A Detailed Chemical Kinetic Investigation of a Tri-Component Diesel Surrogate Ignition and Combustion under HCCI Engine Conditions

بحث حركية التفاعلات الكيميائية التفصيلية لاشعال واحتراق بدائل وقود الديزل الثلاثية التركيب فى محركات الشحنة المتجانسة ذات الاشعال بالضغط

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ملخص البحث

يتناول هذا البحث تطبيق الية حركية التفاعلات التفصيلية لبحث خواص الاشعال والاحتراق لبدائل وقود الديزل المكون من ثلاثة مركبات كميائية. في هذا البحث تم دمج حركية التفاعلات الكيميائية لكل من مركب الهيبتان ومركب الطولوين الي حركية التفاعلات الكيميائية لمركب الهكسان الحلقي. واستنادا الي التركيب الكيميائى لوقود الديزل تم اختياركلا من مركبات الهيبتان والطولوين والهكسان الحلقي ليصبحا مركب مثالي للوقود البديل للديزل. و قد اثبتت النتائج المتحصل عليها ان افضل نسبة تركيب للمركبات الثلاثة المقترحة (الهيبتان ــ الطولوين ــ الهكسان الحلقي) في الوقود البديل هي نسبة 8:1:1. وباستخدام تقنية الحل العددي لكود حراري صفري البعد تم الحصول علي النتائج من المركبات الثلاثة التى تم اختبارها ومقارنتها بنماذج تفصيلية لحركية التفاعلات   لوقود احادية وثنائية التركيب مع النتائج المرجعية المأخوذة عن محرك الشحنة المتجانسة ذات الاشعال بالضغط محل الدراسة. وتشير النتائج المتحصل عليها للنموذج الخاص بالتركيب الثلاثي للوقود الجديد الي توافق ملحوظ مع النتائج المعملية و خاصة فيما يتعلق بزوايا تأخير الاشعال. وتشير ايضا النتائج المتحصل عليها لزوايا تأخير الاشعال الي ان نموذج حركية التفاعلات الكيميائية المقترح يمكنه التحصل علي زاوية الاشتعال الذاتي و كامل عملية الاحتراق بشكل دقيق مثلما سجل فى النتائج المعملية المرجعية.بما يظهر اتفاق ملحوظ في النتائج المعملية الخاصة بالمحرك مع النتائج الحسابية المتحصل عليها.

Abstract

This paper presents a new tri-component diesel surrogate fuel chemical kinetic mechanism. The cross reaction mechanism between N-heptane and toluene is added to the third component detailed mechanism of cyclohexane. Based on the composition of the diesel fuel, N-heptane, toluene, and cyclohexane are selected as ideal components for this new diesel surrogate fuel. The best ratio of the selected diesel surrogate fuel components, which representing heptanes, toluene, and cyclohexane with a ratio of 8:1:1 is determined for the three suggested components. Numerically, the result obtained from a Zero-dimensional thermodynamic code for the proposed tri-component mechanism have been intensively validated against a single, and two components detailed chemical kinetic mechanism. Furthermore, the obtained results validated against the referenced experimental engine data. The obtained results of the tri-component mechanism provide a remarkable agreement between the obtained experimental data in terms of ignition delay angles. The obtained results of ignition delay angles show that the suggested chemical kinetics mechanism can capture the auto-ignition angle and the whole combustion process.

Nomenclature/Abbreviations

SOC	Start of Combustion		**EGR**	Exhaust Gas Recirculation
MSN	Means Square Error		**IMEP**	Indicated Mean Effective Pressure
N	Number of Engine Simulation Run		**CN**	Cetan Number
			C/H	Carbon to Hydrogen Ratio

LTO	low Temperature Oxidation
HTO	High Temperature Oxidation
NTC	Negative Temperature Coefficient
HCCI	Homogeneous Charge Compression Ignition
HRR	Heat Release Rate`
RPM	Revolutions Per Minute
TDC	Top Dead Center
ATDC	After Top Dead Center
BTDC	Before Top Dead Center
CI	Compression Ignition
ICE	Internal Combustion Engine
CA	Crank Angle
DI	Direct Injection

Subscripts

atm	Atmospheric Condition
int	Intake pipe
exh	Exhaust Pipe
exp	Experimental
mod	Modeling

1.   Introduction

Crude oil based diesel fuels consist of hundreds of individual chemical components. Therefore, it is challenging to measure the exact composition of each diesel fuel batch that comes from the refinery. Understanding the details of chemical reactions which typically show a nonlinear dependence on all the variables such as the temperature, pressure and the diesel fuel composition and to use them in numerical simulations would be too motivated when realistic diesel fuels are used. As a consequence, the scientific world has adopted the approach of surrogate fuels. Diesel surrogate fuel is simpler represented of fully blended of selected species of known concentrations and that exhibit combustion characteristics similar to those of the real diesel fuel [1-3].

The problem of finding diesel surrogate fuel properties and its chemical reaction mechanisms becomes tractable because it consists of a complex mixture of hundreds of medium and high molecular weight of hydrocarbons. The composition of the surrogate diesel fuel is chosen such that certain important targets are close to those of the real fuel. However, certain guidelines are available for the choice of surrogates based on their intended applications. These guidelines include feasibility (known chemical kinetic mechanism), simplicity (computational capability), similarity (real fluid physical and chemical properties, density, heating value, evaporation characteristics, chemical composition, C/H ratio, and ignition delay), cost, and availability [4-7].

