Computational Singular Perturbation Analysis of Super-knock in SI Engines

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Abstract

Pre-ignition engine cycles leading to super-knock were simulated with a 48 species skeletal *iso*-octane mechanism to identify the dominant reaction pathways that are present in super-knock. To mimic pre-ignition, a deflagration front was generated via a hot spot that is placed over the piston at close proximity to the end-wall. Computational singular perturbation (CSP) was used to analyze the chemical dynamics at various in-cylinder locations: a point at the center of the cylinder where the deflagration front consumes the air/fuel mixture and two points located at 3 mm from the end-wall where super-knock and mild knock occur. The CSP analysis of the point at the center of the cylinder reveals weak two-stage ignition-like dynamics with a short second stage. At the other points, a pronounced two-stage ignition is displayed with a long second stage. A distinct contribution of formaldehyde (CH_2O) at the second stage of ignition that adds to fast explosive modes in the super-knock points is not observed in the point at the center. A comparison between knock and super-knock analysis indicates that a similar set of reactions is responsible for the abnormal behavior but the fast explosive time scales are comparatively slower for knock, indicating lower reactivity, which results in the reduced intensity of knock. The analyzed results decoded important reactions responsible for the occurrence of super-knock.

Keywords: Computational singular perturbation; Pre-ignition; Super-knock

1. Introduction

To achieve clean and efficient operation, modern spark ignition (SI) engines are downsized to reduce fuel consumption and emissions [1]. To compensate for the reduced displacement, the intake pressure is boosted to achieve the desired power, resulting in unwanted premature auto-ignition, known as pre-ignition, of the reactant charge prior to spark timing. Pre-ignition sometimes lead to the occurrence of sharp pressure peaks and high frequency pressure oscillations, called super-knock. Due to their stochastic nature of pre-ignition and super-knock [2], their prediction and preventions of pre-ignition and super-knock have long been a serious technical challenge, in further improvement of efficiency in SI engines [3].

Pre-ignition and super-knock depend on available in-cylinder reactive local hot spots and mixture characteristics [4]. The fundamental questions on this subject are twofold. The first is concerning the source of pre-ignition. External sources such as carbon particles attached to engine walls and oil droplets that escape from the liner, as well as their composition are reported as the dominant source of pre-ignition [5-7]. The second question is about how the pre-ignition event develops into super-knock. Once the pre-ignition forms an initial flame front, the flame propagation increases the temperature and pressure of the end-gas mixture and may cause a secondary auto-ignition in another reactive hot spot, leading to detonation [8]. The amplitude of the pressure pulse generated depends on the rate of change of heat release at the hot spot.

Various direct numerical simulation (DNS) studies with hot spots [4, 8] have been performed to understand super-knock. All these studies focused on bulk mixture properties, gradients of temperature, ignition delay sensitivity and heat release to characterize the effect of the hot spot and resulting auto-ignition front. However, to the author's knowledge there is

limited information about the chemical characteristics of the system such as the dominant reaction pathways and gas species that cause super-knock.

Recognizing the general interest and relevance of pre-ignition and super-knock, full-cycle engine simulations were performed by the authors recently, which successfully reproduced the occurrence of super-knock events depending on the timing of the pre-ignition event [9]. To gain further insights, the simulation data are further analyzed in order to understand the detailed chemical characteristics inside the local unburned mixture that develops super-knock. To this end, detailed computational singular perturbation (CSP) analysis is performed at various selected locations to elucidate the reactions related to super-knock. Since the source of pre-ignition is highly stochastic and not known clearly, the objective of the study is not to identify the source of pre-ignition; instead the study is focused on the chemical behavior of unburned mixture that triggers super-knock after pre-ignition. In what follows, the CSP methodology is described, results are discussed, and concluding remarks are provided.

