Auto-Ignition of a Hexadecane Droplet Mixed with Different Octane Number Fuels at Elevated Pressures To Investigate the Pre-Ignition Behavior

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ABSTRACT: Pre-ignition is an abnormal combustion event that may occur in boosted direct injection gasoline engines, where one or more auto-ignition events are observed before spark ignition. Due to the direct injection of fuel into the cylinder, some liquid fuel may splash off the walls, pulling lubricating oil with it. The auto-ignition of liquid fuel/lubricant droplets is considered as one of the possible sources of pre-ignition. To assess this stochastic phenomenon in a controlled way, the auto-ignition of a single droplet of a hexadecane-fuel mixture was investigated, with hexadecane serving as a surrogate for the lubricating oil. This experiment included suspending a single hexadecane-fuel mixture droplet on a thermocouple bead in preheated air, at a temperature of 300 ± 4 °C, in a constant volume chamber over a wide range of pressures (4–30 bar). Four different fuels with a range of research octane number (RON) between 70 and 120 were mixed with hexadecane at a volume percentage of 75% hexadecane to 25% fuel to investigate the time to ignition of the droplet, designated as TI. The TI was measured by recording the droplet temperature history simultaneously with high-speed droplet imaging. The droplet ignition is triggered by the auto-ignition of the combustible mixture formed by the hexadecane-fuel mixture's vapor that mixes with the hot ambient air around the droplet. An empirical model was proposed to predict the TI in terms of pressure and the mixture's RON. At constant pressure, the rate of evaporation of the mixture's droplet increases with increasing RON. The time to ignition is seen to increase exponentially as the fuel's RON used in the mixture increases. On the other hand, for a given fuel RON, the time to ignition decreases with increasing ambient pressure. The empirical model shows that at pressures above 20 bar, the dilution of hexadecane by the different fuels has no significant effect on delaying the auto-ignition of the droplet.

INTRODUCTION

Automotive manufacturers are continually endeavoring to improve the performance and efficiency of internal combustion engines to reduce fuel consumption and emissions. Downsized boosted gasoline direct injection (GDI) engines are a promising technology to achieve these goals. Downsizing engines allow for extracting the same power from smaller engines, which reduces the amount of the air-fuel mixture that goes into a naturally aspirated engine. However, such technology remains constrained by several abnormal combustion phenomena, such as knock and pre-ignition. A new destructive combustion mode, known as low-speed pre-ignition (LSPI), is occasionally observed in these highly boosted GDI engines.^{1,2} The LSPI combustion mode is characterized as a stochastic phenomenon that results in the transformation of a normal propagating flame to a severe knocking event^{1,2} and begins before the firing of the spark plug. This pre-ignition event may be initiated by an ignition source such as hot spots in the chamber and carbon particle deposits from the previous cycle.

The potential causes of LSPI, such as auto-ignition in the gaseous phase and the ignition of the fuel-air mixture due to either liquid droplets or solid particles, were described by Zaccardi and Escudié.³ The early occurrence of LSPI before the spark timing may lead to flame propagation that results in

too rapid pressure rises due to the advanced combustion phasing. This may cause violent end gas knock or even super-knock for events that transition to developing detonation.⁴ However, not all LSPI cycles exhibit super-knock.⁵

Toyota Motors and JX Nippon Oil and Energy Corporation investigated the effect of fuel compounds on pre-ignition under high-temperature and high-pressure conditions.⁶ They investigated the effects of pre-ignition temperature, which, under their conditions, was lower compared to a naturally aspirated engine. They reported that pre-ignition temperature showed a better correlation with the motor octane number (MON) and auto-ignition temperature compared to the research octane number (RON). However, the complete mechanism of the fuel reaction was not determined in their study.⁶

Amann et al.¹ demonstrated that fuel chemical composition had a strong impact on the occurrence and intensity of LSPI. Their study showed an increase in LSPI occurrence with fuel blends with high levels of aromatics. On the contrary, oxygenated fuels and low aromatic blends reduced the frequency of LSPI occurrence. Furthermore, they observed different knock and auto-ignition characteristics of the test