N-heptane is often used as a single component surrogate diesel fuel since it has a comparable Cetane number (CN) as European diesel [8, 9]. However, CN does not seem to be representative enough of the ignition characteristics of the diesel fuel. Those probably because the Cetane number experimental determination does not cover a real and a wide range of engine conditions and because the physical delay time can also affect the ignition timing. In that regard, the surrogate fuel consisting from a 50% n-heptane and 50% toluene mixture (by mass) had been proposed to simulate the auto-ignition time of diesel fuel in HCCI combustion [10]. As a practicability, cycloalkanes are a significant component of the conventional diesel fuel (up to approximately 35%), jet fuels (up to 20%), and gasoline (up to 10%) [11, 12]. Because of the high proportion of cycloalkanes in practical fuels, detailed mechanisms for cycloalkanes are needed to simulate this chemical class. These mechanisms need to be valid under the conditions found in internal combustion engines so that, when

they are inserted into surrogate fuel models, they can be used to simulate diesel combustion in homogeneous charge compression ignition (HCCI) application. Such surrogate fuel component model is valuable in optimizing the design and performance of that engine and minimizing their pollutant emissions. Also, Cycloalkanes can raise soot emission levels because they are known to dehydrogenate and produce aromatic, which can lead to the production of polycyclic aromatics that are thought to be inception sites for soot growth [13, 14]. As such, validated chemical kinetic mechanisms for cycloalkanes are needed to treat the oxidation of cycloalkanes under engine conditions. In that regards, the representative surrogate for cycloalkanes, cyclohexane was chosen to represent the major reaction characteristics of cycloalkane oxidation processes [15, 16].

In the present study, N-heptane and N-heptane/toluene chemical kinetic mechanisms have been numerically studied to validate a new tri-components diesel surrogate kinetics model. N-heptane reaction mechanism consists of the 550 species and 2450 reactions proposed by Curran [17]. The N-heptane mechanism has been added to the toluene reaction mechanism. The toluene mechanism consists of the 285 species and 1427 reactions proposed by the Pitz [18]. Twelve co-oxidation reactions between the individual components of N-heptane and toluene blends have included in our detailed chemical kinetics mechanism [19]. The resulting chemical kinetic mechanism of N-heptane/toluene finally consists of 644 species and 2796 reactions. The tri-component mechanism is constructed by combining the two components of N-heptane/toluene mechanism into a cyclohexane mechanism which contains 1081 species and 4269 reactions by the Silke et al. [20]. However, the proposed mechanism contains 1140 species and 4578 reactions.

2.   Numerical Model

HCCI combustion is considered as a new era of the internal combustion engine technology, which will achieve high and low engine efficiency, emissions, respectively. As the HCCI combustion process is mainly controlled by the chemical kinetics, so the detailed chemical kinetics mechanisms of hydrocarbon fuel must be placed in the core of the study [21]. However, due to the lack of information concerning consistent between the internal combustion engine experimental and simulation results of diesel fuel ignition characteristics under HCCI engine conditions, a new diesel fuel surrogate kinetic mechanism has been developed in this work by merging N-heptane, toluene, and cyclohexane. The proposed mechanism has been implemented in the CHEMKIN software [22]. Numerically, the results obtained from a Zero-dimensional thermodynamic code for the proposed tri-component model have been intensively validated against a single and two-components detailed kinetic mechanisms in addition to the engine experimental data. CHEMKIN code solves the coupled chemical kinetic and energy equations and permits to use a variety of boundary and initial conditions for HCCI engine application. The engine parameters have to be specified directly by the user interface of the Internal Combustion Engine Reactor Model. The major advantage of such an approach is that the pressure changes can be related directly to the amount of fuel chemical energy released by combustion, while retaining the simplicity of treating the combustion chamber contents as a single zone. The gaseous mixture introduced into the simulation zone is assumed to be an ideal homogeneous mixture with uniform composition and thermodynamic properties. The gas movement inside the combustion chamber and the chamber geometry design has no effect on combustion performance [23].

Table 1 the main fuel specifications for the studied fuel

Fuel	N-heptane _ toluene _ cyclohexane (mass ratio %)	Cetane Number	C/H Ratio	Lower Heating Value(MJ/kg)	Density（g/ml）at 20°C
N-heptane	100_0_0	56	5.25	44.3	0.679
N-heptane + toluene	50_50_0	32.5	7.1	42.32	0.773
Surrogate A	80_10_10	47	6.6	43.82	0.709
Surrogate B	70_20_10	42.3	5.9	43.45	0.727
Surrogate C	70_10_20	42.7	5.6	43.73	0.718
Surrogate D	60_30_10	37.6	5.8	43.03	0.745
Diesel	Commercial Diesel fuel	52.1	6.8	42.65	0.838

The main target of this work is to predict the exact ignition timing of different diesel surrogates with detailed mechanisms under diesel HCCI conditions and analyze the chemical behavior of different components. Hence, we design six types of surrogate fuels, including single component, two component, and different ratios of tri-component surrogates. Table 1 shows the fuel properties of diesel fuel and its surrogates, including Cetane number, C/H, lower heating value, and density.

The global Woschni model [24] for heat transfer has frequently been used for HCCI engine studies, even though the conditions in the engine vary significantly from those considered in the original work aimed at CI engines [25]. Also, engine heat release analysis sub model has been used in this model to trace and study an individual cycle in the cylinder combustion. As the initial condition for calculations, it was assumed that the intake valve closes at BTDC 140 ^{O}CA with a cylinder pressure of one atmosphere, which produces the best observed fuel free pressure profile around TDC.

3.   Diesel HCCI experiment

Heavy duty commercial single cylinder diesel engines have been prepared to investigate the basic performance characteristics of diesel HCCI engines combustion and emissions. The experimental study will specifically address a number of challenges faced the diesel HCCI engines such as the fuel/air mixture homogeneity, control of ignition timing, heat release rate, emissions over a wide range of loads, speeds, different percentages of EGR rate, different values of port fuel injection pressure, and finally adjusting both of fuel and charged airline temperature [26]. The test engine was adjusted to run with pure diesel fuel in HCCI mode over a wide range of operating conditions to analyze the engine performance and validate our simulation models. This engine will be equipped to handle the heated air and/or fuel in addition to the possibility to change the engine loads at fixed speed.

Test engine used in this study was naturally aspirated, four-stroke, and water-cooled. Fuel/air homogenous mixture was formed during suction and compression strokes, in which the fuel supply mode was changed from the direct fuel injection to port fuel supply. The specifications of the engine were given in Table2.

