FUEL EFFECTS ON DRIVEABILITY AND HYDROCARBON EMISSIONS OF SPARK-IGNITION ENGINES DURING STARTING AND WARM-UP PROCESSES

by

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ABSTRACT

A methodology which can assess the fuel effects on engine starting and warm-up behaviors, including vehicle driveability and hydrocarbon emissions, had been established. The approach includes (i) developing a simulated cold start and warm-up testing procedure for SI engines, (ii) devising a time-resolved, speciated hydrocarbon emissions sampling unit, (iii) formulating a fuel composition model for gasoline, and (iv) modeling the mixture preparation process to explain fuel volatility effects on the engine starting and warm-up behaviors.

The effects of fuel volatility and degree of enrichment on the vehicle driveability and hydrocarbon emissions of modern four-valve SI engines with port-fuel-injection during starting and warm-up processes were studied. A simulated engine cold start procedure for SI engines in a laboratory environment under precisely controlled conditions was established to quantify the vehicle driveability during engine starting and warm-up processes. A time-resolved exhaust gas sampling unit was designed to measure the evolution of the total and speciated hydrocarbon emissions from SI engine during the simulated cold start procedure. A sequence of exhaust samples was drawn and stored by the sampling unit for gas chromatography analysis.

A fuel composition model based on major species present in the fuel was formulated. The model accurately predicts the ASTM distillation curves and Reid Vapor Pressure for both hydrocarbon type fuels and oxygenate-added fuels. Based on this fuel composition model and an isothermal flash calculation, a mixture preparation model which can calculate the extent of evaporation of fuels and the vapor composition of the air/fuel mixture present in the engine intake manifold on a time-resolved basis was developed.

The starting and warm-up attributes of engine by the simulated cold start procedure is found to correlate well with a single parameter - the vapor equivalence ratio (Φ_vapor) of air/fuel mixture calculated by the mixture preparation model. An extended mixture preparation model which further incorporates the liquid-fuel-pool dynamics correctly predicts that the first firing cycle of an engine with different fuels always occurs when Φ_vapor equals to 0.7. The model also illustrates that the fuel species distribution of the hydrocarbon emissions follow the volatility of the fuel components: the light-end components are the major emitted HC species in the early cycles. The contribution from the heavy-end components increase in the later cycles due to the accumulation of these components from the previous cycles and the temperature increase of intake manifold as the engine warms up. The mixture preparation model can be used to access the fuel effects on the startability of SI engines and species distribution of hydrocarbon emissions during cold start, as well as design of the optimal injection strategy for target vapor concentration for engine cold start.

Thesis Advisor: Wai K. Cheng,
Associate Professor of Mechanical Engineering
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NOMENCLATURE

a  port diameter
ASTM  American Standard of Testing and Materials
B  Bore
BDC  bottom dead center
DOHC  double overhead cam
ECU  engine control unit
F/A  fuel-to-air mass ratio
(P/F/A)_s  stoichiometric fuel-to-air mass ratio
f_{BL}  fraction of air in the boundary layer
f_c  fraction of air in equilibrium with the fuel
FID  flame ionization detector
FFID  fast-response flame ionization detector
FTP  Federal Test Procedure
GC  Gas Chromatography
GIMEP  Gross Indicated Mean Effective Pressure
HC  Hydrocarbon
iC8  iso-octane
ID  inner diameter
IVC  intake valve close
IVO  intake valve open
L  stroke
M  Methyl
m_{air}  mass flow rate of air
MBT  maximum brake torque
m_{i,v}  mass of fuel species i in vapor phase
m_{ij}  interaction coefficient of component i and j
MIR  Maximum Incremental Reactivity
MTBE  methyl-tertiary-butyl ether
n  normal
N  cycle number
NBP  normal boiling point
nC5  normal-pentane
NMHC  Non-Methane Hydrocarbon
NMOG  Non-Methane Organic Gas
P  pressure
P_c  critical pressure
ppmC1  parts per million carbon atom
ppbC1  parts per billion carbon atom
R  gas constant
Re  Reynolds number
RMS  root-mean-square
rpm  revolutions per minute
RVP  Reid Vapor Pressure
SI engine  Spark-Ignition engine
species_{i,v}  ppmC1% of species i in vapor phase
T  temperature
T10  10% distillation temperature
T20  20% distillation temperature
T80  80% distillation temperature
T90  90% distillation temperature
T_c  critical temperature
tDC  top dead center
tM   tri-Methyl
v    specific volume
V    volume
V_a  mean port air velocity
V_d  displacement volume
VLE  vapor liquid equilibrium

δ*  boundary layer displacement thickness
Φ_{inj} supplied fuel equivalence ratio, based on the amount of fuel injected
Φ_{vapor} vapor fuel equivalence ratio, based on the amount of fuel evaporated
σ   standard deviation
τ_d  decay time constant of RMS
τ_r  rise time constant of GIMEP
ω   acentric factor
CHAPTER 1

INTRODUCTION

1.1 Background

Vehicle driveability and hydrocarbon (HC) emissions during starting and warm-up are among the most important considerations of spark-ignition (SI) engines and fuel designs. It is desirable to start and warm-up the engine smoothly while keeping HC emissions below the regulated level.

Vehicle driveability attributes, such as the ease of starting, smooth operation during warm-up, hesitation and stumble in acceleration and/or deceleration, are features directly felt by drivers. They are perceived measures of the engine and fuel performance by the customers. Traditionally, driveability of a vehicle using a particular fuel is evaluated subjectively on the road by trained drivers [1]. While the test program reflects actual on-road conditions, the process is rather expensive, time consuming, and undesirable vehicle behaviors are determined based on qualitative information which can not be used for engine and fuel designs in a straight forward manner. Therefore, there is a need to devise a test and analysis method in a laboratory
environment under precisely controlled conditions to evaluate the vehicle driveability quantitatively during starting and warm-up processes of engines.

Undesirable vehicle behaviors during engine transients are mostly caused by deviations of the in-cylinder mixture air/fuel ratio from optimal composition. For example, stable operation of SI engines depends on the development of a homogeneous air/fuel mixture which must be of a combustible composition to burn. Effective operation of the three-way catalytic converter further dictates that the mixture equivalence ratio must be within a narrow window around stoichiometric. It is widely known that deviations of air/fuel ratio present in the combustion chamber are due to incomplete evaporation of the injected fuel and/or time lags introduced from the storage and release of liquid fuel in the intake manifold in the mixture preparation process. These phenomena are directly related to the volatility of the fuel components. These effects are even more prominent at low temperature.

In order to compensate the incomplete evaporation of fuel during cold start, fuel enrichment and high Reid Vapor Pressure (RVP) fuels are currently used to ease the starting and warm-up of engines. Substantial fuel enrichment, however, penalizes the fuel economy and causes high level of tailpipe HC emissions. The use of high RVP fuels enhances the evaporative emissions of hydrocarbons from fuel system. With the fuel economy and low HC emissions regulations, there are severe requirements for the fuel design and the engineering of the mixture preparation process to ensure good driveability and low HC emissions in all weather conditions. Fundamental studies of fuel volatility and enrichment effects on mixture preparation process is essential to optimize vehicle driveability and HC emissions during engine starting and warm-up processes.

SI engines are the dominant mobile source of airborne organics. The HC emissions from the SI engine significantly affect air quality through their effects on smog (ozone and other organic complexes) formation, and through their health effects on human being in terms of
toxicity. Thus there are emissions regulations that require substantial reduction of the passenger cars HC emissions in terms of the Federal Tier I and Tier II standards and in terms of the California Air Resources Board series of Low emissions vehicles standards (from Transition low emissions to Ultra Low emissions) [2]. More stringent requirements are expected in the future. Because of these emissions requirements, considerable efforts have been mounted on relating the HC emissions to the engine design parameters [3] and the fuel parameters [4]. The specific objective of this study is concentrated on the latter ones.

Currently, the major reduction of the emissions from SI engines is achieved by the catalytic converter. The catalytic converter is not effective before it reaches its operating temperature. Thus substantial amount (> 80%) of the tailpipe HC emissions from a production vehicle during the Federal Test Procedure (FTP) driving mode is produced during the first minute or so of operation, prior to catalyst light off [5, 6]. In this period, the cold emissions are essentially the engine-out ones and they are major contributors to the total vehicle HC emissions.

While the current HC emissions regulations are based on the total HC emissions (either as total Non-Methane Hydrocarbon - NMHC, or as Non-Methane Organic Gas - NMOG which includes the oxygenates), it is recognized that different HC species have different impacts on air quality. For example, the olefins have a substantially higher contribution to ozone formation than the paraffins; species such as 1-3 butadiene are toxic. The species ozone forming potential has been assessed in terms of a Maximum Incremental Reactivity (MIR) index [7]. Therefore, to evaluate the impact of SI engine HC emissions on air quality, it is important to consider the effects of the individual emissions species.

Not only the amount of total HC emissions changes with time from engine started, but also the composition of emissions also changes continuously in the warm-up process. The composition of the fuel entering the combustion chamber early in the cold start is skewed toward to the more volatile components [8]. The time evolution of the exhaust composition reflects the
change of the in-cylinder species resulted from the mixture preparation process due to the wild range of volatility of species present in gasoline. This phenomenon will cause the ozone forming reactivity of exhaust gas to change substantially during the warm-up process because of the different MIR of each species.

There are two major motivations in studying the fuel effects on the time dependence of the engine-out speciated HC emissions in starting and warm-up: (i) The predominant part of the total emissions in the FTP is due to the first minute of operation. Thus the engine-cut species which are still changing in this period are of considerable importance. (ii) The exhaust HC species depend on the fuel species which are delivered into the engine. Thus the evolution of the exhaust species distribution could substantially elucidate the mixture preparation process during warm-up.

The fuel composition has major impact on the SI engine HC emissions. The effects could be physical in nature, such as through the component volatility which affects the mixture preparation process; or chemical in nature, such as through the kinetics of oxidation and conversion to intermediate products. The effects were observed in a large scale fleet test program (the Auto-Oil Program): the relationships of both the engine-out and tailpipe HC emissions to the 90% distillation point (T90) of the fuels are found to be statistically significant [9]; and in analysis of the speciated emissions of individual vehicles, the aromatics components of the fuel are found to have a higher (~1.5 times, which is roughly vehicle independent) survival fraction through the engine processes than the other fuel components [10]. The fuel component related findings illustrate the importance of the fuel effects.

The thermodynamic properties of a fuel determine its evaporative characteristics and have major effects on the mixture preparation process in a fuel-injected SI engine. The effects are especially important in the cold-start/warm-up processes and in acceleration/deceleration transients. It is, however, difficult to accurately model the volatility properties of gasoline which
contains numerous chemical species. For many of these species, the thermodynamic properties as well as the species-to-species interactions are not well-known. Empirical formula had been used to relate the fuel vapor pressure as a function of temperature [11]. This approach, however, does not reflect the fuel composition and does not address the known fact that the light fuel components evaporate faster than the heavy ones. The importance of the fuel vapor composition in engine transient behavior is further illustrated by the driveability problems encountered when using gasoline / methyl-tertiary-butyl ether (MTBE) blends: MTBE is more volatile than a large fraction of the fuel hydrocarbon components; the stoichiometric requirement for MTBE is, however, substantially different from a hydrocarbon. This disproportionate fraction of MTBE in the fuel vapor during the start-up process makes the air/fuel ratio calibration for the hydrocarbon-type fuel no longer valid. In order to better understand the fuel volatility and composition effects on vehicle driveability and HC emissions during starting and warm-up of engines, a component-based fuel composition model which can represent the thermodynamic properties of practical fuels and oxygenate-blended fuels is needed.

Mixture preparation in a port-fuel injected engine is a complex process. The fuel is usually injected when the intake valve is closed. At part-throttle operation, there is a backflow of hot burned gas from the cylinder when the valve opens. This hot backflow facilitates the evaporation process. Then the forward flow induced by the piston motion carries the fuel vapor into the cylinder. Liquid fuel film may also be driven into the cylinder by this flow. Thus mixture preparation process involves fuel atomization, evaporation of fuel droplets and liquid film on the port wall and the back of the intake valve, liquid film surface flow, and the heating of the intake port region by the reverse flow of the burned gas when the intake valve opens [12]. It is widely known that volatility properties of fuel have major effects on the mixture preparation process in a fuel-injected engine. The effects are especially important in the engine starting and warm-up processes when incomplete evaporation of injected fuel is more prominent than at the

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fully warm-up condition. In order to understand the fuel effects on the mixture preparation process, the development of a mixture preparation model based on the fuel composition model, fuel volatility properties and some other physical phenomena occurred in the intake port is necessary.

The development of a fuel composition model and a mixture preparation model taking volatility of fuel species into account are essential parts of this thesis. These models could be used to further explore engine and fuel designs for optimal engine behaviors in the starting and warm-up processes. Unlike at the fully warm-up engine condition when all the sensors function normally and thus closed-loop control is available, open-loop control is currently used for the air/fuel ratio control during starting and warm-up processes. The mixture preparation model developed in this thesis would enable optimal fuel injection schedule for engine cold-start process based on the fuel volatility properties.

1.2 Objective

The objective of this thesis is to study the fuel volatility, fuel component, and fuel enrichment effects on starting and warm-up behaviors, including driveability and hydrocarbon emissions, of spark-ignition engines. The following four tasks which will be present in detail in the following chapters are necessary in order to accomplish this objective:

(i) developing a engine cold start testing procedure in a laboratory environment and analysis method to quantify vehicle driveability during starting and warm-up processes (chapter 2 and 3),

(ii) devising a time-resolved exhaust gas sampling unit for total and speciated hydrocarbon emissions during starting and warm-up processes (chapter 4),
(iii) formulating a fuel composition model for characterizing the thermo-physical properties of fuels (chapter 5), and

(iv) modeling the fuel effects on mixture preparation process and establishing correlations between fuel properties and engine start-up / warm-up behaviors (chapter 6).

1.3 Approach

A schematic description of the approach for fuel effects on engine start-up behaviors is shown in Figure 1.1. Establishing a suitable set of experiments and an appropriate mixture preparation model are two major parts in this study. Relating the engine starting and warm-up behaviors to the fuel properties is the final goal of this project.

In the experimental part, a test matrix was formulated in order to represent different volatility range of fuel and different fuel enrichment cases. A simulated engine cold start procedure in a laboratory environment under precisely controlled conditions was established to test the vehicle driveability during engine starting and warm-up processes. A speciated, time-resolved exhaust gas sampling system was designed to sample the engine-out exhaust gas at different time to cover the span of evolution of total and speciated hydrocarbon emissions during cold start and warm-up period. Based on the test matrix, the engine was run under the simulated cold start process while the driveability test and exhaust gas sampling were performed.

In the fuel volatility modeling, a fuel composition model based on the major species present in the fuel was formulated. By using a thermodynamics properties database of hydrocarbons and an isothermal flash calculation, volatility of fuel and effects of component interactions on fuel evaporation can be calculated based on the composition model. The validity of this representation was checked by comparing the simulations of some standard volatility test (ASTM distillation curve and Reid Vapor Pressure) calculated from the fuel model with actual
experimental data. Based on the fuel composition model, a mixture preparation model which includes the fuel volatility properties, air flow schedule, fuel flow schedule, and liquid fuel dynamics occurring inside the intake manifold of engine was developed in order to calculate the properties of the air/fuel mixture present in engine intake port on a time-resolved basis. Then correlation of fuel volatility properties calculated from the mixture preparation model with the engine starting and warm-up behaviors from experiments can be established.

1.4 Overview

The organization of the thesis is as follows. The background, objective and approach of this study has been stated in Chapter 1. The development of a simulated cold start procedure on a modified 4-cylinder spark-ignition engine and analysis method for assessing driveability attributes during engine starting and warm-up are described in Chapter 2. Experimental investigation for the fuel volatility and component effects on one of the most important engine starting behaviors, first firing cycle, are studied in Chapter 3. Then the other aspect of engine starting behaviors, hydrocarbon emissions, is explored in detail in Chapter 4, including design of the speciated, time-resolved exhaust gas sampling unit, experimental results and the analysis of time history of speciated hydrocarbon emissions during engine starting and warm-up.

In Chapter 5, Fuel Volatility Modeling, methodology of formulating fuel composition models for practical fuels and simulation of standard volatility tests to verify the fuel composition models are described. Then the development of mixture preparation model and comparison between model results and engine starting and warm-up behaviors described in Chapter 2, 3, and 4 are stated in Chapter 6. Conclusions are addressed in Chapter 7.
Figure 1.1 Approach of fuel effects on engine start-up behaviors
CHAPTER 2

INVESTIGATION OF FUEL VOLATILITY AND ENRICHMENT EFFECTS ON THE STARTING AND WARM-UP DRIVEABILITY

In this Chapter, the effects of fuel volatility and degree of enrichment on the starting and warm-up behavior of a modern four-valve spark-ignition engine with port-fuel-injection were studied. A simulated cold-start procedure for spark-ignition engine was developed to assess engine driveability during starting and warm-up behaviors. A selected matrix of fuels that included various volume ratios of indolene / MTBE and iso-octane / n-pentane was used to study fuel effects on engine behaviors. The modification of the test engine and measurement instrument are described in section 2.1. The test procedure, conditions and test matrix are stated in section 2.2. Comparison of real engine starting with this particular laboratory procedure is also discussed. Then the formulation of four driveability attributes to quantify engine driveability during starting and warm-up processes and experimental data are presented in section 2.3.
2.1 Experimental Apparatus

2.1.1 Test Engine - Nissan SR20DE Engine

All the experiments reported in this chapter were done in a commercial two-liter four-cylinder spark-ignition engine (the Nissan SR20DE) which had been modified for single cylinder operation [13].

The SR20DE is a 16-valve DOHC in-line four-cylinder engine with two branches of intake and exhaust ports for each cylinder. Specifications of the engine are listed in Table 2.1. The engine has a forced swirl and tumble charge motion created by the intake port configuration to enhance combustion through turbulence effects. The injection of fuel occurs during intake

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<td><strong>Valve Diameter</strong></td>
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<td><strong>Maximum Torque</strong></td>
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valve close (IVC). Each port fuel injector generates four jets of fuel. Two of the jets are directed respectively towards the back of the intake valves of the two branches of the intake port; the remaining jets collide together to facilitate atomization. These features are representative of the state-of-the-art design practice.

This engine had been modified for single cylinder operation in order to avoid the interference among multiple cylinders, as shown in Figure 2.1. In this configuration, injection of fuel and combustion only occur at the active (the fourth from the front of engine) cylinder. The distributor had been replaced by a separate electronic ignition controller for the active cylinder. The intake port of the disabled cylinders were blocked off in order to correctly measure the air flow rate of the active cylinder. The exhaust of the active cylinder was separated from those of disabled cylinders for correct reading of air/fuel ratio sensor (Lambda meter) located at the downstream of exhaust port. There was no modification of moving parts, including the

Figure 2.1 Modifications of Nissan single-cylinder engine
camshaft and valvetrain, for the purpose of inertial balance. These modifications result in a single-cylinder engine with displacement volume of 499 cm$^3$ and compression ratio of 9.5, driving the other three cylinders.

The engine is coupled to a dynamometer, which can control the engine either under constant speed mode or under constant torque mode. The dynamometer consists of an induction type motor with a DC current driven clutch and Eddy current brake. For the ease of temperature control, the engine coolant, oil and fuel are cooled by separate water-cooled heat exchangers which differ from the air-cooled radiator available in modern vehicles. There is no control of air temperature which is equal to ambient temperature of test cell.

2.1.2 Measurement Equipment

The cylinder pressure was measured by a Kistler 6051A pizoelectric transducer which was mounted in the cylinder head through the water jacket. The crank-angle resolved pressure data was written directly on a hard disk via a high speed PC data acquisition system. The clock of the acquisition board is triggered by the crank shaft encoder (BEI incremental optical encoder, model H25E) which give a pulse every crank angle degree.

The air flow was measured by a Kurz 505 mass flow meter. This meter utilizes a thermal sensor and automatically compensates for pressure and temperature changes. In order to damp out the highly pulsating intake air flow resulting from the single-cylinder operation, a 55 gallon tank is placed between the air flow meter and intake manifold of engine.

The fuel injected per cycle in steady state was measured by three different methods. (i) The average fuel volumetric flow rate was measured by a Max 213-311 positive displacement flow meter. (ii) The fuel-air equivalence ratio ($\Phi$) at the exhaust was measured by a Horiba oxygen sensor; the fuel flow could then be calculated from the measured air flow and $\Phi$. (iii) The
amount of fuel delivered in each injection as a function of injection duration was calibrated by weighting the injected fuel trapped in a ice-cooled flask so that the fuel delivered in each experiment could be determined from the duration of injection pulse. All three methods gave consistent results (within 3 percent). The values of Φ quoted in the following are those from the oxygen sensor measurement (when the engine has reached steady-state) which was the most readily available quantity from the experiments.

2.2 Experimental Development

2.2.1 Test Conditions and Procedure

The ambient temperature of test cell was at 20 to 22°C for all the experiments. At the beginning of each test run, the engine block, coolant water, engine oil and the fuel were all cooled down to ambient temperature. The cooling process, by air fan and water-cooled heat exchangers, took about 40 minutes to 1 hour to complete, while data collection took only about 5 minutes. Therefore, the number of test runs which could be performed each day was limited.

The engine was motored by dynamometer at constant speed. The dynamometer controller was set at a fixed speed of 900 revolutions per minute (rpm). The throttle position was set to provide an intake pressure of 0.4 bar. These particular engine speed and intake pressure are representative of idle condition in modern vehicles. The spark ignition was on at all time. The spark timing was set at 20 crank angle degrees before top dead center (TDC) for the maximum brake torque of engine at 900 rpm.

At time zero, fuel injection was started by energizing the injector. Data acquisition system was triggered by the bottom dead center (BDC) signal of the first cycle to start to record the crank-angle resolved pressure data. The amount of fuel injected each cycle was fixed. Care
was taken to ensure that the full amount of fuel was injected in the first cycle. The pressure data was recorded for 1800 cycles, which encompassed the complete fuel transient process.

There are significant differences between the actual starting and warm-up processes in a vehicle and the above procedure. For example, in the actual start-up, the engine is cranked by starter motor with considerably lower speed which may vary due to the state of battery; the intake pressure starts out at atmospheric, than drops to lower pressure which depends on the engine speed; and the amount of fuel injected each cycle varies during the start-up transient according to the program of the Engine Control unit (ECU) which takes into account the coolant temperature and the time since first firing. The above procedure, however, provides a precisely defined starting condition in the laboratory environment and retains the essence of the mixture preparation process in the start-up transient. By fixing the amount of fuel injected per cycle, the effect of the ECU programming is decoupled and the fuel effects can be assessed in terms of the physical properties of the fuel.

2.2.2 Test Matrix

A test matrix was formulated in order to incorporate the two major control factors, different fuel types and different enrichment cases, which influence the driveability of engines during starting and warm-up periods.

Fuel matrix

There are two considerations in the fuel blends selection. First, the fuel blends should represent a broad range of volatility so that the effects of volatility on startability and driveability during warm-up could be assessed. Secondly, the fuel blends should be of practical interest.
The first set of experiments were done with a simple binary mixture of n-pentane (nC5) and iso-octane (iC8) so that the fuel composition, and therefore, the thermo-physical properties of the fuel are well defined. By using a binary mixture, there is no ambiguity about the actual composition, as compared to that of practical fuels, such as gasoline, which contain hundreds of species; and there is no lack of information about thermo-physical properties, such as critical pressure and temperature, of some particular species. N-pentane and iso-octane are hydrocarbons with well-documented thermo-physical properties. N-pentane with normal boiling point at 36.1°C is representative of the light-end components of gasoline. Iso-octane with normal boiling point at 99.2°C is representative of the mid-range gasoline components. A binary mixture of different proportions of the two compounds would provide a substantial volatility change.

Of practical interest is the starting behavior of real gasoline and mixture of gasoline and its additives. Gasoline / MTBE (methyl-tert-butyl-ether) blends with different proportions of these two were used in this study. Because of its compatibility with the current refinery process, MTBE is the leading choice of oxygenates to be introduced in reformulated gasoline. Therefore the study of gasoline / MTBE blends is of interest. The MTBE was of laboratory grade (99.8% pure), and the gasoline used in this study was indolene which is a calibration gasoline.

The blending ratios of the fuel blends used in the fuel matrix were:

(i) N-pentane volume percentage (in nC5/iC8 blends):

0, 15, 30, 50, 70, 85, 100;

(ii) MTBE volume percentage (in indolene / MTBE blends):

0, 5, 10, 15, 20, 30, 50, 70, 85, 100.

In the above, 0% indicated pure iC8 (or indolene), and 100% indicates pure nC5 (or MTBE). The fuels were refrigerated to 0°C before blending in order to minimize the evaporative loss of the volatile species in the blending process.
Fuel enrichment

In the rest of this thesis, fuel enrichment will be represent by the fuel-to-air equivalence ratio $\Phi$ [14], defined as in equation (2.1).

\[
\Phi = \frac{(F/A)}{(F/A)_s}
\]  \hspace{1cm} (2.1)

$(F/A)$ is the fuel-to-air mass ratio. The index "s" refers to the value at stoichiometric condition. When $\Phi$ equals unity, the air/fuel mixture is said to be in stoichiometric; when $\Phi$ is less than unity, it is in condition of fuel lean; and when $\Phi$ is larger than unity, it is in fuel rich condition. The injected (or metered) fuel-to-air equivalence ratio $\Phi_{inj}$ is expressed as the amount of fuel injected per cycle relative to the amount of fuel required to have a stoichiometric air/fuel mixture in the cylinder, provided that all the fuel evaporates.

In the normal engine warm-up process, excess fuel is injected to compensate for incomplete evaporation due to the fact that only more volatile species in gasoline will evaporate when intake manifold is cold. The degree of enrichment during warm-up period will depend on the programming of ECU. Typical values of $\Phi_{inj}$ at idle (except for the first few cycles in cranking) is in the range of 1.0 to 1.5, which were empirically determined. In this study, the amount of fuel injected each cycle was fixed (see section 2.2.1). To assess the effects on fuel enrichment, the amount of fuel injected per cycle for different test runs was varied:

$\Phi_{inj} = 1.0, 1.1, 1.2, 1.3, \text{ and } 1.5.$

The test matrix thus included 17 fuels, from pure nC5 to pure iC8, and from pure MTBE to pure indolene. With the five different injected fuel equivalence ratio $\Phi_{inj}$, there are altogether 85 data points. Each operating condition was repeated three times to check the reproducibility of the engine response. Therefore, there were total 255 test runs.
2.3 Data Interpretation - Driveability Attributes

From the crank-angle resolved cylinder pressure data, the cycle-resolved Gross Indicated Mean Effective Pressure (GIMEP) history by using a particular fuel is calculated for 1800 cycles. GIMEP is the work done by the compression and expansion strokes of engine divided by the displacement volume \( (V_d) \). The definition of GIMEP for the \( i \)th cycle is stated in equation (2.2).

\[
GIMEP_i = \frac{\int_{compr.\&expan.}^{} P \, dV}{V_d}
\]

\[(2.2)\]

A typical GIMEP trace versus cycle number of a simulated start-up process is shown as the dotted line in Figure 2.2. The data for this figure were obtained with no fuel enrichment \( (\Phi_{inj} = 1) \) for indolene.

For the early cycles, the GIMEP curve shows a very erratic behavior of firing, misfiring,

---

**Figure 2.2** GIMEP and RMS history of the single-cylinder engine under the simulated start-up procedure by using indolene as fuel
and partial firing. To systematically characterize these behaviors, the GIMEP moving average and the Root-Mean-Square (RMS) error of GIMEP were calculated. The GIMEP moving average for the $i^{th}$ cycle is obtained from the mean values of 25 cycles (current cycle $i$, 12 cycles after $i$, and 12 cycles before $i$) centered at $i$, as shown in equation (2.3).

$$\frac{\sum_{k=i-12}^{i+12} \text{GIMEP}_k}{25}$$  \hspace{1cm} (2.3)

At the beginning of transient when $i < 13$, the averaging was done over the current cycle, all the previous cycles, and 12 cycles after $i$; the $i^{th}$ cycle was given a higher weight so that the total weight added up to 25. The RMS value of GIMEP is an indication of the fluctuations of the GIMEP value around the moving average, as shown in equation (2.4).

$$\text{RMS}_i = \sqrt{\frac{\sum_{k=i-12}^{i+12} \left( \text{GIMEP}_k - \bar{\text{GIMEP}}_i \right)^2}{25}}$$ \hspace{1cm} (2.4)

The RMS values were also obtained from the mean values which were calculated by a 25-cycle moving average centered at the cycle $i$. The choice of 25 cycle averaging for moving average of GIMEP and RMS was a comprise between being able to filter out the fluctuation and to follow the GIMEP development accurately.

The 25-cycle moving average of GIMEP and the RMS values (calculated over the same 25 cycles) of the GIMEP deviation from the moving average are also shown in the Figure 2.2. Misfired cycles and large cycle-to-cycle variations were observed in the early cycles (less than the 50$^{th}$ cycle). Higher RMS values in this period indicate large magnitude of oscillation of GIMEP values around their moving average. As the cycle number was increased, the moving average of GIMEP increased steadily and the RMS values decreased, indicating the improving driveability of engine during the warm-up process. Similar behaviors were also observed when other fuels were used in the simulated engine cold-start process.
The on-the-road driveability demerits felt by the trained driver (see section 1.1) are based on the engine behaviors:

- The ease of starting,
- Idle roughness (due to torque fluctuations),
- Hesitation (throttle delay in acceleration),
- Surge (unevenness in acceleration),
- Stumble (sudden loss of acceleration at fixed throttle opening).

The above behaviors related to the actual engine GIMEP response in the starting and warm-up process. Therefore to characterize the driveability of the tested fuel in the above laboratory procedure, the following parameters are used:

- The first significantly firing cycle, defined as the first cycle which reaches 75% of the steady state value of GIMEP,
- The 1/e rise time constant ($\tau_r$) of the GIMEP moving average, which is the cycle when GIMEP moving average reaches 63.2% (= 1 - 1/e) of its steady state value,
- The 1/e decay time constant ($\tau_d$) of the RMS fluctuation of GIMEP, which is the cycle when RMS value reaches 36.8% (= 1/e) of steady state value of RMS, and
- The RMS value of the GIMEP fluctuations at 3 $\tau_r$, normalized by the steady state GIMEP, and with the steady-state fluctuation ($\sigma(\infty)$) subtracted. It can be represented as:

\[
\text{normalized RMS value at } 3\tau_r = \frac{\sigma(3\tau_r) - \sigma(\infty)}{\text{GIMEP}(\infty)}
\]  

These four parameters are also indicated in Figure 2.2. The choice of the 75% GIMEP threshold for the first significantly firing cycle was somewhat arbitrary, but the results were not sensitive to any reasonably high threshold level.

By comparing the definition of the on-the-road driveability and the four driveability attributes derived from the simulated start-up process, the first significantly firing cycle, the time
scales for GIMEP development (τ_f) and the time scale for GIMEP fluctuation to decay (τ_d) reflect on the ease of starting. The RMS value of the GIMEP fluctuation after the engine has been firing fully (at 3τ_f) but not fully warm-up yet (σ(3τ_f)) is indicative of the torque fluctuation during engine warm-up. It will be shown later in this section and section 6.2 that the four driveability attributes are not independent since the mixture preparation process has a major impact on the engine warm-up behaviors.

Explicit test of the throttle transient during warm-up was not carried out in this simulated starting procedure. Because the fuel flow generally lags the air flow into the cylinder in a throttle transient, the switching of the fuel from off to on at constant air flow in the laboratory start-up procedure may be considered as an extreme case of throttle transient. Therefore the rise time τ_r of the GIMEP is indicative of the throttle transient response of the fuel.

These four driveability attributes, first significantly firing cycle, rise time constant of GIMEP moving average (τ_f), decay time constant of RMS fluctuation (τ_d), and normalized RMS value at 3τ_r, are shown in Figure 2.3 - 2.6 for the iso-octane / n-pentane mixture, and in Figure 2.7 - 2.10 for the indolene / MTBE mixture. There were three repeated test runs for each data point and only the average value of each operating condition was shown in those graphs. These repeated tests show pretty consistent results (within 5%) in term of the four driveability attributes.

For the iso-octane / n-pentane mixture, the first significantly firing cycle (Figure 2.3) occurs earlier with increasing degree of enrichment from Φ_inj equal to 1 to 1.5, and with increasing proportion of n-pentane which is the more volatile component. This is consistent with the notion that the engine starts faster with enrichment and with a more volatile fuel. Because the above four quantities are fundamentally related to the fuel evaporative properties, they are
not independent of each, and they show the same behaviors (Figure 2.3 - 2.6): namely better starting characteristics with enrichment and with the n-pentane fraction in the mixture.

The simulated starting characteristics of indolene / MTBE blends (Figure 2.7 - 2.10) are similar to those of iso-octane / n-pentane mixture. The ease of starting improves with enrichment, and with increase amount of MTBE in the fuel. Because MTBE is relatively volatile (normal boiling point at 55°C) compared to most of the gasoline components, the latter is consistent with the notion that the engine starts faster with a more volatile fuel.

In summary, these four driveability attributes are not independent because similar trends, namely better driveability attributes with enrichment and with increase amount of volatile component, are observed for different attributes which represent either ease of start or smoothness of engine during warm-up. There are also similar trends for these four attributes by using different fuels; binary mixture of iso-octane / n-pentane and multi-component mixture of indolene / MTBE. Since the starting characteristics are related to the evaporative behavior of the fuel in the mixture preparation process, it is desirable to devise a model to account for the combined effects of fuel enrichment, fuel volatility, and fuel component effects on the starting behaviors. The development of mixture preparation model will be described in section 6.1 and correlations of \( \Phi_{\text{vapor}} \) (a volatility parameter calculated by the mixture preparation model) with engine starting and warm-up driveability attributes will be described in section 6.2.
Figure 2.3 First significantly firing cycle by using iso-octane/n-pentane mixtures as fuel

Figure 2.4 GIMEP rise time constant by using iso-octane/n-pentane mixtures as fuel
Figure 2.5 RMS decay time constant by using iso-octane/n-pentane mixtures as fuel

Figure 2.6 Normalized standard deviation of RMS value at 3 GIMEP rise time constant by using iso-octane/n-pentane mixtures as fuel
Figure 2.7 First significantly firing cycle by using indolene/MTBE mixtures as fuel.

Figure 2.8 GIMEP rise time constant by using indolene/MTBE mixtures as fuel.
Figure 2.9 RMS decay time constant by using indolene/MTBE mixtures as fuel

Figure 2.10 Normalized standard deviation of RMS value at 3 GIMEP rise time constant by using indolene/MTBE as fuel
CHAPTER 3

INVESTIGATION OF FUEL COMPONENT EFFECTS
ON THE FIRST FIRING CYCLE

In this Chapter, an important indication of engine startability, the first firing cycle, which was not discussed in previous chapter was studied by using a modified single-cylinder port-fuel-injection spark-ignition engine under the same test procedure as described in previous chapter. A different fuel injection strategy and test matrix were used to put emphasis on fuel component and enrichment effects on engine starting process. The modification of the test engine and measurement instrument were describe in section 3.1. The test procedure, conditions and test matrix were stated in section 3.2. Then the analysis method and experimental data of the engine first firing cycle were presented in section 3.3.

3.1 Experimental Apparatus

3.1.1 Test Engine - Volvo B5254 FS Engine
All the experiments reported in this chapter and Chapter 4 were done on 4-stroke single cylinder SI engine with a modern 4-valve production head (from the Volvo B5254 FS Engine) [15]. The engine specifications are listed in Table 3.1.

The B5254 FS is a 2.5-liter in-line five-cylinder engine with two intake and exhaust valves for each cylinder. This engine had been modified into a single-cylinder engine, as shown in Figure 3.1. The liner and piston of first cylinder, and part of cylinder head and crankshaft associated with first cylinder were sawed and separated from rest of the engine; then fit into a Ricardo Hydra single-cylinder engine (Mark III) mounting. Part of intake manifold with injector sitting hole was used to keep the same fuel injection geometry as that of the original engine. Fuel was injected at the intake port with a Bosch EV1.3A injector which supplied a spray of 20° cone angle aimed symmetrically between the two intake valves. Injections of fuel were done when intake valves were closed (IVC). These modifications result in a single-cylinder engine with displacement volume of 487 cm$^3$ and compression ratio of 10.1.