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Table 1. List of the Previous Works Related to the Droplet Ignition in Conjunction with the Pre-Ignition Phenomenon

authors	experimental procedure	observation
Jatana et al. ¹⁴	Experiments were conducted in a Ford Ecoboost engine. Cyclopentanone, 2-methyl-1-butanol, and ethylbenzene were mixed at 25% concentration with gasoline.	All mixtures approximately doubled the pre-ignition occurrence compared to baseline gasoline fuel.
Fei et al. ¹⁶	Experiments were conducted in a rapid compression machine (RCM). Lubricant oil droplet ignition in the fuel-air mixture was investigated at elevated temperatures and pressures.	For their experimental conditions, the ignition delay time of the fuel-air mixture was not affected by lubricant oil droplets.
Zahdeh et al. ²	Experiments were conducted in a four-cylinder engine. Pre-ignition event was investigated for single and double injection for a different oil.	Ignition of the diluted fuel-oil mixture was identified as a reason behind the auto-ignition of the fuel.
Amann et al. ¹	Experiments were conducted in a boosted gasoline direct injection engine. A standard gasoline fuel with an octane rating of 87 and 5W20 lubricant oil was used.	Among other reasons, the chemical and physical properties of the fuel and lubricant could cause pre-ignition.
Dahnz et al. ¹³	Experiments were conducted in a turbocharged, gasoline direct-injection 4-cylinder engine.	Lubricant oil droplets released from the piston top land into the combustion chamber could cause pre-ignition.
Ohtomo et al. ¹⁰	Experiments were conducted in RCM in a fuel-air mixture environment where a single oil droplet was injected.	The initial droplet temperature had to be higher, in their case, more than 250 °C for the oil vapor to ignite before the fuel-air mixture.
Kuboyama et al. ¹⁵	Experiments were conducted in a four-cylinder engine to investigate the effect of engine operating parameters. Imaging techniques were implemented in the study.	Several sources were observed to be causing pre-ignition in an engine, such as glowing particles, deposit fragments, and lubricant oil droplets.

fuels in the DI-SI engine even with similar RON and MON ratings. Based on their findings and previous studies, they suggested the lubricant or fuel-based hydrocarbon deposits on the piston crevices as the leading cause of LSPI. In a study of the effect of market variations in gasoline composition on aspects of stochastic pre-ignition (SPI), Mansfield et al.⁷ found a strong indication that the main effect of aromatic plus olefin on primary SPI frequency is to enhance deposit dynamics. These deposits increase the possible sites where the number of ignitions can occur and hence increases the frequency of the SPI event.

Kalghatgi and Bradley⁸ concluded that the pre-ignition in turbocharged engines is characterized by (i) higher pressures and temperatures briefly attributing in the rise to gas-phase pre-ignition; (ii) auto-ignition at even higher pressures and temperatures, which might result in severe knock; (iii) injector sprays striking surrounding surfaces and stripping lubricating oil from them; (iv) lubricant mixing with fuel and forming a critically low ignition-delay mixture, with a tendency to auto-ignite in hot charge atmosphere; (v) residue of gas or particles forming hot spots; and (vi) varying pre-ignition characteristics of different fuels. Hence, for a droplet to ignite, there must be a critical amount of heat to initiate the auto-ignition.

Several studies^{9–13} have attributed pre-ignition events to the auto-ignition of lubricant oil-fuel mixture droplets. The fuel spray injected into the cylinder has an interaction with the lubricant oil film on the cylinder walls. The splashing of this injected fuel pulls the oil off the wall and forms droplets of the oil-fuel mixture. The interaction with the fuel dilutes the lubricating oil and changes its properties. Therefore, it is important to understand lubricating oils, with and without fuel dilution, as a possible ignition source in pre-ignition and super knock events.