The fuel employed was commercial Diesel fuel n-heptane with the characteristics shown in table 3. The fuel supplied flow rate was measured by using different combinations of pre-calibrated flow meters and high accuracy digital balance (±0.001gram absolute error).

The air mass flow rate was measured with a high accuracy digital flow meter. The atmospheric temperature in the engine test lab is usually maintained constant, around 30 ^{O}C. The engine coolant temperature was controlled during HCCI experiments. So, the coolant water in the cooling water jacket was kept constant, which is normally kept at 85 ^{O}CA, during all the experimental activities.

The in-cylinder pressure data has been implemented in a thermodynamic diagnostic model to solve numerically the energy equation balance inside the cylinder, assuming uniform pressure and the mean temperature throughout the chamber at each time step. In this regards, the single cylinder engine tests were achieved at the same conditions of the in-cylinder simulation data shown in Table 4.

Table 2 Test Engine specifications

Bore Stroke/Piston Shape	130 mm×120 mm/ω Shape
Displacement	1.592 L
Connecting Rod Length/Crank Radius Ratio	3.742
Compression Ratio	15.1
Fuel Supply Mode	Port fuel Supply
Intake Valve Open	12º BTDC
Intake Valve Close	38º ABDC
Exhaust Valve Open	55º BBDC
Exhaust Valve Close	17º ATDC
Max. Power	20.22KW at 2200 RPM

Table 3 Properties of n-heptane used in our experiment

Molecular Weight	100.202 g/Mol
Density	0.684 g/cm^3
Vapor pressure	40 mm Hg
Surface Tension	0.02012 N/m
Dynamic viscosity	$3.87*10^{-4}$ Pa S
Critical Temperature	540 K
Autoignition Point	204 ^{o}C

As a sequence, the engine conditions were selected to study the most effective parameters affects the oxidation kinetics of any fuel, such as the engine load (quantified by the indicated mean effective pressure (IMEP)), the engine speed and the charge composition (quantified by the EGR percentage). All of these parameter

combinations can be used to present a variety of levels of the in-cylinder pressure and temperature. As can be observed from Table 4, diesel HCCI conditions were achieved by generating a homogeneous fuel/air mixture externally (port fuel supply method) in a specially designed fuel aerosol production chamber. The diesel fuel aerosol is introduced through the creative system of diesel fuel vaporizer into the test engine manifold. The diesel vaporization system consists of a small chamber in which the diesel vapor is fully vaporized by means of fuel flow and cavitation inside the diesel injection nozzle and liquid fuel injection temperature. The diesel fuel vapor enters into the engine enables the process of engine combustion with a fully homogenized mixture. At each engine condition, IMEP was adjusted around the reference values (4 and 6 bar) in order to avoid the onset of the engine knock. EGR rate has been calculated as shown in equation (1):

$$EGR = \frac{[CO_2]_{int} - [CO_2]_{atm}}{[CO_2]_{exh} - [CO_2]_{atm}} \qquad (1)$$

Where $[CO_2]_{atm}$ is the CO_2 content in the atmospheric air, and $[CO_2]_{int}$ and $[CO_2]_{exh}$ are the CO_2 concentration in the intake and the exhaust pipe respectively.

Table 4 Engine experimental operating conditions

Engine Speed (RPM)	EGR Rate (%)	IMEP (bar)	SOC(exp)
1500	40	5.2	-9.88
		2.8	-9.28
		6.3	-13.48
		4.1	-11.28
	60	4.9	-7.48
		2.8	-8.08
		6.2	-7.08
		4.1	-6.68
2000	40	5.9	-10.48
		3.1	-8.88
		5.8	-13.88
		4.4	-11.68
	60	5.6	-5.28
		3.2	-6.08
		7.1	-5.28
		4.6	-8.08

The first aim of the proposed work is to find out the best ratio of the selected diesel surrogate fuel composition by comparing the achieved results from the simulation code for the modeled ignition delay angles with experimental ones obtained from a single cylinder HCCI engine test. Where, the minimum value of the statistical means square error (MSE), which defined by equation (2), can be used as quantitative selection criterion.

$$MSN = \sqrt{\frac{\sum_{i=1}^{N}(SOC_{i\,(exp)} - SOC_{i\,(mod)})^2}{N}} \quad (2)$$

Where N is the number of engine simulation runs, $SOC_{(exp)}$ and $SOC_{(mod)}$ are the experimental, and modeled start of combustion (SOC) (auto-ignition angle), respectively.

4.   Diesel Surrogate Selection

As can be seen from Fig. 1, the value of SOC is being negative if ignition occurs before TDC. The value of SOC is defined in both experimental and simulation data by measuring the crank angle corresponding to 10% of the cumulative heat released during the stage of the high temperature combustion process.

The optimal composition ratio of the suggested components of the diesel surrogate fuel is determined by a quantitative methodology of MSE. The MSN values were calculated for each case of six diesel surrogate components represented in Table 1 at different sixteen engine conditions described in Table 4. The selection criterion of the optimal n-heptane/toluene/cyclohexane compositions is calculated by comparing the modeled ignition delay angles with experimental ones which obtained from the single cylinder engine tests. The measured in-cylinder instantaneous pressure data were used as input data on a thermodynamic diagnostic model in order to obtain the experimental rate of the heat release (HRR), while the same engine conditions were simulated to obtain the modeled HRR by using the internal combustion engine (ICE) sub-routine from CHEMKIN software. However, the experimental data on the diesel HCCI conditions were achieved with externally diesel aerosol production chamber to produce a perfect fuel/air homogeneous mixture. Consequently, the diesel fuel/air mixture was supposed to be a perfect homogeneous during the combustion process.

