume problems, $\frac{dP}{dt}$ plays an important role.

In order to find $\frac{dP}{dt}$ the Ideal gas law has been differentiated.

$$PV = \sum_i N_i R_u T \quad (24)$$

$$V \frac{dP}{dt} = R_u T \frac{d \sum_i N_i}{dt} + R_u \sum_i N_i \frac{dT}{dt} \quad (25)$$

$$P = \sum_i [X_i] R_u T \quad (26)$$

$$V \frac{dP}{dt} = R_u T \sum_i \dot{\omega}_i + R_u \sum_i [X_i] \frac{dT}{dt} \quad (27)$$

Eqn. 23 can be integrated simultaneously with $\dot{\omega}_i$ to determine $T(t)$ and $[X_i](t)$,

$$\frac{dT}{dt} = f([X_i], T) \quad (28)$$

$$\frac{d[X_i]}{dt} = f([X_i], T) \quad i = 1, 2, \dots, N \quad (29)$$

Subjected to the following initial conditions:

$$T(t = 0) = T_0 \quad (30)$$

$$[X_i](t = 0) = [X_i]_0 \quad (31)$$

2.4 Mechanisms:

2.4.1 CRECK Mechanism:

The detailed CRECK mechanism with 435 species and 13532 reactions was used to investigate different ignition characteristics. The more detailed CRECK mechanism with 466 species and 14631 reactions, which contains reactions involved in NO_x formation, was used to determine the NO_x creation and the effect of different composition of n-heptane and methane on NO_x development.

2.4.2 Chalmers Mechanism:

Chalmers mechanism [4] has been used as a reduced mechanism with 73 species and 417 reactions and has been validated using experimental data. By importing required NO reactions in Chalmers mechanism, this mechanism will be able to predict NO_x formation. Modified Chalmers mechanism predicts thermal NO_x , whereas CRECK mechanism is able to predict the thermal and prompt NO_x formation.

2.4.3 LLNL Mechanism:

The detailed LLNL mechanism with 874 species and 3796 reactions developed at Lawrence Livermore National Laboratory has been used to predict the important ignition characteristics of methane/n-heptane air mixture. LLNL mechanism has been validated versus experimental data and it has shown good agreement.

2.4.4 Mechanism Validation:

To validate the mechanisms, the ignition delay for temperatures between 730-1250 K have been compared with experimental data[7], [8] and[14].

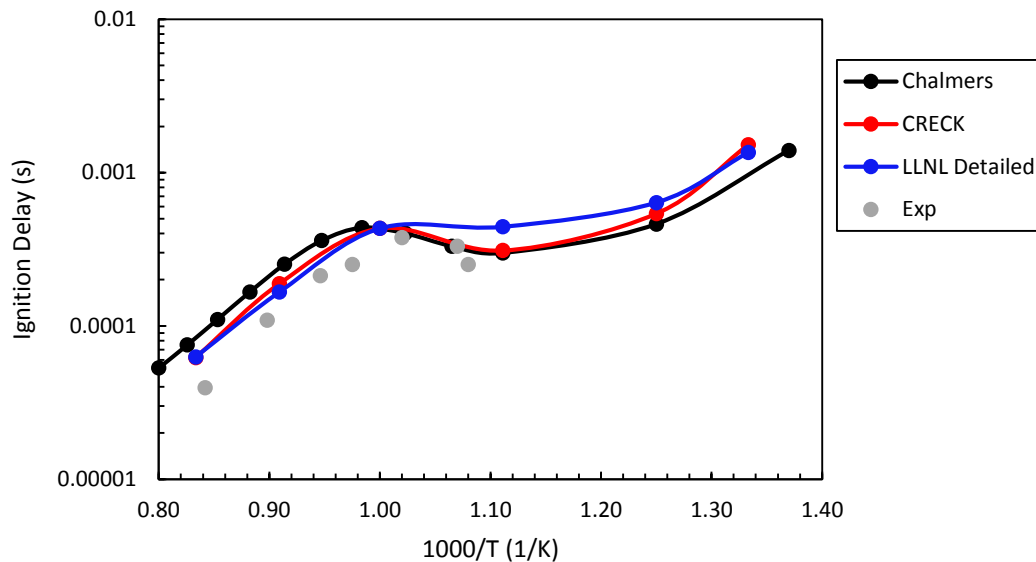


Figure 7 Ignition delay versus 1000/T for n-heptane, 55 atm, $\phi = 1$.

Figure 7 [8] demonstrate the difference between Chalmers and CRECK [5],[6] and LLNL [9],[9],[11],[13] mechanisms and how exact they are in predicting the behavior of pure heptane when we compare them with experimental data. Figure 7 also illustrates the effect of different initial temperatures on ignition delay in a homogeneous reactor with constant pressure. As can be seen at higher temperatures, the CRECK and LLNL mechanisms have more accurate results and it is more compatible with experimental data than Chalmers mechanism, but in the lower temperatures both Chalmers and CRECK mechanisms predict the ignition behavior very well and the difference is trivial. CRECK mechanism predicts the ignition delay behavior very well, however, it is a detailed mechanism and its simulation needs excessive time to be performed. Chalmers mechanism gives a satisfactory result, however, it is not as accurate as CRECK mechanism. Chalmers mechanism can be used in similar cases and the results can be verified by comparing them with experimental data, Figure 7. Chalmers mechanisms for pure methane has been verified using experimental data. At different pressures it has been shown that the mechanisms give the accurate results which are close to experimental data [6] Figure 8.

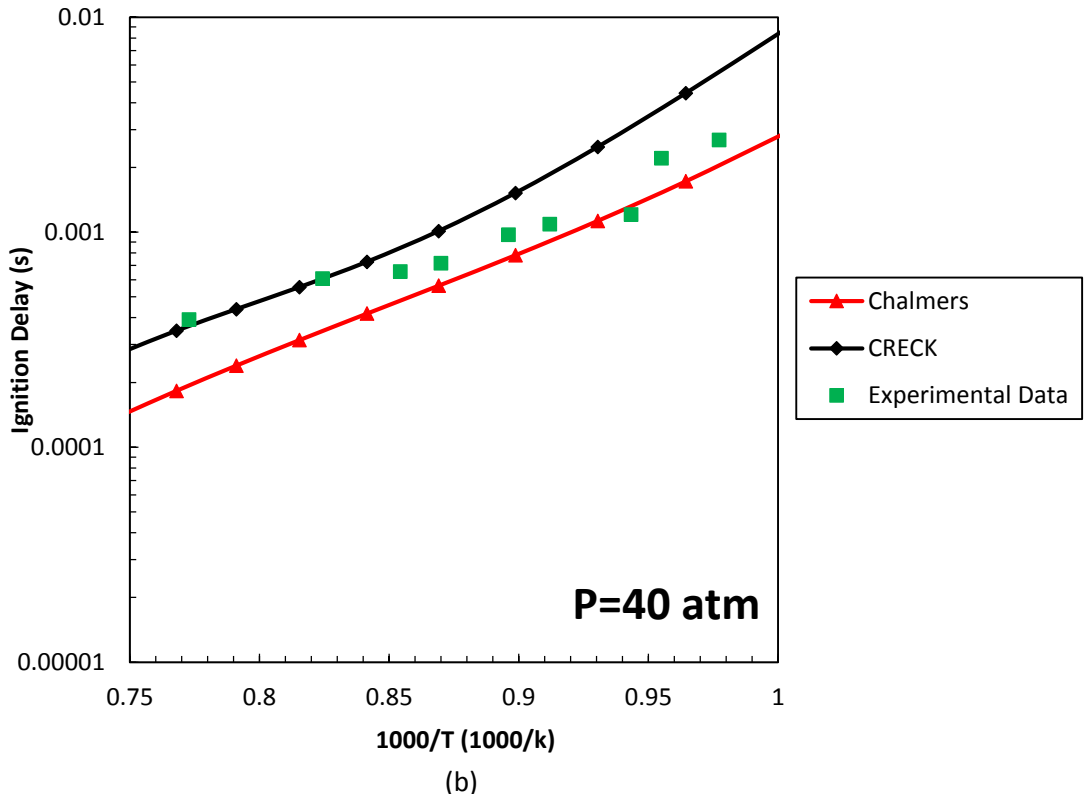
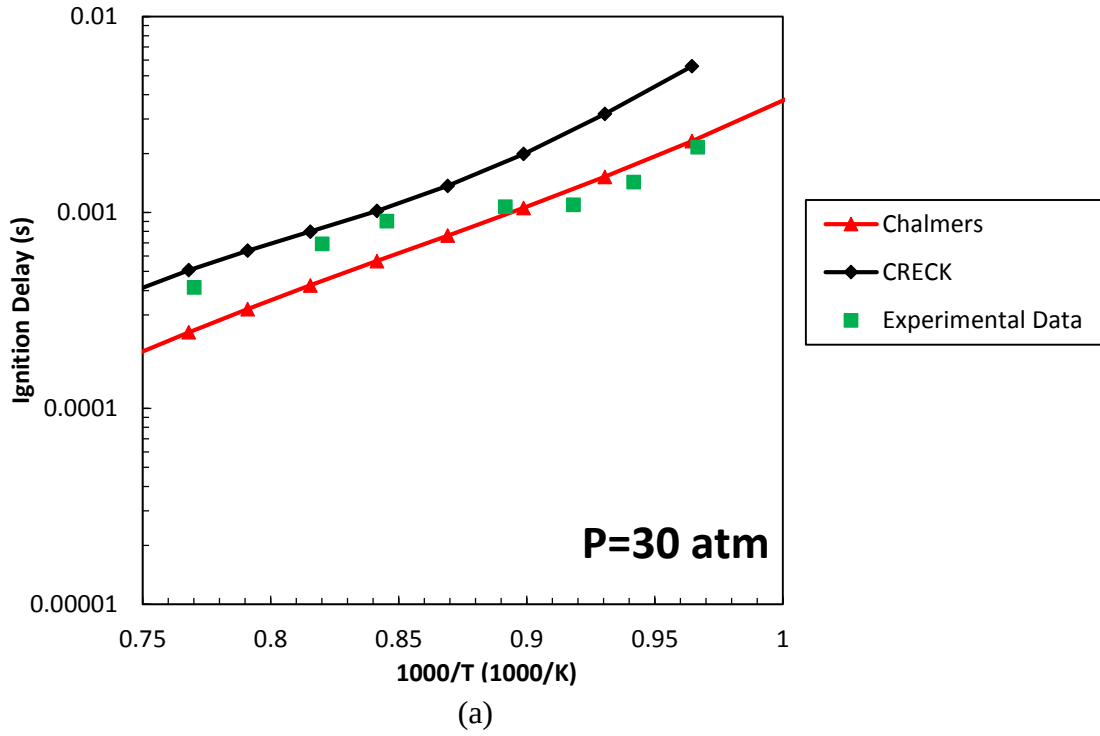


Figure 8 Comparison of ignition delay of CH_4 using Chalmers and CRECK mechanism with the experimental data [8] versus $1000/K$, 55 atm, $\phi=1$. 30 atm (a) and 40 atm (b).

At low temperatures, the Chalmers mechanism has better agreement with measurements, whereas at high temperatures the CRECK mechanism displays better compatibility.

Figure 9 illustrates the Ignition delay of methane using CRECK, Chalmers and LLNL mechanism at different equivalence ratios. The results have been compared with experimental data for temperature ranges from 1000 K to 1350 K. It has been shown that CRECK mechanism has good agreement with experiments at the given equivalence ratios. As the fuel goes richer all the mechanisms have better agreement with experiments. As can be seen LLNL mechanism shows a very similar behavior to CRECK mechanism.

In general, both CRECK and Chalmers mechanisms yield reasonable predictions for the ignition of methane-air mixtures at engine relevant conditions. Based on these validations, Chalmers and CRECK mechanisms are reliable and accurate enough to predict the ignition characteristics of methane in homogenous chamber reactor and diesel engine environments.