By blending ketone (cyclopentanone), alcohol (2-methyl-1-butanol), and ethylbenzene with gasoline to a 25% mass fraction, Jatana et al.¹⁴ found that fuels with similar boiling properties and octane numbers can exhibit similar LSPI number counts but with vastly different LSPI magnitudes and intensities. Kuboyama et al.¹⁵ visually analyzed the pre-ignition phenomena caused by oil droplets in a highly boosted spark ignition engine. They reported that the mixture of lubricant oil and fuel accumulates in the piston crevice area, which ignites at low oxygen conditions. Fei et al.¹⁶ found out that within the pressure range of 27–31 bar, lubricating oil droplet explosion seems to have a positive effect on the amplitude of the pressure oscillation after auto-ignition of the end gas of the ambient

mixture. Their finding leads to the conclusion that, at the environmental and initial conditions applied in their study, the lubricating oil droplet does not make an obvious impact on the ignition delay of the combustible ambient gaseous mixture. However, in their study, the lubricating oil is not mixed with the fuel. The possibility of the dilution of the lubrication oil by the fuel was not considered in their work. This may be the reason why the rate of evaporation of the oil droplet in their study is relatively low. In this current study, the possibility of the lubrication dilution by the fuel is the primary consideration.

Previously, Ohtomo et al.¹⁰ used hexadecane as one of the components for their lubricant oil droplet. Similarly, Distaso et al.¹⁷ also showed that C16–C18 hydrocarbons could be considered as a surrogate for commercial lubricant oil. Moreover, Kuti et al.¹⁸ have also reported that hexadecane can reproduce the chemical ignition delay of large alkanes present in lubricant oils. Since *n*-hexadecane (C₁₆H₃₄) has similar ignition characteristics to that of typical lubricant oils,¹⁸ it is considered as a lubricant surrogate in this work. The previous works on the ignition of the droplet in conjunction with the pre-ignition phenomenon can be summarized in Table 1.

Experiments are carried out in a constant volume combustion chamber to study the effects of the RON and MON at varying pressures on time to ignition to generate a better understanding of their influence when blended with lubricating oil at different concentrations. This may be a more representative situation of what is occurring in the actual engine. To study the characteristics of droplet auto-ignition, a single droplet of the hexadecane-fuel mixture is formed and suspended on the bead of a thermocouple located inside the heated vessel. Similar methods have been widely used for studying single droplet combustion.^{19–21} This method has several advantages, which include the ability to record the temperature history of the droplet. The droplet temperature measurement can be considered as a transient bulk temperature of the inner droplet since there might be some change in the location of the thermocouple bead inside the droplet during the experiment.^{20,21} Temperature data acquisition is synchronized with high-speed imaging to monitor the droplet combustion process and its temperature evolution in real time.

EXPERIMENTAL DETAILS

The experiments are conducted in a cylindrical constant volume (4 L) combustion chamber (CVCC) (Figure 1), which is designed to study

Figure 1. Schematic of the experimental setup with the exaggerated size of the droplet.

single droplet ignition phenomena at elevated initial pressures and temperatures. The CVCC is made of stainless steel 316 L material, and its outer diameter and wall thickness are 320 and 30 mm, respectively. It was pressure tested up to 70 bar via the hydrostatic testing method at room temperature and is capable of operating at 500 °C. It is equipped with three orthogonal pairs of quartz windows that provide optical access to allow photographic diagnostics of the droplet combustion. An in-line heater (Watlow) with a power rating of 3 kW and four heating tapes (Omega STH052-100) with a power rating of 0.738 kW each were installed to heat the chamber to the desired initial temperature.

The experiments reported here were carried out in an air environment at an initial temperature of 300 ± 4 °C and initial pressures ranging from 4 to 30 bar. This temperature was chosen because it was above the auto-ignition temperature of the lubricating oil surrogate but below the auto-ignition temperature of the different diluting fuels. A single droplet injection system was designed and incorporated in the chamber. A capillary tube resides inside a cooling chamber assembly with an actuator system that is water-cooled at 10 °C and prevents the droplet from evaporating or igniting before it is suspended on the K-type thermocouple bead. This allows us to monitor the droplet lifetime temperature from its time of suspension until it is completely consumed. The hexadecane-fuel mixture is delivered to the capillary tube via a syringe pump (Harvard Apparatus PHD 2000). The piston's movement inside the actuator cylinder is controlled by pneumatic solenoid valves (Peter Paul Electronics Co., EH22H90CCH6).

A high-speed camera (PCO, Imager Pro HS, 4M) is used for recording the process from the suspension of the droplet on the thermocouple bead until its auto-ignition utilizing a shadowgraph technique at the frame rate of 500 fps. A LabVIEW-based program is designed to synchronize the activation of the syringe pump for injecting the mixture, the extension, and retraction of the actuator's piston holding the capillary tube, the triggering of the camera, and the temperature data acquisition. The extension of the piston, the camera trigger, and the start of temperature data acquisition are started at the same time. This is immediately followed by the activation of the syringe pump to inject the hexadecane-fuel mixture to form a droplet on the thermocouple bead.