### Table 3.1 Engine specification, Volvo B5254 FS engine

<table>
<thead>
<tr>
<th>Type</th>
<th>in line 5-cylinder, 4 valves/cylinder,</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bore</td>
<td>83 mm</td>
</tr>
<tr>
<td>Stroke</td>
<td>90 mm</td>
</tr>
<tr>
<td>Connecting rod length</td>
<td>158 mm</td>
</tr>
<tr>
<td>Clearance Volume</td>
<td>53.28 cm$^3$</td>
</tr>
<tr>
<td>Displacement</td>
<td>2.435 liters (487 cm$^3$/cylinder)</td>
</tr>
<tr>
<td>Compression Ratio</td>
<td>10.1</td>
</tr>
<tr>
<td>Valve Timing</td>
<td>IVO : 4 BDC</td>
</tr>
<tr>
<td></td>
<td>IVC : 56 ABC</td>
</tr>
<tr>
<td></td>
<td>EVO : 48 BBC</td>
</tr>
<tr>
<td></td>
<td>EVC : 12 ATC</td>
</tr>
<tr>
<td>Valve Diameter</td>
<td>intake : 31 mm</td>
</tr>
<tr>
<td></td>
<td>exhaust : 28 mm</td>
</tr>
</tbody>
</table>
The engine is coupled to an Eaton Dynamatic AF 6360 dynamometer which can maintain the engine at desired constant speed. For the ease of temperature control, the engine coolant, oil and fuel are cooled by heat exchangers at the beginning of start-up procedure to shorten the time for cooling the engine. Since the engine takes about 40 minutes to reach fully warm-up temperature (about 90°C) at low speed (900 rpm) and low load (0.4 bar intake pressure), engine coolant and oil are heated by 1 KW electric heaters to shorten the warm-up time. There is no control of air temperature which is equal to ambient temperature of test cell.

### 3.1.2 Measurement Equipment

The cylinder pressure was measured by a spark plug type (Kistler 6117A) piezoelectric transducer which was mounted in the cylinder head through the spark plug. The charge amplifier
for the pressure transducer was Kistler 5010. The crank-angle resolved pressure data were written directly on a hard disk via a high speed PC data acquisition system (Global Lab). The clock of the acquisition board was triggered by a crank shaft encoder which gave a pulse every crank angle degree. The signal of bottom dead center (BDC) in compression stroke was used to distinguish between engine cycles.

The volumetric flow rate of air was measured by a laminar flow meter installed at the upstream of the throttle valve. In order to damp out the highly pulsating intake air flow resulting from the single-cylinder operation, a 125 liter mixing tank was placed between the throttle valve and intake of engine.

The fuel injected per cycle in steady state was measured by the method (ii) described in section 2.1.2 : the fuel-air equivalence ratio (Φ) at the exhaust was measured by a Horiba oxygen sensor; the fuel flow could then be calculated from the measured air flow and Φ. From the discussion in section 2.1.2, the fuel flow measured by the three different methods are consistent (within 3%), and values measured by method (ii) were the most readily available quantity from the experiments. Therefore, the values of Φ quoted in the following are also those from the oxygen sensor measurement.

3.2 Experimental Development

3.2.1 Test Conditions and Procedure

The ambient temperature of test cell was at 18 - 20°C for all the experiments. At the beginning of each test run, the engine block, coolant water, engine oil and the fuel were all cooled down to ambient temperature by heat exchangers.
The engine was motored by dynamometer at constant speed. The dynamometer controller was set at a fixed speed of 900 rpm. During the motoring, the throttle position was set to provide an intake pressure of 0.4 bar. These engine speed and intake pressure are representative of idle condition in modern vehicles, and same as the operating conditions described in section 2.2.1. The spark ignition was on at all time. The spark timing was set at 22 crank angle degrees before top dead center (TDC) for the maximum brake torque of engine at 900 rpm.

At time zero, data acquisition system was trigger-started by the bottom dead center (BDC) signal of the first cycle to record the crank-angle resolved pressure data. Fuel injection started at the same cycle by energizing the injector. The pressure data was recorded for 100 cycles, which was enough to detect the first firing cycle of engine for all the fuels listed in the fuel matrix (see section 3.2.2) under ambient temperature.

In modern vehicles, the amount of fuel injected in each cycle varies during the start-up transient according to the program of the ECU which takes into account the coolant temperature and the time since first firing. Although programming of ECU is different from car to car, the amount (and also the $\Phi_{\text{inj}}$) of the first one or two injections are usually several times larger than the rest of the cycles to ensure consistent firing from the first cycle.

In the following definition of fueling strategy, one unit of fuel is defined as the amount that would constitute a stoichiometric ($\Phi = 1$, see section 2.2.2 for definition of $\Phi$) mixture at steady state as measured by an exhaust gas oxygen sensor when engine is fully warm-up. Therefore, $\Phi_{\text{inj}}(N) = n$ will represent that $n$ unit of fuel injected at the $N^{th}$ cycle.

In order to take the enrichment effects of the first cycle into account, a electronic controller is designed to vary the duration of the first injection pulse. The way the controller works is followed: several units of fuel were injected in the first cycle ($\Phi_{\text{inj}}(1) = n$, where $n$ can
be varied); followed by single unit of injection in the subsequent cycles (for $N > 1$, $\Phi_{\text{inj}}(N) = 1$). The stoichiometric amount of fuel ($\Phi_{\text{inj}} = 1$) was determined at the engine fully warm-up condition by varying the injection pulse width until the reading of exhaust gas oxygen sensor was 1. It is recognized that this starting procedure is different from that of a real engine because it has no cranking process and its fueling strategy is different. The procedure, however, retains the essential engine warm-up effects on mixture preparation, is well controlled, and is relatively simple so that the fuel volatility effects could readily be assessed.

3.2.2 Test Matrix

A test matrix was formulated in order to incorporate the two major control factors, fuel component effects and fuel enrichment effects, which influence the startability of engines.

Fuel matrix

The rationales behind the fuel blends selection are as following. The fuel blends should represent a broad range of volatility so that the effects of volatility on startability could be assessed. In order to study the fuel component effects, the binary mixture should contain the components from the two major categories of hydrocarbons in gasoline, paraffins and aromatics, which have quite different thermal-physical properties. And the blends are of practical interest.

The fuel species selected and their properties are tabulated in Table 3.2. The fuel blends used and their mixing ratio is listed in Table 3.3. There were one single-component fuel, three binary mixture, one gasoline, and one mixture of gasoline and its additive in the fuel matrix. Iso-Octane, with normal boiling point at $99.2^\circ C$ which is representative of the mid-range components in a gasoline, was used as the single-component fuel and the base component in the binary mixture. The binary blends were: iso-octane and n-pentane at volume ratio of 80/20 to study the
Table 3.2 Properties of the fuel components

<table>
<thead>
<tr>
<th>Fuels</th>
<th>Molecular Weight</th>
<th>Specific Gravity</th>
<th>Normal Boiling Pt.(C) or Distillation Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>72.1</td>
<td>0.631</td>
<td>36.1</td>
</tr>
<tr>
<td>n-Decane</td>
<td>142.3</td>
<td>0.743</td>
<td>174.1</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>106.2</td>
<td>0.869</td>
<td>139</td>
</tr>
<tr>
<td>iso-Octane</td>
<td>114.2</td>
<td>0.696</td>
<td>99.2</td>
</tr>
<tr>
<td>MTBE</td>
<td>88.2</td>
<td>0.731</td>
<td>54.8</td>
</tr>
<tr>
<td>Indolene</td>
<td>~110</td>
<td>~0.82</td>
<td>T10 = 53.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T50 = 105.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T90 = 151.7</td>
</tr>
</tbody>
</table>

Table 3.3 Composition of fuel blends

<table>
<thead>
<tr>
<th>Fuel blend</th>
<th>Volume ratio</th>
<th>Mass ratio</th>
<th>Mole ratio</th>
<th>Carbon ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-Octane</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>iso-Octane/n-Pentane</td>
<td>80/20</td>
<td>81.5/18.5</td>
<td>73.6/24.6</td>
<td>81.7/18.3</td>
</tr>
<tr>
<td>iso-Octane/n-Decane</td>
<td>90/10</td>
<td>89.5/10.5</td>
<td>91.4/8.6</td>
<td>89.5/10.5</td>
</tr>
<tr>
<td>iso-Octane/m-Xylene</td>
<td>75/25</td>
<td>70.6/29.4</td>
<td>69.1/30.9</td>
<td>69.1/30.9</td>
</tr>
<tr>
<td>Indolene</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>Indolene/MTBE</td>
<td>90/10</td>
<td>90.9/9.1</td>
<td>88.9/11.1</td>
<td>~</td>
</tr>
</tbody>
</table>

The effects of a light-end component in the mixture: iso-octane and n-decane at 90/10 to study the effects of a heavy-end component in the mixture; and iso-octane and m-xylene at 75/25 to study the effects of aromatics on the mixture. Therefore, by selecting n-pentane (paraffin), n-decane (paraffin) and m-xylene (aromatic), a broad range of volatility (BP from 36.1 to 174.1℃) was obtained and the effects of paraffins and aromatics on engine performance can be assessed.

The reason for using these particular mixing ratio (80/20, 90/10, and 75/25) was based on the specification of indolene listed in Table 3.4 [16]. The number of carbon atoms in gasoline hydrocarbons typically range from 4 to 12. Percentage of the species outside this range is very small (less than 0.5%). The sum of the volume percentages of light-end species (from C₃ to C₅) in indolene equals to 19.14% (= 0.02 + 6.90 + 12.22) which is very close to 20%. Therefore
20% of n-pentane by volume was used in the binary mixture iso-octane and n-pentane to study the effects of light-end components on engine starting behaviors. The total volume percentage of heavy-end species (from C\textsubscript{10} to C\textsubscript{12}) in indolene is 7.50% (= 4.66 + 2.35 + 0.49) and that of aromatics is 28.77%. Therefore, 10% of n-decane and 25% of m-xylene in the other two binary mixtures were used to study the effects of heavy-end components and aromatics.

Of practical interest is the starting behavior of real gasoline and mixture of gasoline and its additives. A calibration gasoline, indolene, was used to represent a practical fuel. The specification of indolene is listed in Table 3.4. Indolene and MTBE (methyl-tert-butyl-ether) blends with volume ratio of 90/10 were used in this study. Because of its compatibility with the current refinery process, MTBE is the leading choice of oxygenate to be introduced in reformulated gasoline. Usually about 10 - 11% by mass of MTBE is used in reformulated gasoline to replace some of the olefins and aromatics in regular gasoline. Therefore, 10% of MTBE was used in the fuel blends to approximate the properties of reformulated gasoline.

The liquid fuels were refrigerated to 0°C before they were blended together to avoid evaporative losses of light-end components.

<table>
<thead>
<tr>
<th>Carbon number</th>
<th>Paraffins</th>
<th>Aromatics</th>
<th>Olefin &amp; others</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>3 -</td>
<td>0.02</td>
<td>~</td>
<td>0.00</td>
<td>0.02</td>
</tr>
<tr>
<td>4</td>
<td>6.81</td>
<td>~</td>
<td>0.09</td>
<td>6.90</td>
</tr>
<tr>
<td>5</td>
<td>9.93</td>
<td>~</td>
<td>2.29</td>
<td>12.22</td>
</tr>
<tr>
<td>6</td>
<td>6.47</td>
<td>1.71</td>
<td>1.70</td>
<td>9.88</td>
</tr>
<tr>
<td>7</td>
<td>8.37</td>
<td>14.21</td>
<td>0.81</td>
<td>23.38</td>
</tr>
<tr>
<td>8</td>
<td>28.76</td>
<td>1.95</td>
<td>0.32</td>
<td>31.04</td>
</tr>
<tr>
<td>9</td>
<td>1.59</td>
<td>7.16</td>
<td>0.31</td>
<td>9.06</td>
</tr>
<tr>
<td>10</td>
<td>1.17</td>
<td>3.11</td>
<td>0.38</td>
<td>4.66</td>
</tr>
<tr>
<td>11</td>
<td>0.83</td>
<td>0.58</td>
<td>0.94</td>
<td>2.35</td>
</tr>
<tr>
<td>12 +</td>
<td>0.08</td>
<td>0.05</td>
<td>0.36</td>
<td>0.49</td>
</tr>
<tr>
<td>Total</td>
<td>64.03</td>
<td>28.77</td>
<td>7.20</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Fuel enrichment

The detail of fueling strategy used in this study is explained in section 3.2.1. The unit of fuel injected in the first cycle \( \Phi_{\text{inj}}(1) \) was varied from 1 (stoichiometric) to 7 (rich) for different fuel blends, with increment of 1. For all of the fuel blends, when \( \Phi_{\text{inj}}(1) \) was equal to or larger than 7, engine fired at the first cycle (see section 3.3). Therefore, increasing \( \Phi_{\text{inj}}(1) \) to 8 or larger values is not necessary for the purpose of detecting engine firing. Followed by the first cycle, single unit of fuel was injected in the subsequent cycles (for \( N > 1 \), \( \Phi_{\text{inj}}(N) = 1 \)).

The test matrix included 6 fuels and 7 different \( \Phi_{\text{inj}}(1) \). Thus there are altogether 42 data points presented in the following section. Each operating condition was repeated three times to check the reproducibility of the engine response. Therefore, there were total 126 (= 42 x 3) test runs.

3.3 Data Interpretation - First Firing Cycle

From the crank-angle resolved cylinder pressure data, the cycle-resolved Gross Indicated Mean Effective Pressure (GIMEP) history by using a particular fuel is calculated for 100 cycles. Definition of GIMEP and the equation of calculating GIMEP are stated in section 2.3 and equation (2.2). From the definition of GIMEP, the engine produces positive work output during compression and expansion strokes when the GIMEP is larger than zero. This positive work is generated by the release of chemical energy of fuel through combustion and the expansion of the hot burned gas. Therefore, in the following paragraphs, a firing cycle is defined as a cycle with positive value of GIMEP; a misfiring cycle is a cycle when GIMEP equals zero.

Typical GIMEP trace versus cycle number of a simulated engine start-up process are shown in Figure 3.2 and Figure 3.3. The data for Figure 3.2 were obtained with no fuel
enrichment in the first cycle ($\Phi_{\text{inj}}(1) = 1$) for indolene. The engine did not fire until the 16th cycle. Thus the first firing cycle number of this case was 16. In Figure 3.3, the fuel used was also indolene while the $\Phi_{\text{inj}}(1)$ was increased to 7. The first firing cycle under this condition was 1. After the first firing cycles, misfired cycles and large cycle-to-cycle variations were observed in both Figure 3.2 and Figure 3.3. Similar behaviors were also observed when using different fuels and different $\Phi_{\text{inj}}(1)$.

The relationships between first firing cycle versus the unit of first fuel injection $\Phi_{\text{inj}}(1)$ by using the fuels listed in Table 3.3 are shown in Figure 3.4 to 3.9. There were three repeated test runs for each $\Phi_{\text{inj}}(1)$ and all the data points are shown in those graphs (some of them are overlapping). These repeated tests show pretty consistent results in term of the first firing cycle (± 1 cycle).

For iso-octane, the first firing cycle (Figure 3.4) occurs earlier with increase enrichment of the first injection: when $\Phi_{\text{inj}}(1)$ was increased from 1 to 7, number of first firing cycle was decreased from 8 (or 9) to 1. Similar trends were also observed by using other five fuel blends (Figure 3.5 to Figure 3.9). This is consistent with the notion that the engine starts faster with enrichment of fuel which is also demonstrated by the experimental results described in section 2.3.

When there is no enrichment for the first cycle ($\Phi_{\text{inj}}(1) = 1$), the first firing cycles by using different fuel blends are listed in the second column of Table 3.5. By comparing those numbers for iso-octane and three binary blends, there seems to be a trend that the first firing cycle occurs earlier with increasing proportion of volatile component (n-pentane) and later with increasing proportion of heavy-end components (n-decane and m-xylene). Similarly, the first firing cycle of indolene and MTBE mixture (15 or 16) is somewhat smaller than that of indolene (16 or 17) due to the addition of MTBE. MTBE is relatively volatile (normal boiling point at
55°C) compared to most of the indolene components. This is consistent with the notion that the engine starts faster with a more volatile fuel (see section 2.3). When $\Phi_{\text{inj}}(1)$ was increased, the observation described above was still valid: namely earlier occurrence of the first firing cycle with the fraction of more volatile components in the mixture. But there is no direct comparison for those numbers between the binary mixture and practical fuels.

In Figure 3.4 to Figure 3.9, the $\Phi_{\text{inj}}(1)$ required to fire the engine at the first cycle by using different fuel blends are listed in the third column of Table 3.5. Intuitively, the more volatile is the fuel blend, the less is the required $\Phi_{\text{inj}}(1)$ to fire the engine at the first cycle. By comparing the values for iso-octane and the three binary blends, there is the trend that the $\Phi_{\text{inj}}(1)$ required to fire the engine at the first cycle decreases with the increase of proportion of volatile component (n-pentane), and increases with increase of proportion of heavy-end components (n-decane and m-xylene). The numbers for indolene and indolene / MTBE blends are the same. There is also no direct comparison for those numbers between the binary mixture and practical fuels.

In summary, the ease of starting improves with enrichment and with increase amount of volatile components in the fuel blend. From the experimental data of Figure 3.4 to Figure 3.9,

**Table 3.5 Relationship Between First Firing Cycle and $\Phi_{\text{inj}}(1)$ for Different Fuel Blends**

<table>
<thead>
<tr>
<th>Fuel blend</th>
<th>First Firing Cycle at $\Phi(1) = 1$</th>
<th>$\Phi(1)$ to fire engine at the first cycle</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-Octane</td>
<td>8 or 9</td>
<td>5</td>
</tr>
<tr>
<td>iso-Octane/n-Pentane</td>
<td>6 or 7</td>
<td>3</td>
</tr>
<tr>
<td>iso-Octane/n-Decane</td>
<td>11 or 12 or 13</td>
<td>6</td>
</tr>
<tr>
<td>iso-Octane/m-Xylene</td>
<td>13 or 14</td>
<td>7</td>
</tr>
<tr>
<td>indolene</td>
<td>16 or 17</td>
<td>3</td>
</tr>
<tr>
<td>indolene/MTBE</td>
<td>15 or 16</td>
<td>3</td>
</tr>
</tbody>
</table>

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some behaviors of the first firing cycle of engine related to the fuel component and enrichment effects had been addressed. First, the first firing cycle occurs earlier with increasing degree of enrichment of first injection $\Phi_{inj}(1)$ for all of the fuel blends in test matrix. Secondly, for the same $\Phi_{inj}(1)$, first firing cycle occurs earlier with increasing proportion of volatile components and later with increasing proportion of heavy-end components. Finally, the $\Phi_{inj}(1)$ required to fire the engine at the first cycle decreased with increasing proportion of volatile components, and increased with increasing proportion of heavy-end components.

Some of aspects of the first firing cycle had not been explained yet. For example, the first firing cycle at $\Phi_{inj}(1) = 1$ for iso-octane is 8 (or 9) and that of indolene is 16 (or 17) (see 2nd column of Table 3.5). This observation, however, does not necessarily mean that iso-octane is more volatile than indolene because the boiling points of some of the species (e.g. n-pentane, BP = $36.1^\circ$C) in indolene is actually lower than that of iso-octane ($99.2^\circ$C); The required $\Phi_{inj}(1)$ to fire the engine at the first cycle for iso-octane is 5 and that of indolene is 3 (see 3rd column of Table 3.5). These two comparisons of the first firing cycle between iso-octane and indolene seem to be contradictory at the first sight because it is not possible to explain the fuel component and volatility effects on engine starting behaviors by only looking at the specific properties (e.g. boiling point) of selected fuel species. The starting characteristics are related to the evaporative behavior of the fuel in the mixture preparation process; it is desirable to devise a model to account for the combined effects of fuel enrichment, fuel volatility, and fuel component effects on the starting behaviors. The development of mixture preparation model will be described in section 6.1 and section 6.3, and correlations of $\Phi_{vapor}$ (vapor equivalence ratio of the air/fuel mixture present in the combustion chamber) with the first firing cycle of engine will be described in section 6.4.
Figure 3.2 GIMEP trace of the simulated engine start-up process by using indolene as fuel at $\Phi_{\text{in}}(1) = 1$

Figure 3.3 GIMEP trace of the simulated engine start-up process by using indolene as fuel at $\Phi_{\text{in}}(1) = 7$
**Figure 3.4** First firing cycle versus the unit of first fuel injection $\Phi_{in}(1)$ by using iso-octane as fuel.

**Figure 3.5** First firing cycle versus the unit of first fuel injection $\Phi_{in}(1)$ by using iso-octane/n-pentane mixture (volume ratio = 80/20) as fuel.
Figure 3.6 First firing cycle versus the unit of first fuel injection $\Phi_{\text{inj}}(1)$ by using iso-octane/n-decane mixture (volume ratio = 90/10) as fuel.

Figure 3.7 First firing cycle versus the unit of first fuel injection $\Phi_{\text{inj}}(1)$ by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel.
**Figure 3.8** First firing cycle versus the unit of first fuel injection $\Phi_{in}(1)$ by using indolene as fuel

**Figure 3.9** First firing cycle versus the unit of first fuel injection $\Phi_{in}(1)$ by using indolene/MTBE mixture (volume ratio = 90/10) as fuel
In this Chapter, the study of another aspect of engine starting and warm-up behaviors, hydrocarbon emissions, is described. A sampling system was developed to measure the evolution of the speciated hydrocarbon emissions from a single-cylinder SI engine in a simulated starting and warm-up procedure. A sequence of exhaust samples was drawn and stored for gas chromatography analysis. The time resolution of the sampling unit was of the order of 1 to 2 engine cycles at 900 rpm. Four different fuels were used to investigate the fuel effects on speciated hydrocarbon emissions under either firing or motoring condition. The design of the time-resolved exhaust gas sampling unit is first described in section 4.1. The verification of the performance of the sampling unit is described in section 4.2. The test procedure, conditions and test matrix are stated in section 4.3. The specification of the gas chromatography applied in this study was briefly described in section 4.4. Then the fuel effects on the time history of fuel and
non-fuel species of hydrocarbons in exhaust gas during starting and warm-up processes by using different fuels are presented in section 4.5 [17].

4.1 Design of Time-Resolved Exhaust Gas Sampling Unit

The design requirements for the exhaust gas sampling unit are:

(i) The sampling unit must be able to perform time-resolved sampling because the time history of speciated hydrocarbon emissions can provide insight to the relationship between fuel evaporation during mixture preparation process and hydrocarbon emissions during cold start.

(ii) There must be storage units to store exhaust gas samples for gas chromatography analysis.

(iii) The amount of exhaust gas sample captured by the sampling unit must be enough for the GC analysis. GC requires at least 5 c.c. of gas sample for each analysis run.

(iv) The resolution of the sampling unit must be in the order of the time for one engine cycle, and the sample should not aggregate over different cycles in order to study the highly transient behaviors of hydrocarbon emissions during cold-start and warm-up processes.

(v) The time delay between the inlet of exhaust gas sample to the storage unit of sampling system must be small (less than one engine cycle) in order to correctly interpret the evolution of hydrocarbon emissions.

(vi) The storage unit of the sampling system must be able to prevent the hydrocarbons stored in the unit from chemical reactions in order to keep the composition of chemicals in the storage unit unchanged before analysis.

The most commonly used technique to detect the total hydrocarbon concentration in exhaust gas of spark-ignition engines is the flame ionization detector (FID) [18, 19]. In a FID, chemi-ionization takes place when hydrocarbon molecules are introduced into a hydrogen flame.
The magnitude of the current generated is proportion to the concentration (ppmCl) of aliphatic carbon atom in the sampled gas. The resolution of a fast-response FID (FFID) is in the order of several milliseconds. It can be used to measure the crank-angle-resolved hydrocarbon concentration due to its high resolution. However, FFID can only measure total hydrocarbon concentration (violates requirement (ii)).

Another technique used by some of researchers was the wall-mounting rapid-acting sampling valves installed on either cylinder head or exhaust pipe of engine [20]. The duration of the sampling window of the valve is about 3 ms. It can also be used to measure the crank-angle-resolved hydrocarbon concentration. In order to have enough sample for hydrocarbon analyzer, gas sample was repeatedly taken over the same crank angle for many cycles. Thus it can only be used to measure the hydrocarbon concentration under steady-state operation of engine (violates requirement (iv)).

Tedlar bags coupling with solenoid valves were also used by researchers [8, 21, 22] to investigate the species distribution of hydrocarbon emissions. However, the sampling windows used were quite coarse in order to fill the bag with an approximate volume of 10 liters: they range from 3 to 30 seconds which would correspond to many engine cycles (violates requirement (iv)). Therefore, this technique is not suitable for purpose of studying highly transient evolution of hydrocarbon emissions during engine starting and warm-up processes.

In order to fulfill the requirements described above, a exhaust gas sampling unit capable of storing 16 samples was designed and shown in Figure 4.1. Only one of the sixteen sampling cylinders and the components associated with it are shown in the figure. The specification of some components of the sampling unit is stated in Table 4.1. The dimensions of the sampling unit is shown in Figure 4.2.

The sample was taken by a sampling probe placed at the exhaust runner (see Figure 4.1). Its tip was located at the center line of the exhaust runner and about 15 cm from the exhaust
Table 4.1 Specification of components of the sampling unit

<table>
<thead>
<tr>
<th>component</th>
<th>specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>bypass circuit</td>
<td>1/4&quot; copper tubing, ID = 0.175&quot;</td>
</tr>
<tr>
<td>3-way directional solenoid valve</td>
<td>ss body, 1/32&quot; orifice, response time ~ 10 ms</td>
</tr>
<tr>
<td>2-way valve (bottom of cylinder)</td>
<td>type = ball valve, 1/4&quot; male NPT x 2</td>
</tr>
<tr>
<td>3-way valve (top of cylinder)</td>
<td>type = ball valve, 1/4&quot; male NPT x 3</td>
</tr>
<tr>
<td>sampling cylinder</td>
<td>ss, inside volume = 150 cc, 1/4&quot; female NPT</td>
</tr>
<tr>
<td>sampling probe</td>
<td>1/8&quot; ss tubing, ID = 0.05&quot;</td>
</tr>
<tr>
<td>splitter</td>
<td>ss, 1 inlet, 16 outlet, inside volume ~ 10 cc</td>
</tr>
</tbody>
</table>

valves. The inner space of the exhaust runner between the exhaust valves and the sampling location was roughly equal to the engine displacement volume (487 c.c. for Volvo B5254 FS engine, see section 3.1.1). This configuration was intent to provide enough space for the exhaust gas of one cycle to be fully mixed so that representative (cycle-averaged) sample can be captured. The other end of the sampling probe was connected to a splitter which was used to divide the sample gas into 16 parts. Each part of the sample was directed to one of the sixteen sampling cylinders for storage.

The flow between the splitter and the sampling cylinder was controlled by a fast-acting three-way directional solenoid valve. The operation modes of the solenoid valve are as follows: before the solenoid valve was energized, the sample gas was directed to the bypass circuit; when the solenoid valve was energized, the sample gas was directed to the sampling cylinder. At 900 rpm, one engine cycle corresponds to 0.13 second which is large compared to the response time (duration from fully closed to fully opened) of the solenoid valves (~ 10 ms) so that aperture uncertainty is not significant.

During the process of taking sample, the bypass circuit was connected to a vacuum pump which generated a flow of sample from exhaust pipe, through the splitter and de-energized solenoid valves, to the bypass circuit due to the pressure gradient. Therefore, there was essentially no "dead volume" in the sampling system due to this continuous flow of sample and small inner volume (less than 10 c.c.) of the splitter. Before the sampling process, all the
sampling cylinders were evacuated by vacuum pump through the three-way ball valve at the top of the sampling cylinder. When the solenoid valve was at the energized state during the sampling, the sample in the splitter was sucked into the sampling cylinder due to pressure gradient between the splitter and sampling cylinder. The sample was stored in the sampling cylinder, then diluted by nitrogen through the three-way ball valve. After the sampling process, all the 2-way ball valves at the bottom of sampling cylinders and the 3-way ball valves at the top of sampling cylinders were closed to ensure no leakage of sample from cylinder.

All the components of the sampling units were covered by two 3/16-inch aluminum plates at the top and bottom of the sampling unit and surrounded by 1-1/4 inch fiber glass insulation. It is known that the condensation of water may block the sampling loops, especially the orifice (1/32-inch in diameter) of the solenoid valve, and the condensation of heavy hydrocarbons in the sampling loops will change the composition of hydrocarbons captured by the sampling cylinder. The inside space of the sampling unit can be heated by the heating tapes to prevent the condensation of water vapor and heavy hydrocarbons in the sampling loops. The temperature of the heating tapes was controlled by the Omega temperature controller and feedback by a K-type thermocouple.

The timing and the duration of the sampling windows was computer controlled for maximum flexibility. A IBM-compatible PC and a digital/AD/DA IO board were used to program the sampling events (open and close of each solenoid valve). The sampling sequence was indexed to the engine cycles using the BDC-compression pulse. The duration of the opening of the solenoid valves was timed by a real time clock (Intel 8254). Because of the pulsating nature of the exhaust flow, the sampling duration was typically set to 1 or 2 engine cycle periods to ensure that the sample taken did fully represent the cycle-averaged exhaust mass, but with sufficient time resolution to capture the emissions evolution during the warm-up process (see section 4.2 Verification of Time-Resolved Exhaust Gas Sampling Unit). Then the digital signal

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of the sampling events from the computer was amplified by the driver circuit which provided 24-volt DC current to the solenoid valves.

All the dimensions and arrangement of the components of the sampling unit shown in Figure 4.2 was designed to shorten the length of sampling loops or increase the flow speed in order to minimize the transport time of sample from sampling point to sampling cylinder. But they were also constrained by the fact that there must be enough space to fit 16 sampling cylinders and other components associated with them. The 1/8-inch tubing (ID 0.05"") was used in the loop from sampling probe to sampling cylinder in order to comprise between increasing flow speed and preventing water and heavy hydrocarbons from concentration. In this configuration, the delay time of the sample from sampling point to the sampling cylinder was less than one engine cycle (see section 4.2).

After the sampling, the sampling cylinders were typically filled to ~ 20 torr (~ 0.03 bar abs.) of sample gas at the sampling duration of 0.13 second (one engine cycle at 900 rpm). Right after sample collection, the cylinders were filled with a metered amount of nitrogen to ~ 900 torr (~ 1.2 bar abs.) before they were sent off for gas chromatography (GC) analysis. This pressure which was slightly higher than atmospheric pressure provided a pressure gradient to transport the sample from sampling cylinder to GC. The equipment designed to measure the pressure of sampling cylinders and to dilute the sample is shown in Figure 4.3. First the 2-way ball valves was closed while the 3-way ball valves was directed to the vacuum pump until the pressure reading was less than 0.1 torr. Then the 3-way ball valves was closed while the 2-way ball valves was opened to measure the pressure of the sample in the cylinder. Right after that, the 3-way ball valve was directed to the supple of nitrogen which was regulated at ~ 20 psi until the reading of pressure was about 900 torr.
**Figure 4.1** Time-resolved exhaust gas sampling unit

**Figure 4.2** Dimensions of the time-resolved exhaust gas sampling unit
Figure 4.3 Equipment for measuring the pressure of exhaust gas and diluting the sample in the sampling cylinder

4.2 Verification of Time-Resolved Exhaust Gas Sampling Unit

In order to correctly interpret the evolution of hydrocarbon emissions (requirement (v) in section 4.1), the time delay between the inlet of exhaust gas sample to the storage unit must be less than one engine cycle. The transit time from the sample entry point to the storage cylinder was estimated from the bypass flow rate (measured), the flow rate to the cylinder (inferred from the pressure rise of the cylinder after the sample was captured), and the geometry of the sampling system. This transit time under typical operating condition was ~ 50 ms. This time was approximately evenly divided between the residence time in the inlet tubing, in the cavity of the splitter, and in the connection from the splitter to the solenoid valve. The flow was choked at the solenoid valve: the transit time from the valve to the sampling bottle was negligible.

To test the time resolution of the system, the total hydrocarbon values measured by the sampling system were compared to those measured by a fast FID (see section 4.1). The engine used was the Volvo B5254 FS single-cylinder engine. The specification and modification of the
engine was described in section 3.1.1. These two systems started taking sample simultaneously at the BDC of the first engine cycle. The inlets of both measurement systems were located at the same distance (15 cm) from the exhaust valve of engine. The comparison of the total HC concentration measured by these two systems are shown in Figure 4.4 and Figure 4.5.

![Figure 4.4 Comparison between HC measurements from fast-FID and from sampling unit (A single unit of fuel was injected at the first cycle with the ignition turned off.)](image)

In Figure 4.4, the engine was motored at 900 rpm with ignition turned off. The throttle was set to provide an intake pressure of 0.4 bar. A single pulse of 7 units of fuel (indolene) was injected; there was no further fuel injection afterwards. There was no firing in the combustion chamber due to the fact that there is no ignition. The exhaust hydrocarbon measured by the fast FID are shown as the continuous dotted line in Figure 4.4. Here and in all hydrocarbon concentrations reported in this thesis, the concentration is in terms of ppmC1 (parts per million carbon atom). The resolution of fast FID is in the order of several milliseconds which is much
smaller than 0.13 second (equal to one engine cycle). The sampling system measurements are shown as solid symbols. The sampling window width was at 0.13 second and exhaust gas samples were taken at consecutive cycles. The ordinate of the data points (in this and in all subsequent figures of this thesis) were set at the center of the individual sampling windows. There is excellent agreement between the two measurement systems. Therefore, the resolution of the sampling system is at least in the order of one engine cycle (0.13 sec at 900 rpm).

![Graph](image)

**Figure 4.5** Comparison between HC measurements from fast-FID and from sampling unit (One unit of fuel was injected each cycle with the ignition turned on.)

In Figure 4.5, the two measurement systems are compared under firing condition. The operating conditions of the engine are the same as described in section 3.2.1, but the first injection pulse of fuel was equal to 1 unit: the engine speed was kept constant at 900 rpm; the intake pressure was at 0.4 bar; the ignition was on. The test was started by injecting one unit of fuel for each cycle. The Gross Indicated Mean Effective Pressure (GIMEP) (see section 2.3 for the definition of GIMEP) in Figure 4.5 shows that there was no firing in the first 6 cycles. The
hydrocarbon concentration increased in these cycles due to the accumulation of liquid fuel in intake port and cylinder. The subsequent few cycles show low GIMEP and misfiring behaviors. The features was captured by the fast FID : the hydrocarbon concentration dropped after a burn cycle and increased after a misfired cycle. The sampling system measurement also captured these features, but with a phase delay of about one cycle and a damped amplitude of the HC fluctuation. This delay and damping may be attributed to the fact that the sampling system is averaging the exhaust gas over 1 cycle.

The overall performance of the sampling system is deemed satisfactory in that it could average the pulsating exhaust gas over about one cycle so that the sample taken does fully represent the cycle-averaged exhaust mass. The resolution was of the order of one to two cycles; this is of sufficient resolution to capture the emissions evolution during the normal warm-up process.

4.3 Experimental Development

4.3.1 Test Conditions and Procedure

All the experiments reported in this chapter were done on the Volvo B5254 FS Engine (see section 3.1.1 for its specification and modification). The simulated start-up procedure described in section 3.2.1 was used. The engine and fuel were initially at ambient temperature (~20°C). The engine speed was fixed at 900 rpm by dynamometer. The throttle position was set to provide an intake pressure of 0.4 bar. These engine speeds and intake pressure are representative of engine idle condition and same as operating conditions described in section 3.2.1. For the motoring case, the ignition was off; for firing case, the ignition was on at all time. The spark
timing was set at 22 crank angle degrees before top dead center (TDC) for maximum brake
torque of engine at steady state under the operating conditions described above.

Before the sampling process, all the sampling cylinders were evacuated by vacuum pump
through the three-way ball valve at the top of the sampling cylinder (see Figure 4.1). The air
inside the sampling cylinders were pumped out until the pressure reading was less than 0.1 torr.
During the sampling process, the bypass circuit was connected to a vacuum pump in order to
generate a continuous flow of exhaust gas from the exhaust pipe, through the splitter and de-
energized solenoid valves, to the bypass circuit.