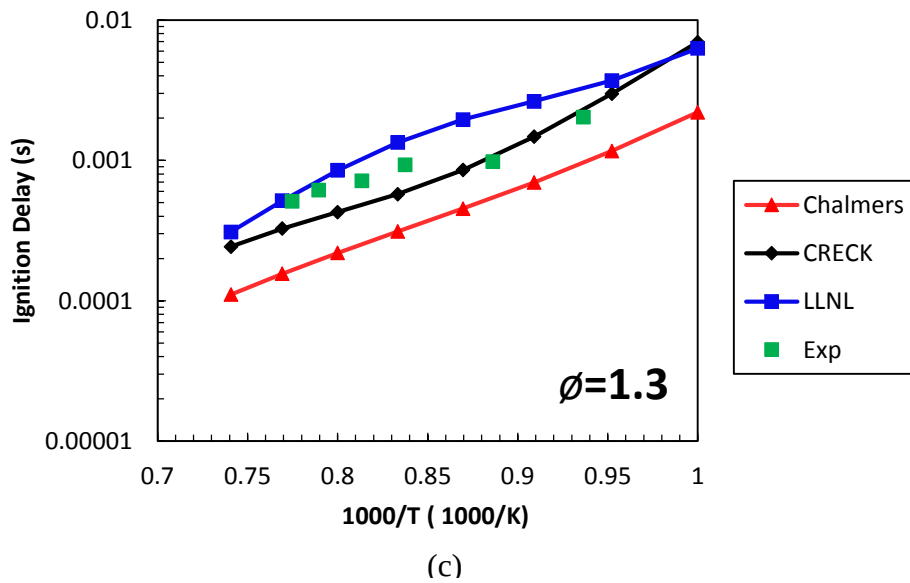
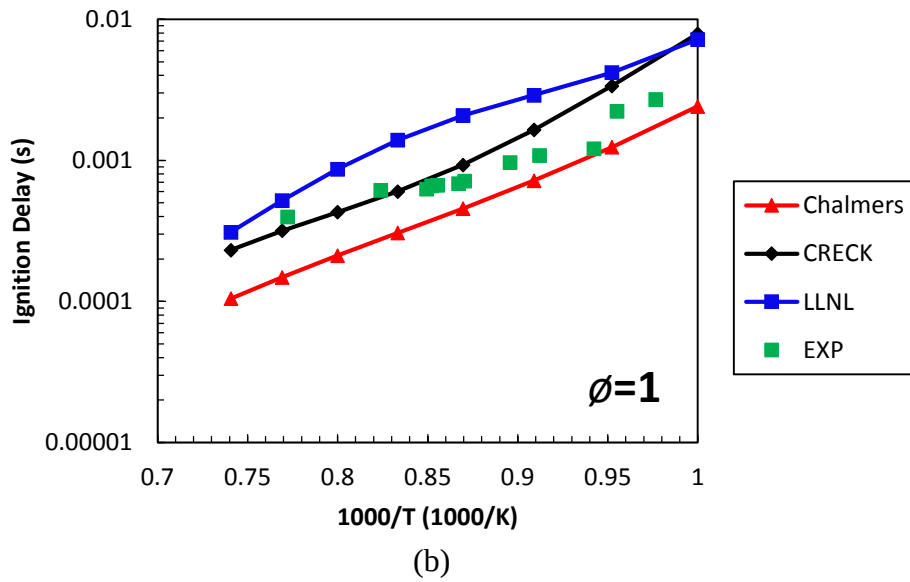
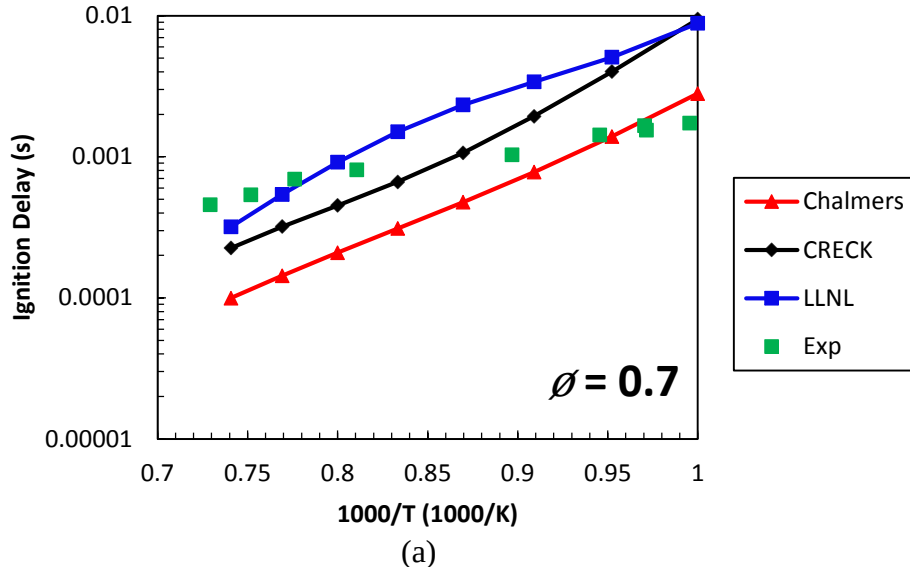


Figure 9 Comparison of ignition delay of CH_4 using Chalmers and CRECK and LLNL mechanisms with the experimental data [14] versus $1000/T$ at 40 atm, $\phi = 0.7$ (a), $\phi = 1$ (b) and $\phi = 1.3$ (c).

Chapter 3

Ignition Characteristics of homogenous systems

3.1 Terminology

Having validated the Chalmers and CRECK mechanism against the experimental data of ignition delay at different high pressures, results now focus on characterizing the ignition behavior of n-C₇H₁₆/CH₄ blends. In addition, a sensitivity study was performed to identify the dominant reactions associated with the ignition of these blends at engine relevant conditions.

Adding CH₄ to n-heptane have a direct relation with ignition delay when calculated with CRECK mechanism, adding methane results in higher ignition delay. With 70% n-heptane 30% methane by volume, the ignition delay is increased by 31.1 μ s. In fact with CRECK mechanism as methane is added to n-heptane, the ignition delay increases continuously.

Chalmers mechanism is unable to predict the ignition behavior of n-heptane/air mixture when methane is added. With given initial parameters (55 atm, $\phi = 1$), when methane is first added, the ignition delay decreases and then at 35% n-heptane – 65% CH₄ the ignition delay goes back to the same value it had without any methane being added. After 35% n-heptane – 65% CH₄, as methane is added the ignition delay increases until the point where ignition does not occur when we have 5% n-heptane – 95% CH₄.

Figure 10 shows the ignition delay versus temperature for five different composition of n-heptane and methane at 55 atm and $\phi = 1$. These five compositions have been chosen because they can present the behavior of blend fuel very well. For all of the cases with Chalmers mechanism in which the mole fraction of CH₄ in the fuel is less than 50% of the blended fuel, the effect of CH₄ appears to be small, especially at temperatures above 1000 K. For temperatures below 1000 K, the ignition delay for all five blends exhibit the NTC behavior.

“The phenomenon of Negative Temperature Coefficient (NTC) is an critical feature of the chemical kinetics of large hydrocarbons at low to intermediate temperature ranges, and is realistically relevant to the intrinsically low-temperature ignition processes governing engine knock, accidental explosions, and finally the recent development of the homogeneous charge compression ignition (HCCI) engines” [9]. NTC region declares for specified range of temperature as we decrease temperature, the ignition delay decreases too.

As we decrease the initial temperature, it is expected that the ignition delay will increase, but, the studies have shown for temperatures lower than 1000 K and higher than 750 K, the ignition delay decreases as the initial temperature goes lower. However, these ranges vary from mechanism to mechanism. For Chalmers mechanism this range starts from 800 K and it ends to 1050 K. As can be seen for pure methane, the NTC region does not appear and as the temperature is decreased the ignition delay increases continuously.

As can be seen in Figure 10, at a constant pressure, the effect of adding CH₄ is more significant in the NTC region. As methane is added, the ignition delay decreases slightly (10% - 50% CH₄) and then it starts to increase as we add more methane to blended fuel. Ignition delay increases dramatically for compositions with 65% or more CH₄, and the ignition behavior is increasingly influenced by the CH₄ oxidation chemistry. In order to examine this aspect further, the ignition delay times for blends with CH₄ content varying from 0 to 100% are plotted in Figure 10.

As the amount of CH₄ in the blend exceeds 65%, the ignition delay time for temperatures above 1050 K increases slower than for temperatures below 1050 K. Both CRECK and Chalmers mechanism predict the same result, but CRECK mechanism leads to more accurate results. Figure 10 shows the ability of the Chalmers mechanism to find the ignition data when CH₄ exceeds 90%.

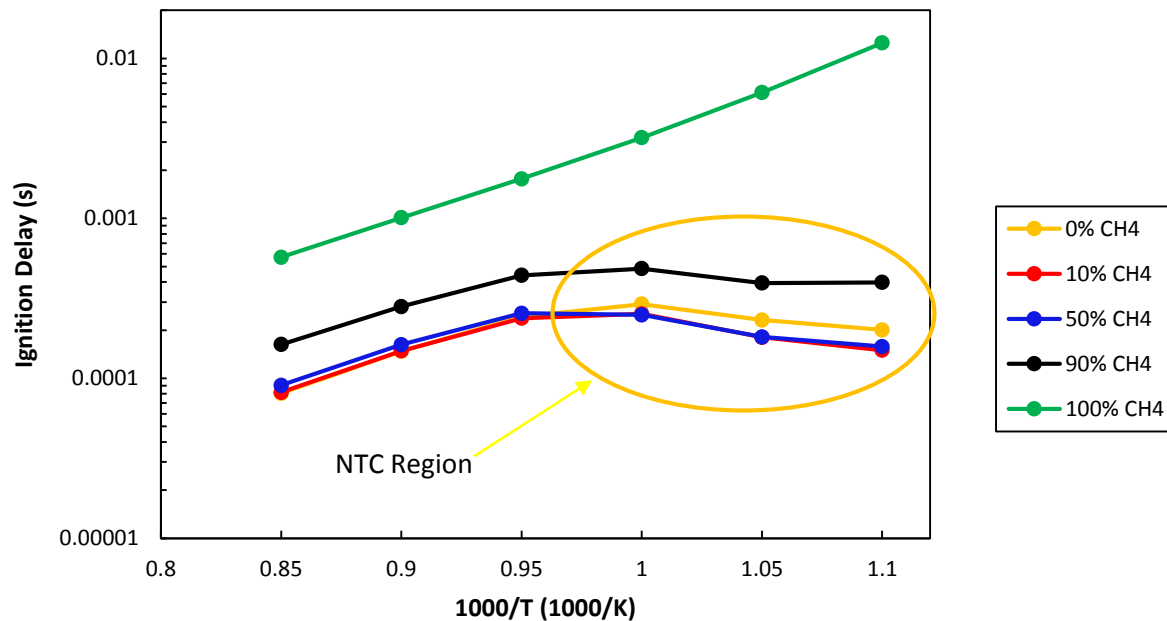


Figure 10 ignition Delay versus 1000/T, Chalmers mechanism, 55 atm, $\Phi=1$.

Finding the exact point: the Chalmers mechanism predicts different behavior for the composition. As can be seen when methane is added in pure heptane at first it decreases the

ignition delay. After adding more methane, however, it reaches to the point that its ignition delay is equal to ignition delay of pure methane. Then as the mole fraction of methane is increased, it keeps increasing more and more. as can be seen from Figure 10 the point that they are almost equal to each other is between 30-40% CH₄ by volume fraction in whole fuel.