2. Problem Specification

The main scope of this paper is the analysis of the existing SI engine simulation data reproducing a super-knock event [9]. Fig. 1 shows the geometry of the engine used in simulations and the cut-sections of the mesh generated for the study. The specifications and operating conditions selected for the study are provided in Table 1. A base mesh size of 4 mm was used initially to generate the mesh, which was further refined with adaptive mesh refinement (AMR) based on the temperature difference (5 K) between adjacent cells. The Kelvin Helmholtz/Rayleigh Taylor spray breakup model was used to represent the spray break-up behavior [10, 11]. The droplets were grouped into parcels and injected with each parcel

containing 50 droplets. Collision between droplets was modeled using the no-time counter algorithm [12]. The radius of the evaporating droplet is calculated using the Frossling correlation. The droplets that impinge on the walls during injection form a wall film, which was accounted for with a wall film model [13]. Physical properties of *iso*-octane were used to represent the fuel spray behavior. A multi-zone approach, based on a well-stirred reactor model, was used to capture endgas auto-ignition coupled with the G-equation model to describe govern the pre-ignition flame propagation. In the multizone approach the cells are grouped based on temperature and equivalence ratio bins of 5 K and 0.05 increments [14, 15]. The in-cylinder simulations were performed using the Reynolds-averaged Navier-Stokes (RANS) method in conjunction with the renormalization group (RNG) k-epsilon model [16]. The heat loss from walls was calculated using the model developed by Han and Reitz [17]. The reader may refer to [9] for detailed information on the models used in the study.

Fig. 1. (a) Geometry of the SI engine, (b) Y-slice with mesh at mid-section of cylinder, (c) Z-slice with mesh at 8 mm from spark plug.

In the simulation cases under study, a pre-ignition event was represented by a hot spot of 1 mm radius with a temperature of 2000 K. The temperature of 2000 K was selected to initiate the pre-

Table 1. Engine specifications and operating conditions for the study.

Specifications	Values	Operating conditions	Values
Bore	85 mm	RPM	1200
Stroke	90 mm	Intake temperature	300 K
Connecting rod length	138 mm	Intake pressure	2 bar
Compression ratio	9.5	Global equivalence ratio	1
Valves	2-intake,2-exhaust valves	Fuel	<i>iso</i> -octane
Spark plug energy	40 mJ	Spark time	5 CAD aTDC

ignition front immediately after its introduction in the cylinder. The hot spot was placed over the piston close to the liner and was initiated at -20 CAD of TDC. A deflagration front was subsequently generated from the hot spot and propagates into the mixture. Three spatial locations were selected for the CSP analysis (see Fig. 2). Point A is located at center of the cylinder where no pressure peaks or oscillations are observed. The deflagration flame consumes the fuel at point A and hence no auto-ignition is observed. Points B and C are located at 3 mm from the end-wall opposite to the location of the pre-ignition hot spot, and develop super-knock with high pressure peaks and oscillations. The two points were selected based on their unique behavior so that the CSP analysis could reveal the dominant reactions that contribute to super-knock at these two points. The pressure histories at points A, B and C are shown in Fig. 2, exhibiting intense pressure oscillations at points B and C.

3. Computational Diagnostic Tools

Computational singular perturbation (CSP) is an algorithmic method of asymptotic analysis that has been widely used for the investigation of various combustion and biological processes. The reader may refer to [18, 19] for a more detailed description of the method. In the

Fig. 2. In-cylinder pressures and locations for points A, B and C, selected for CSP analysis at Z plane (8mm from spark plug).

current study, the following CSP tools were employed: (i) the eigenvalue participation index (EPI) which is a slightly modified version of the time scale participation index (TPI), and measures the absolute contribution (while the TPI measures the relative contribution) of each reaction to the characteristic time scale [20, 21] and (ii) the CSP Pointer (CSP Po), which identifies the scalar variables that mostly relate to the dominant CSP mode [22-25]. A reaction with a positive (negative) EPI value favors (opposes) the explosive character of the time scale, therefore it tends to promote (oppose) the ignition process. Moreover, high CSP Po values of the dominant mode identify scalar variables, which have a large impact on the evolution of the process.