At time zero, data acquisition system was triggered by the bottom dead center (BDC)
signal of the first cycle to start to record the crank-angle resolved pressure data. At the same
time, the sampling system was also triggered by the BDC signal to start sampling. The pressure
data was recorded for 1000 cycles, which is enough to encompass the fuel transient behaviors
during cold start. Fuel injection started at the first cycle. The amount of fuel injected at the first
cycle can be varied by a electric controller (see section 3.2.1). Several units of fuel were injected
in the first cycle; followed by single unit of injection in the subsequent cycles (see section 3.2.1
for the definition of the unit of fuel).

After the sampling, the sampling cylinders were typically filled with exhaust gas to ~ 18
torr at the sampling duration of one engine cycle (0.13 sec) and ~ 35 torr at the sampling duration
of two engine cycle (0.26 sec). Right after sample collection, the samples were diluted by
nitrogen and the cylinders were pressurized to ~ 900 torr (~ 1.2 bar abs.) before they were sent
off for gas chromatography (GC) analysis. In these conditions, the dilution ratio (= final pressure
/ initial pressure) of the sample was ~ 50 at the sampling duration of one engine cycle and ~ 25 at
the sampling duration of two engine cycle.

4.3.2 Test Matrix
Fuel matrix

The fuel species selected and their properties are tabulated in Table 4.2. The fuel blends used and their mixing ratio are listed in Table 4.3. Iso-octane, with normal boiling point at 99.2°C which is representative of the mid-range components in a gasoline, was used as the single-component fuel and the base component in the binary fuel mixture. The binary blends were: iso-octane and n-pentane at volume ratio of 80/20 to study the effects of a light-end component in the mixture; iso-octane and n-decane at 90/10 to study the effects of a heavy-end component in the mixture; and iso-octane and m-xylene at 75/25 to study the effects of aromatics on the mixture. The reason for using these particular mixing ratio (80/20, 90/10, and 75/25) in Table 4.3 had been explained in section 3.2.2. Therefore, a broad range of volatility (BP from 36.1 to 174.1°C) was obtained and the effects of paraffins and aromatics on hydrocarbon emissions can be assessed by using this selection of binary mixtures. Of practical interest is the starting behavior of real gasoline. A calibration gasoline, indolene, was used to represent a practical fuel. The specification of indolene is listed in Table 3.4.

Table 4.2 Properties of the fuel components

<table>
<thead>
<tr>
<th>Fuels</th>
<th>Molecular Weight</th>
<th>Specific Gravity</th>
<th>Normal Boiling Pt.(°C) or Distillation Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>72.1</td>
<td>0.631</td>
<td>36.1</td>
</tr>
<tr>
<td>n-Decane</td>
<td>142.3</td>
<td>0.743</td>
<td>174.1</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>106.2</td>
<td>0.869</td>
<td>139</td>
</tr>
<tr>
<td>iso-Octane</td>
<td>114.2</td>
<td>0.696</td>
<td>99.2</td>
</tr>
<tr>
<td>Indolene</td>
<td>~110</td>
<td>~0.82</td>
<td>T10 = 53.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T50 = 105.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>T90 = 151.7</td>
</tr>
</tbody>
</table>
Table 4.3 Composition of fuel blends

<table>
<thead>
<tr>
<th>Fuel blend</th>
<th>Volume ratio</th>
<th>Mass ratio</th>
<th>Mole ratio</th>
<th>Carbon ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-Octane/n-Pentane</td>
<td>80/20</td>
<td>81.5/18.5</td>
<td>73.6/24.6</td>
<td>81.7/18.3</td>
</tr>
<tr>
<td>iso-Octane/n-Decane</td>
<td>90/10</td>
<td>89.5/10.5</td>
<td>91.4/8.6</td>
<td>89.5/10.5</td>
</tr>
<tr>
<td>iso-Octane/m-Xylene</td>
<td>75/25</td>
<td>70.6/29.4</td>
<td>69.1/30.9</td>
<td>69.1/30.9</td>
</tr>
<tr>
<td>indolene</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
</tbody>
</table>

Test Matrix

The operating conditions for the firing cases for all of the fuel blends and motoring cases for iso-octane / m-xylene mixture and indolene are shown in Table 4.4. The purpose of the motoring cases was to exclude non-fuel species in exhaust gas in order to study the relationships between mixture preparation process and hydrocarbon emissions during cold start. The detail of fueling strategy used in this study is explained in section 3.2.1. The unit of fuel injected in the first cycle ($\Phi_{inj}(1)$, see section 3.2.1 for definition) was varied from 1 (stoichiometric) to 10 (rich) for different fuel blends to ensure firing of engine from the first cycle: more volatile fuel requires less $\Phi_{inj}(1)$; less volatile fuel requires more $\Phi_{inj}(1)$. For the motoring cases, the same $\Phi_{inj}(1)$ was used as those of the same fuel blends for firing cases, for the purpose of consistency. Followed by the first cycle, single unit of fuel was injected in the subsequent cycles (for $N > 1$, $\Phi_{inj}(N) = 1$). The unit of fuel injected in the first cycle for different fuel blends are listed in the third column of Table 4.4. The sampling durations were either 0.13 or 0.26 second, which corresponded to one or two engine cycle, for each case. Different sampling periods were used according to the transient behaviors of the fuel blends in terms of hydrocarbon emissions: the cases with less volatile fuel blends or under firing condition required longer time to reach steady state.
Table 4.4 Test matrix for hydrocarbon emission sampling

<table>
<thead>
<tr>
<th>Fuel blend</th>
<th>Ignition</th>
<th>Φ(1) injection</th>
<th>Sampling duration</th>
<th>Sampling period</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-Octane/n-Pentane</td>
<td>Firing</td>
<td>4</td>
<td>0.26 sec</td>
<td>0 - 75 sec</td>
</tr>
<tr>
<td>iso-Octane/n-Decane</td>
<td>Firing</td>
<td>10</td>
<td>0.26 sec</td>
<td>0 - 15 min</td>
</tr>
<tr>
<td>iso-Octane/m-Xylene</td>
<td>Motoring</td>
<td>10</td>
<td>0.13 sec</td>
<td>0 - 3 min</td>
</tr>
<tr>
<td>iso-Octane/m-Xylene</td>
<td>Firing</td>
<td>10</td>
<td>0.26 sec</td>
<td>0 - 15 min</td>
</tr>
<tr>
<td>indolene</td>
<td>Motoring</td>
<td>7</td>
<td>0.13 sec</td>
<td>0 - 3 min</td>
</tr>
<tr>
<td>indolene</td>
<td>Firing</td>
<td>7</td>
<td>0.26 sec</td>
<td>0 - 15 min</td>
</tr>
</tbody>
</table>

4.4 Gas Chromatography Analysis

Speciation analysis was performed by a HP 5890 GC (Gas Chromatography). Method 2 established by the Auto-Oil Program was followed. Details of the speciation technique are listed in Reference [23] (which lists the retention indices). Some of the instrument parameters for Method 2 are listed in Table 4.5. Typical analysis time for each sample was about 1 hour for each sample. Each sample in one of the sampling bottles was analyzed twice to check the reproducibility.

Hydrocarbons were identified by comparing the observed retention times with those found by calibration standards or retention indexes from comparisons with tables. The GC retention time calibration was updated twice a day by running a calibration gas mixture. The calibration gas is a 23-component mixture containing all C₄ - C₁₃ n-alkanes, plus ethene, 2M-propene, 13-butadiene, benzene, 224tM-pentane, toluene, p-xylene, o-xylene, and 124tM-benzene, all with a concentration of approximately 5 ppbC1.

Method 2 was primarily designed to measure C₄ to C₁₂ hydrocarbons (except for 1M-cyclopentane, benzene, 233tM-pentane, and toluene). Thus some of the species can not be separated by Method 2. For example, the C₁ and C₂ hydrocarbons became a single peak in the
GC spectrum; the peaks of 233tM-pentane and toluene, of which the retention indices are very similar, overlapped. Besides the above, there may be some species whose retention indices are very close can not be separated by this method. More discussion about this problem is described in section 6.6.5.

Table 4.5 Instrument parameters of GC analysis

<table>
<thead>
<tr>
<th>parameter</th>
<th>Method 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>pre-column</td>
<td>2m x 0.32 mm i.d. deactivated fused silica</td>
</tr>
<tr>
<td>column</td>
<td>60 m DB-1, 0.32 mm i.d., 1um film thickness</td>
</tr>
<tr>
<td>sample loop</td>
<td>5mL, maintained at 120C</td>
</tr>
<tr>
<td>column head pressure</td>
<td>140 kPa (set for propane retention time)</td>
</tr>
<tr>
<td>FID hydrogen</td>
<td>110 kPa for a flow of 32 mL/min</td>
</tr>
<tr>
<td>FID air</td>
<td>290 kPa for a flow of 400 mL/min</td>
</tr>
<tr>
<td>FID make up N2</td>
<td>280 kPa for a flow of 32 mL/min</td>
</tr>
<tr>
<td>detector temperature</td>
<td>300C</td>
</tr>
<tr>
<td>temperature</td>
<td>T = -80C for 0.01 min</td>
</tr>
<tr>
<td></td>
<td>T = -80C to -50C at 20C/min</td>
</tr>
<tr>
<td></td>
<td>T = -50C for 2.5 min</td>
</tr>
<tr>
<td></td>
<td>T = -50C to 250C at 6C/min</td>
</tr>
<tr>
<td>valve timing sequence</td>
<td>on at 0.01 min; off at 1.50 min</td>
</tr>
</tbody>
</table>

4.5 Data Interpretation

4.5.1 iC8 / m-Xylene Mixture - Motoring

The exhaust speciated emissions were first measured for the binary mixture of iso-octane and m-xylene at the blending ratio of 75/25 with ignition off. It is the simplest case in the test matrix because of the non-firing condition (no product species) and the simple composition of the mixture. Thus, the species in the exhaust gas were only iso-octane and m-xylene, the two components in the fuel. This data also serve as a reference for the evaporative behaviors of hydrocarbons in the mixture preparation process, which will be discussed in Chapter 6.
The top line shown in Figure 4.6 is the evolution of total HC concentration (in ppmC1) which is the sum of concentrations of iso-octane and m-xylene. Total hydrocarbon concentration rises rapidly in the first 5 cycles or so, and then increases gradually to 142,000 ppmC1 at 3 minutes. The "steady-state" value is shown as an open symbol on the right end of the graph. It roughly corresponds to the stoichiometric air/fuel ratio for the mixture (138,000 ppmC1) and is consistent with the amount of injected fuel ($\Phi_{\text{inj}} = 1$).

![Graph showing HC concentration over cycles](image)

**Figure 4.6** Total and exhaust speciated HC concentrations (ppmC1) by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel under engine motoring condition

Speciated emission concentrations for iso-octane and m-xylene in ppmC1 are also plotted in Figure 4.6. The concentration of iso-octane rises faster than that of m-xylene. The corresponding values for each species normalized by the total hydrocarbon concentration are plotted in Figure 4.7. The percentage of the more volatile species, iso-octane (with normal boiling point 99.2 °C) in exhaust gas is initially high, then drops gradually to the steady state
value. The percentage of the less volatile species, m-xylene (with normal boiling point 139°C) increases very fast with ~ 10 cycles, then increases more gradually and approaches steady state value. Therefore, for iso-octane/m-xylene mixture, the hydrocarbons in exhaust gas are dominated by the more volatile species in the first few cycles. In the first sample, for example, iso-octane contributes 92.81% of total hydrocarbon. This is significantly higher than the concentrations in the fuel (in terms of carbon atoms, iso-octane 68.89%, m-xylene 31.11%; see Table 4.3). At steady state, the values for iso-octane and m-xylene (66.45% and 31.74%), which are represented by open symbols at the right hand side of the graph, are very close to the values in the fuel (68.89% and 31.11%). This shows the consistency between the composition of injected fuel and that of the vaporized fuel.

**Figure 4.7** Normalized exhaust HC concentrations (ppmC1%) of fuel species by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel under engine motoring condition
In summary, before the engine fires, the fuel components delivered to the engine and subsequently to the exhaust are dominated by the more volatile species of the fuel. At the steady state, the total hydrocarbon concentration is consistent with the amount of injected fuel ($\Phi_{\text{inj}} = 1$). The fact that the composition of individual species in exhaust gas at steady state are very close to the values in the fuel demonstrates the consistency between the composition of injected fuel and that of the vaporized fuel.

4.5.2 iC8 / m-Xylene Mixture - Firing

The fuel used and the engine operating condition were the same as the previous case, except that the ignition was turned off and the speciated emission data was more complicated in this case due to the partial decomposition products.

Figure 4.8 are the evolution of GIMEP, and concentrations (in ppmCl) of the fuel species, iso-octane, and m-xylene. From the GIMEP, it can be identified that there was a very strong firing in the first cycle, followed by some partial firings in the first few cycles. The first strong firing was due to the large injection unit of fuel in the first cycle; the partial firing may be due to the incomplete evaporation of m-xylene in the early cycles.

The normalized concentrations (as % of the total hydrocarbon emissions) of the iso-octane and its major decomposition products, iso-butene (2-methyl propene) and propene [24], are shown in Figure 4.9. Because iso-octane is the more volatile component of the two fuel components (normal boiling points: iso-octane, 99.2°C; m-xylene, 139°C), the exhaust concentration in the initial cycles shows a higher value than the steady state value (the open symbol at the right of the graph). This is consistent with the results of motoring case by using the same fuel stated in the previous section. The trend of the concentration of its major product species, iso-butene and propene, follows that of iso-octane.
Emissions of m-xylene and its major decomposition products, toluene and benzene, are shown in Figure 4.10. The level for benzene and toluene in the graph are magnified 10 times. Initially the m-xylene concentration was low; it took approximately 150 cycles for the value to reach steady state. The same trend was also observed for the m-xylene emission in the motoring case. This is due to the fact that the fuel delivered to the engine and subsequently the exhaust were dominated by the more volatile species (iso-octane in this case) of the fuel. The time development of benzene and toluene followed that of the m-xylene, suggesting that they were fragmented products from the partial oxidation of the m-xylene.

Figure 4.11 is the accounting of the hydrocarbon species in the exhaust gas. Iso-octane, iso-butene and propene account for ~ 90% of the hydrocarbon initially. Thus, the HC emissions were dominated by the more volatile species in the fuel and its product species in the early cycles. As the engine warmed up, there was an increase of emissions from m-xylene and the aromatic by-products which are relatively small in concentration compared to the m-xylene. At the steady state, the fuel species emissions were: iso-octane, 46.24%; m-xylene, 22.77%. The ratio is 2.03 which is slightly smaller than the ratio in fuel (69.1% / 30.9% = 2.24, by carbon atoms). This may be due to the higher partial oxidation rate of iso-octane than that of m-xylene. The total emissions of iso-octane, iso-butene, propene, m-xylene, toluene, and benzene account for about 90% of the total emissions throughout the cycle. The rest of the emissions are the unidentified species which account for about 10%.

The steady state value of the toluene to xylene ratio was 0.063 in this experiment in which the mixture was stoichiometric ($\Phi_{\text{inj}} = 1$). This result is consistent with those of Reference [25] in which a binary mixture of (mostly) xylene (80.3%) and ethyl-benzene (19.6%) was used. They obtained a value of 0.056 at $\Phi = 0.9$, and 0.093 at $\Phi = 1.15$ when the engine was running at 1500 rpm and 3.8 bar IMEP. In both circumstances, toluene was formed as an aromatic intermediate from high temperature xylene oxidation. The mechanism involves the displacement
of a methyl group from the xylene by an H atom to form toluene and a methyl radical [26]. It is of interest to note that the species ratios from very different engines and operating conditions give similar result.

In summary, the hydrocarbon emissions by using the iso-octane/m-xylene mixture are dominated by the more volatile species (iso-octane) in the fuel and its product species (iso-butene and propene) in the early cycles. As the engine warms up, there is an increase of emissions from m-xylene and the aromatic by-products. The total emissions of the identified species, iso-octane, iso-butene, propene, m-xylene, toluene, and benzene, account for about 90% of the total emissions throughout the cycle.

![Graph of HC Concentration vs Cycle](image)

**Figure 4.8** GIMEP and exhaust speciated HC concentrations (ppmC1) of fuel species by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel under engine firing condition
Figure 4.9 Exhaust speciated HC concentrations (ppmC1%) of iso-octane and its major product species, 2M-propene and propene, by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel under engine firing condition.

Figure 4.10 Exhaust speciated HC concentrations (ppmC1%) of m-xylene and its major product species, toluene and benzene, by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel under engine firing condition.
4.5.3 iC8 / nC5 Mixture - Firing

The engine was fired with iso-octane/n-pentane mixture (80/20 by volume) and the same engine operating condition as the previous case. There were decomposition product species in the exhaust gas from the partial oxidation of the fuel species.

The Gross Indicated Mean Effective Pressure (GIMEP), total hydrocarbon emissions, and exhaust fuel species concentrations are shown in Figure 4.12. Also shown are the values at 75 cycles (represented by the open symbols at the right of the graph) at which the hydrocarbon emissions may be considered steady state in this case. The steady state assumption was checked by noting that the total hydrocarbon as monitored continuously by a conventional FID did not change further. By checking the value of GIMEP trace, the engine fired at the first injected cycle; there was no misfired cycle. The GIMEP, total hydrocarbon, and fuel species emissions all stabilized after about 6 cycles. The smooth running and the fast stabilization of the GIMEP
behaviors may be attributed to the relatively volatile nature of this fuel mixture. For example, the normal boiling point of both components (iso-octane, 99.2°C; n-pentane, 36.1°C) are below the T50 point (105.0°C) of indolene. In the previous section, it took about approximately 150 cycles for iso-octane/m-xylene mixture to reach steady state. Thus iso-octane/n-pentane mixture which is more volatile than iso-octane/m-xylene mixture is much easier to reach stabilization of GIMEP and the steady state of hydrocarbon emissions. The absolute concentration of iso-octane stayed roughly constant throughout the starting and warm-up. The n-pentane and total hydrocarbon concentrations was slightly higher in the first two samples.

The normalized concentrations (as percentage of the total hydrocarbon concentration, in ppmC1) of iso-octane and its major intermediate products, iso-butene and propene, are shown in Figure 4.13. Propene is also produced from n-pentane decomposition [27]. Therefore in principle, whether iso-octane or n-pentane is the source molecule of propene could not be identified. But the time development of propene followed that of iso-octane and differed from that of the n-pentane (see Figure 4.14), suggesting that iso-octane should be the major source of propene in this case. The iso-butene and propene profiles follow closely that of their parent molecule, iso-octane. For the initial few cycles, these normalized concentrations were below the steady state values. This is because of the presence of a relatively larger amount (as compared to the fuel composition) of the lighter n-pentane and its by-products (mainly ethene, see Reference [27]). The normalized ppmC1% of n-pentane and its product species, C1&C2 group, are shown in Figure 4.14 (The C1 and C2 compounds were not resolved by the limit of the speciation technique applied in this study, and are therefore reported together.).

In the original fuel, the iso-octane / n-pentane proportion was 4.46 (= 81.7% / 18.3%, in term of carbon atoms, see Table 4.3). When the steady state condition was reached in the exhaust, the normalized concentration for iso-octane was 54.42% (Figure 4.13) and that for n-pentane was 8.27% (Figure 4.14). Thus the ratio of iso-octane / n-pentane in exhaust gas at
steady state is 6.58 (= 54.42% / 8.27%) which is quite different from that in fuel. This may be
due to the smaller partial oxidation rate of iso-octane than that of n-pentane in this case. The
remaining 40% of exhaust hydrocarbon were the intermediate products of incomplete oxidation.

An accounting of the emissions species according to their original molecules is shown in
Figure 4.15. The lower trace is the normalized concentration of the exhaust iso-octane plus its
major decomposition products, iso-butene and propene. To this, n-pentane and the C₁ & C₂
partial oxidation products are added to produce the upper trace. In this case, iso-octane are the
relatively less volatile species in the mixture. Therefore, the hydrocarbon emissions are
dominated by the more volatile species, n-pentane, in the fuel and its product species in the first
few cycles. From the upper trace, it can be found that the fuel species and their major
intermediate products account for ~ 90% of the total hydrocarbon emissions throughout the
warm-up process. This result is similar to that of iso-octane/m-xylene firing case described in
the previous section.

In summary, iso-octane/n-pentane mixture which is more volatile than iso-octane/m-
xylene mixture is much easier to reach stabilization of GIMEP and the steady state of
hydrocarbon emissions. Due to the lower partial oxidation rate of iso-octane than that of n-
pentane, the ratio of iso-octane/n-pentane in exhaust gas at steady state is 6.58 which is larger
than that (4.46) in fuel. From the accounting of emissions species, it can be found that the
hydrocarbon emissions are dominated by the more volatile species, n-pentane, and its product
species in the first few cycles. The fuel species and their major intermediate products account
for ~ 90% of the total hydrocarbon emissions throughout the warm-up process.
Figure 4.12 GIMEP, exhaust total HC and fuel species concentrations (ppmC1) by using iso-octane/n-pentane mixture (volume ratio = 80/20) as fuel under engine firing condition

Figure 4.13 Exhaust normalized HC concentrations (ppmC1%) of iso-octane and its major product species, 2M-propene and propene, by using iso-octane/n-pentane mixture (volume ratio = 80/20) as fuel under engine firing condition
Figure 4.14 Exhaust normalized HC concentrations (ppmC1%) of n-pentane and its major product species, C1&C2 groups, by using iso-octane/n-pentane mixture (volume ratio = 80/20) as fuel under engine firing condition.

Figure 4.15 Exhaust species distribution by using iso-octane/n-pentane mixture (volume ratio = 80/20) as fuel under engine firing condition.
4.5.4 iC8 / nC10 Mixture - Firing

The fuel used in this case was iso-octane/n-decane mixture in the volume ratio of 90/10. In Figure 4.16 are the evolutions of GIMEP, and concentrations (in ppmC1) of the fuel species: iso-octane, and n-decane. From the GIMEP, it is noted that there was a very strong firing in the first cycle, followed by some partial firings in the first few cycles. The first strong firing was due to the large amount of fuel injected in the first cycle; the partial firing may be due to the incomplete evaporation of the mixture in the early cycles. Similar behaviors had also been observed by using the iso-octane/m-xylene mixture (see Figure 4.8). Also shown in Figure 4.16 are the values at 15 minutes (represented by the open symbols at the right of the graph) at which the hydrocarbon emissions may be considered "steady state" in this case. For the concentration of fuel species, there are almost no n-decane present in the exhaust gas during the first few cycles. Its concentration then increases to 175.1 ppmC1 at the "steady state", which is much smaller than the concentration of iso-octane (2174.2 ppmC1 at steady state).

The normalized concentrations (ppmC1%, as % of the total hydrocarbon emissions) of the fuel species, iso-octane, n-decane; and iso-butene (2-methyl propene) and propene, which are the major product species for iso-octane partial oxidation, are shown in Figure 4.17. Very little of the non-volatile n-decane was found in the exhaust in the first 40 or so cycles. During this time, probably most of the fuel delivered to the engine was iso-octane. Therefore, the exhaust are dominated by the more volatile species (iso-octane in this case) in the fuel initially. The n-decane concentration in the exhaust did not reach steady state until 150 cycles. It is noted that for the previous case with iso-octane / n-pentane mixture, steady state was reached in about 6 cycles; with iso-octane/m-xylene mixture, steady state was also not reached until 150 cycles. It appears that the time scale to reach steady state is limited by the less-volatile component of the binary mixture.
Figure 4.16 GIMEP and exhaust speciated HC concentrations (ppmCl) of fuel species by using iso-octane/n-decane mixture (volume ratio = 90/10) as fuel under engine firing condition

Figure 4.17 Exhaust normalized HC concentrations (ppmCl%) by using iso-octane/n-decane mixture (volume ratio = 90/10) as fuel under engine firing condition
An accounting of the exhaust species is shown in Figure 4.18. The large number of intermediate products of the n-decane partial oxidation [28] were not identified. At the steady state, the fuel species contributions to the exhaust were: iso-octane, 55.29%; n-decane, 4.45%. The ratio of iso-octane to n-decane is 12.42 which is larger than the ratio in fuel (89.5% / 10.5% = 8.52, by carbon atoms). This may be due to the fact that there was more liquid n-decane going down to the sump than iso-octane because it is much less volatile than liquid iso-octane. The total emissions of iso-octane, iso-butene, propene, and n-decane account for about 85% of the total emissions throughout the cycle. Thus other intermediate species contribute to about 15% of the total hydrocarbon emissions.

![Graph showing exhaust species distribution](image)

**Figure 4.18** Exhaust species distribution by using iso-octane/n-decane mixture (volume ratio = 90/10) as fuel under engine firing condition

In summary, the hydrocarbon emissions by using the iso-octane / n-decane mixture are dominated by the more volatile species (iso-octane) in the fuel and its product species (iso-butene and propene) in the early cycles. Very little of the non-volatile n-decane was found in the
exhaust in the first 40 or so cycles. In the steady state, the ratio of iso-octane to n-decane is larger than the ratio in fuel. The total emissions of the identified species, iso-octane, iso-butene, propene, and n-decane, account for about 85% of the total emissions throughout the cycle.

4.5.5 Indolene - Motoring

To set up as a reference the fuel species evaporative behaviors of practical fuels in the mixture preparation process, the exhaust speciated emissions were measured for indolene with the ignition turned off.

![Figure 4.19 Exhaust total HC (ppmC1) by using indolene as fuel under engine motoring condition](image)

Shown in Figure 4.19 is the evolution of the total hydrocarbon which rises rapidly in the first 5 cycles or so, and then increases more gradually. The "steady-state" value measured at 3 minutes from the commencement of injections is shown as an open symbol on the right end of
the graph. That value (140,762 ppmC1) roughly corresponds to the stoichiometric air/fuel ratio for indolene and is consistent with the amount of injected fuel ($\Phi_{inj} = 1$).

The speciated emission concentrations in units of ppmC1 are plotted in Figure 4.20 to Figure 4.22; the corresponding values normalized by the total hydrocarbon concentration (Figure 4.19) are plotted in Figure 4.23 to Figure 4.25. The species shown in Figure 4.20 and Figure 4.23 are the volatile ones: normal boiling point < T20 of indolene. The species shown in Figure 4.21 and Figure 4.24 are the moderately volatile ones: normal boiling point between T20 and T80 of indolene. The species shown in Figure 4.22 and Figure 4.25 are the relatively less volatile ones: normal boiling point > T80 of indolene. There are trends which were also observed in the previous sections: the amount of the volatile species in exhaust gas is initially high, then drops very fast (~ 5 cycles); the amount of moderately volatile species increase gradually and approach steady state value after 10 or so cycles; the amount of relatively less volatile species is almost zero initially, then increases gradually to the "steady-state" value.

The hydrocarbons in the exhaust gas of the motored engine are dominated by the volatile species of indolene in the first few cycles. In the first sample window, for example, butane and 2M-butane together contribute to 40.14% (butane 14.01%, 2M-butane 26.13%) of total hydrocarbon. This is significantly higher than the concentrations in the fuel (in terms of carbon atoms, the fuel contains 4.9 % butane and 6.4% 2M-butane; 11.3% together). In the first few cycles, the absolute concentrations of butane and 2M-butane are higher than those values in steady state. This is due to the enrichment in the larger unit of the first injection (7 units of fuel were used) and most of fuel species evaporated in the early cycles are volatile ones.

The less volatile species increase gradually to their "steady state" values which are represented by the measurement at 3 minutes since injection commenced. These data points are plotted as open symbols at the right hand side of the graphs. When the graph is plotted with the horizontal scale set to 3 minutes in Figure 4.25, the points with the open symbol do line up with
Table 4.6 Comparison of the fuel composition (as percentage of carbon atom) and measured exhaust composition in the non-firing run

<table>
<thead>
<tr>
<th>Fuel species</th>
<th>C1 % in fuel</th>
<th>C1 % in exhaust (motoring)</th>
<th>normal boiling point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>butane</td>
<td>4.87</td>
<td>4.37</td>
<td>-0.5</td>
</tr>
<tr>
<td>2M-butane</td>
<td>6.36</td>
<td>9.39</td>
<td>27.83</td>
</tr>
<tr>
<td>23dM-butane</td>
<td>1.83</td>
<td>1.78</td>
<td>58</td>
</tr>
<tr>
<td>benzene</td>
<td>2.19</td>
<td>1.18</td>
<td>80.11</td>
</tr>
<tr>
<td>23dM-pentane</td>
<td>4.02</td>
<td>4.26</td>
<td>89.8</td>
</tr>
<tr>
<td>toluene + 233&amp;234tM-pentane</td>
<td>25.43</td>
<td>29.66</td>
<td>110.6/114.8/113.4</td>
</tr>
<tr>
<td>224tM-pentane</td>
<td>10.12</td>
<td>7.54</td>
<td>99.2</td>
</tr>
<tr>
<td>m&amp;p-xylene</td>
<td>0.91</td>
<td>1.17</td>
<td>~</td>
</tr>
<tr>
<td>124tM-benzene</td>
<td>3.13</td>
<td>1.58</td>
<td>169.3</td>
</tr>
</tbody>
</table>

The data trend. Note that at 3 minute, the 124tM-benzene value is higher than that of m&p-xylene. This is consistent with the fuel composition. The steady state composition is compared with the fuel composition (in terms of carbon atoms as percentage of total carbon atoms) in Table 4.6. The normal boiling points of the fuel components are also listed. There is general agreement but there are differences. These differences may be explained as follows. (i) The indolene fuel used in the experiment was, unfortunately, not the same batch as that used in identifying the fuel components; so there may be significant batch-to-batch composition difference in the fuel. (ii) The less volatile fuel components may remain liquid in the engine (may retain in the port and liner surfaces, or may enter the oil circuit). The effect is that the relative concentrations of the high boiling point components such as 124tM-benzene are lower, and those of the light components are enhanced.

In summary, before the engine fires, the fuel delivered to the engine and subsequently the exhaust are dominated by the volatile species (normal boiling point < T20) of the fuel in the first few (~ 5) cycles. The moderately volatile species (with normal boiling between T20 and T80)
increase gradually and approach steady state value after 10 or so cycles. The heavy-end species (normal boiling point > T80) take more than 100 cycles to get to the steady state value.

![Graph showing exhaust HC concentrations over cycles](image)

**Figure 4.20** Exhaust HC concentrations (ppmCl) of light-end components by using indolene as fuel under engine motoring condition
Figure 4.21 Exhaust HC concentrations (ppmC1) of mid-range components by using indolene as fuel under engine motoring condition

Figure 4.22 Exhaust HC concentrations (ppmC1) of heavy-end components by using indolene as fuel under engine motoring condition
Figure 4.23 Exhaust normalized HC concentrations (ppmC1%) of light-end components by using indolene as fuel under engine motoring condition

Figure 4.24 Exhaust normalized HC concentrations (ppmC1%) of mid-range components by using indolene as fuel under engine motoring condition
**Figure 4.25** Exhaust normalized HC concentrations (ppmC1%) of heavy-end components by using indolene as fuel under engine firing condition

### 4.5.6 Indolene - Firing

The fuel used and the operating conditions of the engine were the same as the previous case, except that the ignition was on. The first injection was 7 units of fuel, followed by one unit in each subsequent injection (This was the same fueling schedule as in the non-firing experiment stated previous section). The sampling windows were at cycles 3, 5, 7, 11, 15, 19, 23, 30, 37, 75, 112, 225, 450 and 6750. The last one was at fully warm-up condition (at 15 minutes).

The GIMEP and total HC emissions are shown in Figure 4.26. The engine fired in the first two cycles, and this was followed by several cycles of misfiring (cycles 3-8). The vaporized fuel which was not got burned during these misfiring cycles increased the HC emissions captured in the tailpipe. That is the reason why the total HC concentration in 7th cycle (24,300 ppmC1) was much higher than rest of cycles. There were substantial cycle-to-cycle GIMEP variations in the first 50 or so cycles. For example, there was a very weak firing (the GIMEP was ~ 0.2 bar) in
the 14th cycle. This partial firing also made the HC concentration in the 15th cycle higher. Therefore, the total exhaust HC followed the trend of the GIMEP - the misfired cycles had higher HC emissions.

![Graph showing HC concentration and GIMEP over cycles with data points and labels](image)

**Figure 4.26** GIMEP and exhaust total HC (ppmC1) by using indolene as fuel under engine firing condition

There are, however, several noticeable features:

(i) In Figure 4.19, the HC measured in the motoring case shows that the mixture delivered to the cylinder should increase quickly and there should be no misfiring cycles. The observation of misfiring in Figure 4.26 was due to the ignition of the mixture in the intake manifold by the back flow of the hot burned gas from the cylinder. This back-firing occurred at IVO of the second cycle. The process consumed most of the fuel in the port left over from the first cycle which was enriched; thus negating the benefit of the enrichment strategy. There was still sufficient fuel delivered to the cylinder in cycle two, but the GIMEP was more than a factor of two lower than the first cycle. For cycle 3 onwards, the effect due to enrichment in the first
cycle was completely eliminated and the process was essentially equivalent to using single unit of fuel throughout. It is noted that in Figure 4.5 with single unit of fuel delivery, the engine did not fire for 7 cycles and the subsequent firing cycles were sporadic. This behavior is very similar to the observation in Figure 4.26.

(ii) In the sequence of misfiring cycles 3-8, the HC emissions increased from cycle 5 to cycle 7; but the level at each cycle was substantially less than the stoichiometric amount (which was at ~ 140,000 ppmC1).

(iii) The exhaust HC value at cycle 11, which followed cycle 10, a cycle of finite but very low IMEP (of 0.2 bar or ~ 6% of the steady state value), was substantially lower than that of cycle 7, which followed a misfired cycle.

(iv) The exhaust HC values at cycles 19, 23, 30 and 37 were not that different from the steady state value although the GIMEP values were substantially lower than the steady state value, and there were large cycle-to-cycle fluctuations (but no misfiring).

The above observations may be explained by the multi-component nature of the fuel. The previous results (from Figure 4.20 to Figure 4.25) show that the more volatile components are the major species that are delivered into the engine in the beginning of the starting process. In this case, when 7 units of fuel was injected in the first cycle, the evaporation of the light components was enough to deliver to the cylinder a combustible mixture for firing in the first cycle. In the second cycle, however, due to the back-firing described earlier, the mixture delivered to the engine contained substantially less fuel which made the GIMEP substantially lower. Then, because the fuel nominally provided by the left-over from the first injection was essentially consumed by the back firing, the mixture delivered to the cylinder in cycles 3 to 8, was not adequate for firing. The HC value measured at the exhaust, however, increase during this period. This increase may be attributed to the following:
(i) There is a build up of a wall film in the intake port due to the liquid fuel not delivered to the cylinder in the current cycle. The increase amount of this wall film increases the total mixture delivery into the cylinder via a higher evaporation rate (due to the larger surface area) and a larger amount of strip-atomized droplets from the port wall into the cylinder during the forward flow of the intake process [29].

(ii) As the wall film accumulates, the concentration of the less volatile gasoline components in the film increases since those components are the ones that are predominantly left over from the previous cycles. This concentration increase facilitates the evaporation of these less volatile components and thus the total amount of fuel vapor delivered into the cylinder.

After cycle 30 or so, the exhaust total HC was not much different from the steady state value although the GIMEP was about 1/3 of the steady state value and there were substantial cycle-to-cycle GIMEP variations. The exhaust HC values, however, indicated that at this stage of warm-up, there was complete combustion. The lower GIMEP and the cyclic variation were due to (a) not all the injected fuel was delivered into the cylinder (see figure 4.5) so that the trapped charge was lean; as a result, the energy content of the charge was lower than the steady state value; and (b) because of the lean operating condition, there were substantial late burn cycles and large variations in burn-rate. These late burn cycles and cyclic variations were also evident in the pressure trace. However, a heat release analysis of the pressure trace was not successful because of the large uncertainty both in the residual gas fraction and in the fuel amount in the mixture. In particular, the analysis by itself could not resolve whether the low IMEP was due to the less energy content of the charge or due to late burning.