The time duration for the extension and residence time of the capillary tube in the hot environment is set at 1 s each. This is to avoid a longer exposure of the capillary tube to the hot environment inside the vessel that could trigger the early ignition of the hexadecane-fuel mixture before the suspension of the droplet. After the hexadecane-fuel mixture droplet is suspended on the bead of the thermocouple, the piston is retracted to the cooling chamber. The time duration for the temperature data acquisition is set such that the suspension, auto-ignition of the droplet, and complete burnout of the droplet are recorded.

A precise syringe pump with an accuracy of $\pm 1\%$ and reproducibility of $\pm 0.1\%$ was used to inject the same amount of the

mixture during the droplet generation every test. In combination with the developed automation system to record the data and control the injected quantity, the data collected from at least 10 trials for each running condition were averaged. This leads to good repeatability and high accuracy in maintaining the amount of the injected mixture. Therefore, despite the shape of the droplet that is not complete spherical, the time to ignition (TI) recorded from every test was based on the same quantity of the injected mixture. Several preliminary tests had been carried out to find the suitable position of the thermocouple relative to the injection needle to suspend the droplet on the thermocouple bead. The inclination angle of the thermocouple was set such that the amount of the mixture injected is sufficient to form a droplet, which is very close to the sphere in shape. If the amount of the injected mixture is very less, the droplet cannot be suspended as the amount of the mixture will only create a thin coating on the thermocouple wire. On the other hand, if the amount of the mixture injected is too much, the droplet will not be suspended as it will drop immediately due to its weight; these observations were also reported during the suspension of the droplet of highly viscous heavy fuel oil on the thermocouple bead.²² Due to this, the combination of the inclination angle of the thermocouple wire and the amount of the mixture injected has to be defined carefully so the droplet can be suspended on the thermocouple bead.

The baseline case of this study for the pre-ignition was done by suspending a droplet of pure hexadecane, the lubricating oil surrogate without fuel dilution. To study the effect of the interaction between the oil and the fuel, hexadecane was mixed with FACE-I, PRF-91, PRF-95, and toluene individually, which have the octane number of 70, 91, 95, and 120, respectively (see Table 2). Relevant properties of

Table 2. Matrix for Tested Fuels

hexadecane (vol %)	FACE-I (RON = 70) (vol %)	PRF-91 (RON = 91) (vol %)	PRF-95 (RON = 95) (vol %)	toluene (RON = 120) (vol %)
100				
75	25			
75		25		
75			25	
75				25

hexadecane and fuels used are listed in Table 3. The boiling point, flash point, and autoignition temperature of PRF-91 and PRF-95 presented in Table 3 are estimated based on the ratio of the mixture of iso-octane and *n*-heptane.

To assess the effect of diluting fuel's RON to its ignition behavior, pure air was used in the current study. Since the auto-ignition temperature of hexadecane is lower than those of fuels, the presence of the volume fraction of fuel in the hexadecane-fuel mixture is expected to delay the process of droplet ignition. The temperature of the vessel was set at 300 ± 4 °C, so it was higher than the autoignition temperature of hexadecane, but it is lower than that of the fuels used. The tests were carried out for different pressures, while the temperature was maintained constant at 300 ± 4 °C. The time to ignition (TI) of the droplet recorded from the suspension of the droplet until it ignited was plotted against different ambient pressures.

RESULTS AND DISCUSSIONS

The typical temperature history of the droplet ignition is shown in Figure 2, together with snapshots of the droplet from the initial injection of the mixture onto the thermocouple bead till the end of the combustion phase. The thick black line represents the average temperature of 10 independent experiments with a 1.6 mm diameter droplet of 75 vol % *n*-hexadecane and 25 vol % toluene in the air at 300 ± 4 °C and 10 bar pressure. The gray vertical fringe at the background represents the standard deviation of these experimental data.