For a system of N scalar variables (species plus temperature), there are a total of N CSP modes, for which the basis vectors are approximated by the right and left eigenvectors of the

Jacobian of the chemical source term [26, 27]. The characteristic time scale for each chemical mode is approximated by $\tau_n = |\lambda_n|^{-1}$, where λ_n is the eigenvalue of the n-th CSP mode ($n=1,\dots,N$). This kind of analysis is meaningful if there exists a large gap between the time scales of two adjacent modes, which will allow decomposition into fast (or exhausted) and slow (or active) modes. The fastest of the slow time scales, corresponding to the *fastest active mode*, is the one that characterizes the evolution of the system and the corresponding amplitude the largest of all modes. In homogeneous auto-ignition, the fastest active time scale is usually of explosive nature, and characterizes the action of slow and active chemical processes that drive the system away from equilibrium to result in ignition processes [20, 27].

Therefore, the main objective of the CSP analysis is to first identify the characteristic time scales of explosive nature, and then to explore the important reactions that contribute to their generation. Additional insight is obtained by investigating the scalar variables associated most to the related CSP modes.

The CSP analysis was applied to points A-C shown in Fig. 2 throughout the temporal evolution, which allows to compare flame and super-knock chemistry and identify differences between them. In general, the results of point B and C were found to be both qualitatively and quantitatively similar. Consequently, in the following, only the results for point B will be presented and unless otherwise stated, the conclusions will be representative for both points that exhibit super-knock. The chemical kinetics mechanism that was used includes $N=48$ species and $K=152$ reversible reactions and has been validated in a wide range of initial conditions [28]. The top dead center (TDC) of the engine cycle is at 1080 CAD for all figures presented below.

4. The Dynamics of the Systems

The time scales that characterize the dynamics of the spatial points A and B are displayed in Fig. 3, with black solid and red dashed lines representing dissipative and explosive time scales, respectively. As shown in each case, almost all time scales are of dissipative nature except for few (at most two in each case) that are the explosive ones; a fast one and a slow one. In both cases, a time scale gap is generated and the fast explosive time scale ($\tau_{e,f}$) is among the fastest of the slow time scales. The gap among the time scales suggests that a valid reduced model can be constructed, while the placement of ($\tau_{e,f}$) suggests that this is the characteristic time scale during the process. In addition, it was found that the amplitude of the fast explosive mode is always much larger compared to the rest, in both cases under examination. Therefore, in the following, the analysis will focus on the reactions that have the largest contribution to $\tau_{e,f}$ and on the species that are mostly associated to the related fast explosive mode.

Fig. 3. The developing time scales for point A (left) and point B (right). Solid black and dashed red lines represent dissipative and explosive time scales, respectively.

The evolution of the explosive time scales along with temperature is displayed in Fig. 4 for both spatial points A and B. For a comparison of the CSP diagnostics between the two points, the x-axis has been normalized against the CAD at the maximum temperature gradient for each point, respectively (1079.18 for point A and 1091.55 for point B). Note that, while both cases

may appear to represent auto-ignition of the local mixture, the mixture at point A did not undergo auto-ignition but was rather engulfed by the flame propagation. Therefore, the temperature rise shown for point A shows the flame propagation time scale. The temporal points (P₁-P₆) where the CSP diagnostics will be discussed next are also marked in Fig. 4 for spatial points A and B.

Fig. 4. The developing explosive time scales (τ_e) and the temperature evolution for points A (solid black and blue) and B (dashed red and orange).

Figure 4 reveals that in both cases, a fast explosive time scale initially exists, gradually accelerating and at some point meets a slow one and then both disappear. Briefly afterwards a fast explosive time scale re-appears, accelerating more quickly until it starts to decelerate rapidly, meets a slow explosive time scale and then both disappear. The second merging point is just before temperature reaches its maximum rate of change. The disappearance and reappearance of the fast explosive time scale briefly afterwards is typical of multi-stage ignition [25,29]. Therefore, based on the profiles of the explosive time scales, it is concluded that both cases exhibit two-stage ignition chemistry, although the extent of the second stage is much more pronounced for point B. Again, the behavior at point A indicates an early arrival of the flame

front while the local mixture is undergoing the first stage ignition, and the subsequent second stage ignition chemistry was driven by the flame passing.