The absolute concentrations of the speciated emissions are shown in Figure 4.27 to Figure 4.29; the normalized values (as % of the total exhaust HC) are shown in Figure 4.30 to Figure 4.32. Only the fuel species are shown in those graphs. The species in Figure 4.27 and Figure 4.30 are the volatile ones (with NBP < T20 of the fuel); in Figure 4.28 and Figure 4.31
Table 4.7 Comparison of species concentration in indolene and exhaust species concentration of cycle 7, as percentage of total HC (on ppmC1 basis)

<table>
<thead>
<tr>
<th>Fuel species</th>
<th>C1 % in fuel</th>
<th>C1 % in exhaust (motoring)</th>
<th>normal boiling point [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>butane</td>
<td>4.87</td>
<td>5.97</td>
<td>-0.5</td>
</tr>
<tr>
<td>2M-butane</td>
<td>6.36</td>
<td>12.75</td>
<td>27.83</td>
</tr>
<tr>
<td>23dM-butane</td>
<td>1.83</td>
<td>2.47</td>
<td>58</td>
</tr>
<tr>
<td>benzene</td>
<td>2.19</td>
<td>1.85</td>
<td>80.11</td>
</tr>
<tr>
<td>23dM-pentane</td>
<td>4.02</td>
<td>4.71</td>
<td>89.8</td>
</tr>
<tr>
<td>toluene + 233&amp;234tM-pentane</td>
<td>25.43</td>
<td>21.49</td>
<td>110.6/114.8/113.4</td>
</tr>
<tr>
<td>224tM-pentane</td>
<td>10.12</td>
<td>7.73</td>
<td>99.2</td>
</tr>
<tr>
<td>m&amp;p-xylene</td>
<td>0.91</td>
<td>0.34</td>
<td>~</td>
</tr>
<tr>
<td>124tM-benzene</td>
<td>3.13</td>
<td>0.10</td>
<td>169.3</td>
</tr>
</tbody>
</table>

are the ones with intermediate NBP (with NBP between T20 and T80); and in Figure 4.29 and Figure 4.32 are the relatively less volatile ones (with NBP > T80).

In the non-firing cycles 3-8, the exhaust concentrations of all the fuel species increase (Figure 4.27 to Figure 4.29). This increase indicates that a higher equivalence ratio mixture was being delivered into the cylinder in these consecutive cycles; the process finally led to a firing cycle at cycle 9 (That was probably a partial burn cycle because of the low GIMEP). The measured normalized exhaust fuel species concentrations at cycle 7 (third sampling data point in Figures 4.30 to Figure 4.32) are shown in Table 4.7 together with their concentrations in the fuel (as percentage carbon atoms). The results show that at this point, the light components (with NBP < T20 of the fuel, shown in first box of Table 4.7), were at a higher fraction in the exhaust than in the fuel composition. The intermediate boiling range components (with NBP between T20 and T80, shown in the second box of Table 4.7), were at a slightly lower or at about the same percentage as in the fuel. The heavy components (with NBP > T80), were at a much lower percentage in the exhaust.
The correlation between the fuel species in the fuel and in the exhaust is shown in Figure 4.33. For each component, the data points are the values throughout the warm-up process. The values at 15 minute which is considered to be the fully warm-up values, are marked with crosses (the aromatics and paraffins are marked with + and x respectively.). When the engine is cold, no correlation was found between the fuel component percentage concentrations and those of the exhaust. This is because of that the actual components being delivered to the engine are weighted by the respective volatility behavior. When the engine is fully warmed up, there is good correlation between the fuel paraffins and the exhaust fuel paraffins ($R^2 = 0.845$), and between the fuel aromatics and the exhaust fuel aromatics ($R^2 = 0.997$). The correlations are shown as least-square-fit lines in Figure 4.33. Both fits (for the paraffins and the aromatics respectively) go through the origin within the accuracy of the fit.

The above correlations are consistent with previous findings in the Auto-Oil Program [5, 10]. The slope of each fit has been interpreted as a measure of the survival fraction of the individual species [30]. The ratio of the slope of the aromatics fit to that of the paraffin fit is $\sim 1.9$. This is consistent with the previous finding [5, 10] that the aromatics have a higher survival rate (factors of $\sim 1.5$ to 1.8 higher) than the paraffins.
Figure 4.27 Exhaust HC concentrations (ppmCl) of light-end components by using indolene as fuel under engine firing condition

Figure 4.28 Exhaust HC concentrations (ppmCl) of mid-range components by using indolene as fuel under engine firing condition
Figure 4.29 Exhaust HC concentrations (ppmC1) of heavy-end components by using indolene as fuel under engine firing condition

Figure 4.30 Exhaust normalized HC concentrations (ppmC1%) of light-end components by using indolene as fuel under engine firing condition
Figure 4.31 Exhaust normalized HC concentrations (ppmC1%) of mid-range components by using indolene as fuel under engine firing condition

Figure 4.32 Exhaust normalized HC concentrations (ppmC1%) of heavy-end components by using indolene as fuel under engine firing condition
Figure 4.33 Correlation between exhaust fuel species concentrations and concentrations in indolene under engine firing condition.
A fuel volatility model based on the major species in the fuel has been formulated. The model accurately predicts the ASTM distillation curves and Reid Vapor Pressure (RVP) for hydrocarbon fuels. The model was used to assess the fuel effects on the extent of evaporation and the vapor composition in the mixture preparation process (discussed in Chapter 6). The organization of this chapter is as follows. The thermodynamics calculation is briefly described first in section 5.1. Then the representation of the fuel by its major components is described in section 5.2; this is referred to as the Major-Component fuel model [31]. Finally, the validity of the representation is checked by comparing the actual ASTM distillation curve (section 5.3.1) and the RVP (section 5.3.2) of the fuel to values calculated from the fuel model using the thermodynamics calculation. More details about the topics in this Chapter was discussed in Reference [31] and Reference [32].

5.1 Introduction to Thermodynamics Calculations
The volatility characteristics of the fuel is calculated using a thermodynamics data base and a flash evaporation computer subroutine provided by NIST [33]. The data base consist of the thermophysical properties and interaction coefficients of 116 compounds which include mostly hydrocarbons plus nitrogen, oxygen, and water. The Peng-Robinson equation of state model [34] was used to calculate the vapor-liquid equilibrium (VLE) of mixtures. The Peng-Robinson equation of state is in the form as below,

\[ P = \frac{RT}{v-b} \left( \frac{a(T)}{v(v+b)+b(v-b)} \right) \]  
(5.1)

where,

\[ a_{\text{mix}} = \sum_i \sum_j x_i x_j n_{ij} \]  
(5.2)

\[ b_{\text{mix}} = \sum_i x_i b_i \]  
(5.3)

Constant \( a_{ij} \) and \( b_i \) in equation (2.4) and (2.5) are functions of critical temperature \( T_c \), critical pressure \( P_c \), and acentric factor \( \omega \). Constant \( m_{ij} \) in equation (2.4) is the binary interaction coefficient between component \( i \) and \( j \). In this way, the non-linear species interaction was calculated through binary interaction coefficients [35, 36]. A typical output of isothermal flash calculation [37] by using a mixture of \( n \)-pentane, iso-octane, and nitrogen as input of the subroutine is illustrated in Table 5.1. The interaction coefficients between the components listed in Table 5.1 is stated in Table 5.2.

The oxygenates, such as MTBE and methanol, are not part of the NIST database. These compounds, however, could be added to the database by providing a small amount of thermophysical information and by using the extended corresponding state principle. The basic information for MTBE and methanol used in the calculations is shown in Table 5.3 [38]. The
binary interaction coefficients for the oxygenates and the hydrocarbon species are not known. These values are set to unity because of lack of information. The physical model for the species interaction were based on non-polar compounds which are a good approximation to the hydrocarbons. Because of the nature of the polar / non-polar interaction which is very different from the non-polar / non-polar interaction, the assumption of unity interaction coefficient may lead to errors, especially in the case of methanol which is highly polar.

Table 5.1 A output of isothermal flash calculation by using a mixture of n-pentane, iso-octane, and nitrogen as inputs

<table>
<thead>
<tr>
<th>Component</th>
<th>Feed</th>
<th>Liquid</th>
<th>Vapor</th>
<th>Kvalue</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-pentane</td>
<td>0.1</td>
<td>0.274075</td>
<td>7.60E-02</td>
<td>0.277236</td>
</tr>
<tr>
<td>224-trimethylpentane</td>
<td>0.1</td>
<td>0.724404</td>
<td>1.39E-02</td>
<td>1.91E-02</td>
</tr>
<tr>
<td>nitrogen</td>
<td>0.8</td>
<td>1.52E-03</td>
<td>0.910164</td>
<td>598.189</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.12124</td>
<td>0.87876</td>
<td>Feed Fraction</td>
</tr>
<tr>
<td></td>
<td>41.0463</td>
<td>102.567</td>
<td>32.5584</td>
<td>Molecular Weight</td>
</tr>
<tr>
<td></td>
<td>0.878169</td>
<td>6.49E-03</td>
<td>0.998433</td>
<td>Comp. Factor, Z</td>
</tr>
<tr>
<td></td>
<td>5.01E-02</td>
<td>6.78661</td>
<td>4.41E-02</td>
<td>D, mol/liter</td>
</tr>
<tr>
<td></td>
<td>-42.5756</td>
<td>-241.019</td>
<td>-15.1969</td>
<td>H, kJ/mol</td>
</tr>
<tr>
<td></td>
<td>216.975</td>
<td>294.81</td>
<td>206.236</td>
<td>S, J/mol.K</td>
</tr>
<tr>
<td></td>
<td>57.7643</td>
<td>203.535</td>
<td>37.6527</td>
<td>Cp, J/mol.K</td>
</tr>
<tr>
<td></td>
<td>1.26632</td>
<td>1.28732</td>
<td>Cp/Cv</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1096.65</td>
<td>299.189</td>
<td>Sound Speed, m/s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-4.73E-02</td>
<td>0.418065</td>
<td>JT, K/bar</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5298.36</td>
<td>146.528</td>
<td>Visc., uP</td>
<td></td>
</tr>
</tbody>
</table>

(VLE=PRS, PROPS=EXCST)

Table 5.2 Interaction coefficients between n-pentane, iso-octane, and nitrogen

<table>
<thead>
<tr>
<th></th>
<th>nC5</th>
<th>iC8</th>
<th>N2</th>
</tr>
</thead>
<tbody>
<tr>
<td>nC5</td>
<td>1</td>
<td>0.992</td>
<td>0.889</td>
</tr>
<tr>
<td>iC8</td>
<td>0.992</td>
<td>1</td>
<td>0.855</td>
</tr>
<tr>
<td>N2</td>
<td>0.889</td>
<td>0.855</td>
<td>1</td>
</tr>
</tbody>
</table>
Table 5.3 Thermophysical properties of MTBE and methanol

<table>
<thead>
<tr>
<th>property</th>
<th>unit</th>
<th>MTBE</th>
<th>methanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tc</td>
<td>K</td>
<td>497.1</td>
<td>512.6</td>
</tr>
<tr>
<td>Pc</td>
<td>bar</td>
<td>33.86</td>
<td>79.88</td>
</tr>
<tr>
<td>Vc</td>
<td>l/mole</td>
<td>0.33264</td>
<td>0.11779</td>
</tr>
<tr>
<td>M</td>
<td>g/mole</td>
<td>88.15</td>
<td>32.04</td>
</tr>
<tr>
<td>Tb</td>
<td>K</td>
<td>328.3</td>
<td>338.0</td>
</tr>
<tr>
<td>Cp (ideal gas)</td>
<td>J/mole K</td>
<td>-------</td>
<td>43.9</td>
</tr>
<tr>
<td>H (fusion)</td>
<td>kJ/mole</td>
<td>9.829</td>
<td>3.177</td>
</tr>
</tbody>
</table>

5.2 Methodology for Formulating a Fuel Composition Model - Major-Component Fuel Model

The composition of practical gasoline is complex, with 100 plus species of hydrocarbons. For reformulated gasoline, there are also significant amount of oxygenate compounds. But the flash evaporation computer subroutine described in section 5.1 can only calculate the VLE of a mixture containing up to 20 components. Therefore, a reasonable representation which contains less than 20 components for the real fuel is required for the isothermal flash calculation. The fuel composition model introduced in this section is to represent the practical fuel by a few major components in a logical way.

To illustrate the process, the methodology of formulating a Major-Component fuel model was applied to indolene, for which the species concentrations are known [16]. The procedure of formulating a Major-Component fuel model is illustrated in Table 5.4 and stated as below:

(i) Divide the fuel species into groups, according to their carbon number.

(ii) For species with 6 and higher carbon atoms, the group is further subdivided into non-aromatics and aromatics.
(iii) The component with 4 or less carbons are grouped as one; the compounds with 12 or more carbons are grouped as one.

(iv) For each group, the major component, defined as the species with the highest weight percent in each group, is selected to represent the group.

Table 5.4 Major-Component fuel model for indolene

<table>
<thead>
<tr>
<th>Group</th>
<th>C no.</th>
<th>Molar %</th>
<th>Volume %</th>
<th>Mass %</th>
<th>Major component</th>
<th>species %</th>
<th>Representation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4</td>
<td>4</td>
<td>9.12</td>
<td>6.92</td>
<td>5.47</td>
<td>n-butane</td>
<td>8.46</td>
<td>n-butane</td>
</tr>
<tr>
<td>C5</td>
<td>5</td>
<td>14.15</td>
<td>12.22</td>
<td>10.48</td>
<td>2M-butane</td>
<td>8.84</td>
<td>2M-butane</td>
</tr>
<tr>
<td>C6</td>
<td>6</td>
<td>8.42</td>
<td>8.17</td>
<td>7.46</td>
<td>23dM-butane</td>
<td>2.12</td>
<td>23dM-butane</td>
</tr>
<tr>
<td>C6r</td>
<td>6</td>
<td>2.54</td>
<td>1.71</td>
<td>2.05</td>
<td>benzene</td>
<td>2.54</td>
<td>benzene</td>
</tr>
<tr>
<td>C7</td>
<td>7</td>
<td>8.36</td>
<td>9.17</td>
<td>8.64</td>
<td>23dM-pentane</td>
<td>3.99</td>
<td>23dM-pentane</td>
</tr>
<tr>
<td>C7r</td>
<td>7</td>
<td>17.62</td>
<td>14.21</td>
<td>16.77</td>
<td>toluene</td>
<td>17.62</td>
<td>toluene</td>
</tr>
<tr>
<td>C8</td>
<td>8</td>
<td>23.77</td>
<td>29.09</td>
<td>28.05</td>
<td>224tM-pentane</td>
<td>8.79</td>
<td>224tM-pentane</td>
</tr>
<tr>
<td>C8r</td>
<td>8</td>
<td>2.10</td>
<td>1.95</td>
<td>2.30</td>
<td>m-sylene</td>
<td>0.79</td>
<td>m-sylene</td>
</tr>
<tr>
<td>C9</td>
<td>9</td>
<td>1.41</td>
<td>1.90</td>
<td>1.87</td>
<td>225tM-hexane</td>
<td>0.75</td>
<td>225tM-hexane</td>
</tr>
<tr>
<td>C9r</td>
<td>9</td>
<td>6.86</td>
<td>7.16</td>
<td>8.51</td>
<td>124tM-benzene</td>
<td>2.42</td>
<td>i-Proply benzene</td>
</tr>
<tr>
<td>C10</td>
<td>10</td>
<td>3.76</td>
<td>4.66</td>
<td>5.30</td>
<td>4M-nonane</td>
<td>0.43</td>
<td>n-decane</td>
</tr>
<tr>
<td>C11</td>
<td>11</td>
<td>1.60</td>
<td>2.35</td>
<td>2.57</td>
<td>C11 isoparaffins</td>
<td>0.22</td>
<td>n-undecane</td>
</tr>
<tr>
<td>C12</td>
<td>12</td>
<td>0.29</td>
<td>0.49</td>
<td>0.53</td>
<td>C12 isoparaffins</td>
<td>0.02</td>
<td>n-dodecane</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>56.99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In Table 5.4, the first two columns show the carbon number and the group identity (r in the first column indicates aromatics). Column 3, 4 and 5 are the sum of the molar, volume, and mass percentage of all the species in the particular group. The major component, i.e., the species with the highest weight percent in each group is shown in column 6. The actual weight percents of these species in indolene are shown in column 7.

The fuel composition is represented by these major components and the percentage of each group. The particular major component species, however, may be outside the database of the 116 compounds in the NIST program. Thus a compromise has to be made by replacing the particular species with one in the database with similar properties and the same carbon number.
This is the case for the \( C_9, C_{10}, C_{11}, \) and \( C_{12} \) groups. The 124-tri-Methyl benzene is represented by iso-propyl benzene, 4M-nomane by n-decane, \( C_{11} \) iso-paraffins by n-undecane, and \( C_{12} \) iso-paraffins by n-dodecane. The final species for representing indolene are shown in column 8 of Table 5.4.

Thus the major-component fuel model (for indolene) consists of representing the fuel by the species in column 8 of Table 5.4, and with the percentage for each representing species listed in column 3, 4, and 5. In this way, there are only 13 components in the fuel model to represent indolene in the flash evaporative subroutine which can only handle up to 20 components at the same time. This simplification from the real fuel composition (over 100 species) to a 13-component Major-Component fuel model will be verified by comparing the actual ASTM distillation curve (section 5.3.1) and the RVP (section 5.3.2) of the fuel to values calculated from the fuel model using the thermodynamics calculation.

5.3 Verification of Fuel Composition Model

5.3.1 Simulation of ASTM Distillation Test

To test its validity, the Major-Component fuel model was used to simulate the ASTM distillation curve for different fuels. The ASTM distillation curve was chosen because it is the most readily available information for fuels regarding their volatility.

Details of the ASTM distillation procedure and the apparatus are stated in Reference [39] and Reference [40]. Fuel is distilled from a distillation flask and the temperature read by the thermometer as a function of the liquid condensate collected constitutes the ASTM distillation curve. The process is not in equilibrium and there are significant thermal gradients within the
apparatus. As described below, several important provisions have to be made to render an equilibrium flash calculation representing the ASTM distillation process.

To develop the method, the distillation process of a binary mixture of 50% iso-octane and 50% n-pentane is simulated. The distillation data are from Reference [41], and are shown as solid symbols in Figure 5.1. In this case, the species are known and are well represented by the thermodynamics database. Therefore the only unknown is the manner of the simulation process.

![Figure 5.1 ASTM distillation curve for iso-octane/n-pentane mixture (50/50)](image)

In the first simulation, the composition of the liquid was fixed. Isothermal flash calculations at a fixed pressure of 1 atmosphere were done with increasing temperatures starting from 300 K. The results (see open-square symbols of Figure 5.1) are obviously not correct because the liquid composition changes as the lighter n-pentane boils off.

In the next simulation, the isothermal flash calculations were repeated. At each temperature step, however, the vapor volume larger than the volume of the distillation flask was
removed to simulate the vapor removal by the condenser. Since the vapor composition was different from the original composition because of the preferential boiling off the lighter component, the content of the flask (vapor plus liquid) acquired a different composition for the next temperature step. In this manner, the composition change during the distillation process was simulated.

The results of the above simulation are shown as the open-rhombus symbols in Figure 5.1. The portion of the simulated distillation curve near the end point is in agreement with the data, but the initial boiling point and the first part of the distillation curve are substantially off.

It is well known that the presence of air greatly facilitates gasoline evaporation [42]. To account for the substantially lower initial boiling point of the data, 0.005 mole of nitrogen per mole of fuel was added to the mixture at the start of the simulation. (The use of nitrogen instead of air was for the convenience of simulation. Since the interactions between nitrogen and oxygen with the hydrocarbons are essentially the same, the use of nitrogen in place of air should not make any difference). The amount corresponds to the air space above the fuel in the distillation flask. During the distillation process, the amount of nitrogen was decreased linearly between the initial boiling point and the end point.

The results of the simulation in the presence of nitrogen are shown as open-circle symbols in Figure 5.1. The simulation is in very good agreement with the distillation data. The results are not sensitive to the exact amount of nitrogen was introduced. When twice the amount of nitrogen was introduced, the results are essentially the same (open-triangle symbols in Figure 5.1). Thus, by implementing the details of the ASTM distillation process, an equilibrium flash calculation could simulate the process well. A computer program (ASTMDIS.f, written in FORTRAN) which simulates the ASTM distillation process is listed in Appendix A.

The procedure was next tested with a multi-component fuel of a known composition. An eight-component fuel of Reference [43] was used. The composition is shown in Table 5.5. Since
Table 5.5 Composition and model of a synthetic gasoline

<table>
<thead>
<tr>
<th>Simulated fuel</th>
<th>Major-Fuel-Component model</th>
<th>Simulated fuel</th>
<th>Major-Fuel-Component model</th>
</tr>
</thead>
<tbody>
<tr>
<td>component</td>
<td>mass %</td>
<td>group</td>
<td>major component</td>
</tr>
<tr>
<td>unit</td>
<td>[%]</td>
<td></td>
<td>[%]</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>20</td>
<td>C5</td>
<td>n-Pentane</td>
</tr>
<tr>
<td>i-Pentane</td>
<td>20</td>
<td>C5</td>
<td>i-Pentane</td>
</tr>
<tr>
<td>cyclePentane</td>
<td>5</td>
<td>C5</td>
<td>cyclePentane</td>
</tr>
<tr>
<td>1-Hexane</td>
<td>5</td>
<td>C6</td>
<td>1-Hexane</td>
</tr>
<tr>
<td>Toluene</td>
<td>18</td>
<td>C7</td>
<td>Toluene</td>
</tr>
<tr>
<td>n-Octane</td>
<td>5</td>
<td>C8</td>
<td>n-Octane</td>
</tr>
<tr>
<td>i-Octane</td>
<td>20</td>
<td>C8</td>
<td>i-Octane</td>
</tr>
<tr>
<td>i-propylBenzene</td>
<td>7</td>
<td>C9</td>
<td>i-propylBenzene</td>
</tr>
<tr>
<td>total</td>
<td>100</td>
<td></td>
<td>total</td>
</tr>
</tbody>
</table>

The thermophysical data for all the components are available in the NIST database, the major-fuel component model is an exact representation of the fuel. The results are shown in Figure 5.2. The good agreement between the calculated values and data gives confidence in the simulation procedure.

Figure 5.2 ASTM distillation curve for a eight-component synthetic gasoline
In order to further demonstrate the effectiveness of the simulation procedure, the methodology of simulating the ASTM distillation curves were applied to several Auto-Oil Program fuels [44], for which the species concentrations and ASTM distillation curves are published. Specifically, the method are applied to Fuel A, which is the industry-average fuel; Fuel B which is a certification fuel; Fuel F, which is a low aromatic, low olefin and low T90 fuel; and Fuel MM, which contains 14.8% of MTBE. The Major-Component fuel model for these fuels formulated by the methodology described in section 5.2 are list in Table 5.6 to Table 5.9.

It is noted that the sum of all the species in the specification of these fuels does not add up to 100% (88.4% for Fuel A; 92.2% for Fuel B; 93.9% for Fuel F; 94.6% for Fuel MM) because there are unidentified compounds in the speciation analysis. For the purpose of formulating the Major-Component fuel model, the weight percentage of these unidentified compounds is distributed uniformly across the different groups. In this manner, the "normalized" weight percentages for each group are used instead of the actual percentage of each group. It is also noticed that due to the different analysis method, the maximum carbon number of the identified species for these fuels is only 10, instead of 12 for the case of indolene (see Table 5.4).

The simulated ASTM distillation curves for these fuels are shown in Figure 5.3 to Figure 5.6. For the non-oxygenate fuels (Fuel A, B, and F; Figures 5.3 - 5.5), there is good agreement between the simulation results and the data except at the high end of the boiling range. This discrepancy is attributed to that the model assumes the unidentified species in the fuel speciation analysis are distributed uniformly among the major components. In reality, the unidentified species are most likely to be the ones with high molecular weight (high carbon number) and low volatility. Thus at the high end of the boiling range, the percentage evaporate for the actual fuel is less than that for the fuel model at the same temperature.
For Fuel MM which contains 14.8% of MTBE (Figure 5.6), the agreement between the simulation and data is not as good, especially beyond the ~60% distillation point. The disagreement may be due to the inadequate modeling of the interaction coefficients between the polar MTBE molecules and the non-polar hydrocarbon species.

Based on the Major-Component fuel model of indolene listed in Table 5.4, the ASTM distillation curve of indolene were also simulated. By comparing the Major-Component fuel model of indolene with those of Fuel A, B, F, and MM (Table 5.6 to Table 5.9), it is found that there is no unidentified species in the specification of indolene due to different analysis method; and the maximum carbon number of indolene model is 12 while those of Fuel A, E, F, and MM are 10. Therefore, the indolene model is essentially a better representation than the models for Fuel A, B, F, and MM because the specification information for indolene is more complete.

The experimental data and the simulation of the ASTM distillation curve for indolene are shown in Figure 5.7. There is good agreement between the simulation results and the data for the whole distillation range. At the high end of the boiling range, better match between the simulation results and the data for indolene is observed because indolene model is a better representation of the fuel composition compared with those of Fuel A, B, F, and MM. Therefore, the Major-Component fuel model is a reasonable and logical representation for the practical fuel.
Table 5.6 Major-Component fuel model for Fuel A in the Auto/Oil Program

<table>
<thead>
<tr>
<th>Carbon Group</th>
<th>Mass % (actual)</th>
<th>Mass % (normalized)</th>
<th>Major Component</th>
<th>species %</th>
<th>% for model</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>C4</td>
<td>4.8</td>
<td>n-Butane</td>
<td>4.7</td>
<td>5.9</td>
</tr>
<tr>
<td>5</td>
<td>C5</td>
<td>10.6</td>
<td>i-Pentane</td>
<td>4.4</td>
<td>12.1</td>
</tr>
<tr>
<td>6</td>
<td>C6</td>
<td>17.6</td>
<td>i-Hexane</td>
<td>4.9</td>
<td>19.1</td>
</tr>
<tr>
<td>7</td>
<td>C7</td>
<td>8.9</td>
<td>2M-Hexane</td>
<td>1.5</td>
<td>10.0</td>
</tr>
<tr>
<td>7</td>
<td>C7r</td>
<td>5.5</td>
<td>Toluene</td>
<td>5.5</td>
<td>6.6</td>
</tr>
<tr>
<td>8</td>
<td>C8</td>
<td>12.0</td>
<td>i-Octane</td>
<td>3.3</td>
<td>13.5</td>
</tr>
<tr>
<td>8</td>
<td>C8r</td>
<td>13.6</td>
<td>m-Xylene</td>
<td>7.5</td>
<td>15.1</td>
</tr>
<tr>
<td>9</td>
<td>C9</td>
<td>2.4</td>
<td>n-Nonane</td>
<td>0.5</td>
<td>3.5</td>
</tr>
<tr>
<td>9</td>
<td>C9r</td>
<td>9.2</td>
<td>i-propylbenzene</td>
<td>2.9</td>
<td>9.2</td>
</tr>
<tr>
<td>10</td>
<td>C10</td>
<td>3.8</td>
<td>n-Decane</td>
<td>0.5</td>
<td>5.0</td>
</tr>
<tr>
<td>total</td>
<td>88.4</td>
<td>100.0</td>
<td>35.7</td>
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<td>100.0</td>
</tr>
</tbody>
</table>

Figure 5.3 ASTM distillation curve for Fuel A of the Auto-Oil Program
Table 5.7 Major-Component fuel model for Fuel B in the Auto/Oil Program

<table>
<thead>
<tr>
<th>Carbon no.</th>
<th>Group</th>
<th>Mass % (actual)</th>
<th>Mass % (normalized)</th>
<th>Major Component</th>
<th>species %</th>
<th>% for model</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>C4</td>
<td>4.2</td>
<td>5.0</td>
<td>n-Butane</td>
<td>4.1</td>
<td>5.0</td>
</tr>
<tr>
<td>5</td>
<td>C5</td>
<td>15.4</td>
<td>16.2</td>
<td>i-Pentane</td>
<td>12.3</td>
<td>16.2</td>
</tr>
<tr>
<td>6</td>
<td>C6</td>
<td>6.7</td>
<td>7.4</td>
<td>i-Hexane</td>
<td>1.5</td>
<td>7.4</td>
</tr>
<tr>
<td>7</td>
<td>C7</td>
<td>7.9</td>
<td>8.7</td>
<td>2M-Hexane</td>
<td>1.9</td>
<td>8.7</td>
</tr>
<tr>
<td>7</td>
<td>C7r</td>
<td>16.7</td>
<td>17.5</td>
<td>Toluene</td>
<td>16.7</td>
<td>17.5</td>
</tr>
<tr>
<td>8</td>
<td>C8</td>
<td>23.0</td>
<td>23.7</td>
<td>i-Octane</td>
<td>14.7</td>
<td>23.7</td>
</tr>
<tr>
<td>8</td>
<td>C8r</td>
<td>6.5</td>
<td>7.3</td>
<td>m-Xylene</td>
<td>4.7</td>
<td>7.3</td>
</tr>
<tr>
<td>9</td>
<td>C9</td>
<td>1.9</td>
<td>2.7</td>
<td>n-Nonane</td>
<td>0.6</td>
<td>2.7</td>
</tr>
<tr>
<td>9</td>
<td>C9r</td>
<td>7.7</td>
<td>8.5</td>
<td>i-propylbenzene</td>
<td>1.8</td>
<td>8.5</td>
</tr>
<tr>
<td>10</td>
<td>C10</td>
<td>2.2</td>
<td>3.0</td>
<td>n-Decane</td>
<td>0.4</td>
<td>3.0</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>92.2</td>
<td>100.0</td>
<td></td>
<td>58.7</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Figure 5.4 ASTM distillation for Fuel B of the Auto-Oil Program
Table 5.8 Major-Component fuel model for Fuel F in the Auto/Oil Program

<table>
<thead>
<tr>
<th>Carbon no.</th>
<th>Group</th>
<th>Mass % (actual)</th>
<th>Mass % (normalized)</th>
<th>Major Component</th>
<th>species %</th>
<th>% for model</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>C4</td>
<td>4.3</td>
<td>5.0</td>
<td>n-Butane</td>
<td>4.2</td>
<td>5.0</td>
</tr>
<tr>
<td>5</td>
<td>C5</td>
<td>12.6</td>
<td>13.2</td>
<td>i-Pentane</td>
<td>6.4</td>
<td>13.2</td>
</tr>
<tr>
<td>6</td>
<td>C6</td>
<td>19.6</td>
<td>20.2</td>
<td>i-Hexane</td>
<td>5.9</td>
<td>20.2</td>
</tr>
<tr>
<td>7</td>
<td>C7</td>
<td>9.9</td>
<td>10.5</td>
<td>2M-Hexane</td>
<td>2.4</td>
<td>10.5</td>
</tr>
<tr>
<td>7</td>
<td>C7r</td>
<td>10.5</td>
<td>11.1</td>
<td>Toluene</td>
<td>10.5</td>
<td>11.1</td>
</tr>
<tr>
<td>8</td>
<td>C8</td>
<td>21.1</td>
<td>21.7</td>
<td>i-Octane</td>
<td>19.7</td>
<td>21.7</td>
</tr>
<tr>
<td>8</td>
<td>C8r</td>
<td>8.2</td>
<td>8.8</td>
<td>m-Xylene</td>
<td>4.6</td>
<td>8.8</td>
</tr>
<tr>
<td>9</td>
<td>C9</td>
<td>2.0</td>
<td>2.6</td>
<td>n-Nonane</td>
<td>0.5</td>
<td>2.6</td>
</tr>
<tr>
<td>9</td>
<td>C9r</td>
<td>4.3</td>
<td>4.9</td>
<td>i-propylbenzene</td>
<td>1.3</td>
<td>4.9</td>
</tr>
<tr>
<td>10</td>
<td>C10</td>
<td>1.4</td>
<td>2.0</td>
<td>n-Decane</td>
<td>0.2</td>
<td>2.0</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>93.9</td>
<td>100.0</td>
<td></td>
<td>35.7</td>
<td>100.0</td>
</tr>
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</table>

Figure 5.5 ASTM distillation curve for Fuel F of the Auto-Oil Program
Table 5.9 Major-Component fuel model for Fuel MM in the Auto/Oil Program

<table>
<thead>
<tr>
<th>Carbon no.</th>
<th>Group</th>
<th>Mass % (actual)</th>
<th>Mass % (normalized)</th>
<th>Major Component</th>
<th>species %</th>
<th>% for model</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>C4</td>
<td>1.9</td>
<td>2.1</td>
<td>n-Butane</td>
<td>1.8</td>
<td>2.1</td>
</tr>
<tr>
<td>5</td>
<td>C5</td>
<td>11.6</td>
<td>12.3</td>
<td>i-Pentane</td>
<td>5.1</td>
<td>12.3</td>
</tr>
<tr>
<td>6</td>
<td>C6</td>
<td>28.4</td>
<td>30.0</td>
<td>i-Hexane</td>
<td>9.3</td>
<td>30.0</td>
</tr>
<tr>
<td>7</td>
<td>C7</td>
<td>6.6</td>
<td>7.0</td>
<td>2M-Hexane</td>
<td>1.3</td>
<td>7.0</td>
</tr>
<tr>
<td>7</td>
<td>C7r</td>
<td>10.5</td>
<td>11.1</td>
<td>Toluene</td>
<td>10.5</td>
<td>11.1</td>
</tr>
<tr>
<td>8</td>
<td>C8</td>
<td>5.8</td>
<td>6.1</td>
<td>i-Octane</td>
<td>1.1</td>
<td>6.1</td>
</tr>
<tr>
<td>8</td>
<td>C8r</td>
<td>7.5</td>
<td>7.9</td>
<td>m-Xylene</td>
<td>4.3</td>
<td>7.9</td>
</tr>
<tr>
<td>9</td>
<td>C9</td>
<td>1.2</td>
<td>1.3</td>
<td>n-Nonane</td>
<td>0.2</td>
<td>1.3</td>
</tr>
<tr>
<td>9</td>
<td>C9r</td>
<td>4.4</td>
<td>4.6</td>
<td>i-propylbenzene</td>
<td>1.4</td>
<td>4.6</td>
</tr>
<tr>
<td>10</td>
<td>C10</td>
<td>1.8</td>
<td>1.9</td>
<td>n-Decane</td>
<td>0.1</td>
<td>1.9</td>
</tr>
<tr>
<td>5</td>
<td>MTBE</td>
<td>14.9</td>
<td>15.7</td>
<td>MTBE</td>
<td>14.9</td>
<td>15.7</td>
</tr>
<tr>
<td>total</td>
<td></td>
<td>94.6</td>
<td>100.0</td>
<td></td>
<td>50.0</td>
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</tr>
</tbody>
</table>

Figure 5.6 ASTM distillation curve for Fuel MM of the Auto-Oil Program
Figure 5.7 ASTM distillation curve of indolene

5.3.2 Simulation of Reid Vapor Pressure Test

To further test the Major-Component fuel model, the Reid Vapor Pressure (RVP) of the fuels are computed. The simulation duplicates the RVP test procedure [45]: liquid fuel at 0°C is connected to a vapor chamber filled with air at 37.8°C (100°F) and four times the fuel volume. The equilibrated pressure of the air/fuel mixture at constant volume and at temperature of 37.8°C is calculated. A computer program (RVP.for, written in FORTRAN) which simulates the RVP test is listed in Appendix B.

The experimental data and simulation results for several of the Auto-Oil fuels and indolene are shown in Table 5.10. There is good agreement between the measured and calculated RVP.

The RVP for blends of gasoline / methanol and gasoline / MTBE were measured using a commercially available RVP apparatus (Precision Scientific Model 74893). The gasoline used
was indolene. The measured values are shown as solid symbols in Figures 5.8 and 5.9. The computed values using the Major-Component fuel model are shown as open symbols. For the indolene / MTBE blends, there is good agreement between the measured and computed RVP. For the indolene / methanol blends, the computed values show the same trend as the measured ones - that the RVP first increases and then decreases with the increase of methanol content. There is, however, substantial quantitative difference. The difference may be due to the polar nature of the methanol molecules.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>0.6</td>
<td>0.61</td>
<td>0.55</td>
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<tr>
<td>Simulation [bar]</td>
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<td>0.59</td>
<td>0.58</td>
<td>0.47</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 5.10 RVP calculation and comparison to measured value

![Graph showing the Reid Vapor Pressure (RVP) of a methanol/indolene mixture at different methanol volume percentages.](image)

Figure 5.8 Reid Vapor Pressure of methanol/indolene mixture at different blending ratios

125
Figure 5.9 Reid Vapor Pressure of MTBE/indolene mixture at different blending ratios
CHAPTER 6

MODELING FUEL EFFECTS ON

THE MIXTURE PREPARATION PROCESS AND

COMPARISON OF MODEL WITH EXPERIMENTAL DATA

Mixture preparation in a port-fuel injected engine is a complex process. The fuel is usually injected when the intake valve is closed. At part-throttle operation, there is a backflow of hot burned gas from the cylinder when the valve opens. This hot backflow facilitates the evaporation process. Then the forward flow induced by the piston motion carries the fuel vapor into the cylinder. Liquid fuel film may also be driven into the cylinder by this flow. Thus mixture preparation process involves fuel atomization, evaporation of fuel droplets and liquid film on the port wall and the back of the intake valve, liquid film surface flow, and the heating of the intake port region by the reverse flow of the burned gas when the intake valve opens [12]. Instead of a detailed modeling of the above processes, a simplified model is employed in this chapter to examine the fuel effects on mixture preparation process due to the fact that volatility
of fuel significantly influences the mixture preparation process, especially during cold-start and warm-up periods.