Table 3. Properties of Hexadecane, Isooctane, *n*-Heptane, Toluene, and FACE-I

no.	chemicals	boiling point (°C)	flash point (°C)	auto-ignition (°C)	RON	DCN
1	hexadecane	286.9	135	202	−263.5	105
2	isooctane	117.72	−12.22	447	100	14.79
3	<i>n</i> -heptane	98.38	−3.88	215	0	54.16
4	toluene	110.6	6	480	120	6
5	PRF-91	116.0 (estimated)	−11.5 (estimated)	426.1 (estimated)	91	20.57
6	PRF-95	116.8 (estimated)	−11.8 (estimated)	435.4 (estimated)	95	18.16
7	FACE-I	37.5–123	NA ^a	NA	70	30.92

^aNA, not applicable.

Figure 2. Temperature history of pre-ignition event of the 75% volume fraction of hexadecane + 25% volume fraction of toluene at a pressure of 10 bar.

followed by the gradual decrease in temperature until it reaches near ambient. The energy liberated by the combustion of the oil-fuel droplet is small compared with the heat capacity of the ambient air, so little change in bulk temperature is observed.

Unlike the work done by Fei et al.,¹⁶ the tests in the current work demonstrated that the presence of fuel in the hexadecane mixture increases the evaporation rate of its droplet. The vapor of the mixture then mixed with the hot ambient air and formed a combustible mixture from which the ignition of the droplet is triggered. Figure 2 also shows the auto-ignition temperatures of hexadecane and toluene. While the auto-ignition temperature of hexadecane is lower than that of toluene, its boiling temperature is higher than that of toluene. Therefore, mixing with toluene will result in a lower boiling temperature than that of pure hexadecane.

Consequently, the evaporation rate of the hexadecane-toluene mixture is higher than that of pure hexadecane. On the other hand, since the auto-ignition temperature of toluene is higher than that of hexadecane, it causes the auto-ignition temperature of the hexadecane-toluene mixture to be higher than that of pure hexadecane. As a result, the presence of toluene increases the evaporation rate of the mixture, but the time to ignition of the hexadecane-toluene mixture is longer than that of pure hexadecane.

The series of pictures that show the evaluation of the evaporation of the droplet before its ignition is presented in Figure 3 for hexadecane mixed with FACE-I, PRF-91, PRF-95, and toluene. In these images, it is clearly shown that the auto-ignition of the droplet is preceded by droplet evaporation. It is also evident from Figure 3 that, for the hexadecane-FACE-I mixture, the ignition occurred when the droplet is still partly visible. While for the mixture with PRF-91, PRF-95, and toluene, the ignition occurred when the droplet is not visible anymore. This condition suggests that the entrapment of a more volatile component within the heated droplet could lead to the fragmentation of droplet due to the internal pressure build up.²⁴

Using the plot presented in Figure 2, the time for the droplet to ignite, TI, is defined as the time interval between the minimum temperatures (A) until the time where the ignition of the droplet is first obvious (B). Point B is indicated by the sudden increase in $\frac{dT}{dt}$ in the temperature history. The TI describes the time needed for the droplet to be heated and evaporated, and its vapor mixes with the hot ambient air to form the combustible mixture that can ignite. To verify this, the plot of $\frac{dT}{dt}$ of the hexadecane-PRF95 mixture is superimposed on its temperature history data and presented in Figure 4. Based on the series of images in Figure 3c, which

The process of the suspension, evaporation, and ignition of the droplet mixture can be elaborated as follows:

- Image 1 shows the dripping of the hexadecane-toluene mixture from the capillary tube. It is evident that, as soon as the hexadecane-toluene mixture touches the thermocouple bead, the temperature drops gradually (recall that the mixture is held in a low-temperature zone until injected).
- Image 2 shows the droplet successfully suspended on the thermocouple bead. It is shown in the temperature history that the decrease in temperature becomes steeper after the droplet is successfully suspended.
- Image 3 shows the start of the droplet evaporation that coincides with point A where the minimum temperature is reached in the temperature history. Heat transferred from the hot surroundings toward the droplets results in the evaporation of the droplet. Internal conduction results in the interior of the droplet, also increasing in temperature. As evaporation occurs, the hexadecane-toluene mixture vapor diffuses into the hot ambient air.
- Image 4 shows the start ignition of the droplet. One of the primary characteristics of droplet ignition under high-pressure conditions is the Stefan flow of fuel vapor from the droplet surface that is slow due to the increase in boiling temperature and the decrease in diffusion coefficient.²³ The ignition is followed by a steep increase in the temperature until it reaches its maximum, after which the flame started to diminish.
- Image 5 shows the condition where the flame has completely consumed all the oil-fuel mixture. This is