Fig. 2 shows pronounced differences between experimental and modeled HRR curves for different diesel surrogate fuel component mass ratio. The simulation results indicated that the start of combustion angle delayed with respect to the different modeled surrogate component ratio. From the simulation and experimental results of the diesel surrogate HCCI combustion chemistry analysis, it was found that, the different tested surrogate fuels displays two-stage heat release or two stage combustion process involving low temperature oxidation (LTO) stage followed by high temperature oxidation (HTO) stage separated by a time delay between them is attributed to negative temperature coefficient (NTC). The first stage of heat release is associated with low temperature kinetic reactions (Low Temperature Oxidation, LTO) and the second that much stronger one (main reaction) is the High Temperature Oxidation (HTO). The time delay between LTO and HTO is attributed to the Negative Temperature Coefficient regime (NTC). About 7–10% of the energy is released during the LTO and the rest is released during HTO, as shown in Fig.1. The modeled LTO and HTO stages show very sharp and narrow peaks as a consequence of the single-zone characteristics of the CHEMKIN sub-routine. Fig. 2 shows the

comparison of HRR for the different mass ratio of the suggested three components of diesel surrogate fuel with the resulted profiles obtained from experimental activity at engine speed 1500 RPM, EGR 40%, IMEP 4.1bar. Different surrogate fuel component mass ratio shows a pronounced difference in both of LTO and HTO peak timing. By reducing the N-heptane and increasing both of toluene and cyclohexane mass ratios the LTO and HTO peaks will be reduced and retarded, respectively.

However, to find out the best composition ratios by mass for the tri-components, diesel surrogate fuel the quantitative criteria of MSE have been calculated for the each surrogate at different sixteen engine conditions. The obtained results are represented in Fig. 3 which provides a lowest MSE value for the suggested ratio for the "surrogate A" which consist of 80% N-heptanes, 10% toluene, and 10% cyclohexane in mass. Also, the experimental and the modeled HRR of the suggested tri-component surrogate ratio have been compared with the modeled results obtained from single and two-component mechanisms as shown in Fig. 4 at different engine conditions.
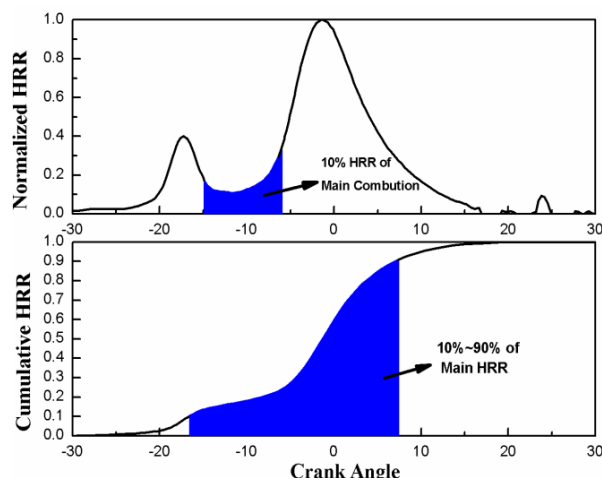
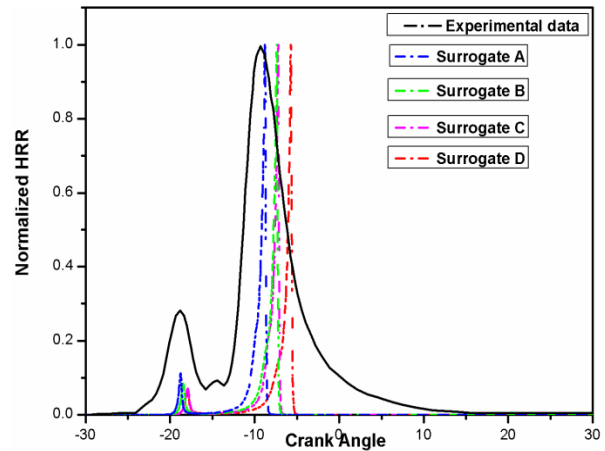**Figure 1 Definitions of the start of combustion and combustion duration**

Figure 2 Experimental and modeled HRR for different diesel surrogate fuel components at the case of: n=1500 RPM, EGR=40%, IMEP=4.1bar
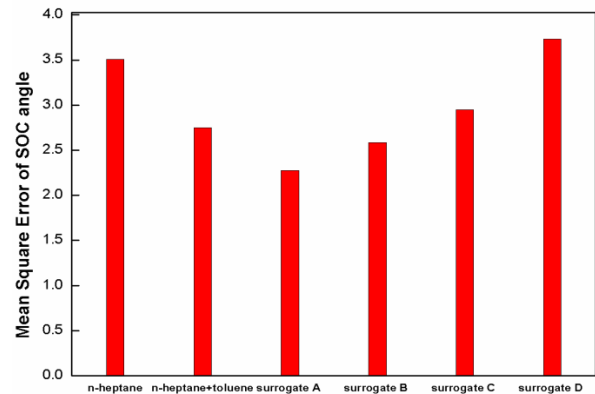

Figure 3 MSE values for different diesel surrogate fuel compositions

For further validation based on single, two, three component surrogate fuel with experimental data to provide more insight into the certainty analysis for our suggested mechanism, the obtained simulation results from a Zero-dimensional thermodynamic code for our proposed tri-component model have been intensively validated against a single and two-component detailed kinetic models in addition to the different experimental engine data as shown in Figure 4. The results have been obtained from tri-component model simulation analysis shows quite well agreement with the experimental data. The obtained results at various engine operating conditions also show a good