In section 6.1, a mixture preparation model based on the volatility characteristics of fuel species is developed. Output of the model is a volatility parameter, $\Phi_{vapor}$, which represents the extend of vaporization of fuel during mixture preparation process. Then the correlations of $\Phi_{vapor}$ with the starting and warm-up driveability attributes from section 2.3 are presented in section 6.2. In order to study the evolution of fuel concentrations in the combustion chamber during cold-start, in section 6.3, the mixture preparation is extended by incorporating the "liquid fuel pool dynamics" with the model developed in section 6.1. The correlations of $\Phi_{vapor}$ calculated by this extended model with the first firing cycle of engine are described in section 6.4. In section 6.5, the effects of thermal environment in the intake port on mixture preparation process are discussed by including the effects of the increase in temperatures on the back of intake valves and intake port wall during the warm-up process. Then the time history of the speciated vapor concentrations delivered to the cylinder is calculated by the mixture preparation model and it is related to the speciated engine-out hydrocarbon emissions (discussed in Chapter 4) in section 6.6

6.1 Model Development - volatility parameter $\Phi_{vapor}$ and $F_{BL}$

The objective of this chapter is to study the fuel effects on mixture preparation process as applied to a typical modern spark-ignition engine. The strategy is to define a parameter derived from the fuel volatility characteristics and the engine operating conditions (intake manifold pressure, temperature, and degree of fuel enrichment), and to examine whether the engine behaviors during start-up can be explained by this parameter. In order to characterize the fuel effects on mixture preparation process, a model which is based on the properties of fuel species is developed in this section.
The conceptual picture of the mixture preparation model is described in Figure 6.1. The model schematizes that the mixture entering into the cylinder comprises two parts: one part consists of the fuel vapor that mixes uniformly with a fraction of the intake air in the vapor boundary layer so that this air/vapor mixture is in thermodynamic equilibrium with the liquid film in the port; the other part consists of just pure air. For this simplified model, the liquid fuel that enters the cylinder is assumed not to significantly affect the gaseous charge composition. Thus the fuel components affects the starting process via their influence on the total vapor concentration and species concentrations in the thermodynamically equilibrated vapor boundary layer.

![Diagram of mixture preparation model]

**Figure 6.1** The conceptual picture of the mixture preparation model

The above procedure of partitioning the intake air into two parts is necessary for the following reason: if all the intake air were assumed to be in equilibrium with the injected fuel, all the fuel would have evaporated even at very low temperature. In the model, the injected fuel
is assumed to be in equilibrium with a fraction of the intake air in one cycle due to the fact that the actual process is far from equilibrium.

Using an analysis of the mass diffusion boundary layer thickness, the portion of air to mix with the fuel vapor and to equilibrate with the liquid fuel can be estimated. The estimate is based on a typical 2-valve engine at idle/light load condition (engine stroke and bore both at 8.7 cm, intake port diameter 4 cm, operating at 0.4 bar intake pressure and 900 rpm). The mean port-air-velocity $V_a$ based on the mean piston speed is:

$$V_a = (B/a)^2(2NL) = 12.3 \text{ (m/s)} \quad (6.1)$$

where $B$, $a$, $N$, and $L$ are the engine bore, port diameter, revolutions per second, and stroke. The Reynolds number based on the port diameter is then $1.25 \times 10^4$. For a steady-state pipe flow this Reynolds number would be in the transient regime.

The mass boundary layer thickness is calculated by assuming that the Schmidt number is unity so that the thickness is the same as the momentum boundary layer (displacement) thickness $\delta^*$. The latter value is calculated based on the flat plate formula [46] evaluated at a longitudinal distance equal to the port diameter $a$. The fraction $f_{BL}$ of the intake air in the vapor mass boundary layer is thus:

$$f_{BL} = \frac{4\delta^*}{a}$$

$$= \frac{4 \cdot 1.721}{Re^\frac{1}{4}} = 6\% \text{ for laminar flow}$$

$$= \frac{4 \cdot 0.046}{Re^\frac{1}{4}} = 1\% \text{ for turbulent flow} \quad (6.2)$$
Because the pulsating nature of the intake process, there is not enough time for the flow to become fully turbulent. (The forward flow period at 900 rpm is ~30 ms. At the mean port-air-velocity, the flow would cover a runner length to diameter ratio of ~9, which is much less than the entrance length to establish a fully development turbulent flow.) The laminar value is therefore more appropriate as a measure of the vapor boundary layer thickness in this case.

Therefore, 6% of the total intake air each cycle is assumed to be in equilibrium with the fuel. Using this amount of air, the equilibrium composition of the vapor/air/liquid mixture may be calculated using the isothermal flash calculation at the intake port temperature and pressure. From the vapor/liquid equilibrium (VLE) data (see section 5.1) calculated by the isothermal flash calculation, a volatility parameter, $\Phi_{\text{vapor}}$, which is a indication of extend of vaporization of fuel, is calculated as:

$$\Phi_{\text{vapor}} = \frac{\sum \left[ m_{f,v,i} \cdot (A/F)_{s,i} \right]}{m_{\text{air}}}$$  (6.3)

In the above, $m_{f,v,i}$ is the mass of the individual vapor components calculated by an equilibrium flash evaporation of the injected fuel in 6% of the intake air, $(A/F)_{s,i}$ is the corresponding stoichiometric air-fuel ratio of the $i^{th}$ component in fuel model, and $m_{\text{air}}$ is the total mass of the intake air in one cycle. The procedure of calculating $\Phi_{\text{vapor}}$ of a particular fuel under particular engine operating conditions is written as a computer program (EAD.for, written in FORTRAN) listed in Appendix C, and explained in the following paragraphs.

The inputs of the model include the composition of the fuel and air, amount of fuel and air for each cycle, and intake pressure and temperature. Composition of the injected fuel is represented by the Major-Component fuel model (explained in section 5.2) of the fuel, and
composition of air is represented by nitrogen and oxygen with molar ratio of 3.773 : 1. The relative amount of injected fuel and total air for each cycle is represented by the injected fuel-air equivalence ratio $\Phi_{\text{inj}}$ (see section 2.2.2). The intake pressure and temperature are the measured values from the experiments described in section 2.2.1. Based on these input, the equilibrium composition of the vapor/air/liquid mixture may be calculated using the isothermal flash calculation, assuming that 6% of the air is in equilibrium with vapor and liquid fuel. From the VLE data, $\Phi_{\text{vapor}}$ of the fuel can be calculated and is the output of the mixture preparation model.

6.2 Correlations of $\Phi_{\text{vapor}}$ with Starting and Warm-Up Driveability Attributes

Based on the mixture preparation model described in previous section, $\Phi_{\text{vapor}}$ for different fuel blends and different enrichment cases ($\Phi_{\text{inj}}$) listed in Table 6.1 (the same test matrix described in section 2.2.2) was calculated. In these calculations, following inputs for the model were specified: the same engine operating condition as that of driveability experiments (0.4 bar intake pressure, 22°C manifold temperature, see section 2.2.1); the composition of iso-octane / n-pentane mixtures and indolene / MTBE mixtures used are listed in Table 6.2 and Table 6.3; and the Major-Component fuel model for indolene is listed in Table 5.4. The correlations of $\Phi_{\text{vapor}}$ with different driveability attributes (also see Reference [47]) derived from engine experiments (see Figure 2.3 to Figure 2.10 in section 2.3) are explained in the following paragraphs.

<table>
<thead>
<tr>
<th>nC5 volume % in iC8/nC5 blends</th>
<th>0, 15, 30, 50, 70, 85, 100</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE volume % in indolene/MTBE blends</td>
<td>0, 5, 10, 15, 20, 30, 50, 70, 85, 100</td>
</tr>
<tr>
<td>Injected fuel equivalence ratio</td>
<td>1.0, 1.1, 1.2, 1.3, 1.5</td>
</tr>
</tbody>
</table>
The correlation of $\Phi_{\text{vapor}}$ to the First Significant Firing Cycle is shown in Figure 6.2. The 85 data points (5 enrichments x 17 fuel blends) in the graph represent the complete test matrix are shown in Table 6.1. The solid symbols are for the iso-octane / n-pentane mixture; the open symbols are for indolene / MTBE mixture. The different enrichments are denoted by symbols of different shapes. The data points for each symbol are from the different mixture proportions. For example, the different mixture proportions of the iso-octane / n-pentane mixture at injected equivalence ratio $\Phi_{\text{inj}} = 1$ are explicitly marked on the figure. Note that for n-pentane content of over 50%, all the fuel has evaporated according to the model, and therefore all these data points have $\Phi_{\text{vapor}}$ equal to the injected equivalence ratio $\Phi_{\text{inj}}$ of 1.

The correlation shown in Figure 6.2 is remarkable, given the extensiveness of the data set which includes different enrichments, fuel types and blending ratios; and the range of y-axis values which span more than an order of magnitude. If we ignore the 6 data points at the extreme right-hand side (beyond $\Phi_{\text{vapor}} \sim 1.2$) of the figure because after all, the minimum value for the y-axis is 1, the data could be fit by a power law:
First Significant Firing Cycle $\propto \Phi_{\text{vapor}}^{-n}$, $n = 5.3$ \hspace{1cm} (6.4)

Since the four start-up parameters are fundamentally related to the fuel volatility characteristics, they all have similar correlation to the value of $\Phi_{\text{vapor}}$. This is shown in Figure 6.3 to Figure 6.5. Because we are interested in the operating regions where the fuel effects are prominent, power-law least square fits are applied to the data points on the left side of these figures. The functional relationships are:

- GIMEP rise time constant, $\tau_r$ $\propto \Phi_{\text{vapor}}^{-n}$, $n = 4.54$ \hspace{1cm} (6.5)
- RMS decay time constant, $\tau_d$ $\propto \Phi_{\text{vapor}}^{-n}$, $n = 4.71$ \hspace{1cm} (6.6)
- RMS value at $3\tau_r$, $(\sigma(3\tau_r) - \sigma(\infty))/\text{GIMEP}(\infty)$ $\propto \Phi_{\text{vapor}}^{-n}$, $n = 4.33$ \hspace{1cm} (6.7)

(In the last quantity, the "background" intrinsic engine IMEP fluctuation $\sigma(\infty)$ which is not related to the fuel volatility has been subtracted out. If this were not done, the value of $n$ would have be much lower - $\sim 2.8$). The engine start-up parameters are roughly inversely proportional to $\Phi_{\text{vapor}}$ to the fifth power. Thus the engine start-up is very sensitive to the fuel volatility properties.

This high sensitivity of the start-up parameters to the fuel volatility is important in terms of fuel formulation. Balance, however, has to be made between good start-up performance and evaporative loss.

The data presented in Figure 6.2 to Figure 6.5 indicated that good start-up characteristics are achieved when $\Phi_{\text{vapor}} > 1$. We have not, however, tested whether this value is universal for all engines. If so, this value may be a practical design target for enrichment strategy during engine starting and warm-up processes.
Figure 6.2 First significantly firing cycle as a function of the vapor equivalence ratio $\Phi_{\text{vapor}}$ for the entire test matrix

Figure 6.3 GIMEP rise time constant as a function of the vapor equivalence ratio $\Phi_{\text{vapor}}$, for the entire test matrix
Figure 6.4 RMS decay time constant as a function of the vapor equivalence ratio $\Phi_{\text{vapor}}$ for the entire test matrix

Figure 6.5 Normalized RMS value of the GIMEP fluctuation after 3 GIMEP rise time constant as a function of the vapor equivalence ratio $\Phi_{\text{vapor}}$ for the entire test matrix
6.3 Model Extension - Liquid Fuel Pool Dynamics and $F_c$

During engine starting and warm-up processes when the coolant and engine parts are at lower temperatures than the fully warm-up condition, the injected fuel which does not evaporate in one cycle will accumulate to form liquid puddles inside the intake manifold. Visualization of mixture preparation process at intake port of a port-fuel injection SI engine [12] confirms this build-up. These liquid fuel puddles persist during the whole engine warm-up period. They play an important role in the formation of the air/fuel mixture in engine transients, such as cold-start, warm-up, and acceleration/deceleration of the engine. With accumulation of liquid fuel inside the intake manifold, correct metering of fuel to form combustible mixture during engine transients becomes difficult. For example, the time lag introduced by the storage and release of liquid fuel in the intake manifold during engine transient conditions can cause substantial deviations of air/fuel ratio in the combustion chamber from stoichiometric. Therefore, the objective of this section is to extend the mixture preparation model developed in section 6.1 by incorporating the mechanism of liquid fuel pool dynamics.

The conceptual picture for the extended mixture preparation model which includes the liquid fuel pool dynamics is shown in Figure 6.6. Two major features of the model are explained as below:

(i) In order to model the non-equilibrated behaviors of the mixture preparation processes, the mixture entering into the cylinder is schematized to comprise two parts: one part consists of the fuel vapor that mixes uniformly with a fraction of the intake air so that this air/vapor mixture is in thermodynamic equilibrium with the liquid film in the port; the other part consists of air only. The fraction of air which is in equilibrium with the fuel is defined as the "effective fraction of air in equilibrium with fuel", denoted by $f_c$. 

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(ii) The injected fuel which does not evaporate during the current cycle is assumed to stay in intake manifold with the accumulated liquid fuel pool from previous cycles. Then this liquid fuel pool is assumed to mix with the fuel flow of next cycle, and interact with the intake air next cycle to reach equilibrium.

Figure 6.6 The conceptual picture for the "extended" mixture preparation model

In the first feature, the procedure of partitioning the intake air into two parts is necessary for the following reason: if all the intake air were assumed to be in equilibrium with the injected fuel, all the fuel would have evaporated even at very low temperature according to the thermodynamic calculation. For example, in Figure 4.4 (see section 4.2), a single pulse of 7 units of fuel was injected at the first cycle with the ignition turned off; there was no further fuel injection afterwards. The exhaust HC measured by the fast-FID and the sampling unit both detected continuous and decreasing concentration of hydrocarbon in exhaust gas until 15 cycles. Thus there was still fuel evaporating from the liquid fuel pool formed at the first injection of
fuel. If all the fuel injected in the first cycle was vaporized within the first engine cycle, there could have been no more fuel evaporating from the liquid fuel pool and no HC as detected by fast-FID and sampling unit at exhaust pipe in the subsequent cycles. Therefore, the fuel injected in the current cycle does not have enough time to reach equilibrium. In order to model this non-equilibrated process, the fuel inside the intake manifold (including the injected fuel of the current cycle and the liquid fuel puddles from previous cycles) is assumed to be in equilibrium with the effective fraction of intake air in that cycle.

The second feature implies that the liquid fuel which does not evaporate and accumulate from previous cycles may still have the chance to evaporate at current and later cycles. In the example described in the previous paragraph, the exhaust HC detected by the fast-FID and the sampling unit show that, at the 15th cycle, there is still fuel evaporating from the liquid fuel pool formed after the first injection of fuel. This example thus demonstrates the importance of the contribution of liquid fuel pool to air/fuel mixture formation. In order to model correctly the mixture preparation process, the liquid fuel pool dynamics has to be included.

The extended mixture preparation model which includes both these two mechanisms is written as a computer program (ACCU.for, written in FORTRAN) listed in Appendix D. The inputs of the model include the composition of the fuel and air, amount of fuel and air for each cycle, and intake pressure and temperature. Composition of the injected fuel is represented by the Major-Component fuel model (explained in section 5.2) of the fuel, and composition of air is represented by nitrogen and oxygen with molar ratio of 3.773 : 1 (because N₂ and O₂ are major components of air). The relative amount of injected fuel and total air for each cycle is represented by the injected fuel-air equivalence ratio Φ_inj (see section 2.2.2). The intake pressure and temperature used in the simulation are the measured values from the experiments. Based on these input, the equilibrium composition of the vapor/air/liquid mixture may be calculated using
the isothermal flash calculation. From the VLE data, $\Phi_{\text{vapor}}$ (see equation 6.3 for the definition) of each cycle, which is the output of the model, can be calculated.

The effective fraction of intake air in equilibrium with fuel, $f_a$, was decided by comparing with the in-cylinder hydrocarbon concentration data measured by Younggy Shin [15]. This data was measured by a fast-FID installed in the top of combustion chamber of the Volvo single-cylinder engine (see section 3.1.1 for engine specification). Detail information about the in-cylinder fast-FID measurement can be found in Reference [18] and Reference [19]. The engine was motored at 900 rpm by dynamometer with ignition turned off. The intake pressure was 0.527 bar and the ambient temperature was 300°K. The fuel used was indolene. Fuel injection started at the first cycle with injected equivalence $\Phi_{\text{inj}}$ of 0.92; followed by the same $\Phi_{\text{inj}}$ for each cycle. The in-cylinder fast-FID measurement for each cycle was converted to $\Phi_{\text{vapor}}$ and represented by the solid symbols in Figure 6.7.

![Figure 6.7 Comparison of $\Phi_{\text{vapor}}$ calculated by the mixture preparation model with the in-cylinder fast FID data under engine motoring condition](image)

Motoring at 900 rpm, $P_i = 0.527$ [bar], $T = 300$[K]
Fuel : indolene, $\Phi_{\text{inj}} = 0.92$

$\Phi_{\text{vapor}}$

- $f_a = 1\%$
- $f_a = 5\%$
- $f_a = 0.5\%$
- in-cylinder FID data

Cycle

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The same operating conditions was used to calculate the $\Phi_{\text{vapor}}$ by the mixture preparation model: intake pressure 0.4 bar; ambient temperature 300°K (the temperature of intake port is assumed to be the same as ambient temperature because there is no firing of engine). The Major-Component fuel model of indolene listed in Table 5.4 was used as input of the model to represent composition of indolene. Three values of $f_e$ was used in the simulations: $f_e = 0.5, 1, \text{ and } 5\%$. The comparison of the $\Phi_{\text{vapor}}$ calculated by mixture preparation model with $\Phi_{\text{vapor}}$ measured by the in-cylinder fast-FID are shown in Figure 6.7.

In Figure 6.7, the value of $f_e$ was first decided by matching the $\Phi_{\text{vapor}}$ of the first cycle. It was found that, besides the first cycle, the in-cylinder fast-FID data correlated well with the simulation at the following cycles by using a single value of $f_e = 1\%$. There are also several noticeable features in Figure 6.7:

(i) In the first cycle, there is no liquid fuel accumulated from previous cycles. Only the fuel vaporized from the injected fuel at the current cycle constitutes the $\Phi_{\text{vapor}}$ of the first cycle. Thus only the first mechanism in the mixture preparation model was used in the first cycle when $\Phi_{\text{vapor}}$ was calculated and when $f_e$ was first decided.

(ii) In the following cycles, the simulation start to accumulate the liquid fuel which does not evaporate each cycle automatically according to the liquid fuel pool dynamics in the mixture preparation model. The simulation with $f_e = 1\%$ can still match the trace of fast-FID measurement well for the later cycles when both mechanisms was used in the simulation. This validates the mechanism of accumulation of liquid fuel in the mixture preparation model. If there is no liquid fuel pool dynamics in the model, the calculated $\Phi_{\text{vapor}}$ for each following cycle should be the same as that of first cycle because all the inputs (composition of fuel, $\Phi_{\text{nj}}$, pressure, and temperature) to the model for each cycle are identical. With the mechanism of accumulation of liquid fuel, the fuel species which does not evaporate and accumulate in the intake manifold are mostly less volatile components in the fuel. Therefore, the amount and composition of the
fuel in intake port (including the current injected fuel and liquid fuel puddles), thus the inputs of the model, are changing cycle by cycle. It is the reason why the \( \Phi_{\text{vapor}} \) is increasing as the cycle number increases.

(iii) From (ii), it is found that the amount and composition of liquid fuel in the intake manifold during warm-up process are changing all the time. Even if the composition and amount of fuel for each cycle are different, \( f_e = 1\% \) still holds for the calculation of all the cycles. This fact illustrates that the model of an effective fraction of air in equilibrium with fuel is a good one.

(iv) When \( f_e \) is larger than 1\%, the simulated \( \Phi_{\text{vapor}} \) overestimates the measured values; when \( f_e \) is smaller than 1\%, the simulated \( \Phi_{\text{vapor}} \) underestimates the measured values. As cycle number increases, the difference among simulated values with different \( f_e \) seems become smaller.

Therefore, 1\% of the total intake air each cycle is assumed to be in equilibrium with the fuel for the mixture preparation model. In Figure 6.7, it is found that \( f_e = 1\% \) is valid when the fuel is indolene, and when the amount and composition of liquid fuel in the intake port are changing. In next section, it will be demonstrated that \( f_e = 1\% \) is also valid for using different type of fuels as inputs of the model.

In Figure 6.7, the \( \Phi_{\text{vapor}} \) measured by the in-cylinder fast-FID are converted from the actual hydrocarbon concentration in the combustion chamber. Therefore, the \( \Phi_{\text{vapor}} \) estimated by the extended mixture preparation model which correlates well with the fast-FID data is the actual fuel/air equivalence ratio in the combustion chamber for that particular cycle. It is different from the \( \Phi_{\text{vapor}} \) calculated by the model described in section 6.1, although the definition for both \( \Phi_{\text{vapor}} \) are the same.

Unlike the \( \Phi_{\text{vapor}} \) calculated by the extended mixture preparation model, the \( \Phi_{\text{vapor}} \) calculated by the model in section 6.1 was not meant to be the actual fuel/air equivalence ratio in combustion chamber in a specific cycle. It is a volatility parameter derived from the fuel properties and the engine operating conditions to represent the effects of "relative" volatility of
fuel on the engine starting and warm-up behaviors. For example, the engine start-up parameters are roughly inversely proportional to $\Phi_{\text{vapor}}$ to the fifth power (see section 6.2). That is, better driveability of engine can be obtained when the fuel with higher $\Phi_{\text{vapor}}$ is used. Besides, $\Phi_{\text{vapor}}$ calculated by the model in section 6.1 does not correspond to the hydrocarbon concentration of any particular cycle. It is an indication of the overall performance of the fuel for engine operated under starting and warm-up periods. Although with the same name and definition, it is completely different from the $\Phi_{\text{vapor}}$ calculated by the extended mixture preparation model. Therefore, it is not surprise to find that the $f_{\text{BL}}$ for the model in section 6.1 is 6%, while the $f_e$ for the extended mixture preparation model described in this section is 1%.

6.4 Correlations of $\Phi_{\text{vapor}}$ with First Firing Cycle of Engine

In this section, the mixture preparation process of the simulated engine cold-start procedure described in Chapter 3 was simulated by the extended mixture preparation model described in section 6.3. The $\Phi_{\text{vapor}}$ for each cycle from the first fuel injection to the 25th cycle was calculated by the model, and compared with the engine first firing cycles data by using different fuels.

The inputs for the simulation of $\Phi_{\text{vapor}}$ was based on the test procedure described in section 3.2.1: the engine was fired with the 6 different fuels stated in Table 3.3 at 900 rpm, 0.4 bar intake pressure, and 20°C ambient temperature (the temperature of intake port is assumed to be the same as ambient temperature because there is only several firing cycles within the first 25 cycles for most of the cases); the units of fuel injected in the first cycle ($\Phi_{\text{inj}}(1)$) were varied from 1 to 7 units, followed by one unit of fuel in each subsequent cycles; composition of fuel blends are listed in Table 6.4; composition of indolene is represented by the Major-Component fuel model of indolene listed in Table 5.4.
Table 6.4 Composition of the fuels used in the first firing cycle test

<table>
<thead>
<tr>
<th>Fuel blend</th>
<th>Volume ratio</th>
<th>Mass ratio</th>
<th>Mole ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-Octane</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>iso-Octane/n-Pentane</td>
<td>80/20</td>
<td>81.5/18.5</td>
<td>73.6/24.6</td>
</tr>
<tr>
<td>iso-Octane/n-Decane</td>
<td>90/10</td>
<td>89.5/10.5</td>
<td>91.4/8.6</td>
</tr>
<tr>
<td>iso-Octane/m-Xylene</td>
<td>75/25</td>
<td>70.6/29.4</td>
<td>69.1/30.9</td>
</tr>
<tr>
<td>indolene</td>
<td>~</td>
<td>~</td>
<td>~</td>
</tr>
<tr>
<td>indolene/MTBE</td>
<td>90/10</td>
<td>90.9/9.1</td>
<td>88.9/11.1</td>
</tr>
</tbody>
</table>

The simulated values of $\Phi_{\text{vapor}}$ for different fuel blends at each cycle are represented by the dotted lines in Figure 6.8 to Figure 6.13. The different lines in each graph represent the $\Phi_{\text{vapor}}$ by using different units of fuel injected at the first cycle, from $\Phi_{\text{inj}}(1) = 1$ to 7.

The first firing cycle data for the 6 different fuel blends obtained by the simulated cold-start procedure described in Chapter 3 are shown in Figure 3.4 to Figure 3.9. The same data for these fuels are also shown by symbols in Figure 6.8 to Figure 6.13 in order to compare the first firing cycle of engine with the $\Phi_{\text{vapor}}$ calculated by the mixture preparation model. For example, the first firing cycle for iso-octane when $\Phi_{\text{inj}}(1)$ equals 1 is either 8 or 9 cycles (there are 3 repeated test runs for each operating condition, see section 3.2.2), as shown in Figure 3.4. In Figure 6.8, the three data points lay on the lowest line which is the trace of the simulated $\Phi_{\text{vapor}}$ when $\Phi_{\text{inj}}(1)$ equals 1. The cycle numbers (horizontal axis values) for these three points are also either 8 or 9 cycles. Therefore, the values in the vertical axis correspond to these 3 points are the simulated $\Phi_{\text{vapor}}$ for the operating condition of these points. In this way, the information described by Figure 6.8 to Figure 6.13 is the predicted values of fuel/air equivalence ratio ($\Phi_{\text{vapor}}$) present the combustion chamber when the engine starts to fire.

In the lowest line ($\Phi_{\text{inj}}(1) = 1$) of Figure 6.8, for example, the engine does not fire until $\Phi_{\text{vapor}}$ equals to about 0.7 (cycle number equals to 8 or 9). For the top line ($\Phi_{\text{inj}}(1) = 7$) of Figure
6.8, the engine fires at the first cycle where the $\Phi_{vapor}$ equals to about 0.95. By comparing the first firing cycles of all the seven lines in Figure 6.8, it is noted that the engine starts to fire whenever $\Phi_{vapor}$ is larger or equal to 0.7. For all of the other fuels in Figure 6.9 to Figure 6.13, similar results are observed: there is no first firing cycle occurring at the cycle where $\Phi_{vapor}$ is less than 0.7.

All of the data points in Figure 6.8 to Figure 6.13 are redrawn in Figure 6.14: the same type of symbols represent the first firing cycles with the same fuel, but with different $\Phi_{inj}(1)$; different types of symbols represent the first firing cycles for different fuels. The correlation between the first firing cycles and the $\Phi_{vapor}$ shown in Figure 6.14 is remarkable, given the extensiveness of the data set (126 test runs) which includes different fuel types (wild range of volatility) and different enrichment ($\Phi_{inj}(1) = 1$ to 7). It is noticed that all the first firing cycle occur whenever $\Phi_{vapor}$ is larger than or equal to 0.7 (There are some points with $\Phi_{vapor}$ larger than 0.7 locating at the vertical line of the first cycle). Therefore, under this particular operating condition (900 rpm, 0.4 bar intake pressure, MBT spark timing), $\Phi_{vapor}$ equals 0.7 is the lean burn limit of the air/fuel mixture (the minimum amount of fuel required to ignite the mixture in the combustion chamber). That is, whenever the $\Phi_{vapor}$ is larger 0.7, the engine starts to fire at that cycle. This correlation demonstrates that the extended mixture preparation model can correctly predict the total vapor concentration (or $\Phi_{vapor}$) for each cycle present in the combustion chamber during cold-start for different fuel types and fuel different enrichment.

There are also some noticeable features in Figure 6.8 to Figure 6.13 which also show that this model can simulate well the evaporative behaviors of fuel species in the mixture preparation process:

(i) For single component fuel (iso-octane) and the fuel blends with heavy-end components (iso-octane / n-decane and iso-octane / m-xylene mixtures), the $\Phi_{vapor}$ values increase
as the cycle number increases for all the values of $\Phi_{\text{inj}}(1)$. For the fuels with light-end components, including iso-octane / $n$-pentane mixture, indolene, and indolene / MTBE mixture, at $\Phi_{\text{inj}}(1) = 1$, the $\Phi_{\text{vapor}}$ also increases as the cycle number increases. This is due to the build-up of the liquid puddles inside the intake manifold. The contribution of the injected fuel to the $\Phi_{\text{vapor}}$ of the current cycle is the same for each cycle (before the first firing cycle) because the operating condition and thermal environment of the engine does not change. The only difference is the amount of liquid fuel accumulated in the intake manifold. Therefore, the liquid fuel accumulated from the previous cycles can still evaporate at the later cycles even if the operating condition and the thermal environment are the same as those of the previous cycles. This behavior is successfully captured by the liquid fuel pool dynamics (see section 6.3) of the extended mixture preparation model.

(ii) For the fuels with light-end components, including iso-octane / $n$-pentane mixture, indolene, and indolene / MTBE mixture, there is a spike of the $\Phi_{\text{vapor}}$ at the first cycle when $\Phi_{\text{inj}}(1)$ is larger 1. When the fuel is injected into the intake manifold during cold-start, most of the species evaporate to form the air/fuel mixture are the more volatile (light-end) species in the fuel. Therefore, the $\Phi_{\text{vapor}}$ of the first few cycles come mostly from these light-end components. When $\Phi_{\text{inj}}(1)$ is larger than 1 unit of fuel, the $\Phi_{\text{vapor}}$ of the first cycle, which is mostly constituted by the light-end components of more than 1 unit of fuel, may be larger than those of several following cycles because $\Phi_{\text{inj}}$ for these cycles are kept at constant of 1 unit.

In Figure 3.5, Figure 3.8, and Figure 3.9, it is noticed that there is a “discontinuity” of the first firing cycle from $\Phi_{\text{inj}}(1) = 2$ to 3. For example, the first firing cycle of indolene for $\Phi_{\text{inj}}(1) = 1$ is 16 (or 17); that for $\Phi_{\text{inj}}(1) = 2$ is 15 (or 16); but the first firing cycle for $\Phi_{\text{inj}}(1) = 3$ suddenly drops to 1. In Figure 6.12, it can be found that this “discontinuity” is due to the big spike ($\Phi_{\text{vapor}} \approx 0.9$, which is larger than the lean burn limit of 0.7) at the first cycle for $\Phi_{\text{inj}}(1) = 3$. However,
\( \Phi_{vapor} \) of the first cycle for the \( \Phi_{inj}(1) = 1 \) and \( \Phi_{inj}(1) = 2 \) are about 0.3 and 0.6, which are less than the lean burn limit. Therefore, the engine will not fire until \( \Phi_{vapor} \) reaches 0.7 in these cases.

Besides the first firing cycle, the criterion for successful engine firing, \( \Phi_{vapor} \) is larger or equal to 0.7, is applicable to all other cycles under the same operating condition. In Figure 6.15 to Figure 6.20, the dotted lines represent the simulation of \( \Phi_{vapor} \) for each cycle which are the same lines as those in Figure 6.8 to Figure 6.13: the different lines in each graph represent the \( \Phi_{vapor} \) by using different units of fuel injected at the first cycle, from \( \Phi_{inj}(1) = 1 \) to 7. All the firing cycles are represented by solid symbols while misfiring cycles are represented by empty symbols (only one of the three repeated test runs for each fuel is shown in these graphs). It is found that all the firing cycles occur when \( \Phi_{vapor} \) is larger or equal to 0.7 (some misfiring cycles with \( \Phi_{vapor} \) larger than 0.7 is due to the cycle-to-cycle variations when \( \Phi_{vapor} \) is close to the border line of 0.7). This phenomenon is even more prominent with fuel blends with presence of light-end components, such as the blends of iso-octane / n-pentane, indolene, and indolene / MTBE mixture. For example, in Figure 6.19, the fuel used is indolene and the third line in this graph represents the case with first injection unit \( \Phi_{inj}(1) \) equals to 3. In the third line of Figure 6.19, the first point whose \( \Phi_{vapor} \) is equal to about 0.9 is a firing cycle, followed by several misfiring cycles because \( \Phi_{vapor} \) for those cycles is less than 0.7. The engine did not fire until the 13\textsuperscript{th} cycle when \( \Phi_{vapor} \) finally approach to 0.7.
Figure 6.8 Correlation of the first firing cycle with the $\Phi_{\text{vapor}}$ by using iso-octane as fuel

Figure 6.9 Correlation of the first firing cycle with the $\Phi_{\text{vapor}}$ by using iso-octane/n-pentane mixture (volume ratio = 80/20) as fuel
Figure 6.10 Correlation of the first firing cycle with the $\Phi_{vapor}$ by using iso-octane/n-decane mixture (volume ratio = 90/10) as fuel

Figure 6.11 Correlation of the first firing cycle with the $\Phi_{vapor}$ by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel
Figure 6.12 Correlation of the first firing cycle with the $\Phi_{\text{vapor}}$ by using indolene as fuel.

Figure 6.13 Correlation of the first firing cycle with the $\Phi_{\text{vapor}}$ by using indolene/MTBE mixture (volume ratio = 90/10) as fuel.
Figure 6.14 Correlation of the first firing cycle with the $\Phi_{vapor}$ for the entire fuel matrix

Figure 6.15 Correlation of firing and misfiring cycles with $\Phi_{vapor}$ by using iso-octane as fuel
Figure 6.16 Correlation of firing and misfiring cycles with $\Phi_{vapour}$ by using iso-octane/n-pentane mixture (volume ratio = 80/20) as fuel.

Figure 6.17 Correlation of firing and misfiring cycles with $\Phi_{vapour}$ by using iso-octane/n-decane mixture (volume ratio = 90/10) as fuel.
Figure 6.18 Correlation of firing and misfiring cycles with $\Phi_{\text{vapor}}$ by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel.

Figure 6.19 Correlation of firing and misfiring cycles with $\Phi_{\text{vapor}}$ by using indolene as fuel.
6.5 Effects of Thermal Environment of the Intake Port on the Mixture Preparation Process

During Engine Starting and Warm-Up

One of the major control variables which influence the extend of vaporization of fuel during mixture preparation process is the temperature in the intake manifold. In previous sections, ambient temperature was used to represent the thermal environment of intake manifold for the simulations based on the assumption that the temperatures of the engine and the fluids (intake charge air and fuel flow) was initially the same as ambient temperature; and the thermal environment of the intake port did not change much if the engine was only fired for several cycles. If the engine was fired for a longer period of time, this assumption would not be right. For example, during engine warm-up process, the coolant temperature, which is close to the temperature of intake port wall, typically increases from ambient temperature (~ 20°C) to fully warm-up condition (~ 90°C) within 20 minutes. Temperature of intake valves may change even
more dramatically because the intake valves are in direct contact with the hot burned gas in the combustion chamber. Thus the intake manifold temperature are highly transient during the engine starting and warm-up periods.

The thermal environment of the intake manifold of a port-fuel injection engine during warm-up process involves many complex heat transfer phenomena: heating of the intake valves by the hot burned gas in the combustion chamber; heating of the intake port region by the reverse flow of the burned gas when the intake valves open; cooling of intake valves and the intake port wall by the injection and vaporization of fuel. A comprehensive heat transfer model is beyond the scope of this thesis. The purpose here is to capture the representative behaviors of intake port which are important to the mixture preparation process. As such, the strategy is to measuring the representative temperatures inside the intake port as the input of the mixture preparation model.