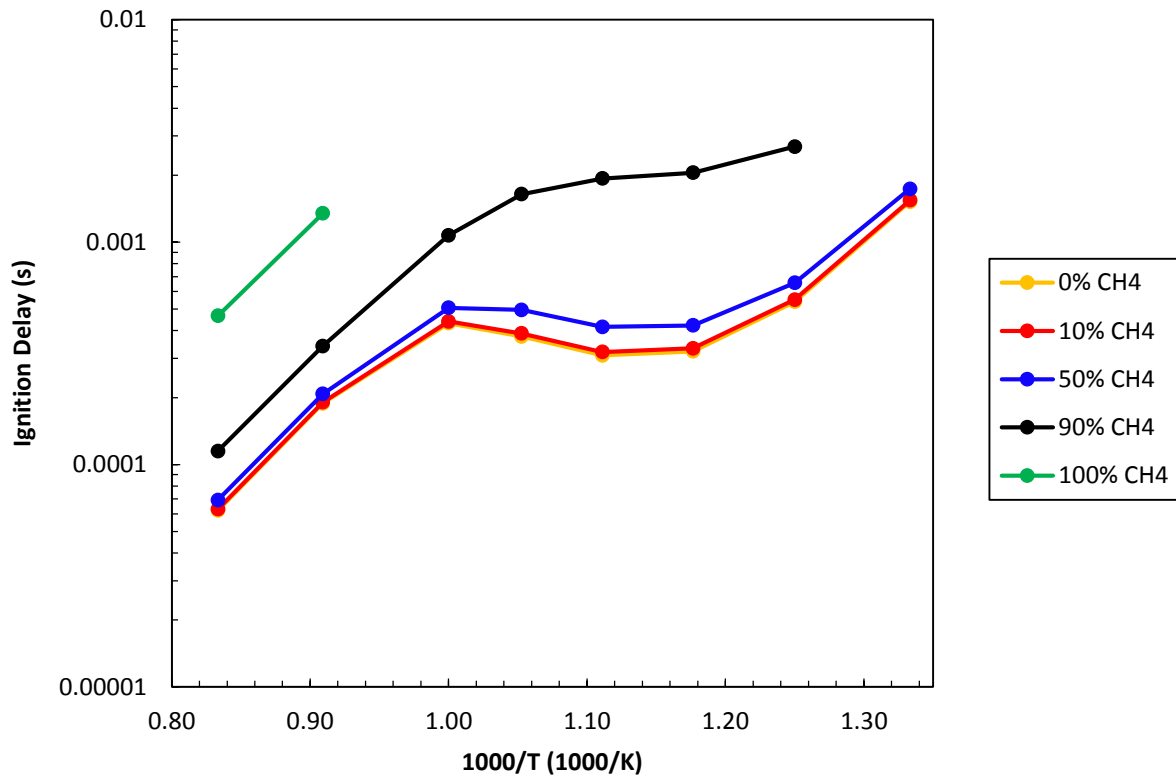


Figure 11 Ignition Delay versus 1000/T, CRECK Mechanism, 55 atm, $\Phi=1$.

As can be seen in Figure 11, at a constant temperature, as we add methane in the composition, the ignition delay increases continuously. The ignition delay increases slightly when methane is added at no more than 50% in the composition. The NTC region for CRECK mechanism starts from 850 K and it disappears as we hit 1000 K. Figure 11 illustrates that pure methane can only ignite when the temperature is above 1100 K. The results just discussed show that the inlet temperature of the fuel-air mixture is a potential tuning parameter for ignition. However, relatively high inlet temperatures are often required for proper timing.

Figure 11 shows the effect of NTC region of n-heptane and methane on ignition delay. When the temperature is decreased, it is expected that the ignition delay will increase because the reactants will need more time to react with each other, but for temperatures between 750 K and 1000 K the ignition delay decreases as the temperature drops, Figure 11. Since with

Chalmers mechanism the NTC region occurs in the range of 800 K and 1050 K, the ignition delay for temperature 800 K is less than 1000 K. As more methane is added, ignition delay of 1000 K goes below 800 K, i.e. as methane is added more than 60% by volume fraction, the NTC effect disappears.

The range of NTC region for CRECK mechanism is between 860 K-1000 K, thus the difference between ignition delay of 1200 K and 1000 K is tremendously higher than the difference between 1000 K and 800 K. The ignition delays for 800 K and 1000 K are very close together, due to occurrence of NTC between 860 K and 1000 K.

As can be seen in Figure 12, with Chalmers mechanism, as methane is added to the composition the ignition delay decreases at first and then it increases whereas, both CRECK and LLNL mechanisms have shown the ignition delay grows as methane is added. However for higher temperatures such as 1200 K, all three mechanisms have shown the ignition delay rises as more methane is supplemented. Figure 12 shows the ignition behavior of different compositions of n-heptane and methane over three different initial temperature calculated with LLNL, CRECK, Chalmers mechanisms at pressure of 55 atm and $\phi = 1$.

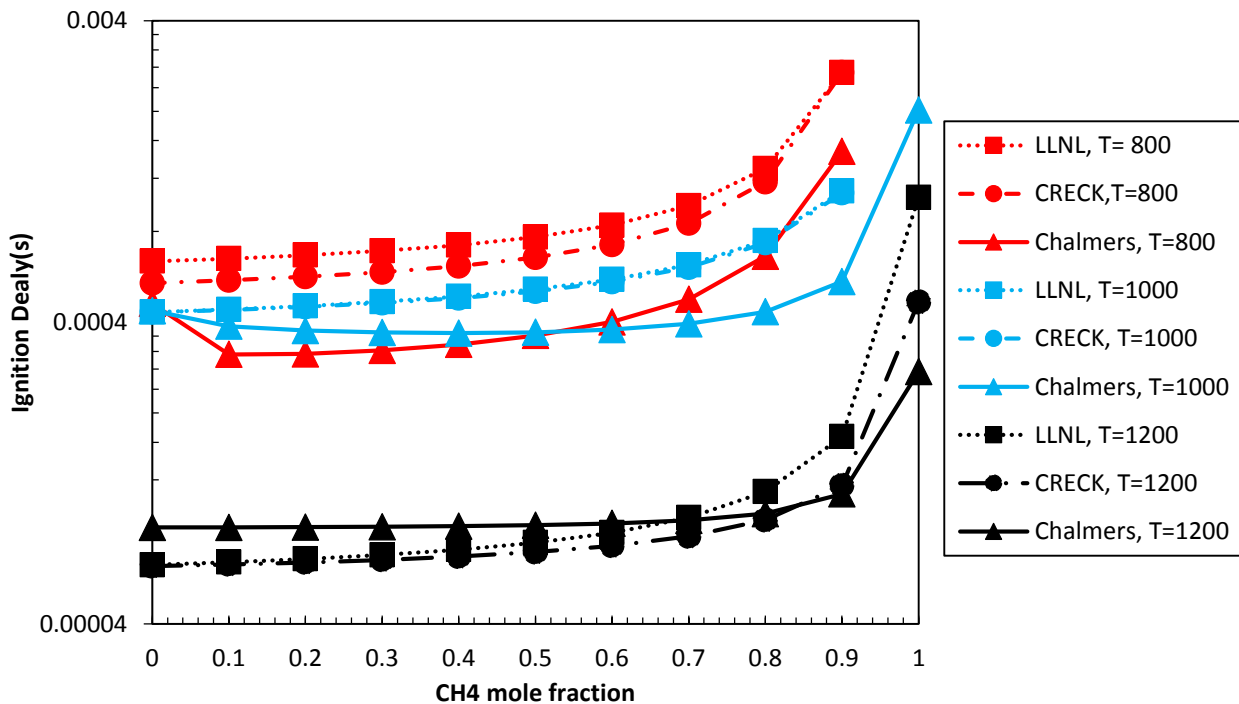


Figure 12 Comparison of ignition delay versus CH₄ mole fraction between CRECK and LLNL and Chalmers mechanisms, 55 atm, $\Phi=1$.

Adding methane to n-heptane could have several pleasant influence on ignition delay, NO_x formation, soot formation, etc. As can be seen in Figure 7, the CRECK mechanism has good agreement with experimental data. As it is expected, as the temperature decreases, the

ignition delay increases until temperature of 970-80 K. After 970-80 K as the temperature goes lower the ignition delay decreases due to NTC region. The more we decrease the temperature the ignition delay decreases until 860 K.

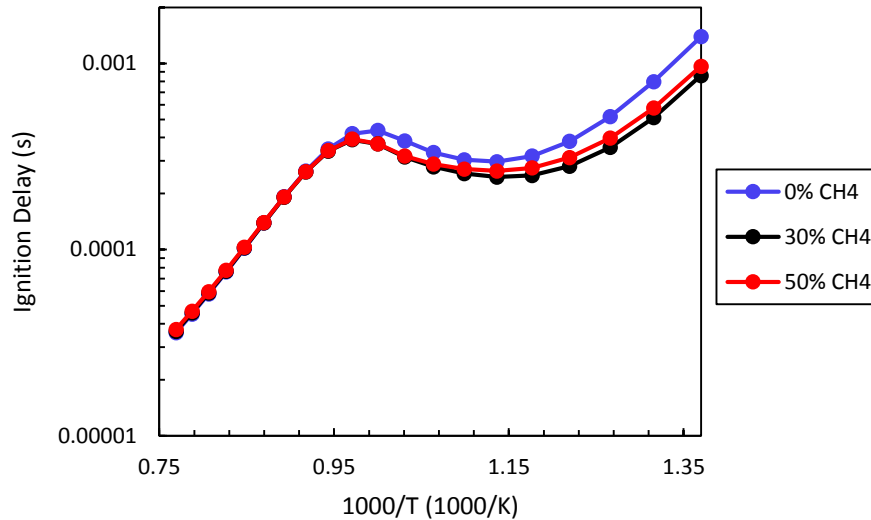


Figure 13 Effect of methane on ignition delay with three different compositions of n-heptane/methane, Chalmers Mechanism, 55 atm, $\Phi=1$, 0% CH₄, 30% CH₄, 50% CH₄.

Figure 13 shows the ignition delay of three different compositions for a wide range of temperatures in more detail. As it can be seen the ignition delay of 50% CH₄ is always higher than 30% CH₄. In addition the ignition delay of 30% CH₄ and 50% CH₄ is lower than 0% CH₄ for all the given initial temperatures.

Different equivalence ratios can have different ignition delays, as can be seen in Figure 14 as the fuel becomes richer the ignition delay decreases. Since CRECK mechanism is not able to predict the ignition delay for compositions with more than 90% CH₄ in low temperatures, at a given time we can't predict the behavior of fuel when CH₄ exceeds 90% mole fraction in blend fuel.

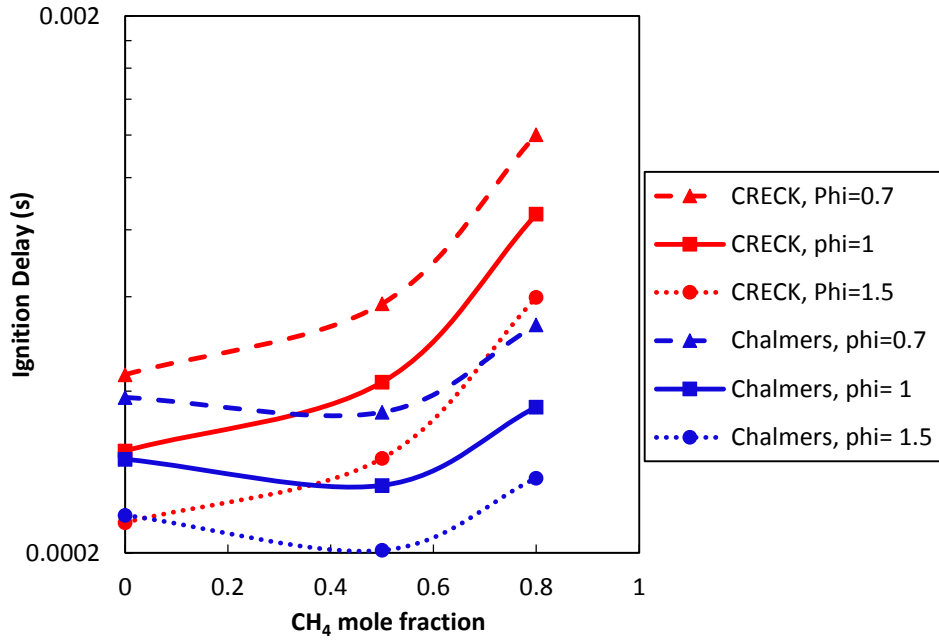


Figure 14 Effect of equivalence ratio on ignition delay using CRECK and Chalmers mechanism. T=900K, 55 atm.