agreement with the engine experimental data. The obtained results of the ignition delay angles show that the suggested chemical kinetics model can capture the auto-ignition timing and the whole combustion process effectively.
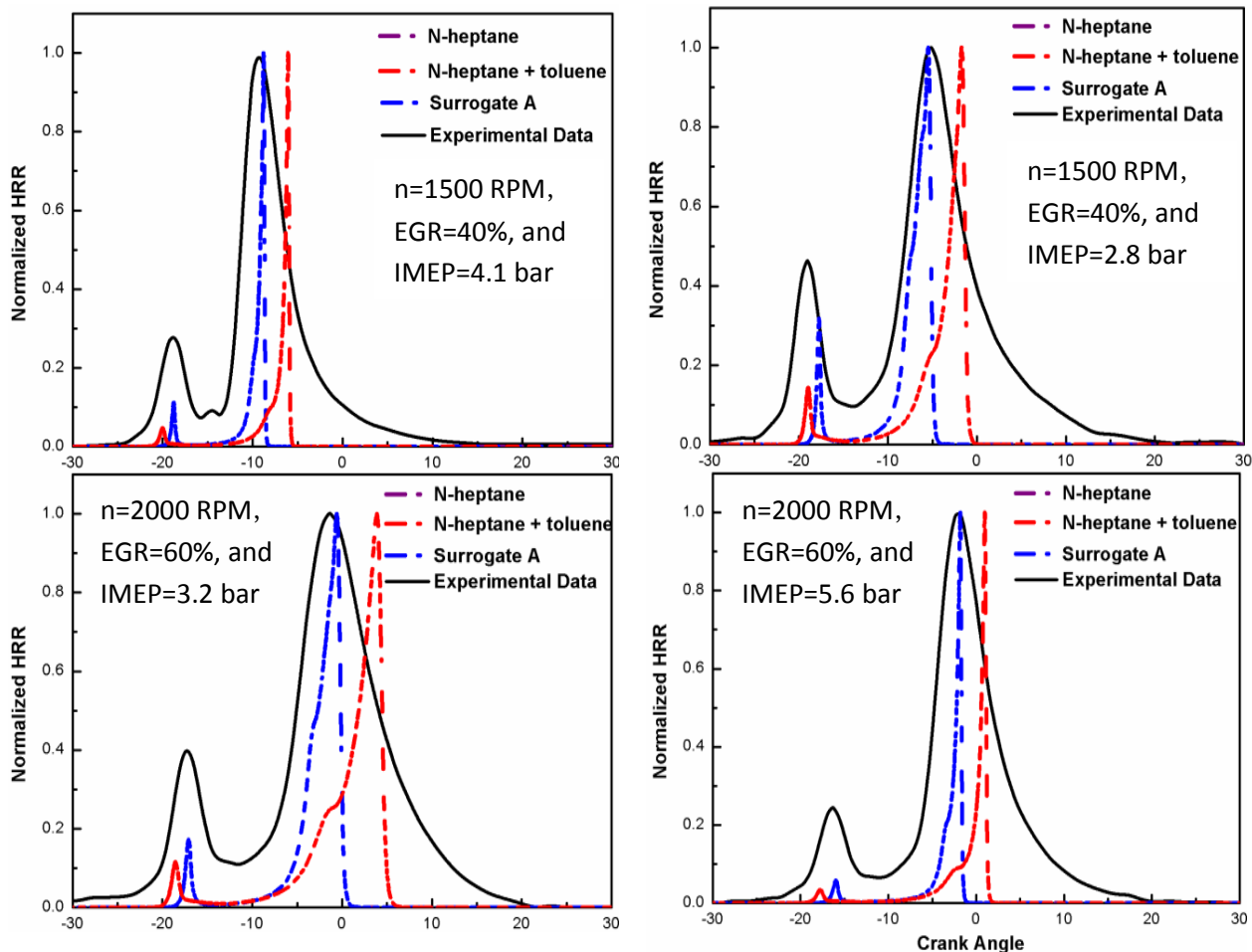

Figure 4 Experimental and modeled HRR for different diesel surrogate fuel chemical kinetic mechanisms evolution at different engine conditions

5.   Kinetic mechanisms analysis

To understand the kinetics involved in the ignition inhibition of the tri-component mechanisms, the following analysis is divided into three parts: (1) sensitivity analysis to find out the key elementary reactions controlling chemistries leading to auto-ignition, (2) OH specie flux analysis to explain the advantages of the tri-component surrogate model compared with the two-component, especially focused on the addition of cyclohexane, and (3) further numerical analysis to investigate the effect of compositional changes in the surrogate mixture.

5.1. Sensitivity analysis

For further examination for the fuel chemistry in the low temperature recation region prior to auto-ignition, a sensitivity analysis was carried out under HCCI condition. Sensitivity analysis was used to

investigate the effect of the parameters change on the solution of the mathematical models. By calculating the ensemble property parameter (e.g., species concentration, temperature, and reaction rate) variation caused by the small changes in the value of a reaction rate constant. Therefore, the definition of the so-called "sensitivity", which can be valued via sensitivity coefficients, resolved through a series of the reaction rate differential equations. The magnitude of the each elemental reaction sensitivity coefficient value can provide information about the importance and interconnection of the parameters and variables. The matrix of the sensitivity coefficients ($\bar{S}$) is defined as:

$$\bar{S} = \frac{\partial \varphi}{\partial \alpha}$$

Where ϕ and α represents the output and the parameter investigated, respectively. In the present study, the sensitivity coefficients of the pre-exponential factor (k) of each reaction rate constant on the species concentration C has been calculated in its normalized form in order to compare between the calculated values. The normalized matrix of the sensitivity coefficients is defined as:

$$\bar{S} = \frac{k_j}{C_i} \frac{\partial C_i}{\partial k_j} = \frac{\partial \ln C_i}{\partial \ln k_j}$$

Where k_j is the jth reaction rate constant, C_i is the ith species concentrations, and $\frac{\partial C_i}{\partial k_j}$ is the sensitivity coefficients of the ith species concentrations to the jth reaction rate constant.