Configuration of the intake port of the Volvo single-cylinder engine (see section 3.1.1) and the locations of the thermocouples measuring the intake port temperature are shown in Figure 6.21. One of the thermocouples was installed on the back of an intake valve, and the other one was on the intake manifold wall and half inch from the intake valve seat. Fuel is injected into the intake manifold to form a cone-shaped spread of fuel by the injector which is located at the top of the intake manifold. The spread of the fuel and the wetted area in the intake port are also shown in Figure 6.21. Most of the injected fuel impinges on the back of the intake valves and the intake manifold wall. Thus most of the accumulated liquid fuel vaporizes from these wetted areas. Therefore, temperatures of intake valves and intake port wall are chosen as two representative temperatures for the mixture preparation process.

The measurement of the intake valve temperature and the intake manifold wall temperature during engine warm-up are shown in Figure 6.22. In this case, the Volvo engine was fired with indolene. The intake manifold wall temperature, which is represented by the bottom line in Figure 6.22, rises slowly from ambient temperature to ~40°C during the first two minutes
of the warm-up process. The intake valve temperature (top line) increases much faster than the intake manifold wall temperature within the first minute, then increases roughly with the same rate as the intake manifold wall temperature after the first minute. The steeper slope of the intake valve temperature within the first minute of warm-up process is due to the direct heating by the in-cylinder burned gas.

The measurement of the intake valve temperature and the intake manifold wall temperature under the motoring condition are shown in Figure 6.23. In this case, the ignition was turned off. Fuel was injected at the first cycle with $\Phi_{\text{inj}} = 1$. The initial difference of the two temperatures was due to the heating of the intake valve by the in-cylinder compressed air before the first fuel injection (The engine was motored by dynamometer for a while before the first fuel injection). The intake manifold wall temperature remained constant; the intake valve temperature decreased because the intake valves were cooled by the injected fuel impinging on the back of the intake valves.

When the engine was firing with indolene, the in-cylinder hydrocarbon concentration was also measured by the fast-FID described in section 6.3. The engine was motored at 900 rpm with ignition on. The intake pressure was 0.548 bar and the ambient temperature was 300°C. Fuel injection started at the first cycle with injected equivalence $\Phi_{\text{inj}}$ of 0.92; followed by the same $\Phi_{\text{inj}}$ for each cycle. The in-cylinder fast-FID measurement for each cycle was converted to $\Phi_{\text{vapor}}$ and represented by the solid symbols in Figure 6.24.

The same operating conditions was used to calculate the $\Phi_{\text{vapor}}$ by the mixture preparation model. The Major-Component fuel model of indolene listed in Table 5.4 was used as input of the model to represent the composition of indolene. The effective fraction of intake air in equilibrium with fuel, $f_e$ was assumed to be 1% (see section 6.3). The intake valve temperature and intake manifold wall temperatures measured by the thermocouples were used as the intake temperatures for the simulation. The simulated $\Phi_{\text{vapor}}$ calculated by using the intake
valve temperature and intake manifold wall temperature are represented by the dotted line and the solid line individually in Figure 6.24. The \( \Phi_{\text{vapor}} \) calculated by the intake valve temperature is slightly higher than \( \Phi_{\text{vapor}} \) calculated by intake manifold wall temperature due to the higher initial temperature of intake valve. The correlation between \( \Phi_{\text{vapor}} \) calculated by mixture preparation model and \( \Phi_{\text{vapor}} \) measured by the in-cylinder fast-FID is very good. The \( \Phi_{\text{vapor}} \) calculated by the intake valve temperature is somewhat closer to the measurement, especially at the first few cycles. (In the period of ~ 50 cycles, there is not a significant difference between the valve and the port temperature.) It may be due to the higher temperature of intake valve which facilitates the vaporization of fuel.

The value of \( \Phi_{\text{vapor}} \) under the engine firing condition can thus be correctly simulated by the mixture preparation model, using the representative temperatures measured by the thermocouples as inputs. In the following sections, all the simulations were done by using the measured intake valve temperature and intake manifold wall temperature as the input of the model. It can also be shown in the following section that the importance of the thermal environment of the intake port becomes even more significant when the engine is fired for a longer period of time.
Figure 6.21 Locations of thermocouples measuring the intake valve temperature and intake manifold wall temperature

Figure 6.22 The measurement of intake valve temperature and intake manifold wall temperature under engine firing condition
Figure 6.23 The measurement of intake valve temperature and intake manifold wall temperature under engine motoring condition.

Figure 6.24 Comparison of $\Phi_{\text{vapor}}$ calculated by the mixture preparation model with the in-cylinder fast FID data under engine firing condition.
6.6 Correlations of Speciated Vapor Concentrations in Air/Fuel Mixture with Time History and Species Distribution of Engine-Out Hydrocarbon Emissions

In this section, the mixture preparation process of the simulated engine cold-start procedure described in Chapter 4 was simulated by the extended mixture preparation model described in section 6.3. A volatility parameter, ppmC1%, derived from the Vapor-Liquid Equilibrium (VLE) data of different fuel blends was simulated and compared with the time history and species distribution of engine-out hydrocarbon emissions described in section 4.5.

The inputs of the mixture preparation model were based on the test procedure described in section 4.3.1: the engine was either motored or fired with the 4 different fuels stated in Table 4.3 at 900 rpm, 0.4 bar intake pressure, and 20°C ambient temperature; the units of fuel injected in the first cycle were varied for different fuels (see Table 4.4 and Table 6.5), followed by one unit of fuel in each subsequent cycles; compositions of fuel blends are listed in Table 6.5; the composition of indolene is represented by a Major-Component fuel model of indolene listed in Table 5.4. The measured intake valve temperature and intake manifold wall temperature for different fuel under either firing or motoring condition are used as the intake temperature of the model. From the VLE data, the ppmC1% of each major components in the fuel model are calculated. The ppmC1% is defined in the following equation:

\[
ppmC1\% = \frac{(species_{i,v})}{\sum_{i}(species_{i,v})} \times 100
\]  \hspace{1cm} (6.8)

where the \((species_{i,v})\) is in the unit of ppmC1. Therefore, ppmC1% of species i represent the ratio of the amount of individual species i in vapor phase to the amount of total vapor fuel.

In the following paragraphs, the ppmC1% of each fuel species in the fuel blends of each case listed in Table 6.5 are simulated by the mixture preparation model. The results of the simulations are then compared with the measured ppmC1% of the species in the exhaust gas.
Table 6.5 Test matrix for the ppmC1% calculation by the mixture preparation model

<table>
<thead>
<tr>
<th>Fuel blend</th>
<th>volume ratio</th>
<th>mass ratio</th>
<th>molar ratio</th>
<th>carbon ratio</th>
<th>Ignition</th>
<th>Φ(1) injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>iso-Octane/n-Pentane</td>
<td>80/20</td>
<td>81.5/18.5</td>
<td>73.6/24.6</td>
<td>81.7/18.3</td>
<td>Firing</td>
<td>4</td>
</tr>
<tr>
<td>iso-Octane/n-Decane</td>
<td>90/10</td>
<td>89.5/10.5</td>
<td>91.4/8.6</td>
<td>89.5/10.5</td>
<td>Firing</td>
<td>10</td>
</tr>
<tr>
<td>iso-Octane/m-Xylene</td>
<td>75/25</td>
<td>70.6/29.4</td>
<td>69.1/30.9</td>
<td>69.1/30.9</td>
<td>Motoring</td>
<td>10</td>
</tr>
<tr>
<td>iso-Octane/m-Xylene</td>
<td>75/25</td>
<td>70.6/29.4</td>
<td>69.1/30.9</td>
<td>69.1/30.9</td>
<td>Firing</td>
<td>10</td>
</tr>
<tr>
<td>indolene</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>Motoring</td>
</tr>
<tr>
<td>indolene</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>~</td>
<td>Firing</td>
</tr>
</tbody>
</table>

6.6.1 iC8 / m-Xylene Mixture - Motoring

The evolution of the speciated hydrocarbon emissions in the exhaust gas by using a binary mixture of iso-octane/m-xylene at blending ratio of 75/25 with the ignition turned off (see section 4.5.1) is compared with the results simulated by the mixture preparation model in this section. The measured ppmC1% of iso-octane and m-xylene are represented by the solid symbols in Figure 6.25 (also in Figure 4.7). The simulated ppmC1% of these two fuel species by using the intake valve temperature and intake manifold wall temperature are represented by the dotted lines and solid lines individually. The simulated ppmC1% values of these two fuel species correlate well with the measured ppmC1% by the GC technique.

The simulated ppmC1% of the fuel species by the mixture preparation model can capture the early depletion of heavy aromatics in the exhaust gas under motoring condition: the percentage of the more volatile species, iso-octane (with normal boiling point 99.2°C) is initially high, then drops gradually to steady state value; the percentage of the less volatile species, m-xylene (with normal boiling point 139°C) is initially small, then approaches steady state value gradually. Therefore, the ratio of iso-octane to m-xylene in the exhaust gas is larger than the proportion in the fuel in the first few cycles. The correlation shows that the initial depletion of heavy-end components in the exhaust gas is due to the difference in the volatility of the fuel.
species in the mixture. The less volatile component, m-xylene in this case, is more difficult to vaporize than the more volatile component (iso-octane) during the mixture preparation process. According to the mixture preparation model, the unvaporized fuel, which comprises mostly the less volatile components, from the early cycles accumulates in the intake port. In the later cycles, the accumulated fuel from the previous cycles mixes with the air in the later cycles, evaporates, and contributes to the air/fuel mixture in the combustion chamber. Thus the percentage of the less volatile components in the mixture increases gradually due to the increased fraction of these components in the liquid fuel accumulated from the early cycles.

As the cycle number increases, the ppmC1% of iso-octane decreases while that of m-xylene increases gradually, as shown in Figure 6.25. At the steady state (not shown in Figure 6.25), the ratio of ppmC1% of iso-octane to m-xylene for both the simulation and measurement in the exhaust gas approach the proportion in the fuel. These ratios are shown in Table 6.6. These results show the consistency between the composition of the injected fuel and that of the vaporized fuel at the steady state.

**Table 6.6 Composition of iso-octane / m-xylene mixture in the injected fuel and in the exhaust gas at the steady state (motoring case)**

<table>
<thead>
<tr>
<th>component [ppmC1%]</th>
<th>injected fuel (1350 cycle)</th>
<th>exhaust (1000 cycle)</th>
<th>simulation (1000 cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iC8</td>
<td>68.9</td>
<td>68.3</td>
<td>69.1</td>
</tr>
<tr>
<td>m-xylene</td>
<td>31.1</td>
<td>31.7</td>
<td>30.9</td>
</tr>
</tbody>
</table>
Figure 6.25 Correlation of the simulated ppmC1% with the speciated HC emissions by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel under engine motoring condition

6.6.2 iC8 / m-Xylene Mixture - Firing

The evolution of the speciated hydrocarbon emissions in the exhaust gas with the binary mixture of iso-octane / m-xylene at the blending ratio of 75/25 under the firing condition (see section 4.5.2) are compared with the results simulated by the mixture preparation model in this section. The measured ppmC1% of the fuel species, iso-octane and m-xylene, are represented by the solid symbols in Figure 6.26 (also in Figure 4.9 and 4.10). The simulated ppmC1% of these two fuel species by using the intake valve temperature and intake manifold wall temperature are represented by the dotted lines and solid lines in the graph individually. The sum of the measured ppmC1% of these two fuel species ranges from 60 to 70% for most of the cycles; the remaining hydrocarbons are product species from the partial oxidation of the fuel species.
Although trends of the measured ppmC1% of iso-octane and m-xylene are similar to that of the simulation, it is not meaningful to compare them without taking the product species into account.

In Figure 6.27, the simulated ppmC1% of the fuel species calculated by the mixture preparation model with the two different temperatures as inputs are duplicated from the previous graph. These values are compared to the exhaust values for which the concentrations of each fuel component and its major product species are combined together: iso-octane is combined by its major product species, iso-butene (see Figure 4.9), and other product species; m-xylene is combined with its major product species, benzene and toluene (see Figure 4.10). In this manner, it is found that the simulated ppmC1% of the iso-octane and m-xylene calculated by using the intake manifold wall temperature correlates well with the sum of the measured ppmC1% of fuel species and their product species. Therefore, the mixture preparation model correctly predicts the vaporization of fuel during the mixture preparation process under the firing condition.

The simulated ppmC1% also captures the early depletion of heavy aromatics in the exhaust gas under the firing condition: the percentage of the more volatile species, iso-octane, and its product species is initially high, then drops gradually to the steady state value; the percentage of the less volatile species, m-xylene, and its product species is initially small, then approaches steady state value gradually. By the correlation with the mixture preparation model, the early depletion of heavy-end component and its product species in the exhaust gas is due to the difference in the volatility of the fuel species in the mixture. The less volatile component, m-xylene in this case, is more difficult to vaporize than the more volatile component (iso-octane) during the mixture preparation process in the early cycles. In the later cycles, the unvaporized fuel, which comprises mostly the less volatile component, from the previous cycles can mix with the air of later cycles and vaporize. This is also true for the motoring case stated in the previous section. In addition, the temperature in the intake port is increased by the heating of burned gas
in the later cycles. The increase of temperature also promotes the evaporation of the accumulated liquid fuel in the intake port.

As the cycle number increases, the ppmC1% of iso-octane and its product species decrease while that of m-xylene and its product species increase gradually, as shown in Figure 6.27. At the steady state (not shown in Figure 6.27), the ratio of the simulated ppmC1% of iso-octane to m-xylene, and the ratio of the measured ppmC1% of iso-octane to m-xylene (including fuel and product species) approach the proportion in the fuel. These ratios are shown in Table 6.7. Therefore, the consistency between the composition of the injected fuel and that of the vaporized fuel at the steady state is true for both the firing and motoring cases (see Table 6.6).

For most of the cycles in Figure 6.27, the simulation by using the intake manifold wall temperature (solid line) correlates well with the measurement. The results suggest that the thermal environment of the mixture preparation process under the firing condition is dominated by the intake manifold wall temperature. But in the first few cycles, the slopes of the curves of measurement are actually closer to that of the curves simulated by using the intake valve temperature (dotted line). It may imply that the vaporization of fuel is dominated by the intake valve temperature in the first few cycles because the injected fuel is primarily aimed at the intake valves. At the later cycles, the representative intake temperature switches to intake manifold wall temperature because most of the liquid fuel is accumulated at the intake port wall, instead of intake valve surface.

**Table 6.7 Composition of iso-octane/m-xylene mixture in the injected fuel and in the exhaust gas at the steady state (firing case)**

<table>
<thead>
<tr>
<th>component [ppmC1%]</th>
<th>injected fuel (6750 cycle)</th>
<th>exhaust (6750 cycle)</th>
<th>simulation (6750 cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iC8</td>
<td>68.9</td>
<td>71.1*</td>
<td>69.1</td>
</tr>
<tr>
<td>m-xylene</td>
<td>31.1</td>
<td>28.9*</td>
<td>30.9</td>
</tr>
</tbody>
</table>

* including the fuel species and product species
Figure 6.26 Correlation of the simulated ppmCl% with the speciated HC emissions (fuel species only) by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel under engine firing condition

Figure 6.27 Correlation of the simulated ppmCl% with the speciated HC emissions (including all the fuel species and product species) by using iso-octane/m-xylene mixture (volume ratio = 75/25) as fuel under engine firing condition
6.6.3 iC8 / n-C5 Mixture - Firing

The evolution of the speciated hydrocarbon emissions in the exhaust gas by using the binary mixture of iso-octane / n-pentane at the blending ratio of 80/20 under the firing condition (see section 4.5.3) are compared with the simulation done by the mixture preparation model in this section. The measured ppmC1% of the fuel species, iso-octane and n-pentane, are represented by the solid symbols in Figure 6.28 (also in Figure 4.13 and 4.14). The simulated ppmC1% of these two fuel species by using the intake valve temperature and intake manifold wall temperature are represented by the dotted lines and solid lines. The difference between these two lines are not so significant because the engine was only fired for 40 cycles and these two temperatures should not differ too much. The summation of the measured ppmC1% of these two fuel species in exhaust is about 60% for most of the cycles in the exhaust gas. Thus about 40% of the hydrocarbons in the exhaust gas are intermediate product species from the partial oxidation of the fuel species.

In Figure 6.29, the simulated ppmC1% of the fuel species are duplicated from the previous graph. But the percentage of the measured exhaust species are summed by the fuel species and its products species: iso-octane is summed by its major product species, iso-butene (see Figure 4.13), and other product species; n-pentane is summed by its major product species, C1 & C2 (see Figure 4.14). The simulated ppmC1% can correlate well with the summation of the measured ppmC1% of fuel species and their product species. Therefore, the mixture preparation model can correctly predict the vaporization of the iso-octane / n-pentane under the firing condition.

The simulated ppmC1% can also capture the early enrichment of light-end in the exhaust gas under the firing condition: the percentage of the light-end component (n-pentane, NBP 36.1°C) and its product species (C1 & C2) is initially high, then drops gradually to the steady state
value; the percentage of the less volatile species (iso-octane, NBP 99.2°C) and its product species is initially small, then approaches steady state value gradually. The early enrichment of light-end component and its product species in the exhaust gas is due to the differentiation of the volatility of the fuel species in the mixture. The more volatile component, n-pentane in this case, is easier to vaporize than the less volatile component (iso-octane) during the mixture preparation process. Thus the ratio of the summation of iso-octane and its product species to the summation of n-pentane and its product species in the first sample (54.6% / 45.4%) is less than the ratio in the fuel (81.6% / 18.4%). In the later cycles, the unvaporized fuel, which comprises mostly the less volatile component (iso-octane), from the previous can mix with the air of later cycles and vaporize. Thus the percentage of iso-octane in the exhaust gas increases in the later cycles.

As the cycle number increases, the ppmC1% of iso-octane and its product species increases while that of n-pentane and its product species increases gradually, as shown in Figure 6.29. At the steady state (not shown in Figure 6.29), the ratio of the simulated ppmC1% of iso-octane to n-pentane, and the that of measured ppmC1% of iso-octane to n-pentane (including fuel and product species) will approach the proportion in the fuel. These ratios are shown in Table 6.8. This result shows the consistency between the composition of the injected fuel and that of the vaporized fuel at the steady state under the firing condition.

Table 6.8 Composition of iso-octane/n-pentane mixture in the injected fuel and in the exhaust gas at the steady state (firing case)

<table>
<thead>
<tr>
<th>component [ppmC1%]</th>
<th>injected fuel (75 cycles)</th>
<th>exhaust (75 cycles)</th>
<th>simulation (75 cycles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iC8</td>
<td>81.6</td>
<td>83.9*</td>
<td>81.9</td>
</tr>
<tr>
<td>n-pentane</td>
<td>18.3</td>
<td>16.1*</td>
<td>18.1</td>
</tr>
<tr>
<td>* including the fuel species and product species</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 6.28 Correlation of the simulated ppmC1% with the speciated HC emissions (fuel species only) by using iso-octane/n-pentane mixture (volume ratio = 80/20) as fuel under engine firing condition

Figure 6.29 Correlation of the simulated ppmC1% with the speciated HC emissions (including all the fuel species and product species) by using iso-octane/n-pentane mixture (volume ratio = 80/20) as fuel under engine firing condition
The evolution of the speciated hydrocarbon emissions in the exhaust gas by using the binary mixture of iso-octane / n-decane at the blending ratio of 90/10 under the firing condition (see section 4.5.4) are correlated with the simulation by the mixture preparation model in this section. The measured ppmC1% of the fuel species, iso-octane and n-decane, are represented by the solid symbols in Figure 6.30 (also in Figure 4.17). The simulated ppmC1% of these two fuel species by using the intake valve temperature and intake manifold wall temperature are represented by the dotted lines and solid lines. The summation of the measured ppmC1% of these two fuel species in exhaust is about 60% for most of the cycles in the exhaust gas. Thus about 40% of the hydrocarbons in the exhaust gas are intermediate product species from the partial oxidation of the fuel species.

In order to compare the measurement with the simulation, product species has to be taken into account. Unlike the iso-octane / m-xylene and iso-octane / n-pentane mixtures, most of the partial oxidation products of the fuel species (iso-octane and n-decane [24, 28]) are the same (except for the iso-butene which is primarily derived from iso-octane). It is difficult to decide whether they originally come from iso-octane or n-decane. However, it is possible to apportion the percentages of partial oxidation products of iso-octane in the exhaust gas by comparing the percentages of iso-octane and its product species obtained in the previous sections.

The three binary mixtures in the test matrix, iso-octane / m-xylene (section 6.6.2) and iso-octane / n-pentane (section 6.6.3), and iso-octane / n-decane (section 6.6.4) mixtures, all consist of iso-octane as the base component. Besides the different “additives” in the mixture, the engine operating conditions for these three firing cases are identical. Therefore, it is reasonable to compare the mechanism of partial oxidation of iso-octane in these three cases.
In Figure 6.27, using the simulation based on the intake manifold wall temperature, the computed composition of the fuel vapor in the mixture correlates well with the exhaust composition when the product HC species are accounted for. This result may be interpreted as follows. If there were no incomplete oxidation (i.e., all the fuel species were converted completely to CO₂, CO, H₂, and H₂O), the exhaust HC would consist of just the fuel species that escape oxidation and the composition would have been the same as computed by the mixture preparation model. With partial oxidation, however, there are intermediate products. Thus the split in the exhaust HC to the fuel species that are “feed-through” and the product species may be obtained from the ratio of the measured product species composition percentage and the computed fuel vapor composition percentage. For example, for the iso-octane / m-xylene mixture, the ratio of the iso-butene (iC₄H₈), as a percentage of the total HC (in ppmC₁) in the exhaust, to the computed amount of iso-octane from the mixture preparation model, as a percentage of the total HC in the unburned gas mixture, is approximately 16% throughout the cycles (plotted as solid circles in Figure 6.31). This ratio does not change in spite of the fact that both the iso-octane and iso-butene fraction changed over the measurement period (see Figure 4.9). What is remarkable is that this value of 16% is also valid for the other two fuel blends. The same observation could also be drawn for the exhaust “unconverted” iso-octane : that for all the three fuel blends, the value is 63%. The remaining 21% (= 1 - 0.16 - 0.63) may be attributed to other product species. Thus the results in Figure 6.31 may be represented by:

\[ [iC₈]_{\text{partial oxidation}} \rightarrow 0.63[iC₈] + 0.16[iC₄H₈] + 0.21[\text{other product species}] \quad (6.9) \]

By using equation 6.9 and the measured ppmC₁% of iso-octane represented by the solid circles in Figure 6.30, the summation of iso-octane and its product species in the exhaust gas by using the iso-octane / n-decane mixture can be estimated. The results are represented by the solid
circles in Figure 6.32. Therefore, the rest of the hydrocarbons in the exhaust gas represented by the solid triangles in Figure 6.32 is the summation of the ppmC1% of n-decane and its product species. In this way, it is found that the simulated ppmC1% of the iso-octane and n-decane calculated by using the intake manifold wall temperature can correlate well with the summation of the measured ppmC1% of fuel species and their product species. Again, the mixture preparation model correctly predicts the vaporization of fuel during the mixture preparation process under the firing condition. Again, it seems that the thermal environment of the mixture preparation process under the firing condition is dominated by the intake manifold wall temperature when heavy-end components are used as fuel.

The simulated ppmC1% can also capture the early depletion of heavy-end component in the exhaust gas under the firing condition: the percentage of the more volatile species, iso-octane, and its product species is initially high, then drops gradually to the steady state value; the percentage of the less volatile species, n-decane, and its product species is initially small, then approaches steady state value gradually. The early depletion of heavy-end component and its product species in the exhaust gas is due to the differentiation of the volatility of the fuel species in the mixture. Similar behaviors were observed when the iso-octane / m-xylene mixture was used (see section 6.6.2).

At the steady state (not shown in Figure 6.32), the ratio of the simulated ppmC1% of iso-octane to n-decane, and the ratio of the measured ppmC1% of iso-octane to n-decane (including fuel and product species) will approach the proportion in the fuel. These ratios are shown in Table 6.9. This shows the consistency between the composition of the injected fuel and that of the vaporized fuel which are also observed in the previous cases at the steady state under the firing condition.
Table 6.9 Composition of iso-octane/n-decane mixture in the injected fuel and in the exhaust gas at the steady state (firing case)

<table>
<thead>
<tr>
<th>component [ppmC1%]</th>
<th>injected fuel</th>
<th>exhaust (6750 cycle)</th>
<th>simulation (6750 cycle)</th>
</tr>
</thead>
<tbody>
<tr>
<td>iC8</td>
<td>89.4</td>
<td>89.2*</td>
<td>89.9</td>
</tr>
<tr>
<td>n-decane</td>
<td>10.6</td>
<td>10.8*</td>
<td>10.1</td>
</tr>
</tbody>
</table>

* including the fuel species and product species

Figure 6.30 Correlation of the simulated ppmC1% with the speciated HC emissions (fuel species only) by using iso-octane/n-decane mixture (volume ratio = 90/10) as fuel under engine firing condition
Figure 6.31 Mechanism of the partial oxidation of iso-octane by using the iso-octane/m-xylene, iso-octane/n-pentane, and iso-octane/n-decane mixtures as fuel

Figure 6.32 Correlation of the simulated ppmC1% with the speciated HC emissions (including all the fuel species and product species) by using iso-octane/n-decane mixture (volume ratio = 90/10) as fuel under engine firing condition
6.6.5 Indolene - Motoring

The evolution of the speciated hydrocarbon emissions in the exhaust gas by using indolene with the ignition turned off (see section 4.5.5) are correlated with the simulation by the mixture preparation model in this section. The measured ppmC1% of the major components (from C4 to C9) of indolene are represented by the solid symbols from Figure 6.33 to Figure 6.41 (also in Figure 4.23, 4.24, and 4.25). The simulated ppmC1% of these major components by using the intake valve temperature and intake manifold wall temperature are represented by the dotted lines and solid lines in those graphs. For some of the major components, like n-butane, 23dM-butane, 23dM-pentane, and m&p-xylene, the simulated ppmC1% match the measured ones. But the simulated ppmC1% of the other major components, 2M-butane, benzene, toluene, iso-octane, and 124tM-benzene, does not match with the measured ppmC1%. However, they seem to have similar trend as the measurement.

There are two possible reasons for this inconsistency. First, as explained in section 4.5.5, the indolene fuel used in the experiment was not the same batch as that used in identifying the fuel composition. There may be substantial batch-to-batch composition difference in fuel. For example, the speciation data for two different batches of indolene have toluene weight percentages of 11.4% and 16.8% respectively, and iso-octane of 6.3% and 10.4%, respectively (the latter ones are from the same speciation data which the composition model of indolene in Table 5.4 was based on). The simulated ppmC1% of the major components of indolene were calculated by using the Major-Component fuel model listed in Table 5.4 as one of the inputs. The composition of indolene which was used to formulate the Major-Component fuel model may be different from that of indolene used in the experiments due to this batch-to-batch difference. Therefore, the simulated ppmC1% of some of the major components does not match with the measured ppmC1%.
The other possible reason for the difference between the measured ppmC1% and the simulated ppmC1% is due to the fact that some species can not be separated by the GC under the specification described in section 4.4. For example, the retention time for toluene, 223tM-pentane, and 234tM-pentane in the GC are very similar. Therefore, the peaks for those species are overlapped in the GC spectrum and can not be separated.

Unfortunately, the batch of the indolene used in the hydrocarbon emissions sampling is not available for Gas-Liquid Chromatography analysis. However, a method to recover the composition of the indolene based on the consistency between the amount and composition of the injected fuel and those of the vaporized fuel at the steady state is developed and stated in the following paragraphs.

For the iso-octane / m-xylene mixture with the well-defined composition (volume ratio = 75/25) under the motoring condition (section 4.5.1), it was found that the steady-state concentration of hydrocarbon (142,002 ppmC1) in the exhaust gas roughly corresponds to the stoichiometric air/fuel ratio for the mixture and is consistent with the amount of the injected fuel ($\Phi_{ij} = 1$). Therefore, the amount of hydrocarbons in the exhaust gas at the steady state will be the same as the amount of injected fuel under the motoring cases. In Table 6.6 (see section 6.6.1), it shows that the composition of the hydrocarbons in the exhaust gas and simulated ppmC1% of the fuel species by the mixture preparation model will approach the composition of the injected fuel at steady state. The same behaviors were also observed for the firing conditions by using the iso-octane / m-xylene (see Table 6.7), iso-octane / n-pentane (see Table 6.8), and iso-octane / n-decane (see Table 6.9) mixtures. Thus for both the motoring and firing conditions, the composition of hydrocarbons in the exhaust gas at the steady state is roughly the same as that of the injected fuel.

This observation by using the binary mixtures with the known compositions may be able to extend to a multi-component fuel like indolene. By assuming that the steady-state
hydrocarbon composition (Figure 6.33 to Figure 6.41) in the exhaust gas is the same as the composition of the injected fuel, the molar percentage of some of the major components can be determined and shown in the third column of Table 6.10. (For some of the rows in Table 6.10, they might represent a mixture instead of a single component. For example, the row for toluene actually represents the mixture of toluene, 223tM-pentane, and 234tM-pentane because they can not be separated by the GC.) The second column of Table 6.10 is the original concentration of the major components used to simulate the ppmC1% shown in Figure 6.33 to Figure 6.41. Based on this "modified" composition of indolene, the ppmC1% of these major components by using the intake valve temperature and intake manifold wall temperature are simulated and represented by the dotted lines and solid lines in Figure 6.42 to Figure 6.50. It is found that the simulated ppmC1% of the major components of indolene by using the "modified" composition in Table 6.10 can correlate well with the measured ppmC1% by the GC technique. Therefore, the mixture preparation model can correctly predict the vaporization of a practical fuel during the mixture preparation process under the motoring condition, provided that the composition of the injected fuel is known.

The simulated ppmC1% can also capture the early enrichment of the light-end components and the early depletion of heavy-end components in the exhaust gas under the motoring condition: the percentage of the more volatile species, like n-butane, 2M-butane, and 23dM-butane, are initially high, then drops to the steady state value within 100 cycles; the percentage of the less volatile species, like m&p-xylene and 1?4tM-benzene, are initially small, then approaches steady state value gradually. The early enrichment of the light-end components and the early depletion of heavy-end components in the exhaust gas are due to the differentiation of the volatility of the fuel species in indolene. The less volatile components are more difficult to vaporize than the more volatile component during the mixture preparation process in the early
cycles. In the later cycles, the unvaporized fuel, which comprises mostly the less volatile components, from the previous can mix with the air of later cycles and vaporize.

Table 6.10 Molar percentage of major components of indolene

<table>
<thead>
<tr>
<th>major component</th>
<th>molar %</th>
<th>modified molar %</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-butane</td>
<td>8.46</td>
<td>8.46</td>
</tr>
<tr>
<td>2M-butane</td>
<td>8.84</td>
<td>14.15</td>
</tr>
<tr>
<td>23dM-butane</td>
<td>2.12</td>
<td>2.12</td>
</tr>
<tr>
<td>benzene</td>
<td>2.54</td>
<td>1.40</td>
</tr>
<tr>
<td>23dM-pentane</td>
<td>3.99</td>
<td>8.36</td>
</tr>
<tr>
<td>toluene</td>
<td>17.62</td>
<td>26.43</td>
</tr>
<tr>
<td>224tM-pentane</td>
<td>8.79</td>
<td>6.15</td>
</tr>
<tr>
<td>m-xylene</td>
<td>0.79</td>
<td>0.79</td>
</tr>
<tr>
<td>i-Proply benzene</td>
<td>2.42</td>
<td>0.63</td>
</tr>
</tbody>
</table>

Figure 6.33 Correlation of the simulated and measured ppmC1% of n-butane by using indolene as fuel under engine motoring condition
**Figure 6.34** Correlation of the simulated and measured ppmC1% of 2M-butane by using indolene as fuel under engine motoring condition.

**Figure 6.35** Correlation of the simulated and measured ppmC1% of 23dM-butane by using indolene as fuel under engine motoring condition.
Figure 6.36 Correlation of the simulated and measured ppmC1% of benzene by using indolene as fuel under engine motoring condition

Figure 6.37 Correlation of the simulated and measured ppmC1% of 23dM-pentane by using indolene as fuel under engine motoring condition
Figure 6.38 Correlation of the simulated and measured ppmC1% of toluene by using indolene as fuel under engine motoring condition.

Figure 6.39 Correlation of the simulated and measured ppmC1% of iso-octane by using indolene as fuel under engine motoring condition.
**Figure 6.40** Correlation of the simulated and measured ppmC1% of m&p-xylene by using indolene as fuel under engine motoring condition

**Figure 6.41** Correlation of the simulated and measured ppmC1% of 124tM-benzene by using indolene as fuel under engine motoring condition
Figure 6.42 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of n-butane by using indolene as fuel under engine motoring condition

Figure 6.43 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of 2M-butane by using indolene as fuel under engine motoring condition
Figure 6.44 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of 23dM-butane by using indolene as fuel under engine motoring condition.

Figure 6.45 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of benzene by using indolene as fuel under engine motoring condition.
Figure 6.46 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of 23dM-pentane by using indolene as fuel under engine motoring condition.

Figure 6.47 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of toluene by using indolene as fuel under engine motoring condition.
Figure 6.48 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of iso-octane by using indolene as fuel under engine motoring condition

Figure 6.49 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of m&p-xylene by using indolene as fuel under engine motoring condition
Figure 6.50 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of 124tM-Benzene by using indolene as fuel under engine motoring condition.
6.6.6 Indolene - Firing

The evolution of the speciated hydrocarbon emissions in the exhaust gas by using indolene as fuel with the ignition turned on (see section 4.5.6) are compared with the simulated ppmC1% calculated by the mixture preparation model in this section. The measured ppmC1% of the major components (from C₄ to C₈) of indolene are represented by the solid symbols in Figure 6.51 to Figure 6.59 (also in Figure 4.30, 4.31, and 4.32). The sudden jump (or drop) of the third data point in each graph is due to the misfiring of engine from cycle 3 to 8. As shown in Figure 4.21, the engine fired in the first two cycles, and followed by several cycles of misfiring (cycle 3-8).

The simulated ppmC1% of these major components based on the original Major-Component fuel model (Table 5.4) by using the intake valve temperature and intake manifold wall temperature are represented by the dotted lines and solid lines in Figure 6.51 to Figure 6.59. As explained in the previous section, the indolene fuel used in the experiment was not the same batch as that used in identifying the indolene composition to formulate the Major-Component fuel model. Therefore, the simulated ppmC1% of the major components based on this original fuel model can not represent the speciated vapor concentration in the combustion chamber.

Fortunately, the batch of the indolene used in the hydrocarbon emissions sampling under the motoring condition is the same as that used for this test run. In previous section, by assuming that the steady-state hydrocarbon composition in the exhaust gas is the same as the composition of the injected fuel, the molar percentage of some of the major components can be modified and shown in Table 6.10. By using this "modified" composition of indolene, the ppmC1% of these major components by using the intake valve temperature and intake manifold wall temperature under firing condition are simulated and represented by the dotted lines and solid lines in Figure 6.60 to Figure 6.68. Again, the measured ppmC1% of the major components of indolene are
represented by the solid symbols in these graphs. There are also some noticeable features in these graphs:

(i) The third data point of the measurement, which corresponds to the misfiring cycles of engine, in each of these graphs always matches well with the simulated ppmC1%. At this point, the vaporized fuel which escaped the combustion process became the hydrocarbon emissions captured in the exhaust pipe. Unlike other firing cycles, there is no product species in the exhaust gas during these misfiring cycles. Therefore, the composition of hydrocarbons in the exhaust gas during the misfiring cycles should be the same as that of vaporized fuel, which is correctly estimated by the mixture preparation model in this point. Thus the mixture preparation model can predict the vaporization of a practical fuel during the mixture preparation process under the firing condition, provided that the composition of the injected fuel is known.

(ii) Besides the third data point, the measured ppmC1% of n-butane, 2M-butane, 23dM-butane, 23dM-pentane, and iso-octane is always smaller than the simulated ones due to the partial oxidation of these fuel species. It is found that the partial oxidation rates for most of the cycles are fairly constant because the measurement has similar trend as simulation. This is also true when the binary mixtures of iso-octane / m-xylene, iso-octane / n-pentane, and iso-octane / n-decane were used as fuels in the previous sections.

(iii) The behaviors of the measured ppmC1% of benzene and toluene are different from other fuel species because they are also product species of other heavier fuel aromatics. For example, the first and second data points of benzene is larger than the simulation due to the conversion from other aromatics in the fuel; the third data point (the misfiring cycles) then matches well with the simulation because there is no conversion of other aromatics to benzene, and there is also no partial oxidation of benzene itself.