3.2 Sensitivity

The below table are the important reaction which have been excluded from sensivity analysis.

Reaction	Reaction description
R5339	$\text{HO}_2 + \text{NC}_7\text{H}_{16} \Rightarrow \text{H}_2\text{O}_2 + \text{NC}_7\text{H}_{15}$
R5337	$\text{OH} + \text{NC}_7\text{H}_{16} \Rightarrow \text{H}_2\text{O} + \text{NC}_7\text{H}_{15}$
R5334	$\text{O}_2 + \text{NC}_7\text{H}_{16} \Rightarrow \text{HO}_2 + \text{NC}_7\text{H}_{15}$
R2795	$\text{OH} + \text{CH}_4 \Rightarrow \text{H}_2\text{O} + \text{CH}_3$
R2017	$\text{NC}_7\text{-OQOOH} \Rightarrow \text{OH} + \text{CH}_3\text{CHO} + .84\text{C}_2\text{H}_4\text{CHO} + .16\text{CH}_3\text{COCH}_2 + .1666667\text{NC}_5\text{H}_{10} + .1666667\text{NC}_7\text{H}_{14}$
R2015	$\text{NC}_7\text{-OOQOOH} \Rightarrow \text{NC}_7\text{-OQOOH} + \text{OH}$
R2014	$\text{NC}_7\text{-OOQOOH} \Rightarrow \text{NC}_7\text{-QOOH} + \text{O}_2$
R2013	$\text{NC}_7\text{-QOOH} + \text{O}_2 \Rightarrow \text{NC}_7\text{-OOQOOH}$
R2012	$\text{NC}_7\text{-QOOH} \Rightarrow \text{OH} + \text{C}_2\text{H}_5\text{CHO} + .9\text{C}_3\text{H}_6 + .25\text{C}_2\text{H}_4 + .2\text{NC}_4\text{H}_8$
R2009	$\text{NC}_7\text{-QOOH} \Rightarrow \text{HO}_2 + \text{NC}_7\text{H}_{14}$
R2008	$\text{NC}_7\text{-QOOH} \Rightarrow \text{NC}_7\text{H}_{14}\text{O} + \text{OH}$
R2006	$\text{NC}_7\text{H}_{15}\text{-OO} \Rightarrow \text{NC}_7\text{-QOOH}$
R2005	$\text{NC}_7\text{H}_{15}\text{-OO} \Rightarrow \text{NC}_7\text{H}_{15} + \text{O}_2$

R2004	$O_2 + NC_7H_{15} \Rightarrow NC_7H_{15}-OO$
R1797	$O_2 + HCO \Rightarrow HCO_3$
R1366	$O_2 + NC_7H_{15} \Rightarrow NC_7H_{14} + HO_2$
R383	$HO_2 + CH_2O \Rightarrow H_2O_2 + HCO$
R259	$HO_2 + CH_2CHCH_2 \Rightarrow OH + CH_2O + C_2H_3$
R256	$HO_2 + CH_3 = CH_2O + OH$
R17	$O_2 + HCO = HO_2 + CO$
R14	$OH + OH (+M) = H_2O_2 (+M)$
R13	$HO_2 + HO_2 = H_2O_2 + O_2$
R5	$OH + HO_2 = H_2O + O_2$

Results have showed the combustion process is initiated by the production of alkyl radical (NC_7H_{16}) with reaction R 5334.



Then NC_7H_{15} goes on two different path with R 1366 and R 2004. Temperature defines which path is dominant.



Figure 15 shows the rate of production of NC_7H_{15} versus time based on two different reaction at $T=850\ K$. as can be seen with respect to time the reaction R 2004 consumes more of NC_7H_{15} and as a result produces more alkyl peroxy radicals ($NC_7H_{15}-OO$), consequently R 2004 is more dominant than R 1366 which produces NC_7H_{14} . So the following set of reaction are more likely to happen within the reactor.

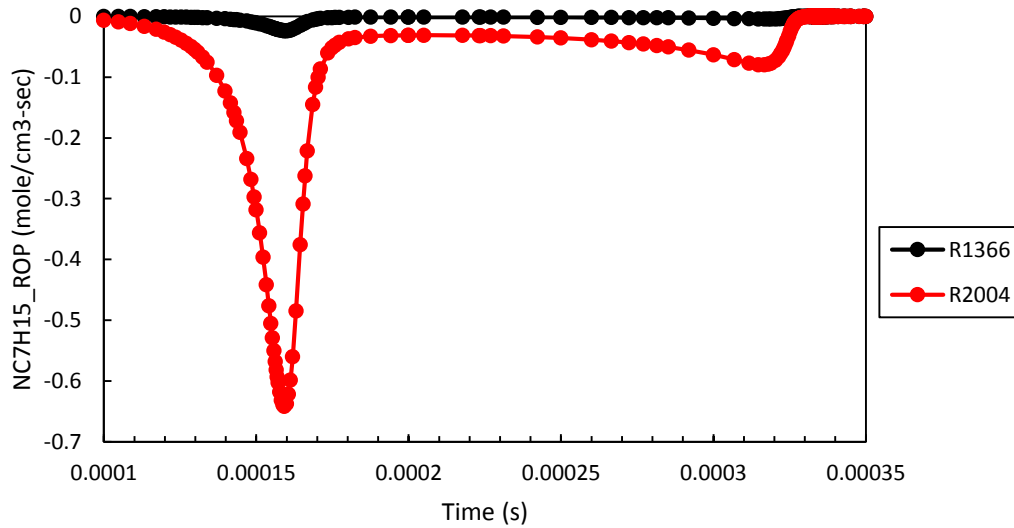


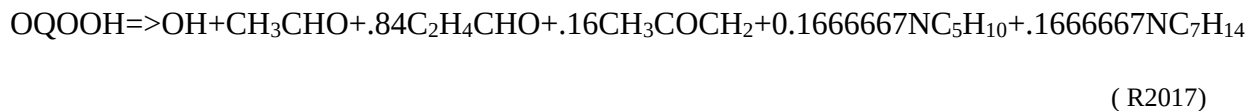
Figure 15 NC₇H₁₅ Rate of production versus time, T=850 K, 55 atm. Φ=1.



And the reverse side of this which produces NC₇-QOOH plays an important role in the direction of combustion; R 2014:



NC₇-



As we can see reaction R 2004 produces alkylperoxy radical (NC₇H₁₅OO) and then because it needs to be able to react faster and easier it isomerizes through reaction R2006 and produces alkylhydroperoxy radical (...-QOOH) which is able to react with oxygen and produces peroxyalkylhydroperoxy radical (...-OOQOOH) through R 2013, Sensivity analysis has shown the reverse of reaction R 2013 and R 2014 has an enormous effect on the reaction path. It consumes NC₇-OOQOOH and produces NC₇-QOOH and O₂. R 2013 decreases ignition delay but R 2014 is very sensitive and has a huge effect on ignition delay.

After NC7-OOQOOH is produced there is a competition between R 2014 and R 2015 as we can see in Figure 16, Reaction R 2014 is dominant and decomposition of peroxyalkylhydroperoxy radical cannot compete with that. Decomposition does, but not comparable to R 2014.

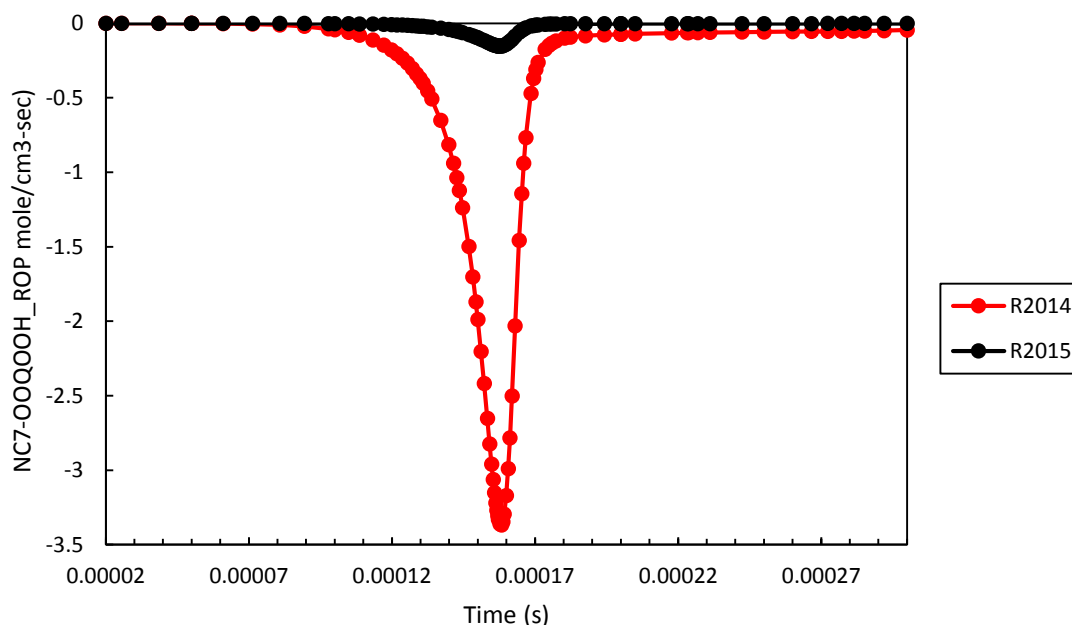


Figure 16 NC7-OOQOOH Rate of production versus time, T=850 K, 55 atm. $\Phi=1$.

R 2015 is a reaction in which peroxyalkylhydroperoxy radical decomposes to ketohydroperoxide and OH which is followed by more decomposition to ketone radical and aldehyde radical and hydroxide and ethanol and heptane and pentene. As it decomposes more and more, the amount of hydroxyl radical (OH) in the reactor increases; thus, reaction R 5337 more easily takes place because there is sufficient OH in there.

The reaction path diagram for this chain branching cycle is drawn in Figure 17. In Figure 18 sensitivity of three different composition of n-heptane and methane has been discussed and compared.