(a) 75% Hexadecane + 25% Face-I (RON=180.13)

(b) 75% Hexadecane + 25% PRF-91 (RON=-174.88)

(c) 75% Hexadecane + 25% PRF95 (RON=-173.88)

(d) 75% Hexadecane + 25% Toluene (RON=-167.63)

Figure 3. Process ignition of the droplet at $P = 10$ bar. Figure 4. Temperature history of the hexadecane-PRF95 mixture and its $\frac{dT}{dt}$ at 10 bar.

the time interval between the dashed line and dashed-dotted line.

To investigate the effect of the pressure on the time of droplet ignition, TI, the temperature history of the hexadecane-PRF-95 droplet mixture at pressures of 4, 10, and 22 bar are presented in Figure 5. It is evident that the

Figure 5. Temperature history of the hexadecane-PRF95 mixture at 4, 10, and 22 bar.

temperature gradient, at the point where the droplet's temperature is minimum, for the pressure of 4 bar is initially comparable to that of 10 and 22 bar. As the temperature starts increasing from its minimum, the gradient at 4 bar increases more slowly compared with those lower than those of 10 and 22 bar.

To show the variation of evaporation rate, the time history of $\frac{dT}{dt}$ for the hexadecane-PRF-95 mixture at the pressure of 4, 10, and 22 bar was superimposed and is presented in Figure 6. It is evident that the rate increase in temperature ($\frac{dT}{dt}$) from the point where the temperature is minimum (A), increases with the increased pressure. Since for all liquids, the coefficient of the thermal conductivity increases with pressure, it suggests that the heat transfer in the current work is dominated by conduction. Consequently, the formation of the combustible mixture between the vapor of the hexadecane-PRF95 mixture with the ambient air at a low pressure needs a longer time to approach the minimum mixture flammability limit. Thus, increasing pressure of the vessel at constant ambient temperature expedites the auto-ignition of the mixture, which leads to the decrease in TI with the increase in the pressure as shown in Figure 5.

To study the role of the fuel's RON at different pressures, the RON is a nondimensional parameter, so TI and P are normalized to make it nondimensional too. The normalized TI (TI^*) is obtained by normalizing the TI of each mixture at each pressure (TI_i) with the TI of pure hexadecane obtained at a pressure of 4 bar ($TI^* = \frac{TI_i}{TI_{\text{Hex-4bar}}}$). The nondimensionalized pressure (P^*) is the vessel pressure normalized by the atmospheric pressure ($P^* = \frac{P}{P_{\text{atm}}}$).

The RON of the hexadecane-fuel mixture is estimated using the following correlation²⁵

$$RON_{\text{mix}} = \sum_i (x_i \cdot RON_i) \quad (1)$$

Figure 6. (a) Comparison of a $\frac{dT}{dt}$ of the hexadecane-PRF95 mixture for the vessel pressure of 4, 10, and 22 bar. (b) Zoom-in view of $\frac{dT}{dt}$.

where x_i is the volume fraction of the i component in the mixture, and RON_i is the RON of the individual components. The RON of hexadecane is estimated using a derived cetane number (DCN).²⁶

$$RON = -293\left(\frac{DCN}{100}\right)^2 - 52\left(\frac{DCN}{100}\right) + 114.1 \quad (2)$$

According to Kubic,²⁷ the DCN is a biased estimate of the cetane number (CN). Using the DCN–CN relation provided by Kubic,²⁷ the hexadecane's RON could be evaluated. They showed that the CN of 100 (that is the cetane number of hexadecane) corresponds to a DCN of 105. Using this DCN, the RON of hexadecane can be estimated as follows:

$$RON = -293\left(\frac{105}{100}\right)^2 - 52\left(\frac{105}{100}\right) + 114.1 = -263.5 \quad (2a)$$

To verify this, estimated RON of hexadecane, the structural group contribution method^{27,28} is used, which is expressed as follows

$$RON = a + b\left\{\sum_i (ON)_i\right\} + c\left\{\sum_i (ON)_i^2\right\} + d\left\{\sum_i (ON)_i^3\right\} + e\left\{\sum_i (ON)_i^4\right\} + f\left\{\sum_i (ON)_i\right\} \quad (3)$$

where $\sum_i (ON)_i$ is the sum of the group contributions for the RON obtained from Table 4, and a , b , c , d , e , and f are correlation constants from Table 5.