Because OH radical is a good indicator for the onset of the oxidation process, the normalized sensitivity coefficients of the OH radical with respect to pre-exponential factor

for "surrogate A" is carried out at the early stage of the low combustion temperature. As shown in Figure 5, the most relevant reactions in this case are related to low temperature mechanisms of n-heptane and cyclohexane of the surrogate fuel mixture. At the onset of the heat release, OH radical are consumed mainly by the cyclohexane abstraction reactions and n-heptane. The production NTC reactions region is primarily driven by the low temperature branching path (mainly by n-heptanes). Toluene, on the contrary, is single stage fuel combustion with the very limited reactivity at low temperatures. The most important abstraction reactions involve the formation of the benzyl radical, which are thermally stable due to electron delocalization and their reaction with oxygen at auto-ignition temperatures is thermodynamically less advantaged. It is interestingly noted from Figure 5 that the cross reactions between n-heptane and toluene have positive sensitivity coefficients, which can increase the overall reactions rate for building up the radical pool as they transform benzyl radicals to the more reactive heptyl radicals. Summed together, the sensitivity bars of the reactions involved in the formation and decomposition of the fuel ketohydroperoxides will demonstrate how the low temperature branching agents reveal the presence of the low temperature mechanism role. Those, is fundamental to initiating the formation of the radical pool leading to the development of the low temperature heat release. The flux analysis is further studied in the next paragraph, highlights that about 94% of the OH radical is generated in this way.
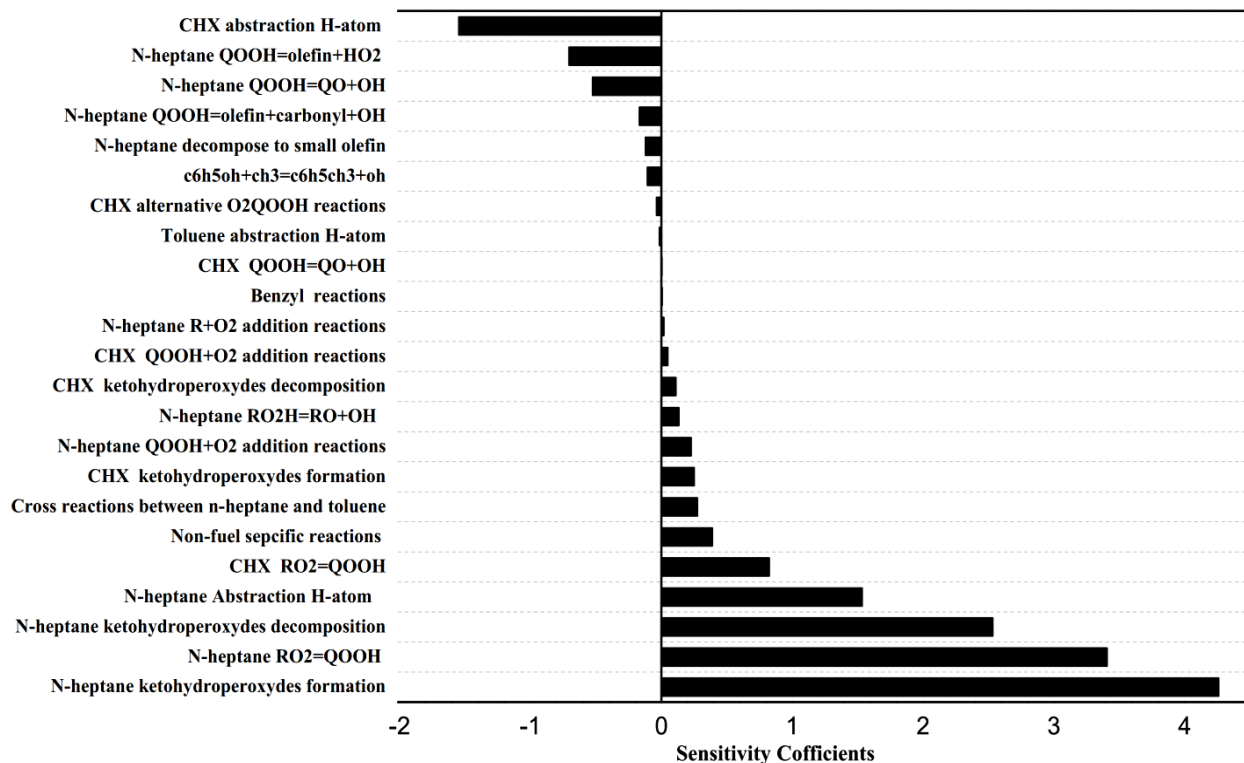
Figure 5 *Sensitivity coefficients of the OH radical with respect to pre-exponentials at the onset of the first stage pressure rise. (In cylinder T=822K, P=41bar, CAD=18 BTDC)*

5.2. Comparative performance of the two-components and "surrogate A" fuel modeling

To understand the main differences between the suggested surrogate chemistry, a local rate of production is conducted for the two surrogates (surrogate A and n-heptane/toluene two-component surrogates) prior to the onset of the first-stage ignition. So, the reactions controlling the first stage events can be examined. At such conditions, only fuel specific reactions are participating in the formation of the initial radical pool and from reactions analysis, the major fuel consumption path for n-heptane and toluene in two surrogates are quite similar. Most notably, the HO_2 and OH production rates at this time before the first stage ignition are respectively higher by nearly a factor of 1.5 and 1.2 for the surrogate A. Figure 6 plots calculated HO_2 and OH molar fractions during the ignition for both n-heptane/toluene two- component and "surrogate A" fuel. It is seen that during the early part of the first stage activity, <10% of toluene conversion, the OH concentration builds up to the similar levels for the two surrogates while the HO_2 concentration is about a factor of 2 lower for the n-heptane/toluene two component fuel. However, later during the first heat stage release, 10%—30% toluene conversion, the concentration of the HO_2 and OH are, respectively higher by a factor of 1.4 and 1.2 (on the average) of the surrogate A fuel. Higher OH radical concentrations are mainly due to cyclohexane low temperature reactions which results in higher reactivity. On the contrary, in the n-heptane/toluene two component mechanisms abstraction reactions on toluene lead to the formation of

the benzyl radicals that do not lead to many reactive OH radical.