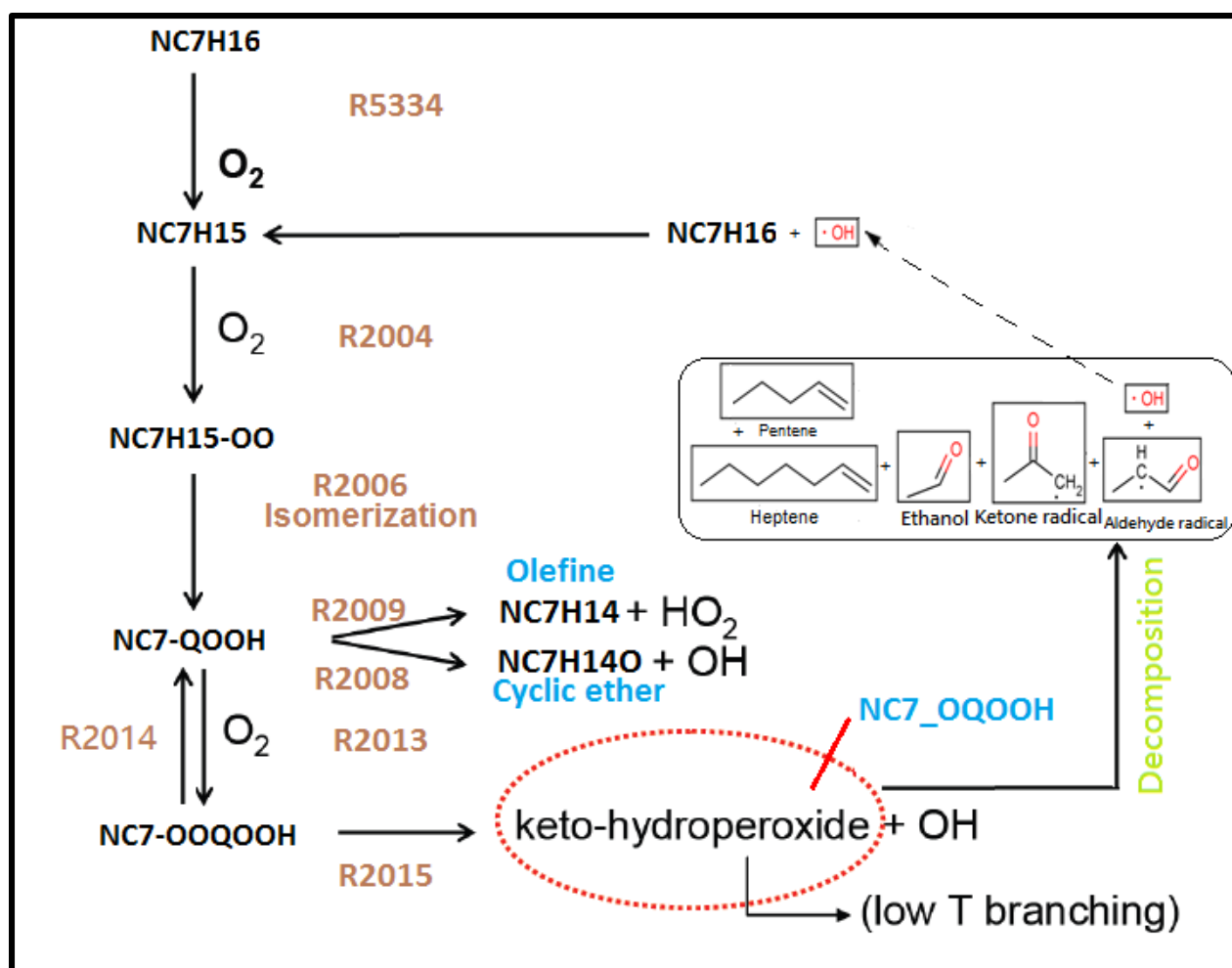


Figure 17 Reaction path diagram of pure heptane.

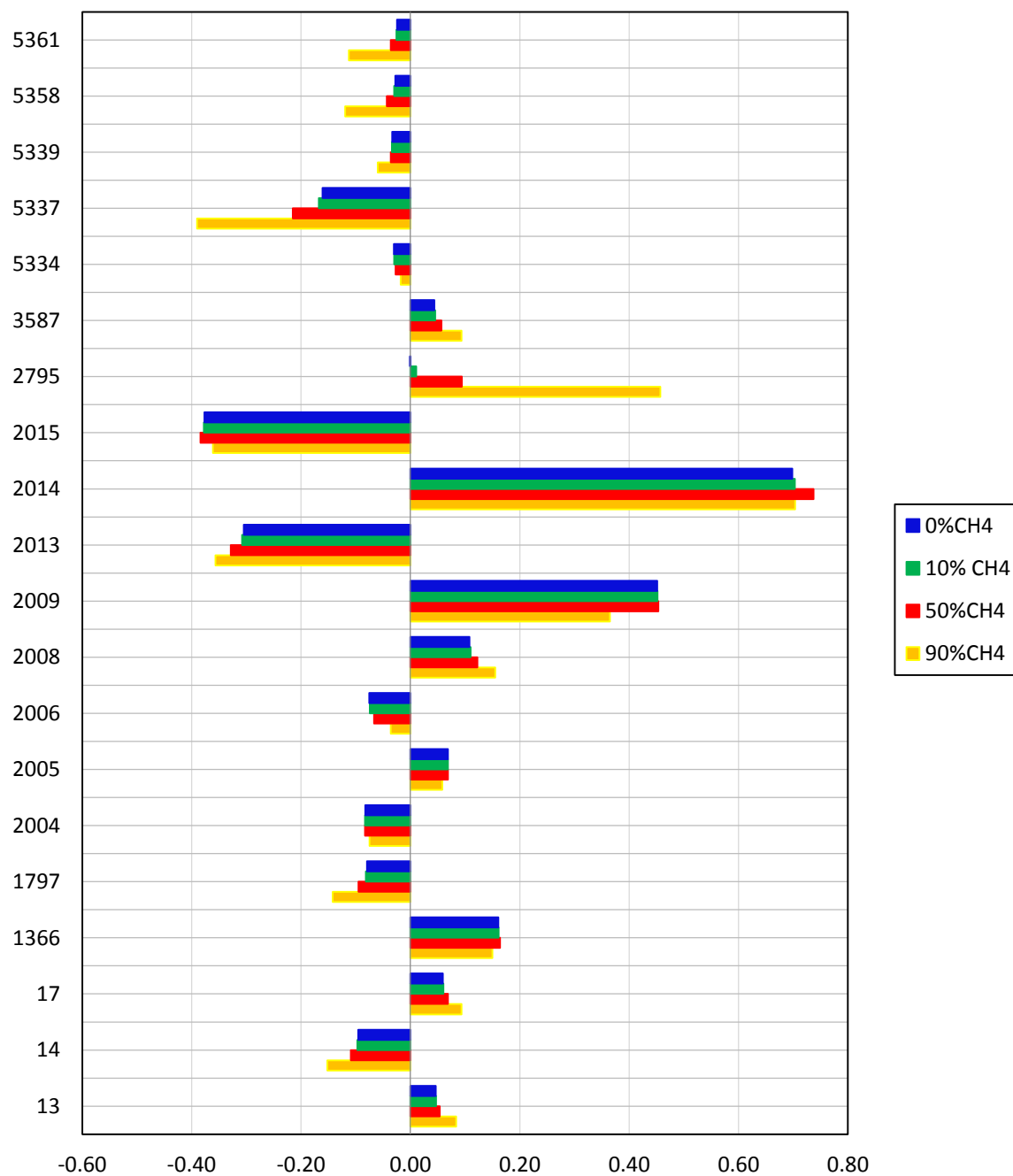


Figure 18 Normalized Sensivity Coefficient for 4 different compositions of n-heptane and methane by CRECK mechanism, 55 atm, T= 850 K, $\Phi=1$. 100% n-heptane- 0% CH₄, 90% n-heptane- 10% CH₄, 50% n-heptane- 50% CH₄ and 10% n-heptane- 90% CH₄.

3.3 Initial Temperature:

Different mechanisms have different prediction of ignition behavior, the purpose of this section is to find the lowest temperature at which ignition occurs for given initial conditions. Table 3 illustrates the minimum temperature needed for start of ignition for different n-heptane-methane composition when the limiting time is 4 msec.

Table 3 Minimum temperature of ignition for different mechanism at a given time of 4 msec.

Limiting time : 4 msec				
CH4	C7H16	CRECK	Chalmers	LLNL(detailed)
0	1	715	685.213	701
0.1	0.9	715	667.1679	702
0.2	0.8	716	667.6692	702
0.3	0.7	717	668.6717	703
0.4	0.6	717	670.1754	704
0.5	0.5	718	672.1805	705
0.6	0.4	721	675.6892	707
0.7	0.3	724	682.2055	710
0.8	0.2	732	698.2456	717
0.9	0.1	765	744.8622	750

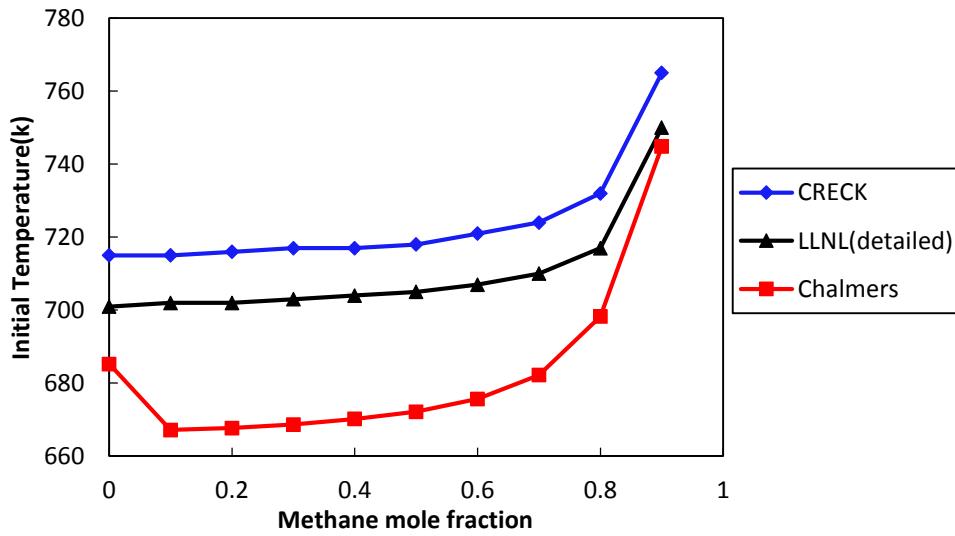


Figure 19 Minimum temperature for ignition computed using LLNL, CRECK, Chalmers mechanism. Given time 4 msec, 55 atm, $\Phi=1$.

Figure 19 shows the lowest initial temperature at which the ignition can occur, with given initial parameters including end point time: 4 msec, pressure: 55 atm, $\phi = 1$. As can be seen the CRECK mechanism predicts highest minimum initial temperatures, whereas with Chalmers mechanism the ignition can occur at lower temperatures.

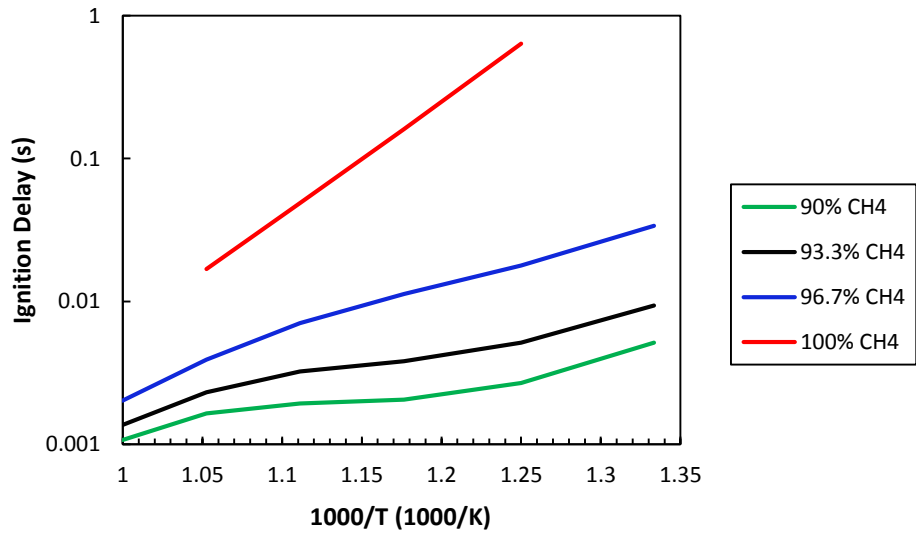


Figure 20 Ignition delay of n-heptane/methane mixtures at 55 atm and $\Phi=1$. Methane mole fraction varies from 90% to 100%

Figure 20 shows the ignition delay for higher amount of methane in the composition with end time of 1 sec. As can be seen the mixture of methane/n-heptane air mixture will finally ignite, it's just the matter of time. Since methane/n-heptane blend ignites at higher temperature, Figure 20 has been drawn for temperature below 1000 K.

NO_x formation has been one of the main problems that plays an important role in the pollution engine cause. As the result shows adding CH_4 to n-heptane/air mixture decreases the amount of NO_x formation, even a change of 1 milligram could cause much less pollution given a long usage time. Also, if we calculate and sum the amount of the reduction in every vehicle with diesel engine in them, it would have significant role on the air.