Table 2 summarizes all the reactions that were identified as important contributors to the generation of $\tau_{e,f}$ in both cases under investigation. In the following, the subscripts "*f*" and "*b*" stand for forward and backward reaction, respectively. Tables 3 and 4 summarize the CSP diagnostics for points A and B. For point A, P₁-P₄ belong to the first ignition stage and P₅-P₆ to the second, while for point B, first stage is represented by P₁-P₃ and second stage by P₄-P₆. In both spatial points, the first stage is dominated by the same set of reactions, while their contributions to $\tau_{e,f}$ are much more enhanced in point B due to the higher temperature. Comparison of the results from P₁ to P₃ shows that the temperature of point B is increased by approximately 80 K compared to point A (see Fig. 5(a)). The temperature stratification in the cylinder is the result of temperature drop caused by fuel evaporation during direct fuel injection and heat transfer between the in-cylinder gas and fuel droplets. Furthermore, since point B is located further away near the end wall, the long duration of the flame propagation compresses and heats up the end-gas. Consequently, point B spends much longer time developing radicals through the first stage chemistry at higher temperature, making it highly reactive by the time the mixture enters the second stage of ignition. On the other hand, point A only develops the first stage ignition chemistry for a short period of time at lower temperature; hence its second stage chemistry becomes active only upon the arrival of the flame.

Note also that during the first ignition stage, point B is by approximately 50% fuel leaner compared to point A. This is attributed to the initial mixture distribution resulting from the large scale flow and mixing, resulting in charge stratification. However, the net chemical reactivity appears to be dominated by the temperature effect.

Table 2: The reactions providing significant contribution to the generation of the fast explosive timescale $\tau_{e,f}$, during the ignition at spatial points A and B.

13	$iC_8H_{18}+O_2 \leftrightarrow C_8H_{17}+HO_2$	34	$C_2H_4+OH \leftrightarrow C_2H_3+H_2O$	84	$HCO+CH_3 \leftrightarrow CO+CH_4$
14	$C_8H_{17}+O_2 \leftrightarrow C_8H_{17}O_2$	52	$H+O_2 \leftrightarrow O+OH$	89	$CH_2O+H \leftrightarrow HCO+H_2$
15	$C_8H_{17}O_2 \leftrightarrow C_8H_{16}OOH$	54	$H_2+OH \leftrightarrow H_2O+H$	91	$CH_2O+OH \leftrightarrow HCO+H_2O$
16	$C_8H_{16}OOH+O_2 \leftrightarrow O_2C_8H_{16}OOH$	64	$HO_2+OH \leftrightarrow H_2O+O_2$	93	$CH_2O+HO_2 \leftrightarrow HCO+H_2O_2$
17	$O_2C_8H_{16}OOH \leftrightarrow C_8KET+OH$	65	$HO_2+HO_2 \leftrightarrow H_2O_2+O_2$	97	$CH_3+O_2 \leftrightarrow CH_2O+OH$
18	$C_8KET \leftrightarrow C_6H_{13}CO+CH_2O+OH$	67	$H_2O_2 (+M) \leftrightarrow 2OH (+M)$	98	$CH_3+HO_2 \leftrightarrow CH_3O+OH$
20	$iC_8H_{18}+OH \leftrightarrow C_8H_{17}+H_2O$	72	$H_2O_2+OH \leftrightarrow HO_2+H_2O$	99	$CH_3+H(+M) \leftrightarrow CH_4(+M)$
23	$iC_8H_{18}+HO_2 \leftrightarrow C_8H_{17}+H_2O_2$	77	$HCO+M \leftrightarrow H+CO+M$	103	$CH_3+HO_2 \leftrightarrow CH_4+O_2$
24	$C_8H_{17} \leftrightarrow C_3H_7+C_3H_6+C_2H_4$				

Table 3: Values of the largest EPI and CSP Po of the fast explosive mode for point A. Refer to Fig. 4 for the selected points P1-P6.