As shown in Figure 7, flux analysis (supplemental data) of OH radical reveals that toluene concentration is almost the same as the cyclohexane in the surrogate mixture (10.6% and 11.6% molar fractions for toluene and cyclohexane respectively). However, apart from n-heptane abstraction reactions, OH radical is mainly consumed by cyclohexane abstraction reactions (12.77% of cyclohexane compared to 2.01% of toluene of OH consumption). This progresses further with low temperature branching and accelerates the overall reaction rate in the early stages of the first stages ignition. The main reactions for cyclohexane and toluene are as follows:

R1: $CHX+OH=CHXRAD+H_2O$

R2: $C_6H_5CH_3+OH=C_6H_5CH_2J+H_2O$
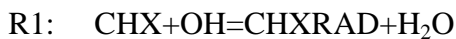
Both reactions are in competition, since R2 corresponds to a termination reaction due to the lower reactivity of the benzyl radical compared to the cyclohexyl radical, and R1 corresponds to a branching reaction (which accelerates the oxidation process). Termination reactions decrease the reactivity of the mixture by eliminating reactive radicals, thus causing lower heat release during the low temperature regime, while the reaction of cyclohexane with OH has the opposite effect.
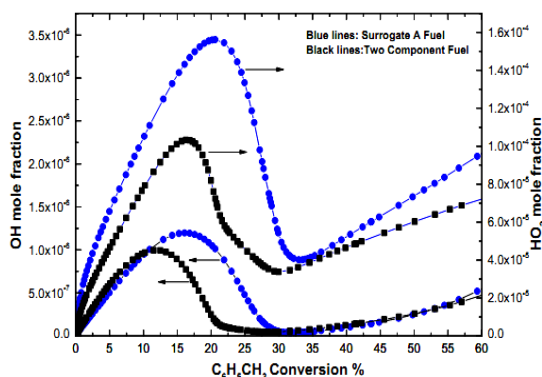

Figure 6 Calculated HO_2 and OH molar fractions during the ignition of two component and three component surrogates with initial conditions (In cylinder T=822K, P=41bar, CAD=18 BTDC)
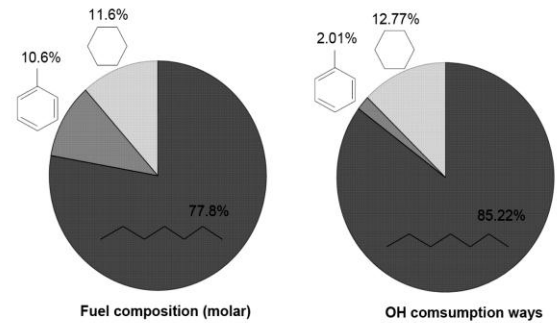

Figure 7 Surrogate-A mixture composition and aggregated OH consumption pathways of OH in respect to its tri-components: analysis conducted at the onset of the first stage pressure rise with initial conditions (In cylinder T=822K, P=41bar, CAD=18 BTDC)

In fact, cyclohexane is almost entirely consumed at the end of the first stage of ignition delay (72% consumed).

5.3. Constant volume analysis of each component performance of new surrogate fuel

In order to investigate the performance of each component in the mixture of the surrogate A fuel and reduce the computational time, constant volume simulation was carried
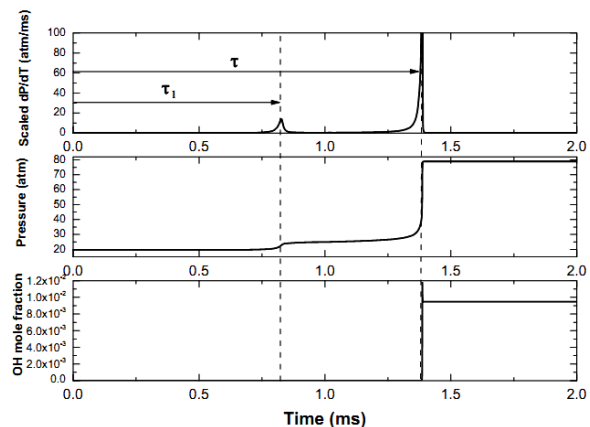

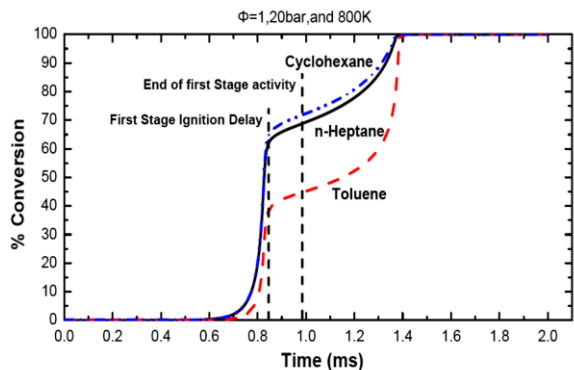*Figure 8 Illustration of ignition delay definition for two-stage combustion*

Fig.9 Percent fuel conversion profiles of tri-surrogate components, with initial conditions of 800 K, Φ=1, and 20 bar for constant volume simulation.
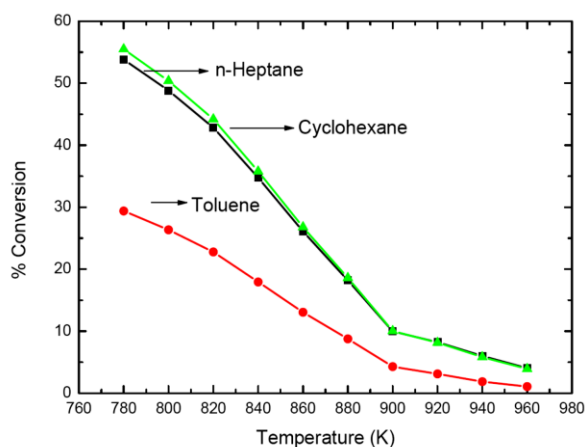