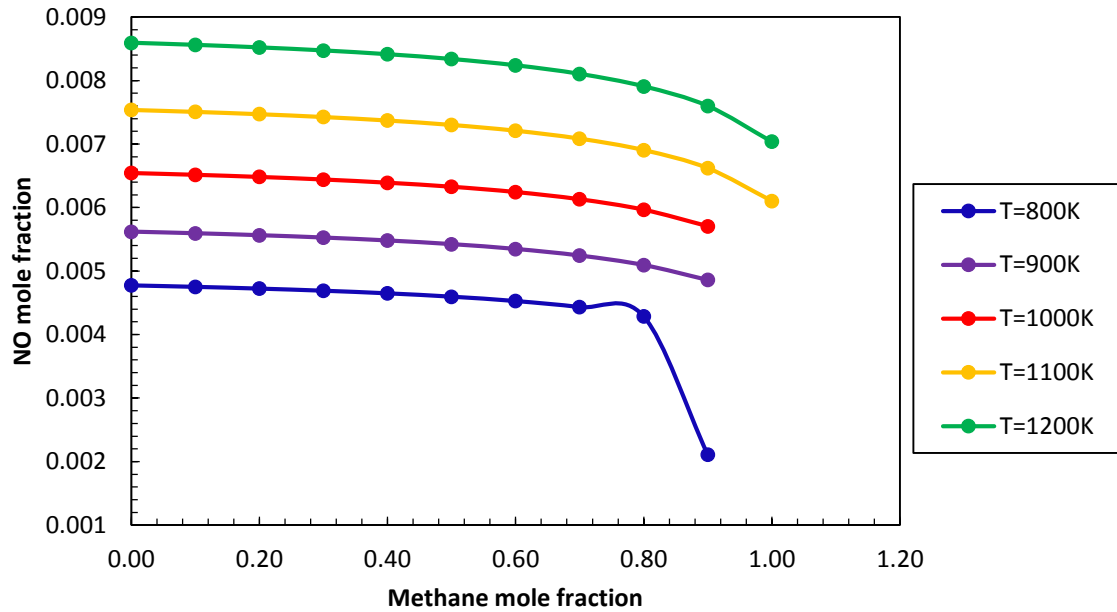


Figure 21 Computed NO mole fraction at EVO as a function of methane mole fraction for various initial temperatures by CRECK mechanism, 55 atm, $\Phi=1$.

As can be seen in Figure 21, as the mole fraction of CH_4 in the fuel increases the amount of NO_x in the cylinder decreases, thus less air pollution. Also, it is obvious that NO_x formation has a direct relation with temperature, i.e. as the temperature goes higher the NO_x forms more and more. Both CRECK and modified Chalmers mechanisms are able to predict the NO_x formation in the cylinder, however, as we go further to NTC region (the temperature around 900- 1000 K) these two mechanisms show more similar results with each other.

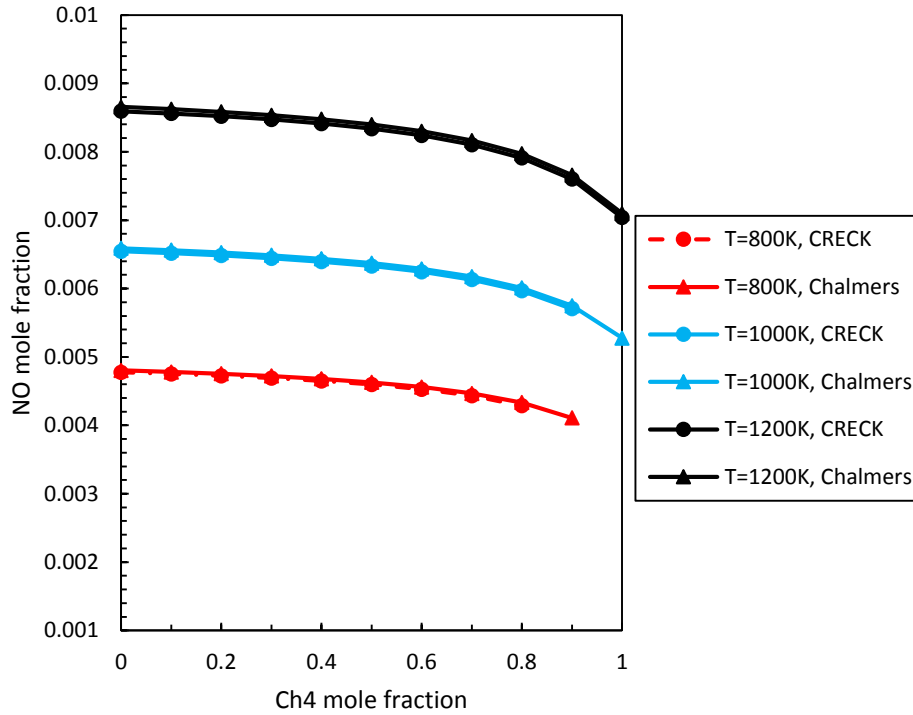


Figure 22 Comparison of NO formation using CRECK and Chalmers mechanism at three initial temperatures for various n-heptane/methane blend compositions at 55 atm, $\Phi=1$.

As can be seen in Figure 22 both CRECK and Chalmers mechanisms have good agreement in predicting the NO_x formation of methane/n-heptane air mixture. As can be seen at higher temperatures the NO_x formation is more dependent on change in methane/n-heptane blend composition. Creck mechanism is unable to predict the ignition behavior of higher percentage of methane in n-heptane composition at lower temperatures.

There are some species which have significant role in soot formation such as: Pyrenes, $\text{C}_{16}\text{H}_{10}$, C_6H_6 and etc. Figure 23 shows that by adding CH_4 to n-heptane/air mixture, soot formation decreases dramatically. As can be seen with higher initial temperature the PAH formation decreases tremendously as more methane is added to n-heptane/air mixture. With initial temperature to be 800 K, the PAH formation is the lowest compared to other cases with higher initial temperatures.

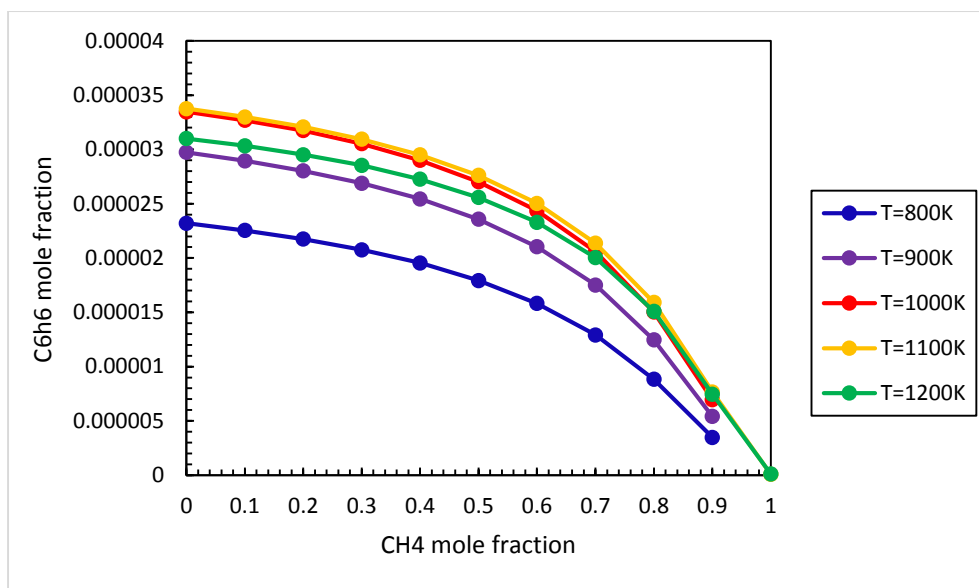


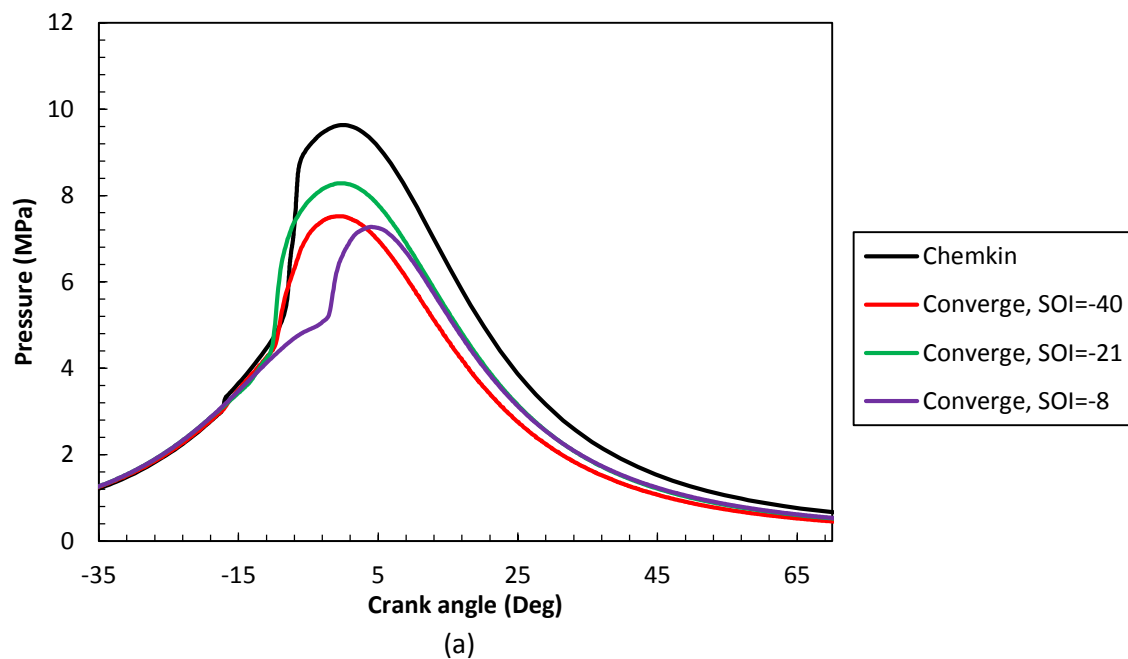
Figure 23 Peak C₆H₆ mole fraction as a function of CH₄ mole fraction for different initial temperature and CH₄ mole fraction computed using CRECK mechanism at 55 atm, $\Phi=1$.

Chapter 4

HCCI and Ignition Stages

4.1 Comparison of Chemkin and Converge Results

Engine simulator reactor of Chemkin: Chemkin is capable of analyzing the HCCI engine, although it is not as powerful as other programs such as KIVA, Converge, but it still can predict the general trend and is able to give the approximate result.



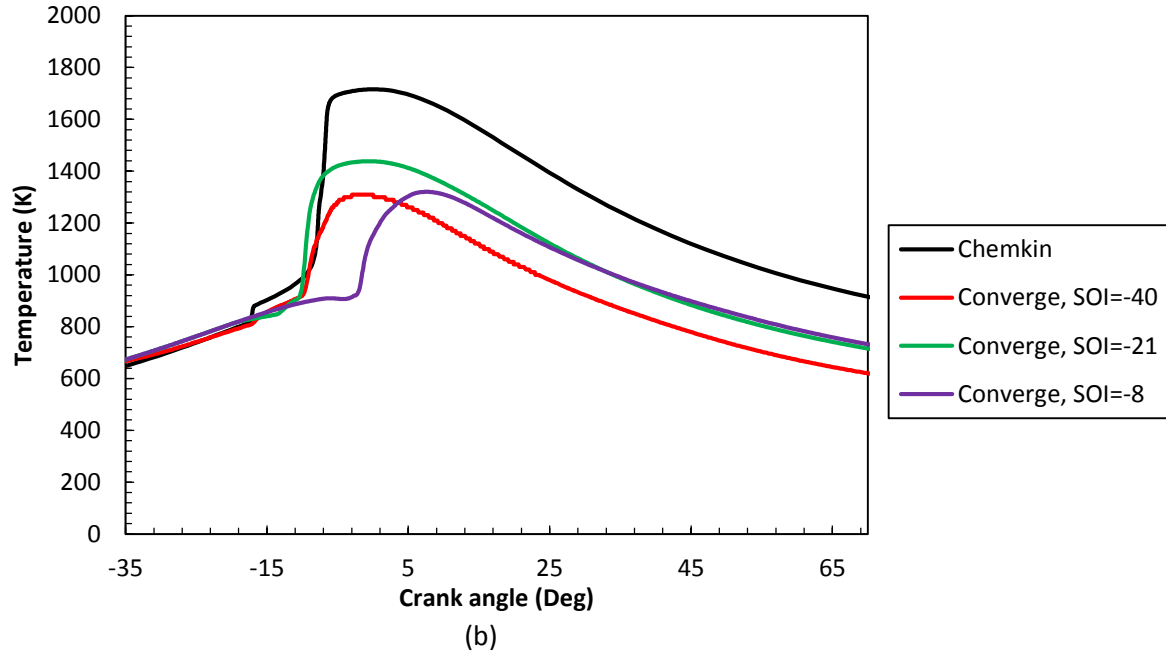


Figure 24 Pressure (a) and Temperature (b) profiles using chemkin and Converge.