Point	P ₁		P ₂		P ₃		P ₄		P ₅		P ₆	
CAD	1057.6063		1063.0029		1068.4015		1078.1095		1078.9730		1079.1356	
CAD/CAD _{ign}	0.98000		0.98500		0.99001		0.99900		0.99980		0.99995	
$\lambda_{e,f}$ [s]	2.34E+02		5.16E+02		9.87E+02		3.19E+03		2.06E+04		1.68E+05	
$\tau_{e,f}$ [s]	4.28E-03		1.94E-03		1.01E-03		3.13E-04		4.85E-05		5.93E-06	
T [K]	649		674		696		754		1216		1523	
$Y_{iC_8H_{16}}$	6.88E-02		6.73E-02		6.57E-02		6.39E-02		3.72E-02		1.39E-02	
EPI	15f	94	15f	210	15f	411	15f	1741	67f	7582	52f	149324
	18f	89	18f	195	18f	369	18f	1559	98f	7541	98f	54529
	16f	68	16f	161	16f	328	15b	-1514	52f	5843	99f	-41966
	15b	-68	15b	-161	15b	-328	16f	1508	13f	4897	64f	-40777
	23f	29	23f	65	23f	122	20f	692	103f	-4344	77f	30166
	97f	14	97f	35	97f	56	98f	418	64f	-3919	54f	26422
	17f	7	17f	20	17f	49	91f	-412	93f	1913	89f	-25597
	16b	-6	16b	-17	16b	-43	17f	339	34f	1543	84f	-21505
CSP Po	$C_8H_{17}O_2$	0.42	$C_8H_{17}O_2$	0.41	$C_8H_{17}O_2$	0.42	C_8KET	0.49	T	1.04	T	1.03
	C_8KET	0.38	C_8KET	0.38	C_8KET	0.37	$C_8H_{17}O_2$	0.48	iC_8H_{18}	-0.05	O_2	-0.07
	HO_2	0.12	HO_2	0.12	HO_2	0.13	HO_2	0.01	H_2O_2	-0.04	H_2	0.06

Fig. 5. (a) Initial in-cylinder temperature, (b) *iso*-octane mass fraction distribution at -20 CAD aTDC (start of deflagration front).

Table 4: Values of the largest EPI and CSP Po of the fast explosive mode for point B. Refer to Fig. 4 for the selected points P1-P6.

Point	P ₁		P ₂		P ₃		P ₄		P ₅		P ₆	
CAD	1069.7229		1075.1801		1080.6565		1090.4638		1091.3369		1091.5003	
CAD/CAD _{ign}	0.98000		0.98500		0.99000		0.99900		0.99980		0.99995	
$\lambda_{e,f}$ [s]	2.35E+03		3.75E+03		5.19E+03		1.17E+03		3.24E+03		2.04E+05	
$\tau_{e,f}$ [s]	4.25E-04		2.67E-04		1.93E-04		8.52E-04		3.09E-04		4.91E-06	
T [K]	735		751		779		926		966		1360	
y_{iC8H16}	3.40E-02		3.57E-02		3.82E-02		4.70E-02		4.30E-02		2.18E-02	
EPI	15f	1106	15f	1935	15f	4077	67f	1608	67f	3513	67f	66097
	16f	959	16f	1693	15b	-3639	24f	-589	24f	-1101	98f	59966
	15b	-958	15b	-1692	16f	3567	98f	380	98f	1028	52f	55658
	18f	879	18f	1490	18f	2798	20f	332	65f	-631	64f	-47725
	98f	213	98f	424	14f	999	93f	306	93f	625	13f	35608
	23f	198	17f	375	14b	-967	65f	-282	103f	-611	103f	-30330
	17f	189	16b	-354	20f	948	23f	279	20f	600	34f	18845
	16b	-177	23f	254	17f	936	91f	-264	91f	-511	91f	17575
					16b	-915	103f	-241	72f	-426	99f	-14856
CSP Po	C ₈ H ₁₇ O ₂	0.43	C ₈ H ₁₇ O ₂	0.49	C ₈ H ₁₇ O ₂	0.58	T	1.00	T	0.94	T	1.33
	C ₈ KET	0.37	C ₈ KET	0.40	C ₈ KET	0.51	H ₂ O ₂	0.14	H ₂ O ₂	0.09	H ₂ O ₂	-0.21
	HO ₂	0.11	HO ₂	0.08	CH ₂ O	-0.11	iC ₈ H ₁₈	-0.08	iC ₈ H ₁₈	-0.03	iC ₈ H ₁₈	-0.07