(iv) Besides the misfiring cycles, the measured ppmC1% of m&p-xylene and 124tM-benzene are always larger than the simulation due to the smaller partial oxidation rates of
aromatics than those of paraffins. The larger survival fractions of aromatics compared to paraffins can also be found in Figure 4.33. These larger survival fractions of m&p-xylene and 124tM-benzene make the relative amount (represented by the ppmC1%) of these aromatics in the exhaust gas looks larger.

The simulated ppmC1% can also capture the early enrichment of the light-end components and the early depletion of heavy-end components in the exhaust gas under the firing condition: the percentage of the more volatile species, such as n-butane, 2M-butane, and 23dM-butane, are initially high, then drops to the steady state value within 100 cycles; the percentage of the less volatile species, like m&p-xylene and 124tM-benzene, are initially small, then approaches steady state value gradually. The early enrichment of the light-end components and the early depletion of heavy-end components in the exhaust gas are due to the differentiation of the volatility of the fuel species in indolene. The less volatile components are more difficult to vaporize than the more volatile component during the mixture preparation process in the early cycles. In the later cycles, the unvaporized liquid fuel accumulated in the intake port, which comprises mostly the less volatile components, from the previous can mix with the air of later cycles and vaporize. The increase of intake temperature also promotes the evaporation of the accumulated liquid fuel in the intake port.

In summary, the mixture preparation model can correctly simulate the vaporization of a practical fuel during the mixture preparation process under the firing condition. The mixture preparation model can predict the hydrocarbon composition in the air/fuel mixture before combustion. Therefore, it provides the information about the “source” of hydrocarbon emissions from SI engines: the amount of fuel species in the combustion chamber before the combustion and the partial oxidation processes.
Figure 6.51 Correlation of the simulated and measured ppmC1% of n-butane by using indolene as fuel under engine firing condition

Figure 6.52 Correlation of the simulated and measured ppmC1% of 2M-butane by using indolene as fuel under engine firing condition
**Figure 6.53** Correlation of the simulated and measured ppmC1% of 23dM-butane by using indolene as fuel under engine firing condition

**Figure 6.54** Correlation of the simulated and measured ppmC1% of benzene by using indolene as fuel under engine firing condition
Figure 6.55 Correlation of the simulated and measured ppmC1% of 23dM-pentane by using indolene as fuel under engine firing condition

Figure 6.56 Correlation of the simulated and measured ppmC1% of toluene by using indolene as fuel under engine firing condition
Figure 6.57 Correlation of the simulated and measured ppmC1% of iso-octane by using indolene as fuel under engine firing condition

Figure 6.58 Correlation of the simulated and measured ppmC1% of m&p-xylene by using indolene as fuel under engine firing condition
**Figure 6.59** Correlation of the simulated and measured ppmC1% of 124tM-benzene by using indolene as fuel under engine firing condition

**Figure 6.60** Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of n-butane by using indolene as fuel under engine firing condition
Figure 6.61 Correlation of the simulated (based on modified indolene composition) and measured ppmCl% of 2M-butane by using indolene as fuel under engine firing condition

Figure 6.62 Correlation of the simulated (based on modified indolene composition) and measured ppmCl% of 23dM-butane by using indolene as fuel under engine firing condition
Figure 6.63 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of benzene by using indolene as fuel under engine firing condition

Figure 6.64 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of 23dM-pentane by using indolene as fuel under engine firing condition
Figure 6.65 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of toluene by using indolene as fuel under engine firing condition.

Figure 6.66 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of iso-octane by using indolene as fuel under engine firing condition.
Figure 6.67 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of m&p-xylene by using indolene as fuel under engine firing condition.

Figure 6.68 Correlation of the simulated (based on modified indolene composition) and measured ppmC1% of 124tM-benzene by using indolene as fuel under engine firing condition.
6.7 The Optimal Fuel Injection Schedule for Engine Cold-Start

A major cause for undesirable engine behaviors is the deviations of the in-cylinder mixture air/fuel ratio from stoichiometric. This deviations during cold-start are due to incomplete evaporation of the injected fuel and/or time lags introduced from the storage and release of liquid fuel in the intake port. To compensate the incomplete evaporation of injected fuel for better driveability during cold-start, fuel enrichment and high Reid Vapor Pressure (RVP) fuels are used to ease the starting and warm-up process. Substantial fuel enrichment, however, penalizes fuel economy and causes high engine-out HC emissions, and the use of high RVP fuels increases the evaporative emissions from the vehicle fuel system. Unlike at fully warm-up condition when all the sensors are functioning normally and the engine is under closed-loop control, air/fuel ratio is under open-loop control during starting and warm-up. A methodology is needed for optimal design of fuel injection schedule for engine cold-start process.

The mixture preparation model developed in section 6.3 is based on the thermo-physical properties of fuel and liquid-fuel-pool dynamics in the intake port. It has correctly simulated the vaporization of a practical fuel during the mixture preparation process. In section 6.4, the good correlation between $\Phi_{\text{vapor}}$ and the engine first firing cycle demonstrates that the total vapor concentration of hydrocarbons in the combustion chamber can be predicted by the model; In section 6.6, the comparison of the simulated ppmC1% with the measured ppmC1% of fuel species in the exhaust gas shows that the vapor composition of hydrocarbons can be simulated by the model. Therefore, both the amount and composition of the vaporized fuel which contributes to the combustion and hydrocarbon emissions of engine can be assessed by the mixture preparation model.
Using the mixture preparation model described above, a design of the optimal fuel injection schedule for engine cold-start is feasible. The objective of the optimal fuel injection schedule is to calculate the required injection equivalence ratio $\Phi_{\text{inj}}$ for each cycle during starting and warm-up processes to obtain a target vapor equivalence ratio $\Phi_{\text{vap}}$ of air/fuel mixture in the combustion chamber before combustion. By modifying the ACCU.for program listed in Appendix D and using a iteration to calculate the required $\Phi_{\text{inj}}$ to fulfill the target $\Phi_{\text{vap}}$, the optimal schedule of $\Phi_{\text{inj}}$ for each cycle during cold-start can be calculated, and the procedure is written as a computer program (ENRICH.for, written in FORTRAN) listed in Appendix E. In order to explain the procedure, an example is stated in the following paragraphs.

In this example, the optimal fuel injection schedule for a real engine cold-start (from cranking) is calculated. The target $\Phi_{\text{vap}}$ is set to be 1 for each cycle during cold-start in order to have stable combustion of engine and reasonable engine-out (both hydrocarbon and NOx emissions) emissions. (The setting of $\Phi_{\text{vap}}$ for cold-start will depend on different design considerations of each vehicle manufacturer and is beyond the scope of this thesis. But $\Phi_{\text{vap}} = 1$ seems to be a reasonable value for most of the situations.) The fuel used is assumed to be indolene and represented by the Major-Component fuel model of indolene listed in Table 5.4 as one of the inputs for simulation. For the purpose of demonstration, the required $\Phi_{\text{inj}}$ is only calculated for the first 50 cycle, starting from the cranking of engine. The thermal environment of intake port is assumed to be unchanged because the engine is only fired for 5 seconds (50 cycles at 1200 rpm). The intake temperature is thus assumed to be constant at 300°K for simulation.

Besides the inputs and operating conditions for the simulation described above, the intake pressure is also required to calculate the $\Phi_{\text{inj}}$. Based on the required $\Phi_{\text{inj}}$ for each cycle, the air mass flow rate is required to calculate the required fuel mass flow rate (see equation (2.1) for the definition of equivalence ratio $\Phi$). These two input parameters, the intake pressure and
the air mass flow rate for each cycle, are highly dynamic for a real engine cold start. For simplicity of the simulation, measured values for these two parameters are used. These two parameters were measured from the starting of a Ford Zetec engine which was cranked by using a battery and a starter motor. The fuel was injected at the first cycle of cranking and the throttle position was set at the idle condition. The measurement for the engine speed and intake pressure are shown in Figure 6.69.

![Graph showing intake pressure and engine speed over cycle number.](image)

**Figure 6.69** Start-up conditions of Ford Zetec engine

Based on the inputs and operating conditions for the simulation described above, the required $\Phi_{\text{inj}}$ can be calculated and shown in Figure 6.70. The dotted line represents that, for each cycle, the target $\Phi_{\text{vapor}}$ is set to be 1. In order to fulfill this requirement, the schedule for the injected equivalence ratio $\Phi_{\text{inj}}$ for each cycle must be equal to the values represented by the solid symbols. For example, the $\Phi_{\text{inj}}$ must be larger than 6 in order to make vapor equivalence ratio $\Phi_{\text{vapor}}$ of the air/fuel mixture in the combustion equal to stoichiometric for the first engine cycle.
As the cycle number increases, the required $\Phi_{\text{inj}}$ is decreased due to two reasons: (i) the liquid fuel which is not vaporized in the previous cycles will evaporate in the later cycles; (ii) the decreasing intake pressure can promote the vaporization of fuel in the intake port.

![Graph showing the required $\Phi_{\text{inj}}$ for target $\Phi_{\text{vapor}} = 1$ during the start-up process of Ford Zetec engine.](image)

**Figure 6.70** Required $\Phi_{\text{inj}}$ for target $\Phi_{\text{vapor}} = 1$ during the start-up process of Ford Zetec engine

The most interesting aspect in this graph occurs at the 5th cycle at which the required $\Phi_{\text{inj}}$ is lower than target $\Phi_{\text{vapor}}$. Even though not all of the current injected fuel (whose $\Phi_{\text{inj}}$ is less than 1) vaporized at this cycle (by checking the VLE data of this cycle, some of heavy species injected at this cycle did not evaporate), the $\Phi_{\text{vapor}}$ is still equal to 1 due to the vaporization of the accumulated liquid in the port and the decreasing intake pressure. After this cycle, the required $\Phi_{\text{inj}}$ has to be slightly larger than unity in order to fulfill the target $\Phi_{\text{vapor}}$. According to the required $\Phi_{\text{inj}}$ in Figure 6.70 and measured air flow rate shown in Figure 6.71, the required fuel
flow rate can be decided (by assuming that the stoichiometric air/fuel ratio for indolene is equal to 14.6) and shown in Figure 6.71.

![Figure 6.71](image)

**Figure 6.71** Required fuel mass flow rate for the target $\Phi_{\text{vapor}} = 1$ during the start-up process of Ford Zetec engine

For the current fuel injection design which is based on empirical results, automotive engineers have already found the similar design requirement for the fuel injection schedule during engine cold start as described in the previous paragraphs: several large injection pulses at the first few cycles to ensure firing from the first engine cycle; then a smaller injection pulse to prevent high level of HC emissions; followed by slightly rich subsequent fuel injections to ensure stable combustion during warm-up process [8]. But the actual amount and timing of the fuel injection are decided by engine-dynamometer tests and varied at different operating conditions of engines. The example described in this section provides a solid evidence and physical explanation for the observation described above. Therefore, the methodology of designing the optimal fuel schedule during cold start developed in this section provides a very useful approach.
to design the fuel injection schedule for more desirable fuel economy, engine driveability, and cleaner air.
A methodology which can assess the fuel effects on engine starting and warm-up behaviors, including vehicle driveability and hydrocarbon emissions, had been established. The approach includes (i) developing a simulated cold start and warm-up testing procedure for SI engines to study the vehicle driveability in a laboratory environment, (ii) devising a time-resolved, exhaust gas sampling unit to investigate the evolution and species distribution of HC emissions during engine starting and warm-up processes, (iii) formulating a fuel composition model to represent the volatility characteristics of practical fuels, and (iv) modeling the mixture preparation process to explain fuel volatility effects on the mixture preparation process.

A simulated engine start-up test procedure had been established in the laboratory to assess the fuel effects on driveability. In this procedure, the engine is motored at part throttle at constant RPM. Then the fuel is switched on and the Gross Indicated Mean Effective Pressure (GIMEP) for each cycle is measured for the whole start-up transient. Engine behaviors are measured quantitatively by the driveability attributes which are the first significantly firing cycle, the rise time constant ($\tau_r$) of the GIMEP, the decay time constant ($\tau_d$) of the GIMEP fluctuation,
and the fluctuation of GIMEP at $3\tau_s$. These four driveability attributes represent either ease of start or smoothness of engine during warm-up, and are not independent since the starting characteristics are related to the evaporative behaviors of the fuel in the mixture preparation process. There are similar trends observed for these four attributes by using a selected matrix of fuels that included various blending ratios of iso-octane / n-pentane and indolene / MTBE mixtures: the driveability attributes improve with enrichment, and with increase amount of volatile components in the fuel blends.

Another important indication of startability, the first engine firing cycle, was also studied by using a modified single-cylinder SI engine under the same test procedure as described above, except that fuel injection strategy was designed to simulate the fuel enrichment in the early cycles used in modern vehicle to ease the starting and warm-up of engine: different units (from 1 to 7) of fuel were injected in the first cycle; followed by single unit of injection in the subsequent cycles. A test matrix which included a single-component fuel, three binary fuels, and two practical fuel blends was used to represent a broad range of volatility and different component effects. The ease of starting improves with enrichment and with increase amount of volatile components in the fuel blend: the first firing cycle occurs earlier with increasing degree of enrichment of first injection $\Phi_{inj}(1)$; for the same $\Phi_{inj}(1)$, first firing cycle occurs earlier with increasing proportion of volatile components.

A time-resolved exhaust gas sampling technique was developed to measure the speciated HC emissions from a SI engine in a warm-up process. The resolution of the sampling was one to two cycles at 900 rpm. Time-resolved speciated HC emissions in a simulated starting and warm-up process were measured with the following fuels: n-pentane / iso-octane, n-decane / iso-octane, m-xylene / iso-octane and indolene. The exhaust HC species followed the volatility of the fuel components: in the early cycles, the light components were the major emitted HC species; as the cycle number increased, the percentages of heavy-end components in the exhaust gas increased.
gradually. For the binary fuel blends when the major decomposition products from the fuel are identified, the total fuel plus major decomposition products could account for ~ 90% of the total HC emissions throughout the warm-up process. For a multi-component fuel such as indolene, the light-end components (components with NBP < T20) contribute significantly to the delivery of the first combustible mixture to the cylinder. For the motoring cases, the total HC concentration in the exhaust is consistent with the amount of the injected fuel.

A fuel composition model, the Major-Component fuel model, for calculating fuel volatility has been developed. The model is based on representing the fuel by its major species. The fuel evaporative characteristics were computed by an equilibrium flash calculations of a mixture of these species using their thermophysical properties and interaction coefficients. The method predicts accurately the ASTM distillation curves and the RVP for hydrocarbon fuels. The predictions, while still good, is less accurate for fuels with oxygenates because of the uncertainty in the polar/non-polar interaction between the oxygenates and the other hydrocarbons. The Major-Component fuel model is a logical representation for the thermophysical properties of the practical fuels.

A mixture preparation model based on the volatility characteristics of fuel species has been developed. The model schematizes that the mixture entering into the cylinder comprises two parts: one part consists of the fuel vapor that mixes uniformly with a fraction of the intake air in the vapor boundary layer so that this air/vapor mixture is in thermodynamic equilibrium with the liquid film in the port; the other part consists of just pure air. In this manner a volatility parameter, $\Phi_{\text{vapor}}$, which represents the extend of vaporization of fuel during mixture preparation process can be calculated by the model. It is found that the driveability attributes derived from the simulated cold-start test can be explained by the $\Phi_{\text{vapor}}$. Over an extensive range of fuel mixture and enrichment, the first significantly firing cycle, the value for $\tau_i$ and $\tau_{di}$, and the GIMEP fluctuation at $3\tau_i$ are inversely proportional to the fifth power of $\Phi_{\text{vapor}}$. 
By incorporating the liquid-fuel-pool dynamics in the intake manifold of engine into the mixture preparation model described above, both the vapor concentration and composition of the air/fuel mixture in the combustion chamber each cycle can be predicted by the model. The vapor concentration of the air/fuel mixture, \( \Phi_{\text{vapor}} \), can correctly predict the occurrence of the first firing cycle of engine. Under the particular operating condition of engine (900 rpm, 0.4 bar), the first firing cycle of engine for all the fuels occurs whenever the \( \Phi_{\text{vapor}} \) is larger than or equal to 0.7. The vapor composition of the air/fuel mixture, ppmC1\%, calculated by the model correlates well with time-resolved, speciated HC emissions data. The model also illustrates that the high proportion of the light-end components in the exhaust in the early cycles is due to the difference in volatility of the species in the fuel blends. As the port warms up and as a steady state liquid pool is formed in the intake, the HC composition delivered to the cylinders shifts back to the fuel composition.

The above results demonstrate that the mixture preparation model could assess the fuel effects on the mixture preparation process, vehicle driveability, and species distribution of time-resolved hydrocarbon emissions during engine starting and warm-up process. This model also provides a knowledge-based methodology to design the optimal fuel injection strategy for target vapor concentration during engine cold start.
REFERENCE


APPENDIX A

PROGRAM ASTMDIS
******************************************************************************
Introduction for main program :
******************************************************************************

ASTMDIS.FOR : 

This program is to calculate the ASTM distillation curve (ASTM D86) of Major-Component fuel model which is the model representation for a practical fuel. (SAE941877)

In this program, subroutines of the NIST Database 4 (NIST Thermodynamical Properties of Hydrocarbon Mixtures, V1.0) is used to calculate the Vapor/Liquid equilibrium data and phase properties of hydrocarbons.

More explanation of the program in the Ph.D. thesis of Kuo-Chiang Chen (section 5.3.1)

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Introduction for subroutines of NIST database which been used in this program :
They are in the program of source1.for, source2.for, and source31.for.
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BUBP(px,t,x,feed,ak,x,psi,nph,ier) :
This subroutine solves the material balance in bubble point pressure calculation. Given the temperature and the feed composition it returns the bubble point pressure.

FLASH(px,t,x,feed,ak,x,psi,nph,ier) :
This subroutine solves the material balance in isothermal flash calculation. Given temperature, pressure, and feed composition it returns the compositions of the resulting phases and the liquid fraction.

INITIALIZE_PROGRAM :
This subroutine initializes the SUPERTRAPP program routines.

PHASE_PROPERTIES(px,t,x,psi,nph,model,props,foxp) :
This subroutine calculates the properties (both transport and equilibrium) of liquid and vapor phases after the FLASH calculation.

SETUP_COMPONENTS(name,feed,nc) :
This subroutine initializes the names, feed fractions and numbers of components for FLASH calculation.
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Index for parameters used in program ASTMDIS :
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ak(i) : K factors for the Major Components as the
output of FLASH calculation

bp(i) : boiling point of each major components.
(check at part 7.1)

bpsmall : initial boiling point of the fuel which is
also the boiling point of the most volatile
component in fuel model.
(check at part 7.2)

feed(i) : mole fractions of Major Components as the
inputs to the FLASH calculation. All feed(i)
must sum to unity before each FLASH or BUBP
calculation.

feedi(i) : initial mole fractions of fuel model from
input file (*.in). (input from part 4.1)

foxp(i,j) : fugacity coefficient of i component in the
j phase, as the output of PHASE_PROPERTIES
subroutine

i : i component
j = 1 : liquid phase
j = 2 : vapor phase

filedat : data filename for V/L equilibrium data &
phase properties at each temperature
step. (input from part 3).

filein : input filename which should contains the
number of species (nci), species name (namei)
and amount of each species (feedi)
(input from part 2).

fileout : output filename. (input from part 3).

fuel : liquid fuel left in the distillation flask
at each temperature step. (initialized as
1 mole at part 8).

fuelvap : total vapor fuel evaporated which is the
summation of actual moles of all components.
(initialized in part 9.6).

ier : error flag as output of FLASH calculation
ier = 0 : no error
ier = 1 : no convergence in FLASH routine

model : model of calculating the phase properties
as one input of the PHASE_PROPERTIES
(initialized as 'exct' in part 5).

name(i) : species names of Major Components & N2 as
input of the FLASH calculation.

namei(i) : initial species for fuel model from input
file (*.in) (input from part4.1)

nc : number of component (including the N2), as
the input of SETUP_COMPONENTS subroutine.

nci : initial number of fuel component in fuel
model from the input file (*.in)
(input from part 4.1)

nph : number of phases which is the output of the
FLASH calculation and also the input for
PHASE_PROPERTIES subroutine
nph = 0 : all vapor
nph = 1 : all liquid
nph = 2 : liquid & vapor phases

props(i,j) : properties of 2 phases as output of the
PHASE_PROPERTIES subroutine
i = 4 : density
j = 1 : liquid phase
j = 2 : vapor phase

psi : liquid fraction from the output of FLASH
calculation, and also the input of the
PHASE_PROPERTIES subroutine

px : pressure for isothermal flash calculation as input for FLASH and PHASE_PROPERTIES subroutines.

sum : summation of normalized feed fraction which is supposed to be 1.0 (used at part 9.1 & 9.7.2).

temp : temperatoty address for the current temperature (used at part 9.7.1, 9.9 & 9.11).

total : total amount of substance in distillation flask which are liquid fuel and air (N2) left in the system. (initialized in part 9).

tx : temperature for isothermal flash calculation as input for FLASH and PHASE_PROPERTIES subroutines.

vc : volume of vapor fuel condensed at 273[K] at each temperature step (calculated at part 9.7.4).

vd : distilled volume collected by condenser at 273[K]. (initialized at part 8 and calculate at part 9.7.4).

vi : initial volume of fuel (1 mole) in distillation flask at 273[K]. (calculated from part 6).

x(i,j) : mole fractions of the phases resulting from FLASH calculation, also the inputs for the PHASE_PROPERTIES subroutines.
i : i component 
j = 1 : saturated liquid phase 
j = 2 : saturated vapor phase

xliq(i) : actual mole of component i in liquid phase at current temperature based on the assumption that initial mole of total fuel is 1. (initialized in part 9.5).

xvap(i) : actual mole of component i in vapor phase at current temperature based on the assumption that initial mole of total fuel is 1. (initialized in part 9.5).

******************************************************************************

1. Declare parameters:
*******************************
imPLICIT DOUBLE PRECISION (A-H,O-Z)
character filein*20
character fileout*20
character filedat*20
character labels(12)*44
character model*5
character name(20)*30
character namei(20)*30
dimension ak(20)
dimension bp(20)
dimension feed(20)
dimension feedi(20)
dimension foxp(20,2)
dimension props(12,2)
dimension x(20,2)
dimension xliq(20)
dimension xvap(20)
data labels '/'Feed Fraction'/'Molecular Weight'/'Z'/'Density'/'Enthalpy'/'Entropy'/'Cp',
2. Read the input filename:
   Refer the standard input file for fuel model/*.in

write('**.*)','input filename?'
read(*,15,err=10)filein
format(a20)
open(2,err=10,file=filein)

3. Read the output filename:
   Refer the standard output file for the distillation
   temperature V.S. distilled percentage/*.out
   Refer the standard data file for V/L equilibrium data
   and phase properties/*.dat

write('**.*)','output filename?'
read(*,25,err=20)fileout
format(a20)
open(3,err=20,file=fileout)
write('**.*)','data filename for V/L data?'
read(*,27,err=26)filedat
format(a20)
open(4,err=26,file=filedat)

4. Read the nc, name(i), and feed(i) from input file
   Refer the standard input file/*.in
   Attention! the sum of total moles of fuel component
   should be equal to 1.0 in/*.in.
   Number of fuel components in fuel model should be less
   than 19.

4.1 Read the composition of fuel model from/*.in

read(2,30)nci
format(10x,i2)
do 50 i=1,nci
   read(2,40)namei(i)
format(10x,a30)
50 continue
do 70 i=1,nci
   read(2,60)feedi(i)
format(10x,d14.6)
70 continue

4.2 Initial amount of N2:
   initial volume of air inside the distillation flask is
   assumed to be roughly equal to 0.5% of fuel in molar
   basis (SAE941877)

name(nci+1) = 'N2'
feedi(nci+1) = 0.005

5. Initialize subroutine:
   The model used in PHASE_PROPERTIES subroutine is EXCST.
   call initialize_program
   model = 'excst'
6. Find the initial volume of mixture at 273[K] :
   N2 is excluded in this calculation!
   The initial volume of the fuel is based on the fact
   that total mole of fuel is equal to 1.0
   props(4,1) is the density of liquid phase
   Pressure throughout the distillation process is assumed
   as 1.0 bar

   \[
   px = 1.0 \\
   tx = 273.0 \\
   nc = nci
   \]
   do 71 i = 1,nci
      name(i) = namei(i)
      feed(i) = feedi(i)
   71 continue
   call setup_components(name,feed,nc)
   call flash(px,tx,feed,ak,x,psi,nph,ier)
   if (ier.EQ.1) then
      write(*,'(A)')'convergence failure in FLASH'
      go to 910
   endif
   call phase_properties(px,tx,x,psi,nph,model,props,foxp)
   \[
   vi = 1/props(4,1)
   \]

7. Find the most volatile component in fuel model :
   Check the boiling point of each component,
   then find the smallest BP as the IBP of the curve.

7.1 Find the BP of each species :
   Using the subroutine BUBP
   Assuming the temperature giving the bubble point
   pressure = 1.0 is the boiling temperature.

   \[
   nc = 1 \\
   feed(1) = 1.0 \\
   do 80 i = 1,nci
      name(1) = namei(i)
      call setup_components(name,feed,nc)
   \]
   do 81 j = 230,1000
      tx = j
      call bubp(px,tx,feed,ak,x,psi,nph,ier)
      if (px .GE. 1.0) then
         bp(i) = tx
         go to 82
      endif
   81 continue
   82 continue
   80 continue

7.2 Find the smallest BP

   \[
   bpsmall = 1000 \\
   do 83 i = 1,nci
      if (((bpsmall - bp(i)) .GE. 0) then
         bpsmall = bp(i)
      endif
   83 continue

7.3 Compare the smallest BP & ambient temperature (300[K])
   to decide the IBP.
if (bpsmall .LT. 300) then
  bpsmall = 300
endif

8. Initialize the calculation of ASTM distillation curve
   at the Initial Boiling Point of the distillation curve.
   The following calculation are all based on the
   assumption that the initial (273[K]) mole of fuel is
   equal to 1.0

fuel = 1.0
vd = 0

 do 90 i = 1,nci
    name(i) = namei(i)
    feed(i) = feedi(i)
  continue
  feed(nci+1) = feedi(nci+1)
 90

9. Loop 900 :

   The distillation temperature will be increased at the
   step of 1[K] for each cycle within this loop.
   Once all the fuel is evaporated (tested at part 9.4),
   this program will jump out of this loop and terminate
   the distillation process at #901.
   Total amount of substance in the distillation flask
   is equal to the sum of liquid fuel and N2 left in the
   system.

 do 900 j = bpsmall,1000
    nc = nci + 1
    px = 1.0
    tx = j
    total = fuel + feed(nci+1)
 900

9.1 Normalize the feed fraction :
   Attention! NIST subroutines require the sum of feed
   fraction equal to unity.

 do 110 i = 1,nci+1
    feed(i) = feed(i)/total
  continue
  sum = 0
 do 120 i = 1,nci+1
    sum = sum + feed(i)
 120
 continue
 if (sum.NE.1) then
    feed(nci+1) = feed(nci+1)+1-sum
 endif

9.2 Calculate V/L equilibrium data and phase properties at
   current temperature :

call setup_components(name,feed,nc)
call flash(px,tx,feed,ak,x,psi,nph,ier)
if (ier.EQ.1) then
   write(*,*)'convergence failure in FLASH'
   go to 910
endif
call phase_properties(px,tx,x,psi,nph,model,props,foxp)
9.3 Write the V/L equilibrium data and phase properties of current temperature into a data file /*.dat

```
write(4,200)'  ',
200    format(a40,a40)
write(4,210)'p = ',p
210    format(a4,1f10.4)
write(4,220)'t = ',t
220    format(a4,1f10.4)
do 240 i = 1,nci+1
240        write(4,230)name(i),feed(i),x(i,1),x(i,2)
        format(a30,3d14.6)
continue
props(1,1) = psi
props(1,2) = 1-psi
do 260 i = 1,12
260        write(4,250)labels(i),props(i,1),props(i,2)
        format(a44,2d14.6)
continue
```

9.4 Check whether all the fuel is evaporated at current temperature:
If all the fuel is in vapor phase, then this distillation process is completed.

```
if (nph.EQ.0) go to 901
```

9.5 Find the actual liquid and vapor composition:
The initial amount of fuel before distillation process is assumed to be 1. Because the feed fraction was normalized in part 9.1, \(x(i,j)\) should be multiplied by 'total' to recover. Because \(x(1,j) + \ldots + x(nc,j) = 1\), \(x(i,j)\) should be multiplied by the liquid or vapor fraction, \(props(1,j)\).

```
do 310 i = 1,nci+1
310        xliq(i) = x(i,1)*props(1,1)*total
continue
do 320 i = 1,nci+1
320        xvap(i) = x(i,2)*props(1,2)*total
continue
```

9.6 Calculate the total volume of liquid fuel left in the distillation flask and the total volume of vapor fuel evaporated during this temperature step:
Caution! N2 should be excluded in this calculation.

```
fuel = 0
fuelvap = 0
do 330 i = 1,nci
330        fuel = fuel + xliq(i)
continue
do 340 i = 1,nci
340        fuelvap = fuelvap + xvap(i)
continue
```

9.7 Calculate the volume of the distilled fuel which is condensed by condenser at 273[K]:
Caution! N2 was excluded.
9.7.1 Initialize:

nc = nci
temp = tx
tx = 273

9.7.2 Normalize feed(i)

do 350 i = 1,nci
   feed(i) = xvap(i)/fuelvap
continue
sum = 0
do 360 i = 1,nci
   sum = sum + feed(i)
continue
if (sum.NE.1) then
   feed(nci) = feed(nci)+1-sum
endif

9.7.3 Calculate V/L data & phase properties:

call setup_components(name,feed,nc)
call flash(px,tx,feed,ak,x,psi,nph,ier)
if (ier.EQ.1) then
   write(*,*),'convergence failure in FLASH'
go to 910
endif
call phase_properties(px,tx,x,psi,nph,model,props,foxp)

9.7.4 Calculate actual condensed volume:

vc = 1/props(4,1)*fuelvap
vd = vd + vc

9.8 Calculate the distilled percentage at each temperature
step:

percent = vd/vl

9.9 Write the ASTM distillation curve (temperature and
distilled percentage) into the output file /*.out

write(3,370)temp,percent
write(*,* )temp,percent
format(2f12.6)

9.10 Specify the feed fractions for next temperature step:
Assume all the vapor fuel is moved out of the system
by condenser. The only fuel left in the distillation
flask is liquid fuel during this temperature interval
and actual moles of these liquid components are
xliq(i) (calculated from part 9.5).

do 380 i = 1,nci
   feed(i) = xliq(i)
continue

9.11 Find the amount of N2 for next temperature interval:
The amount of N2 inside the distillation flask is
assumed to decrease linearly from $b_{psamll}[K]$ to
$bpsamll + 70[K]$. After $bp + 70[K]$, there is no $N_2$ any more.

\[
\text{feed}(nci+1) = \frac{(bpsamll+70-(\text{temp}+1))}{70} \cdot \text{feed}(nci+1) \cdot \text{fuel}
\]
if ($\text{feed}(nci+1) \cdot \text{LT} \cdot 0$) then
$\text{feed}(nci+1) = 0$
endif

10. If all the fuel is evaporated (single phase case):
Then this distillation process is completed and the
distilled percentage is equal to 1.

\[
\text{continue}
\]
\[
\text{percent} = 1
\]
\[
\text{write}(3,905)\text{tx,percent}
\]
\[
\text{format}(2f12.6)
\]
\[
\text{write}(*,*)\text{tx,percent}
\]
\[
\text{write}(*,*)'\text{end}'
\]
\[
\text{continue}
\]
end
APPENDIX A.1

indolene.in:

Input file for ASTMDIS.for (Appendix A), RVP.for (Appendix B), EAD.for (Appendix C), ACCU.for (Appendix D), and ENRICH.for (Appendix E)

The following components and composition of the fuel are the Major-Component fuel model of indolene (Table 5.4)

nc = 13
name(1) = C4
name(2) = ICS
name(3) = 23DMB
name(4) = BNZ
name(5) = 23DMP
name(6) = TOL
name(7) = 224TMP
name(8) = MXYL
name(9) = 225TMH
name(10)= CUMENE
name(11)= C10
name(12)= C11
name(13)= C12
feed(1) = 0.0912
feed(2) = 0.1415
feed(3) = 0.0842
feed(4) = 0.0254
feed(5) = 0.0836
feed(6) = 0.1762
feed(7) = 0.2377
feed(8) = 0.0210
feed(9) = 0.0141
feed(10)= 0.0686
feed(11)= 0.0376
feed(12)= 0.0160
feed(13)= 0.0029
APPENDIX B

PROGRAM RVP
******************************************************************************

Introduction for main program :
******************************************************************************

RVP.FOR :

This program is to calculate the Reid Vapor Pressure (RVP) 
(ASTM D323) of Major-Component fuel model which is the 
model representation for a practical fuel (SAE941877)

In this program, subroutines of the NIST Database 4 (NIST 
Thermodynamical Properties of Hydrocarbon Mixtures, V1.0) 
is used to calculate the Vapor/Liquid equilibrium data and 
phase properties of hydrocarbons.

More explanation of the program in the Ph.D. thesis of 
Kuo-Chiang Chen (section 5.3.2)

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******************************************************************************

Subroutines of NIST database which been used in this 
program :
Please see ASTMDIS.for (Appendix A) for detail  
******************************************************************************

FLASH(px,tx,feed,ak,x,psi,nph,ier) :
INITIALIZE_PROGRAM :
PHASE_PROPERTIES(px,tx,x,psi,nph,model,props,foxp) :
SETUP_COMPONENTS(name,feed,nc) :
******************************************************************************

Index for parameters used in program ASTMDIS :
******************************************************************************

ak(i) : K factors for the Major Components as the 
output of FLASH calculation

da : density of air at 37.8[C].
    (input at part 7.2).
df : density of fuel at 0[C].
    (calculated at part 6).

feed(i) : mole fractions of Major Components as the 
inputs to the FLASH calculation. All feed(i) 
must sum to unity before each FLASH or BUBP 
calculation.

feedi(i) : initial mole fractions of fuel model from 
input file (*.in). (input from part 4.1)

foxp(i,j) : fugacity coefficient of i component in the 
j phase, as the output of PHASE_PROPERTIES 
subroutine

i : i component
j = 1 : liquid phase
j = 2 : vapor phase

filein : input filename which should contains the 
number of species (nci), species name (namei) 
and amount of each species (feedi) 
(input from part 2).

fileout : output filename. (input from part 3).
ier : error flag as output of FLASH calculation
    ier = 0 : no error
    ier = 1 : no convergence in FLASH routine
model : model of calculating the phase properties
        as one input of the PHASE PROPERTIES
        (initialized as 'exst' in part 5).
name(i) : species names of Major Components & N2 as
         input of the FLASH calculation.
namei(i) : initial species for fuel model from input
          file (*.in) (input from part4.1)
nc : number of component (including the N2), as
     the input of SETUP_COMPONENTS subroutine.
cni : initial number of fuel component in fuel
      model from the input file (*.in)
       (input from part 4.1)
nph : number of phases which is the output of the
      FLASH calculation and also the input for
      PHASE PROPERTIES subroutine
      nph = 0 : all vapor
      nph = 1 : all liquid
      nph = 2 : liquid & vapor phases
p : absolute pressure in testing chamber.
    (In part 9.2.2, 9.3.2, 9.4.2).
    Reid Vapor Pressure (in part 9.5).
props(i,j) : properties of 2 phases as output of the
            PHASE PROPERTIES subroutine
            i = 4 : density
            j = 1 : liquid phase
            j = 2 : vapor phase
psi : liquid fraction from the output of FLASH
      calculation, and also the input of the
      PHASE PROPERTIES subroutine
px : pressure for isothermal flash calculation
     as input for FLASH and PHASE_PROPERTIES
     subroutines.
sum : summation of normalized feed fraction which
      is supposed to be 1.0 (used at part 7.4)
tax : temperature for isothermal flash calculation
     as input for FLASH and PHASE_PROPERTIES
     subroutines.
v : initial volume of total air/fuel mixture
    before test (calculated from part 8).
vp : volume of total air/fuel mixture under current
     pressure. (in part 9.2.2, 9.3.2, 9.4.2).
x(i,j) : mole fractions of the phases resulting from
        FLASH calculation, also the inputs for the
        PHASE PROPERTIES subroutines.
        i : i component
        j = 1 : saturated liquid phase
        j = 2 : saturated vapor phase
xa : mole fraction of air (part 7.3)
xf : mole fraction of fuel (part 7.3)

*****************************************************************************

---

1. Declare parameters:

    implicit double precision (a-h,o-z)
    character filein*20
    character fileout*20
    character labels(12)*44
    character model*5

226
character name(20)'*30
character namei(20)'*30
dimension ak(20)
dimension feed(20)
dimension feedi(20)
dimension foxp(20,2)
dimension prosp(i2,2)
dimension x(20,2)
data labels / 'Feed Fraction', 'Molecular Weight', 'Z',
  'Density', 'Enthalpy', 'Entropy', 'Cp',
  'Cp/Cv', 'Sound Speed', 'JT Coefficient',
  'Viscosity', 'Thermal Conductivity' /

2. Read the input filename:
Refer the standard input file for fuel model /*.in

write(*,*)'input filename? (*.in)'
read(*,15,err=10)filein
format(a20)
open(2,err=10,file=filein)

3. Read the output filename:
Refer the standard output file for RVP /*.rvp

write(*,*)'output filename? (*.rvp)'
read(*,25,err=20)fileout
format(a20)
open(3,err=20,file=fileout)

4. Read the nc, name(i), and feed(i) from input file
Refer the standard input file /*.in
Attention! the sum of total moles of fuel component
should be equal to 1.0 in /*.in.
Number of fuel components in fuel model should be less
than 19.