Figure 24 depicts the in-cylinder pressure and temperature during the first and second stages of ignition. The mechanism used in Chemkin is Creck, and Converge simulations have been done with Chalmers mechanism. As can be seen when fuel injects at -21 ATDC, the pressure and temperature profiles are much more similar to Chemkin prediction. When fuel injects sooner, it will have more time to be evaporated and mixed with air, thus the temperature and pressure is higher than when fuel is injected later. On the other hand when fuel is injected it has more time to access to crevice spots. Because of this phenomena, when fuel injects at -40 ATDC, temperature and pressure profiles are below the one with start of injection of -21 ATDC.

4.2 Ignition Stages:

Table 4: Engine parameters

Parameter	Setting
Compression Ratio	17.4
Cylinder clearance volume	28.4 cm ³
Engine speed	1500 rpm
Connecting Rod to crank radius ratio	3.216
Cylinder bore diameter	82 cm
Initial temperature	940 K
Initial pressure	47 atm
Start of Injection	-8 ATDC

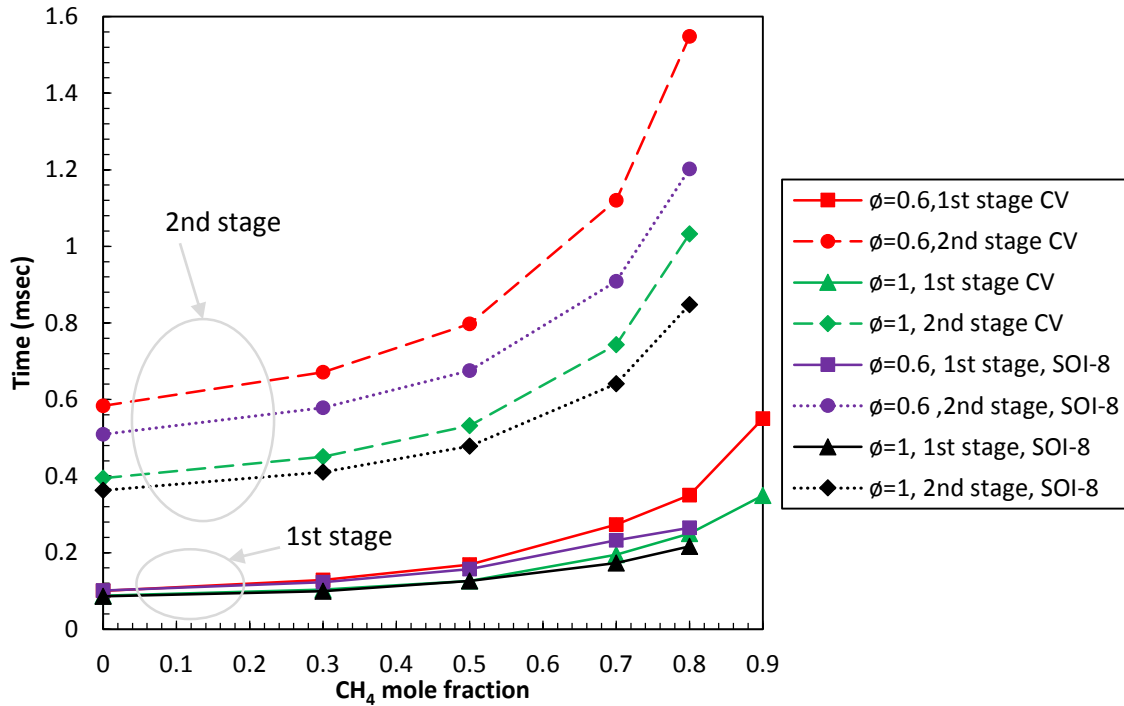
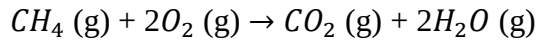


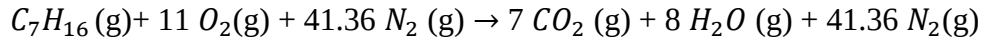
Figure 25 simulation of 1st and 2nd stage ignition delay using constant volume reactor and engine simulator with conditions from Table 4.

Figure 25 compares the ignition stages of a closed homogenous reactor with constant volume and HCCI for two different equivalence ratios, a rich mixture and the other one stoichiometric. Results of 1st stages and 2nd stages with different ϕ for closed homogeneous reactor with constant volume and HCCI engine have a very good compatibility with each other. As can be seen the 2nd stage of constant volume for $\phi = 0.6$, is higher than all other cases. As the fuel becomes leaner the ignition delay decreases both in HCCI engine and constant volume chamber. This happens because as we add methane to the composition the mole fraction of

oxygen decreases. One of the main reasons for this difference is the lack of oxygen in the chamber as CH₄ is added in there. Since each mole of CH₄ needs two mole of oxygen to react with



And each mole of n-heptane needs 11 mole of oxygen to react with



Since the equivalence ratio is a function of both n-heptane and methane, as we add more methane in the chamber, at a constant equivalence ratio, less amount of oxygen will be presented in the chamber, thus the reactions that need oxygen will be less likely to take place. The reactions that lead to an increase in the ignition delay require oxygen.

As can be seen, when the volume is constant ignition delay is always higher than ignition delay in HCCI engine. It happens because firstly, in an engine near top dead center (TDC), the volume changes slightly, whereas in this comparison it has been compared with a constant volume chamber. Since the volume from start of injection until TDC, decreases, pressure increases based on the ideal gas equation and when pressure increases the ignition delay decreases.

As methane is added the 1st stage ignition delay increases sluggishly whereas the 2nd stages rises tremendously. As can be seen the difference between 1st stage and 2nd stage increases as more methane is added to the chamber. The results are shown for compositions up to 80% CH₄, because simulation cannot be done for compositions with more than 80% CH₄ at $\phi = 0.6$.

4.3 Species production/consumption:

Table 5 Engine Parameter.

Parameter	Setting
Compression Ratio	17.4
Cylinder clearance volume	28.4 cm ³
Engine speed	1500 rpm
Connecting Rod to crank radius ratio	3.216
Cylinder bore diameter	82 cm
Initial temperature	940 K
Initial pressure	47 atm
Start of Injection	-116 ATDC

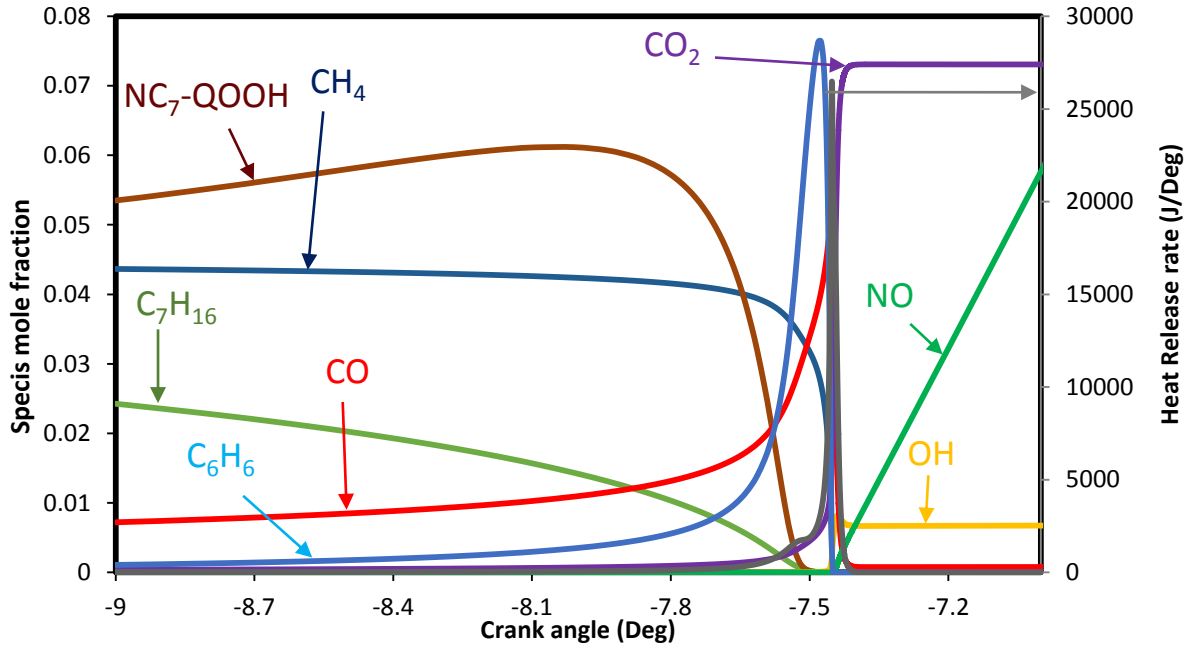


Figure 26 Species mole fraction profile during ignition stages for $\phi = 0.6$ at configuration of Table 5.

Figure 26 shows how important species are consumed or produced. As can be seen n-heptane is being consumed in 1st stage ignition delay, NC₇-QOOH is the main species that is being produced when n=heptane is dissociated. It starts producing in the 1st stage and consuming in 2nd stage ignition delay. Methane remains almost constant in 1st stage ignition delay and starts consuming as 2nd stage is initiated. Benzene starts forming shortly before 2nd stage ignition delay and it stops producing right after 2nd stage ends. CO₂ is being produced with 2nd stage and it remains in the cylinder until the exhaust gas goes out. As can be seen,

the temperature increases as the 2nd stage ignition delay happens. The heat release rate has a close relation with temperature. “Crevice zone is the main source of the HC emission, while the CO emission is mainly from the boundary layer” [35].

Figure 27 shows the temperature profile during 1st stage and 2nd stage ignition delay. As can be seen in the 1st stage of ignition delay there is not that much difference for different composition of n-heptane and methane. For 2nd stage ignition delay the difference between different compositions are vastly different. As more methane is added to the composition the 2nd stage of ignition delay postpones. The final temperature for all five compositions are same, i.e. adding methane to n-heptane does not affect the final temperature.