The enhanced reactivity at point B is highlighted by the fact that its $\lambda_{e,f}$ is much larger throughout the entire stage: ten times larger at P₁ and five times larger at P₃. The EPI values reveal that the largest contributors to $\lambda_{e,f}$ during the first stage (P₁-P₃) in both cases are 15f, 18f, 16f and 15b, the first three favoring the explosive character of $\lambda_{e,f}$, thus, promoting ignition,

while the last one favors the dissipative character of $\lambda_{e,f}$. These reactions compose the typical low-temperature oxidation pathway of *iso*-octane: 15f is the isomerization of $C_8H_{17}O_2$ to $C_8H_{16}OOH$, 16f is the oxidation of $C_8H_{16}OOH$ to $O_2C_8H_{16}OOH$, 18f decomposes C_8KET to products and OH. Reaction 15b competes with 16f and their contributions are practically cancelled. Additional notable positive contributions are provided by 23f (involving C_8H_{17}), 97f/98f (involving CH_3 to form OH) and 17f (the low temperature degenerate branching to form OH). At the same time, reaction 16b competes with 17f in the consumption of $O_2C_8H_{16}OOH$, but the competition works in favor of 17f. Finally, in both cases, the CSP Po identifies RO_2 and C_8KET as the variables mostly related to the fast explosive mode, while HO_2 plays a secondary role.

For point A towards the end of the first stage ignition (e.g., P_4), the temperature is 25 K lower and the mass fraction of iC_8H_{18} is almost two times larger, compared to the respective instant in the super-knock case (e.g., P_3). In contrast, at point B (50 % leaner to point A) the mass fraction of iC_8H_{18} gradually increases during the first stage due to strong local mass fraction gradients, incurring rapid diffusion of fuel in the neighboring mixture (see Fig. 5(b) circled region). Fig. 6 shows the evolution of the mass fraction of iC_8H_{18} for points A and B with $\tau_{e,f}$ overlaid. It is shown that the instant when $\tau_{e,f}$ disappears in the point B case, $y_{iC_8H_{18}}$ reaches a local maximum and after that it decreases due to decomposition of iC_8H_{18} . However, its brief decrease is followed by an unexpected increase during which τ_e reappears but with larger values. The fuel is eventually consumed when $\tau_{e,f}$ starts its final steep acceleration. This behavior is distinctly different from point A where the reappearance of τ_e is accompanied by a rapid consumption of the fuel.

Fig. 6. The developing explosive time scales (τ_e) and y_{iC8H18} evolution for points 1 (solid black and blue) and 3 (dashed red and orange).

These results suggest that point B would probably ignite even earlier if the increase of the fuel after the first stage would not occur, since the second stage would be shorter and as it will be shown next, it would be dominated by the same set of reactions in both cases. In summary, the second stage of point B is characterized by a period over which $\tau_{e,f}$ is accelerating slowly and its values are larger than the last part of the first stage, followed by a period that is rapidly accelerating leading eventually the system to ignition. On the other hand, point A does not develop the second stage chemistry until the arrival of the flame, which raises the local temperature rapidly and induces a steep acceleration of the second stage ignition chemistry. The CSP diagnostics of point B at P_4 and P_5 are representative of the dominant dynamics at the first part of the second stage. Table 4 indicates that the dominant reaction is the chain branching 67f, which decomposes H_2O_2 to two OH molecules, thus promoting ignition.

From the rest of the reactions that have a considerable contribution to $\tau_{e,f}$, the following observations can be made: (i) reaction 98f has a gradually increasing effect, promoting ignition, (ii) reactions 24f, 20f, 23f (the first opposing and the other two promoting ignition) which have a contribution of roughly 20% in total, are related to the consumption of iC_8H_{18} or C_8H_{17} and (iii) except for 67f, hydrogen-related chemistry has a very weak effect. The CSP Po identifies

temperature as the variable mostly related to the fast explosive mode, an indication that these two points fall in the thermal runaway regime. It is noted though, that H_2O_2 is also pointed with a notable value, which is a distinct difference compared to point A. Eventually, as Table 4 shows at P_6 , $\tau_{e,f}$ for point B is led to a rapid acceleration mainly by the contributions of 67f, 98f, 13f. Additionally, the chain branching 52f provides some considerable contribution accelerating the evolution of the system towards ignition.