Fig. 10 Percent fuel conversion profiles of different surrogate components at the end of first stage Ignition delay. Constant volume simulations are conducted at varying initial temperatures with initial pressure of 20 bar, Φ=1.
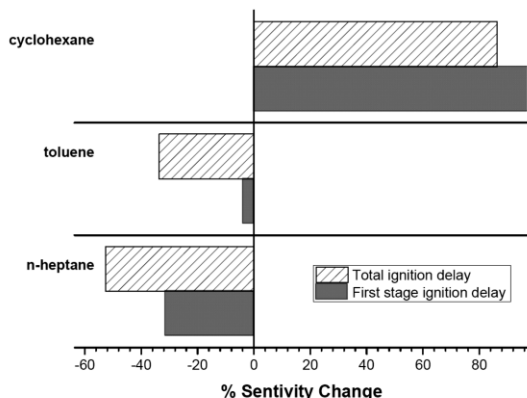

Fig.11 Percent sensitivity on first-stage ignition and total ignition delays based on 10% composition variation, with initial conditions of 800 K and 20 bar for constant volume simulation. The stoichiometric base surrogate composition is varied by doping it with an additional 10% (absolute increase) of each one of the tri-component fuel.

out by CHEMKIN 4.1 package (closed homogeneous batch reactor sub-routine). Because of the two stage ignition combustion, the ignition delay is defined according to the pressure rise curve.

Figure 8 describes the definition of total ignition delay (τ) and the first-stage ignition delay (τ_1). In the current work, τ and τ_1 are reported in units of milliseconds.

Figure 9 plots time variations of the percentage of fuel conversion for the surrogate A using constant volume adiabatic conditions with initial conditions corresponding to 800 K at 20 bar and stoichiometric mixture (Φ=1), with a special emphasis on the first stage ignition event. It is seen that at the end of the first stage ignition, the consumed percentages for n-heptane, toluene, and cyclohexane are approximately 69%, 44% and 72%, respectively. Hence, by the end of the first stage ignition substantial fractions of n-heptane and cyclohexane have achieved, while comparatively less fractions of the toluene have been consumed because the initial temperature is very sensitive to the ignition delay process.

Figure 10 shows the percentage of the fuel conversion for the different surrogate components with different initial temperature at the end of the first stage ignition delay. It is observed that when initial temperature is lower than 900K, the tri-component fuel conversion ratio reduces quickly. However, its influence moderates as the temperature continues to increase. N-heptane and cyclohexane have rapid fuel conversion rate at the first stage ignition delay. Those, is due to the low temperature radical pool effects which enhanced the overall reaction rate by their low temperature branching reactions. Toluene as a radical scavenger is more stable, since toluene does not show any cool flame behavior and it is expected to rapidly convert into stable intermediates, mainly benzyl and phenol by reacting with the very reactive

radical generated during the n-heptane and cylohexane low temperature reactions, thus decreasing the reactivity of the mixture. Finally, as the temperature increases, the fuel conversion percentages are close to zero and the cool flame behavior for low temperature heat release is inhibited.

A further numerical analysis is undertaken to investigate the effect of the compositional change in the surrogate mixture. Once more, surrogate A is used in the analysis. At the same temperature and pressure considered previously, in cylinder T=822K, P=41bar, CAD=18 BTDC, the base surrogate composition has been studied by adding 10% of each components of the n-heptane, toluene, and cyclohexane. The first stage and the total stage ignition delays are described as shown in Figure 8 and the sensitivity to the doped component (X) is calculated as:

$$s = \frac{\tau(base+10\% \ X) - \tau(base)}{\tau(base)} x100$$

$$s = \frac{\tau_1(base+10\% \ X) - \tau_1(base)}{\tau_1(base)} x100$$

Figure 11 shows the obtained sensitivity coefficients. The three different components show a distinctive effect on the first-stage ignition and the total delay. N-heptane shows a pronounced enhancing effect on the reactivity accelerating both the first and the second stage of the ignition. While toluene also reduces two stage ignition delay, which may due to cross reactions between n-heptane and toluene as they transform benzyl radicals to the more reactive heptyl radicals and increase OH production and a faster fuel conversion. Interestingly, cyclohexane has a significant inhibiting effect on both the ignition events, especially for total ignition delay, suggesting that cyclohexane concentration can be used as a "tuning knob" to control the delay between the two stages of the combustion. The peculiar effect of each component, which is

also representative of a chemical class, reinforces the hypothesis that the inclusion of an iso-alkane component or a revised choice of components could improve the agreement between the fuel surrogate and the actual diesel, leading to a better reproduction of the magnitude and the timing of the two ignition stages.

6. Conclusion

A new tri-component diesel surrogate fuel has been proposed and used to simulate the auto-ignition time of an HCCI diesel engine. The main results are summarized as follows:

1. Based on the composition analysis of real diesel, cyclohexane is firstly selected as a new representative component, which is added to the n-heptane/toluene two-component models. The new tri-component model which consists of 1140 species and 4590 reactions is developed by merging available well-developed detailed mechanisms of each component.

2. Experimental and numerical studies are carried out with proposed new model, single and two-component detailed kinetic models. The obtained results show that the suggested chemical kinetics model provides a remarkable agreement with the experimental ones and can capture the auto-ignition angle and the whole combustion process effectively.

3. At the early stage of the low temperature combustion, OH sensitivity analysis of the new model shows that the addition of the cyclohexane can significantly affect the radical pool. The main reactions are related to the low temperature mechanisms of the n-heptane and cyclohexane, while toluene has little influence on the first stage ignition process.

4. Flux analysis reveals that the new tri-component model is more reactive than two-component n-heptane/toluene model

owing to cyclohexane low temperature branching reactions.

In addition, the effect of compositional changes illustrates that the cyclohexane is most reactive species in the surrogate fuel mixture. This indicates that the cyclohexane could be a good candidate to control the delay between the two stages of the combustion. Furthermore, the addition of another component (such as olefins) to the surrogate will be explored in future work to improve the behavior of diesel surrogate compared to that of the target diesel fuel.

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