4.1 Read nci, namei(i), and
feedi(i) from input file:

read(2,30)nci
format(10x,i2)
do 50 i=1,nci
  read(2,40)namei(i)
  format(10x,a30)
continue
do 70 i=1,nci
  read(2,60)feedi(i)
  format(10x,d14.6)
continue

4.2 Composition of air:
Using N2 to simulate the air.

namei(nci + 1) = 'N2'

5. Initialize subroutine:
The model used in PHASE_PROPERTIES subroutine is EXCST.

call initialize_program
model = 'excst'
6. Find the density of fuel at 0[C] (273.15[K]):
N2 is excluded in this calculation! props(4,1) is the
density of liquid phase. Unit of density is [mole/l]

px = 1.0
tx = 273.15
nc = nci
do 71 i = 1,nci
    name(i) = namei(i)
    feed(i) = feedi(i)
continue
    call setup_components(name,feed,nc)
call flash(px,tx,feed,ak,x,psi,nph,ier)
if (ier.EQ.1) then
    write(*,*),'convergence failure in FLASH'
go to 900
endif
    call phase_properties(px,tx,x,psi,nph,model,props,foxp)
    props(1,1) = psi
    props(1,2) = 1-psi
    if (nph.EQ.2) then
        df = 1 / (props(1,1)/props(4,1) + props(1,2)/props(4,2))
    else
        if (nph.EQ.1) then
            df = props(4,1)
        else
            write(*,*),'boiling point of fuel is less than 0[C]'
go to 900
        endif
    endif

7. Find the mole fraction of each component in the
air/fuel mixture:

7.1 Specify name(i):
do 100 i = 1,nci+1
    name(i) = namei(i)
continue

7.2 Density of air at 37.8[C] :
da = 0.0386789

7.3 Mole fraction of fuel & air :
    Assume total mole of the mixture = 1.0
    xf = df / (4*da + df)
xax = 1 - xf
    do 110 i = 1,nci
        feed(i) = feedi(i) * xf
continue
    feed(nci + 1) = xa

7.4 Check whether sum of the mole of all species is equal
to 1.0 :
sum = 0
    do 120 i = 1,nci+1
sum = sum + feed(i)
continue
if (sum.NE.1) then
  feed(nci+1) = feed(nci+1) + 1 - sum
endif

8. Calculate the initial total volume of RVP chamber:
Assume total mole of air/fuel mixture = 1.0
Unit of volume is [l]
Note:
  Volume of air is estimated under 310.95[K]
  Volume of fuel is estimated under 0[C]
vi = xf / df * 5

9. Calculation of RVP:
Start the calculation from 1.0 [bar], then compare the
volume of air/fuel mixture at current pressure with
the initial volume vi.
If these two volumes are the same, then the current
pressure is the RVP of the fuel.
If these two volumes are not the same, then increase
the pressure at the step of 0.1[bar] in loop #200.
Then increase the pressure at the step of 0.01[bar] in
loop #300.
  Then increase the pressure at the step of 0.001[bar] in
loop #400.

9.1 Initialize:
nc = nci + 1
tx = 310.95

9.2 Loop #200:
  Detect the RVP to the order of 0.1
do 200 a = 1.0, 0.3, 0.01
  px = a

9.2.1 Calculate V/L equilibrium data and phase properties
  at current pressure:
call setup_components(name, feed, nc)
call flash(px, tx, feed, ak, x, psi, nph, ier)
if (ier.EQ.1) then
  write(*,*)'convergence failure in FLASH'
go to 900
endif
call phase_properties(px, tx, x, psi, nph, model, props, foxp)
props(1,1) = psi
props(1,2) = 1 - psi

9.2.2 Compare the volume under current pressure with the
  initial volume
if (nph .EQ. 2) then
  vp = (props(1,1)/props(4,1) + props(1,2)/props(4,2))
exthelse
  vp = props(1,2)/props(4,2)
endif
if (vp .LE. vi) then
  p = px
  go to 210
endif
200 continue
210 continue

c 9.3 Loop #300 :
c Detect the RVP to the order of 0.01
do 300 a = (p-0.1), p, 0.01
  px = a

9.3.1 Calculate V/L equilibrium data and phase properties
at current pressure :
call setup_components(name, feed, nc)
call flash(px, tx, feed, ak, x, psi, nph, ier)
if (ier.EQ.1) then
  write(*,*)'convergence failure in FLASH'
go to 900
endif
call phase_properties(px, tx, x, psi, nph, model, props, foxp)
  props(1,1) = psi
  props(1,2) = 1-psi

9.3.2 Compare the volume under current pressure with the
initial volume
if (nph .EQ. 2) then
  vp = (props(1,1)/props(4,1) + props(1,2)/props(4,2))
else
  vp = props(1,2)/props(4,2)
endif
if (vp .LE. vi) then
  p = px
  go to 310
endif
300 continue
310 continue

c 9.4 Loop #400 :
c Detect the RVP to the order of 0.001[bar]
do 400 a = (p-0.01), p, 0.001
  px = a

9.4.1 Calculate V/L equilibrium data and phase properties
at current pressure :
call setup_components(name, feed, nc)
call flash(px, tx, feed, ak, x, psi, nph, ier)
if (ier.EQ.1) then
  write(*,*)'convergence failure in FLASH'
go to 900
endif
call phase_properties(px, tx, x, psi, nph, model, props, foxp)
  props(1,1) = psi
  props(1,2) = 1-psi

9.4.2 Compare the volume under current pressure with the
initial volume

if (nph .EQ. 2) then
    vp = (props(1,1)/props(4,1) + props(1,2)/props(4,2))
else
    vp = props(1,2)/props(4,2)
endif
if (vp .LE. vi) then
    p = px
    go to 410
endif

400 continue
410 continue

9.5 RVP :

gage pressure = absolute pressure - 1.0

p = p - 1.0

10. Write the RVP, and other mixture properties to the
output file :
    Refer the standard output file /*.rvp

10.1 Write the RVP to output file

write(3,*),'RVP [bar] = ',p
write(*,*),'RVP [bar] = ',p
write(3,*),'T[K] = ',tx
write(3,*),'vi = ',vi
write(3,*),'vp = ',vp

10.2 Write the V/L equilibrium data and phase properties
of current pressure into *.rvp

write(3,500)'----------------------------------------',
+ ',
500  format(a40,a40)
do 520 i = 1,nci+1
    write(3,510)name(i),feed(i),x(i,1),x(i,2)
510  format(a30,3d14.6)
520 continue
write(3,*),' '
props(1,1) = psi
props(1,2) = 1-psi
do 540 i = 1,12
    write(3,530)labels(i),props(i,1),props(i,2)
530 format(a44,2d14.6)
540 continue
900 continue
end
APPENDIX C

 subroutine ead(pe,te,phie,pmfe,nce,namee,feede,
 + phiv,nc,name,feed,ak,x,psi,nph,ier,props)
 c
 c*****************************************************************************
 c Introduction for main program : 
 c*****************************************************************************
 c EAD.FOR :
 c 
 c This subroutine is to calculate the vapor equivalence 
 c ratio and other volatility parameters of fuel during the 
 c mixture preparation process of engine by using the Major-
 c Component fuel model which is the model representation for 
 c a practical fuel. (SAE941877)
 c 
 c In this program, subroutines of the NIST Database 4 (NIST 
 c Thermodynamical Properties of Hydrocarbon Mixtures, V1.0) 
 c is used to calculate the Vapor/Liquid equilibrium data and 
 c phase properties of hydrocarbons.
 c 
 c More explanation of the program in the Ph.D. thesis of 
 c Kuo-Chiang Chen (section 6.1)
 c 
 c Professor Wai. K. Cheng
 c Kuo-Chiang Chen
 c MIT Sloan Automotive Laboratory
 c 1995
 c*****************************************************************************
 c*****************************************************************************
 c Introduction for the subroutine EAD :
 c*****************************************************************************
 c Use :
 c call ead(pe,te,phie,pmfe,nce,namee,feede,
 c + phiv,nc,name,feed,ak,x,psi,nph,ier,props)
 c Parameters :
 c
 c (Following parameters should be input from the calling 
 c program before EAD can be performed)
 c
 c pe : intake pressure.
 c te : temperature.
 c phie : enrichment.
 c This parameter must be in the form of the 
 c equivalence Fuel/Air ratio of fuel :
 c phie = 1.0 : stoichiometric
 c phie > 1.0 : rich
 c phie < 1.0 : lean
 c pmfe : partially mixing factor.
 c This parameter represent the percentage of 
 c intake air which is inside the fuel diffusion 
 c boundary layer during the mixture preparation 
 c process.
 c nce : number of component of fuel model.
 c namee : names of component of fuel model.
 c This parameter must be the name or synonym of 
 c this component shown in the STRAPP user's guide.
 c feede : mole fractions of components.
 c Summation of the mole fractions must be 1.
 c
 c (Following parameters will be returned back to the
calling program. Everything returned back to the
calling program will contain N2 and O2 in calculation)

phiv : vapor equivalence ratio.
nc : number of component used in the isothermal flash
calculation.
name : name of component used in the isothermal flash
calculation.
feed : mole fractions of components used in the
isothermal flash calculation.
ak : K factor of each component.
x : mole fraction of components in liquid & vapor
phases.
  x(i,j) : i, component i
         j = 1, liquid
         j = 2, vapor
psi : liquid fraction of mixture.
nph : number of phase.
nph = 0, vapor only
nph = 1, liquid only
nph = 2, vapor & liquid.
ier : error of flag for FLASH calculation.
ier = 0, no error
ier = 1, no convergence in FLASH routine.
props : phase properties.
  props(i,j) :
  j = 1, liquid
  j = 2, vapor
  i = 1, feed fraction
  i = 2, molecular weight
  i = 3, compressible factor, Z
  i = 4, density, D, mole/liter
  i = 5, enthalpy, H, cal/mole
  i = 6, entropy, S, cal/mole.K
  i = 7, heat capacity, Cp, cal/mole.K
  i = 8, Cp/Cv
  i = 9, sound speed, m/sec
  i = 10, JT coefficient, K/bar
  i = 11, viscosity, uP
  i = 12, thermal conductivity, W/M.K

***************************************************************************
***************************************************************************
Parameters Index :

ak(i) : K factor of component i, calculated by
subroutine FLASH.
faratios : stoichiometric fuel/air ratio of fuel (part
5)
feed(i) : feed fraction of component i, input for
subroutine FLASH.
feede(i) : feed fraction of component i, input from main
program
foxp(i,j) : fugacity coefficient of component i in phase
j calculated by subroutine PHASE_PROPERTIES.
ier : error flag of FLASH.
model : model of calculating the phase properties.
       input of subroutine PHASE_PROPERTIES. (part 2)
name(i) : name of component i, input for subroutine
FLASH.
namee(i) : name of component i, input from main program.
nc : number of components, input for subroutine
FLASH.
nce : number of components, input from main program.
nead(i) : series number of component i in the library
STPLIB. (part 4)
nph : number of phase, output of FLASH.
ox(i) : mole of oxygen required for the
stoichiometric combustion per mole of
component i. (part 4)
pe : intake pressure, input from main program.
phie : metered enrichment, input from main program.
phiv : vapor equivalence ratio of fuel (part 7.4).
pmfe : partially mixing factor, input from main
program.
props(i,j) : different phase properties i of mixture in
different phases j calculated by subroutine
PHASE_PROPERTIES.
px : pressure, input for subroutine FLASH.
psi : liquid fraction of mixture, calculated by
subroutine FLASH.
te : temperature, input from main program.
total : sum of moles of fuel, N2, and O2 (per mole
of fuel). (part 7.2)
tx : temperature, input for subroutine FLASH.
x(i,j) : mole fractions of component i and phase j.
calculated by subroutine FLASH.
xn2 : mole of N2 per mole of fuel in the calculation
of equilibrium-air distillation. (part 6)
xo2 : mole of O2 per mole of fuel in the calculation
of equilibrium-air distillation. (part 6)
wfuel : molecular weight of fuel (part 3).
wmoles : molecular weight of component i (part 3).

1. Declare parameters :

1.1 General parameters :

implicit double precision (a-h,o-z)
character namee(20)*30
class name(20)*30
character model*5
dimension x(20,2)
dimension feede(20)
dimension feed(20)
dimension ak(20)
dimension props(12,2)
dimension foxp(20,2)
dimension wmoles(20)
dimension oxy(20)

1.2 Transfer the series numbers of
components from LIBS to SETUP COMPONENTS (in source31.for) to
EAD.FOR
common/nnumcom/nlibs(20) (LIBS)
common/nnumcom/nsetup(20) (SETUP_COMPONENTS)
common/nnumcom/nead(20) (EAD)

common/nnumcom/nead(20)
1.3 Data block for the (O2)s of each component:

(O2)s is the mole of O2 required for the stoichiometric combustion per mole of component i.
This data block is arranged by the same sequence as in the STPLIB.

dimension o2s(119)
data o2s / 2, 3.5, 5, 2*6.5, 3*8, 2*9.5,
    3*9.5, 7*11,
    + 2*11, 8*12.5,
    + 10*12.5,
    + 8*14, 2*15.5,
    + 2*15.5, 17, 18.5, 20, 21.5, 23, 24.5, 26, 27.5,
    + 29, 30.5, 32, 33.5, 35, 36.5, 3, 4.5, 2*6,
    + 2*6, 6*7.5, 9, 10.5,
    + 12, 13.5, 15, 4, 2*5.5, 4.5, 7.5, 9, 10.5,
    + 9, 10.5, 12, 7.5, 9, 4*10.5, 12,
    + 12, 3*13.5, 12, 2*13.5, 14.5, 2*0,
    + 6*0, 1.5, 3, 7.5 /

2. Initialize the model:
The model used in PHASE_PROPERTIES subroutine is EXCST.
model = 'excst'

3. Find the molecular weight of each component in the fuel and molecular weight of the fuel:
nc = 1
feed(1) = 1
px = 1
tx = 273
do 10 i = 1, nce
name(1) = namee(i)
call setup_components(name, feed, nc)
call flash(px, tx, feed, ak, x, psi, nph, ier)
if (ier.EQ.1) then
    write(*,*) 'convergence failure in FLASH at step 3'
go to 900
endif
call phase_properties(px, tx, x, psi, nph, model, props, foxp)
if (nph.EQ.0) then
    wmole(i) = props(2,2)
else
    wmole(i) = props(2,1)
endif
continue
10 continue
wfuel = 0
do 20 i = 1, nce
wfuel = wfuel + wmole(i)*feede(i)
continue
20 continue

4. Find the mole of oxygen required (O2S(I) or oxy(i)) for the stoichiometric combustion per mole of component i:
Defination of O2S(i) is:
1*(CaHbOc) + (oxy(i))*(O2) = (a)*(CO2) + (b/2)*(H2O)

oxy(i) = a + (b/4) - (c/2)

nc = nce
do 100 i=1,nc
   name(i) = namee(i)
   feed(i) = feede(i)
 100 continue

call setup_components(name,feed,nc)
do 110 i=1,nc
   oxy(i) = o2s(nead(i))
 110 continue

5. Calculate the stoichiometric fuel/air ratio (F/A)s for fuel:

faratios = 0
do 200 i = 1,nce
   faratios = faratios + oxy(i)*feede(i)
 200 continue

faratios = wfuel / (faratios*(1*32+3.773*28.01))

6. Calculate mole of air (mole of N2 & mole of O2) per mole of fuel for the equilibrium-air distillation calculation:

   In this calculation, it should be noticed that the partially mixing factor (pmfe) is also included.

   xn2 = (wfuel/(faratios*28.846))*(3.773/4.773)*pmfe
   xo2 = (wfuel/(faratios*28.846))*(1/4.773)*pmfe

7. Calculation of the vapor equivalence ratio by Equilibrium-Air distillation of the fuel under specified pressure, temperature, enrichment, and partially mixing factor:

7.1 Input nc, name(i), feed(i):

   nc = nce + 2
   do 300 i = 1,nce
     name(i) = namee(i)
     feed(i) = feede(i)
 300 continue

   name(nce+1) = 'N2'
   name(nce+2) = 'O2'
   feed(nce+1) = xn2
   feed(nce+2) = xo2

7.2 Normalize feed(i):

   total = 1 + xn2 + xo2
   do 310 i = 1,nc
     feed(i) = feed(i) / total
 310 continue

   sum = 0
   do 320 i = 1,nc
     sum = sum + feed(i)
 320 continue

   if (sum.NE.1) then
     feed(nc) = feed(nc)+1-sum
   endif

7.3 Isothermal flash calculation:
px = pe
tx = te
call setup_components(name, feed, nc)
call flash(px, tx, feed, ak, x, psi, nph, ier)
if (ier.EQ.1) then
  write(*,*)'convergence failure in FLASH at step 7'
  go to 900
endif
call phase_properties(px, tx, x, psi, nph, model, props, foxp)

7.4 Check the phase of mixture & calculate the vapor equivalence ratio :

if (nph.EQ.2) then
  phiv = 0
  do 330 i = 1, nce
    phiv = phiv + x(i,2)*oxy(i)
  330    continue
  phiv = phiv * pmfe * phie / x(nc,2)
else if (nph.EQ.0) then
  phiv = 1
else
  phiv = 0
endif
900 continue
return
end
APPENDIX D

PROGRAM ACCU
*******************************************************************************
Introduction for main program:
*******************************************************************************
ACCU.FOR :

This program is to calculate:
1. vapor equivalence ratio of fuels
2. the amount of accumulated liquid fuel.
3. % of each species in vapor phase

during the mixture preparation process of engine by using
the Major-Component fuel model which is the model
representation for a practical fuel. (SAE941877)

In this program, the liquid fuel is assumed to accumulate
each injection steps.

The injection of fuel:
1. the first injection pulse can be varied and different
   from the subsequent pulses. (total if at the section of
   "initial injection")
2. the subsequent pulses are all the same. (default phi = 1.0)

In this program, EAD subroutine (in Appendix C) is used to

calculate the vapor equivalence ratio

In this program, subroutines of the NIST Database 4 (NIST
Thermodynamical Properties of Hydrocarbon Mixtures, V1.0)
is used to calculate the Vapor/Liquid equilibrium data and
phase properties of hydrocarbons.

More explanation of the program in the Ph.D. thesis of
Kuo-Chiang Chen (section 6.3)
(see Table 5.4 for indolene model)

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Kuo-Chiang Chen
MIT Sloan Automotive Laboratory
1995

*******************************************************************************
*******************************************************************************
1. Declare parameters:
*******************************************************************************
implicit double precision (a-h,o-z)
character fileout*20
character filedat*20
character filedat*20
character filein*20
character fileint*20
character name(20)*30
character namee(20)*30
dimension feed(20)
dimension fee(20)
dimension feedi(20)
dimension ak(20)
dimension x(20,2)
dimension props(12,2)
dimension c(20)  
dimension r(20)  
dimension rn(20)  
dimension xliq(20)  
dimension xvap(20)  

2. Read the output filename:

write(*,*)'output filename for fuel properties?'  
read(*,25,err=20)fileout  
format(a20)  
open(3,err=20,file=fileout)  
write(*,*)'output filename for speciated mole %?'  
read(*,35,err=30)filedat  
format(a20)  
open(4,err=30,file=filedat)

3. Set the intake pressure (pe) and amount of air in equilibrium with fuel, Fe (pmfe):

pe = 0.4  
phie = 1.0  

write(*,*)'size of first injection pulse'  
read(*,*)totalfl

4. Read the nce, namee(i), and feede(i) from input file:

4.1 read the input file for fuel composition:

write(*,*)'input filename for fuel composition?'  
read(*,41,err=40)filein  
format(a20)  
open(5,err=40,file=filein)  

4.2 read the input file for temperature:

either measured intake valve T or intake manifold wall T each cycle can be used for simulation  
(see section 6.5 of Kuo-Chiang Chen's Ph.D. thesis)

write(*,*)'input filename for temperature?'  
read(*,43,err=42)fileint  
format(a20)  
open(6,err=42,file=fileint)  

4.3 read the nce, namee(i), feede(i)

read(5,50)nce  
format(10x,i2)  
do 52 i = 1,nce  
  read(5,51)namee(i)  
  format(10x,a30)  
continue  
do 54 i = 1,nce  
  read(5,53)feede(i)  
  format(10x,d14.6)  
continue

5. Write the heading to the output file:
5.1 *.out

write(3,*)'%
write(3,*)'input file : indolene.in'
write(3,*)'run by d:\strapp\source\ead\accu.for'
write(3,100)'pressure     = ',pe
write(3,100)'enrichment      = ',phiE
write(3,100)'partially mixing factor = ',pmfe
write(3,100)'first injection pulse = ',totalfl
write(3,*)'%
100 format(a26,1f12.6)
write(3,110)'cycle','t','time','phiv','totalfl'
write(3,*)'%
110 format(1a4,2a7,1a7,1a8)

5.2 *.dat

write(4,*)'%
write(4,*)'input file : indolene.in'
write(4,*)'run by d:\strapp\source\ead\accu.for'
write(4,100)'pressure     = ',pe
write(4,100)'enrichment      = ',phiE
write(4,100)'partially mixing factor = ',pmfe
write(4,100)'first injection pulse = ',totalfl
write(4,*)'%

5.2.1 for indolene

write(4,115)'cycle','time','C4','C5','C6','C7','C7r','
+C8','C8r','C9','C9r','C10','C11','C12'
115 format(1a4,1a7,1a3a7)
write(4,*)'%

6. Initial injection:

totalfl = totalfl1
do 120 i = 1,nce
   feede(i) = feedi(i)
120 continue

7. Do loop 900 :
   i is the cycle number
   time is the real time, under 900 [rpm]
   te is the temperature

call initialize_program
do 900 i = 1,5
   time = i
   time = (1/7.5) * time

7.1 Temperature
   measured temperature input file is 95121902.t2 for
   indolene
   t1 : intake valve temperature (2)
   t2 : intake wall temperature (5)
   t3 : moving average of t1 (6)
   t4 : moving average of t2 (7)
   t5 : average of t3 and t4
7.1.1 Or constant intake temperature for motoring case:

\[
t_e = 300.0
\]

read(6,200)ncyclet, timet, t1, t2, t3, t4, t5
format(i5,6f7.2)
te = t2 + 273.15

8. Call EAD:

call ead(pe, te, phie, pmfe, nce, namee, feede,
+ phiv, nc, name, feed, ak, x, psi, nph, ier, props)

9. Find actual moles of components in liquid phase:

totalx1 = 0
do 210 j = 1, nce
   totalx1 = totalx1 + feed(j)
210 continue

do 220 j = 1, nce
   xliq(j) = x(j,1)*psi*totalf/totalx1
220 continue

totalf1 = 0
do 230 j = 1, nce
   totalf1 = totalf1 + xliq(j)
230 continue

10. Calculate the ratios for the major components:
   These ratios are in PPMC1 basis.

10.1 Carbon number of major components (indolene)

   c(1) = 4
   c(2) = 5
   c(3) = 6
   c(4) = 6
   c(5) = 7
   c(6) = 7
   c(7) = 8
   c(8) = 8
   c(9) = 9
   c(10) = 9
   c(11) = 10
   c(12) = 11
   c(13) = 12

10.2 Percentage in ppmC1 in vapor phase:
   PPMC1(i)v/(total PPMC1)v x (100%)

ptotal = 0
do 240 j = 1, nce
   ptotal = ptotal + x(j,2)*c(j)
240 continue

do 250 j = 1, nce
   r(j) = x(j,2)*c(j)*100/ptotal
250 continue

10.2.1 Percentage of major component in indolene:
r(1) = r(1) * 0.93
r(2) = r(2) * 0.62
r(3) = r(3) * 0.25
r(4) = r(4) * 1.00
r(5) = r(5) * 0.48
r(6) = r(6) * 1.00
r(7) = r(7) * 0.37
r(8) = r(8) * 0.38
r(9) = r(9) * 0.53
r(10) = r(10) * 0.35
r(11) = r(11) * 0.11
r(12) = r(12) * 0.14
r(13) = r(13) * 0.069

10.2.2 indolene modification:
(see section 6.6.5, Table 6.10 of Kuo-Chiang Chen's Ph.D. thesis)

r(1) = r(1) * 1.00
r(2) = r(2) * 1.60
r(3) = r(3) * 1.00
r(4) = r(4) * 0.55
r(5) = r(5) * 1.00
r(6) = r(6) * 1.50
r(7) = r(7) * 0.70
r(8) = r(8) * 1.00
r(9) = r(9) * 1.00
r(10) = r(10) * 0.26
r(11) = r(11) * 1.00
r(12) = r(12) * 1.00
r(13) = r(13) * 1.00

11. Calculate the phi_v:

phi_v = phi_v*total_f

12. Calculate the total ppmC1:

12.1 The actual vapor phase:

do 251 j = 1,nce
   xvap(j) = x(j,2)*(1-psi)*total_f/total_x1
continue

total_fv = 0

do 252 j = 1,nce
   total_fv = total_fv + xvap(j)*c(j)
continue

xvap(nce+1) = feed(nce+1)/total_x1/pmfe
xvap(nce+2) = feed(nce+2)/total_x1/pmfe

ppmcl = total_fv/(xvap(nce+1)*xvap(nce+2))*1000000

13. Write the results:

write(3,260)i,te,time,phi_v,total_f,ppmcl
write(*,260)i,te,time,phi_v,total_f,ppmcl
format(i4,2f7.2,1f7.4,1f8.4,1f10.2)

13.1 for indolene
write(4,265)i, time, r(1), r(2), r(3), r(4), r(5), r(6),
+r(7), r(8), r(9), r(10), r(11), r(12), r(13)
format(i4,1f7.2,13f7.2)

14. Check whether all the fuel is evaporated :

if (nph.EQ.0) go to 910

15. Find the feede(i) for next injection :

totalf = totalfl + 1
do 270 j = 1, nce
    feede(j) = (feedi(j)+xliq(j))/totalf
continue

16. End of loop 900 :

continue

910 continue end
APPENDIX E

PROGRAM ENRICH

*****************************************************************************

Introduction for main program:

--------------------------------

ENRICH.FOR:

This program is to calculate the amount of injected fuel required to fulfill the target vapor equivalence ratio:

(1) liquid fuel is assumed to accumulate each injection steps.
(2) injection of fuel is determined by iteration.
(3) EAD subroutine (in Appendix C) is used to calculate the vapor equivalence ratio
(4) Intake pressure and air mass flow rate is using Ford Zetec engine data

In this program, subroutines of the NIST Database 4 (NIST Thermodynamical Properties of Hydrocarbon Mixtures, V1.0) is used to calculate the Vapor/Liquid equilibrium data and phase properties of hydrocarbons.

More explanation of the program in the Ph.D. thsis of Kuo-Chiang Chen (section 6.7)
(see Table 5.4 for indolene model)

Professor Wai. K. Cheng
Kuo-Chiang Chen
MIT Sloan Automotive Laboratory
1996

*****************************************************************************

1. Declare parameters:

***********************************************************************

implicit double precision (a-h,o-z)
character fileout*20
character filedat*20
character fileda2*20
character filein*20
character fileint*20
character name(20)*30
character nameee(20)*30
dimension feed(20)
dimension feede(20)
dimension feedi(20)
dimension ak(20)
dimension x(20,2)
dimension props(12,2)
dimension c(20)
dimension r(20)
dimension rn(20)
dimension xliq(20)
    dimension xvap(20)

***********************************************************************

2. Read the output filename:

*******************************************************************************

write(*,*)'output filename for fuel properties?'
read(*,25,err=20)fileout

*******************************************************************************
format(a20)
open(3, err=20, file=fileout)
write(*,*)'output filename for speciated mole %?'
read(*,35,err=30)filedat
format(a20)
open(4, err=30, file=filedat)

3. Initial set-up :
   pe : intake pressure
   pmfe : fe, fraction of air in equilibrium with fuel
   phivtarg : target vapor equivalence ratio
   phiinj : injected fuel equivalence ratio
   totalfl : total liquid fuel accumulated
   xliq(i) : actual mole of liquid speices
   totalf : total fuel (including current injection & accumulated liquid fuel in intake port)

phie = 1.0
pe = 0.4
te = 300.0
pmfe = 0.01
phivtarg = 1.0
phiinj = phivtarg
totalfl = 0
do 36 i = 1,20
   xliq(i) = 0
continue
   totalf = phiinj + totalfl
4. Read the nce, namee(i), and feede(i) from input file :
   Read the temperature file :
   Read the input file for fuel composition :

4.1 read the input file for fuel composition :
   write(*,*)'input filename for fuel composition?'
   read(*,41,err=40)filein
format(a20)
open(5, err=40, file=filein)

4.2 read the input file of Ford Zetec data (fordlm.dat) :
   fileint = 'ford102.dat'
   open(6, file=fileint)

4.3 read the nce, namee(i), feede(i)
   read(5,50)nce
   format(10x,i2)
do 52 i = 1,nce
   read(5,51)namee(i)
   format(10x,a30)
continue
do 54 i = 1,nce
   read(5,53)feede(i)
   format(10x,dl4.6)
continue

5. Write the heading to the output file :
5.1 *.out
write(3,*)'\n
write(3,*)'input file : indolene.in'
write(3,*)'run by d:\strapp\source\ead\enrich.for'
write(3,100)'pressure    = ',pe
write(3,100)'temperature = ',te
write(3,100)'partially mixing factor = ',pmfe
write(3,100)'target vapor phi = ',phivtarg
write(3,*)'  
100 format(a26,1f12.6)
write(3,110)'cycle','pi','rpm','air','fuel','phiinj','phiv','+
            'totalfl'
write(3,*)'\n
110 format(1a4,1a6,1a7,4a8,1a9)

5.2 *.dat
write(4,*)'\n
write(4,*)'input file : indolene.in'
write(4,*)'run by d:\strapp\source\ead\enrich.for'
write(4,100)'pressure    = ',pe
write(4,100)'temperature = ',te
write(4,100)'partially mixing factor = ',pmfe
write(4,100)'target vapor phi = ',phivtarg
write(4,*)'  

5.2.1 for indolene

write(4,115)'cycle','time','C4','C5','C6r','C7','C7r', +
        'C8','C8r','C9','C9r','C10','C11','C12'

115 format(1a4,1a7,13a7)
write(4,*)'\n
6. Initial injection :
   No liquid fuel accumulated in intake port.
   Only current injection.

do 120 i = 1,nce
   feede(i) = feedi(i)
continue

7. Do loop 900 :
   i is the cycle number
   time is the real time, under 900 [rpm]
   te is the temperature

call initialize_program
do 900 i = 1,20
   time = i
   time = (1/7.5) * time
   te = 300.0

7.1 Ford data file is "fordlm.dat"
It has 4 sets of data for each cycle, only take the
1st for each cycle
intake pressure : fordpi
intake temperature : fordti
speed : fordrpm
air mass flow rate : fordair
exhaust Phi : fordphi
8. Loop 200:

   Iteration to determine injection amount (phiinj):

200

   continue
   call ead(pe,te,phie,pmfe,nce,namee,feede,
              phiv,nc, name, feed, ak, x, psi, np, ier, props)
   phiv = phiv * totalf
   write(*,*) phiv
   dphiv = phivtarg - phiv
   if ((dphiv .GE. 0.005) .OR. (dphiv .LE. -0.005)) then
     phiinj = phiinj * (phivtarg / phiv)
     totalf = phiinj + totalf1
     do 201 j = 1, nce
        feede(j) = (feedi(j) * phiinj + xliq(j)) / totalf
     end
   endif
   phiinjm = phiinj * fordair / 14.6

9. Find actual moles of components in liquid & vapor phase:

9.1 Find xliq(i) & totalf1

210

   totalx1 = 0
   do 210 j = 1, nce
      totalx1 = totalx1 + feed(j)
   continue
   do 220 j = 1, nce
      xliq(j) = x(j,1) * psi * totalf / totalx1
   continue
   totalf1 = 0
   do 230 j = 1, nce
      totalf1 = totalf1 + xliq(j)
   continue

9.2 Find xvap(i) & total ppmCl:

231

   do 231 j = 1, nce
      xvap(j) = x(j,2) * (1 - psi) * totalf / totalx1
   continue
   totalfv = 0
   do 232 j = 1, nce
      totalfv = totalfv + xvap(j) * c(j)
   continue
   xvap(nce+1) = feed(nce+1) / totalx1 / pmfe
   xvap(nce+2) = feed(nce+2) / totalx1 / pmfe
   ppmc1 = totalfv / (xvap(nce+1) + xvap(nce+2)) * 1000000

10. Calculate the ratios for the major components:

   These ratios are in PPMCl basis.

10.1 for indolene
c

c(1) = 4
c(2) = 5
c(3) = 6
c(4) = 6
c(5) = 7
c(6) = 7
c(7) = 8
c(8) = 8
c(9) = 9
c(10) = 9
c(11) = 10
c(12) = 11
c(13) = 12

c
10.2 Percentage in ppmCl in vapor phase:

PPMC1(i)v/((total PPMCl)v x (100%))

c
ptotal = 0
do 240 j = 1,nce
   ptotal = ptotal + x(j,2)*c(j)
240 continue

do 250 j = 1,nce
   r(j) = x(j,2)*c(j)*100/ptotal
250 continue


c
10.2.1 Percentage of major component in indolene:

r(1) = r(1) * 0.93
r(2) = r(2) * 0.62
r(3) = r(3) * 0.25
r(4) = r(4) * 1.00
r(5) = r(5) * 0.48
r(6) = r(6) * 1.00
r(7) = r(7) * 0.37
r(8) = r(8) * 0.38
r(9) = r(9) * 0.53
r(10) = r(10) * 0.35
r(11) = r(11) * 0.11
r(12) = r(12) * 0.14
r(13) = r(13) * 0.069


c
10.2.2 indolene modificatin:

r(1) = r(1) * 1.00
r(2) = r(2) * 1.60
r(3) = r(3) * 1.00
r(4) = r(4) * 0.55
r(5) = r(5) * 1.00
r(6) = r(6) * 1.50
r(7) = r(7) * 0.70
r(8) = r(8) * 1.00
r(9) = r(9) * 1.00
r(10) = r(10) * 0.26
r(11) = r(11) * 1.00
r(12) = r(12) * 1.00
r(13) = r(13) * 1.00


c
11. Write the results:

write(3,260)i,fordpi,fordrpm,fordair,phiinjm,phiinj,phiv,
+totalfl
   write(*,261)i,phiinj,phiv
260 format(i4,1f6.3,1f7.1,2f8.2,2f8.4,1f9.4)
261 format(i4,2f8.4)
c
11.1 for indolene

write(4,265)i,time,r(1),r(2),r(3),r(4),r(5),r(6),
   +r(7),r(8),r(9),r(10),r(11),r(12),r(13)
265 format(i4,1f7.2,13f7.2)
c
12. Check whether all the fuel is evaporated :
c
if (nph.EQ.0) go to 910
c
13. Find the feede(i) for next injection :
c
phiinj = phivtarg
totalf = phiinj + totalfl
do 270 j = 1,nce
   feede(j) = (feedi(j)*phiinj + xliq(j))/totalf
270 continue
c
14. End of loop 900 :
c
900 continue
910 continue
end