The contribution of the hydrogen-related 52f is basically the fundamental difference between point A and B during the second stage, since in the case of point A, reaction 52f has a considerable contribution at an earlier stage (at P_5 in Table 4) compared to point B where it becomes dominant later (at P_6 in Table 4). At the same time, the relative contribution of 98f to $\tau_{e,f}$ is larger for point A but the opposite holds for 67f. Moreover, only reaction 13f, which includes iC_8H_{18} , has a considerable contribution to $\tau_{e,f}$ as opposed to point B where reactions 24f, 20f, 23f were also identified. Finally, the CSP Po identifies temperature as the variable mostly related to the fast explosive mode, verifying that as in point B, the second stage relates to the thermal runaway regime.

To further validate the above findings as the characteristics of super-knock event, an additional engine simulation was performed at the same operating conditions, but with pre-ignition initiated at -5 CAD aTDC. The temperature and fuel distribution are comparable to the pre-ignition cycle, as shown in Fig. 7. The same two locations B and C were examined and it

Fig. 7. (a) Temperature (b) iso-octane mass fraction at start of spark timing, pressures at local point A', B' and C' are shown.

was found that point C for this case only led to mild knock with a lower pressure peak. Therefore, a CSP analysis was applied to this point, which is referred to as C' in order to distinguish it from point C in the previous analysis. Details on the CSP diagnostics for this point are provided in Table 5 and Fig. 8.

To highlight the key findings, point C' exhibited a two-stage ignition characterized by a distinct set of explosive time scales, which were more pronounced compared to point A. The

Fig. 8. The developing explosive time scales (τ_e) and the temperature evolution for points A (solid black and blue) and C' (dashed red and orange).

Table 5: Values of the largest EPI and CSP Po of the fast explosive mode for point C'. Refer to Fig. 8 for the selected points P1-P6.

Point	P ₁		P ₂		P ₃		P ₄		P ₅		P ₆	
CAD/CAD _{ign}	1079.4468		1084.9539		1090.4613		1100.3751		1101.2559		1101.4214	
CAD	0.98000		0.98500		0.99000		0.99900		0.99980		0.99995	
$\lambda_{e,f}$ [s]	1.42E+03		1.30E+03		1.24E+03		2.90E+03		3.83E+04		1.35E+05	
$\tau_{e,f}$ [s]	7.05E-04		7.72E-04		8.05E-04		1.93E-04		2.61E-05		7.40E-06	
T [K]	707		704		703		812		1239		1462	
$y_{iC_8H_{16}}$	5.72E-02		5.73E-02		5.84E-02		6.11E-02		3.32E-02		1.72E-02	
EPI	15f	624	15f	602	15f	609	15f	2417	67f	15778	52f	95708
	18f	552	18f	538	18f	547	20f	2347	98f	14417	98f	46998
	16f	502	16f	480	15b	-483	15b	-2229	52f	9312	64f	-34409
	15b	-502	15b	-480	16f	482	16f	2205	103f	-8921	13f	25923
	23f	145	23f	121	23f	102	18f	1492	13f	7891	99f	-25311
	98f	103	98f	94	98f	81	91f	-1478	64f	-7359	103f	-21764
	17f	82	17f	77	17f	76	14f	1064	93f	4743	89f	-19831
	16b	-74	16b	-68	16b	-68	14b	-1036	34f	3516	77f	17662
	103f	-40	103f	-53	103f	-59	98f	963	65f	-2939	54f	15679
CSP Po	C ₈ H ₁₇ O ₂	0.45	C ₈ H ₁₇ O ₂	0.47	C ₈ H ₁₇ O ₂	0.49	CH ₂ O	0.37	T	1.16	T	1.12
	C ₈ KET	0.39	C ₈ KET	0.41	C ₈ KET	0.44	T	0.26	H ₂ O ₂	-0.14	iC ₈ H ₁₈	-0.07
	HO ₂	0.11	HO ₂	0.08	HO ₂	0.04	C ₂ H ₄	0.15	iC ₈ H ₁₈	-0.06	CH ₂ O	-0.06

temperature at point C' was found to be slightly higher (by 8%) during the first stage of ignition compared to point A. As in point B, the mass fraction of iC₈H₁₈ gradually increased during the

first stage and at the early part of the second stage. The CSP diagnostics revealed that the first stage is dominated by the same set of reactions reported for points A and B, although the characteristic time scale is much faster compared to point A (80% at P_1 , 60% at P_2 and 20% at P_3), an indication of enhanced reactivity. However, $\tau_{e,f}$ of point C' (mild knock) is slower compared to point B (super-knock) (70% at P_1 , 300% at P_2 and 700% at P_3).