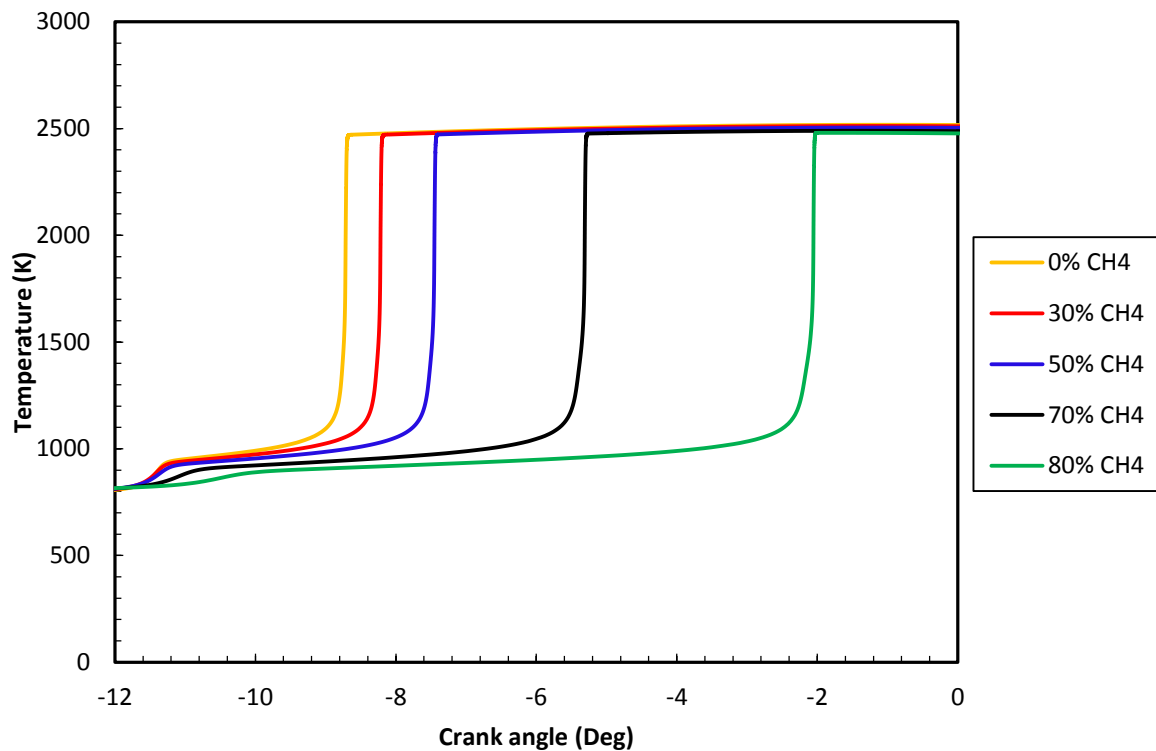


Figure 27 Temperature profile of HCCI engine for 5 different compositions of n-heptane/methane at $\phi = 0.6$ with initial configuration from Table 5.

4.4 Break Mean Effective Pressure (BMEP):

Break Mean Effective Pressure (BMEP) can be a valuable way to measure the engine output performance. Figure 28 shows the BMEP difference for different compositions at different equivalence ratios, stoichiometric, 0.8 and 0.6. As can be seen the BMEP decreases as the fuel becomes leaner. As we add methane to the compositions, BMEP decreases slightly.

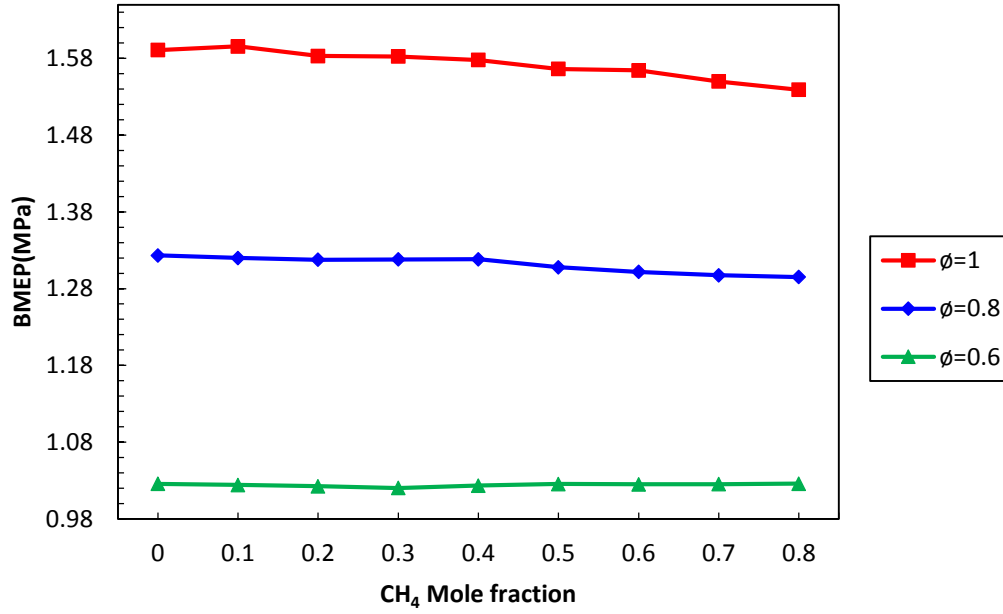


Figure 28 BMEP versus CH₄ mole fraction for different ϕ with initial condition as Table 5.

4.5 Emission Control :

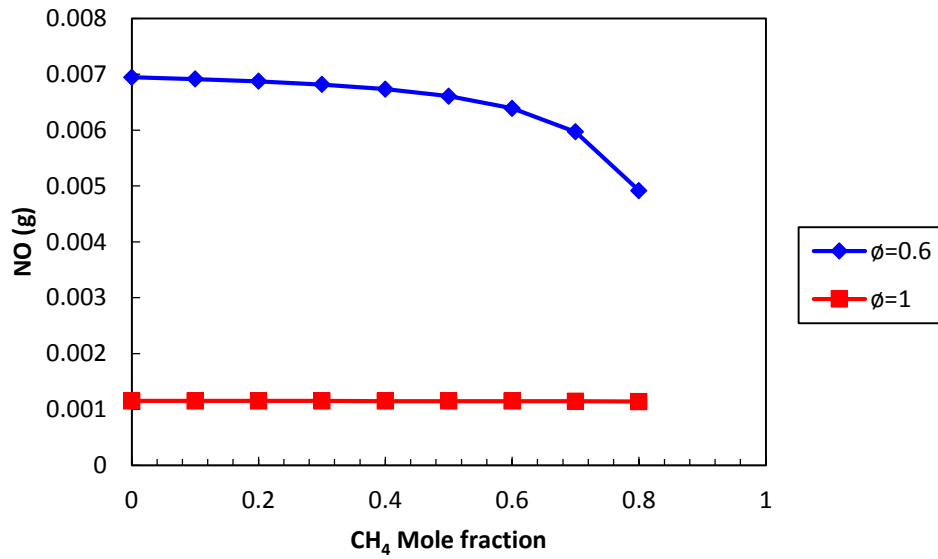


Figure 29 The mass of NO at exhaust valve opening for different ϕ with conditions as Table 5.

Figure 29 shows the NO end point for different compositions of n-heptane and methane at different equivalence ratios. This shows the amount being left in chamber after each ignition. As can be seen the NO formation decreases as the fuel becomes richer. For stoichiometric fuel, adding methane does not affect the NO formation. But for leaner fuels, as more methane is added, the NO formation decreases gradually.

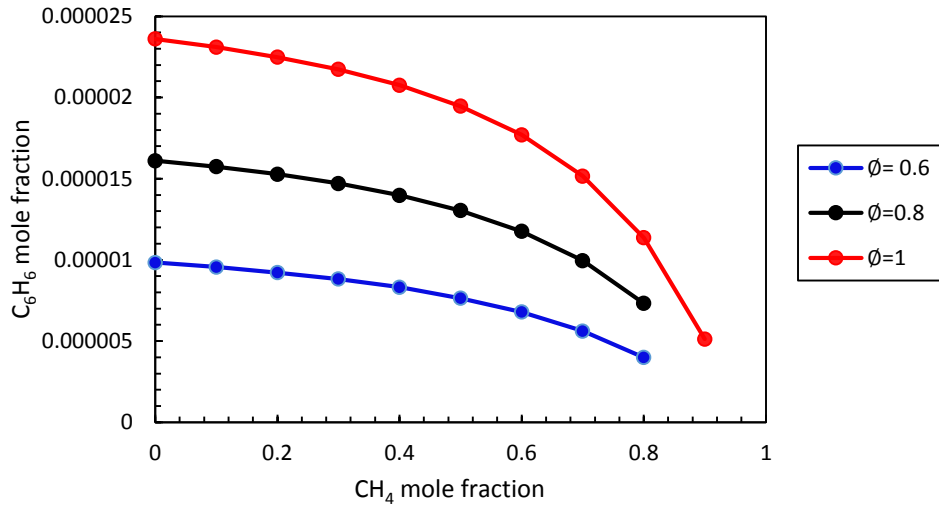


Figure 30 C₆H₆ mole fraction for different ϕ with initial condition as Table 5.

Figure 30 show a clear and direct dependence of PAH emissions on methane/n-heptane fuel proportion and equivalence ratio in an HCCI engine. Figure above illustrates by adding methane to n-heptane, PAH formation is reduced tremendously. It can be understood methane addition has smaller effect on PAH reduction when fuel is leaner. As the fuel goes leaner, PAH formation decreases massively.

Chapter 5

Conclusions

A numerical investigation has been performed to examine the effects of methane addition on the ignition of n-heptane/air mixtures at HCCI conditions. Simulations are performed using the Chemkin software for a constant-pressure reactor, a constant-volume reactor and an HCCI engine. Two detailed mechanisms, namely CRECK and LLNL, and a reduced mechanism, Chalmers, have been used to predict the ignition behavior of n-heptane/methane blends. The mechanisms have been validated using the ignition delay data for n-heptane/air and methane/air mixtures at engine conditions. Results are presented for various n-heptane/methane blends for a range of conditions with temperature in the range 700-1200 K, pressure 30-55 atm, and equivalence ratio 0.6-1.5. Important observations are as follows.

Ignition delay predictions using all the mechanisms exhibit good qualitative agreement with the experimental data for both n-heptane/air and methane/air mixtures. There is also reasonably good quantitative agreement, with the CRECK showing the best overall agreement.

As expected, the addition of methane has significant effect on the ignition of n-heptane/air mixtures. For small amount of methane in the blend, the ignition behavior is essentially determined by n-heptane chemistry. However as the amount of methane is increased, the ignition behavior is strongly influenced by methane chemistry. In contrast, the addition of even a small amount of n-heptane causes a significant decrease in the ignition delays for methane-air mixtures. Ignition delay is also strongly influenced by equivalence ratio (ϕ), as a small change in ϕ from its stoichiometric value causes a significant change in ignition delay.

Results indicate some discrepancy in the Chalmers mechanism for predicting the ignition delays for n-heptane/methane. As the amount of methane in the blend is increased, the CRECK and LLNL mechanisms predict a continuous increase in ignition delay, whereas the Chalmers mechanism predicts first a decrease in ignition delay and then an increase. In addition, the Chalmers mechanism predicts the lowest minimum temperature for ignition within a specified time, while the CRECK mechanism predicts the highest minimum temperature.

A sensitivity analysis is performed using the CRECK mechanism in order to identify the important reactions associated with the ignition of n-heptane/methane blends at engine conditions. Important reactions identified include R5337 ($\text{OH} + \text{NC}_7\text{H}_{16} \Rightarrow \text{H}_2\text{O} + \text{NC}_7\text{H}_{15}$), R2795 ($\text{OH} + \text{CH}_4 \Rightarrow \text{H}_2\text{O} + \text{CH}_3$), and R2013 ($\text{NC}_7\text{-QOOH} + \text{O}_2 \Rightarrow \text{NC}_7\text{-OOQOOH}$). The

sensitivity to these reactions increases as the amount of CH₄ in the blend is increased. In addition, reactions R2015 (NC₇-OOQOOH=>NC₇-OQOOH+OH), R2014 (NC₇-OOQOOH=>NC₇-QOOH+O₂) and R2009 (NC₇-QOOH=>HO₂+NC₇H₁₄) become important at higher pressure. Overall, the heptyl and keto-hydroperoxide play a key role in the ignition of n-heptane/methane blends.

Simulations for the HCCI engine are performed using the Chemkin software with engine simulator option and the 3D CFD code Converge. Results indicate that the Chemkin code can provide reasonable trends in terms of temperature and pressure profiles with respect to the crank angle. In addition, predictions for the HCCI engine using the start of injection (SOI) at 8° before TDC are found to be comparable to those obtained using the constant volume reactor model. Moreover, the results indicate the two-stage ignition behavior for both the constant volume reactor and the HCCI engine. Finally some results are presented on the HCCI engine performance and emissions using the Chemkin software. The addition of methane is found to have a relatively small effect on BMEP. However, NO_x and PAH formation decrease monotonically with the addition of methane.

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