As in the super-knock case (point B), the increased reactivity of point C' during the first stage of ignition is due to the enhanced role of 15f, 16f and 18f (approximately six times larger compared to point A). The contribution of 98f to $\tau_{e,f}$ was the one that increased the most (roughly two orders of magnitude at the early part of the first stage), followed by 17f and 16b (more than ten times larger), as it was previously reported in the analysis of point B. On the other hand, the second stage of ignition was found to be dominated by the hydrogen-related chain branching reactions 67f and 52f, and the iC_8H_{18}/C_8H_{17} -related reactions were found to have secondary role to $\tau_{e,f}$, which is consistent with what was reported for the second stage of point A, but different from the second stage of point B. All these results indicate that the same mechanism drove both the super-knock and the mild-knock cases, with its features being more striking in the super-knock case.

5. Conclusions

Pre-ignition cycles were simulated introducing a hot spot over the piston to initiate a deflagration front at -20 and -5 CAD of TDC. CSP analysis was performed on locations that exhibited super-knock (points B and C) and mild knock (point C') behavior to understand the dominant chemical reactions involved in their ignition and compared to those from a point that is swept by the flame front (point A).

The comparison between points A and B revealed that both points exhibited two-stage ignition behavior based not only on the profiles of their respective $\tau_{e,f}$ but also from the dominant chemical pathways. However, the two-stage ignition is much more pronounced in the super-knock related point B compared to point A, since the latter is swept by the flame and the two-stage profile is very weak. In both cases, the first/second stage relates to the chemical/thermal runaway regime. In general, the chemical pathways dominating the first stage of both spatial points are the typical pathways that are commonly found in the literature. However, during the first stage, point B is more reactive than point A, due to: (i) the enhanced role of 15f, 18f and 16f by one order of magnitude; (ii) the increased effect of 98f by two to three orders of magnitudes; and (iii) the augmented (by 20-30 times) contribution of 17f. These findings are the result of the higher temperature that characterizes point B. Eventually, point B enters the second stage (thermal runaway) earlier than point A, but its fuel mass fraction has increased due to diffusion as a result of local concentration gradients. This event results in the increased role of reactions 24f, 20f, 23f (which include the consumption of iC_8H_{18} and C_8H_{17}), which happens at the expense of the hydrogen-related reactions 67f and 52f. On the other hand, in the case of point A, the second ignition stage is dominated by hydrogen-related chemistry, and mainly reactions 67f and 52f drive the system to ignition.

The analysis of point C' revealed the same characteristics as those observed in the super-knock case but quantitatively milder: (i) a less pronounced two-stage ignition occurs; (ii) the temperature is increased as compared to point A but the increase is not as large as for point B; (iii) the fuel mass fraction gradually increases during the first-stage ignition and increases even more before the initiation of the second stage; (iv) the increased reactivity during the first stage is due to the 15f, 18f, 16f, 98f, 17f, with the effect of the last two being much more significant

(especially 98f). However, the second stage was found to be dominated by hydrogen-related chemistry, resembling the dominant pathway of point A and considerably different from the one observed for point B.

The above findings suggest that the reactivity of the system changes significantly in hot spots, being increased during the first stage, but decreased during the early part of the second stage due to the increase of the fuel mass fraction, which is the result of the local concentration gradients. The increased temperature in the hotspots enhances the effect of the typical first-stage ignition pathway, but significantly more noticeable is the increase of the effect of 98f and 17f.

Acknowledgements

The work was performed with the funding from King Abdullah University of Science and Technology. The simulations utilized the KAUST supercomputing facility.

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