From the molecular structure of hexadecane, there are two groups of ($-CH_3$) and 14 groups of ($>CH_2$). Accordingly, the $\sum_i (ON)_i$ for hexadecane is -122.902 . Using eq 3, the RON of hexadecane can be estimated as follows:

$$RON = 103.6 + 0.231\{-122.902\} + (-0.0226)\{(-122.902)^2\} = -266.2 \quad (3a)$$

Based on the calculation shown in eqs 2a and 3a, it is found that eqs 2 and 3 give a comparable result for the estimation of

Table 4. Group Contribution for Estimation of the Hydrocarbon's Octane Number²⁸

type of hydrocarbon	serial number	group	(ON) _i
paraffins	1	$-CH_3$	-2.315
	2	$>CH_2$	-8.448
	3	$>CH-$	-0.176
	4	$>C<$	11.94
olefins	5	$=CH-$	0.392
	6	$>C=$	8.697
	7	$=CH_2$	3.623
	8	$=C=$	-37.37
	9	$=CH-$ (cis)	6.269
	10	$=CH-$ (trans)	6.449
	11	$\equiv CH$	18.36
cyclic ^a	12	$\equiv C-$	-7.201
	13	$>CH_2$	-4.421
	14	$>CH-$	-2.177
	15	$>C<$	8.916
aromatics ^a	16	$=CH-$	2.879
	17	$>C=$	5.409
	18	$=CH-$	3.591
	19	$>C=$	2.382
	20	$>C=$ (o)	-1.768
	21	$>C=$ (m)	10.24
	22	$>C=$ (p)	11.51

^aGroups 19–22 are all nonfused.

the RON of hexadecane. For the current work, the estimated RON of hexadecane obtained from eq 2 will be used for calculating the RON of the different hexadecane-fuel mixtures. After employing eqs 1 and 2, the RON of the reactants and mixtures used can be estimated and tabulated in Table 6.

Based on the RON of the mixtures presented in Table 6, the plot of P^* against TI^* is shown in Figure 7 for the different oil-fuel mixtures. It is apparent from Figure 7 that the addition of the aforementioned fuels in hexadecane has significantly increased the TI^* of the oil-fuel droplet. For all of the mixtures investigated, the TI decreases exponentially with increasing pressure. It is worth noting the significant increase in the TI^* for P^* lower than 16, while a very small change in the TI^* is shown at P^* higher than 20, showing an asymptotic behavior.

To deduce an empirical relationship for $TI^* = f(RON, P^*)$, curve fitting of the experimental data are plotted in Figure 7a–

Table 5. Correlation Constant for eq 2²⁸

octane number	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
RON	103.6	0.231	−0.0226	0.001	1.42×10^{-05}	1.58
MON	88.87	0.212	−0.0093	0.00104	9.59×10^{-06}	0.339

Table 6. RON of Reactants and Mixtures

reactants/mixtures	RON
hexadecane	−263.5
FACE-I	70
PRF-91	91
PRF-95	95
toluene	120
75% hexadecane + 25% FACE-I	−180.125
75% hexadecane + 25% PRF-91	−174.875
75% hexadecane + 25% PRF-95	−173.875
75% hexadecane + 25% toluene	−167.625

d. These fits can be represented by the exponential model as follows:

$$TI^* = a \cdot e^{(b \cdot P^*)} \quad (4)$$

In this equation, $a = f(RO\text{N})$, and $b = f(P^*)$. Using the log scale in the y axis, the line fit of hexadecane-fuel mixture's TI^* data in Figure 7 can be represented as five parallel straight lines with the same gradient (Figure 8). Referring to eq 4, the value of a represents the interception of each line with the y axis, while b is the slope of the lines. The values of a and b can be tabulated as shown in Table 7.

As presented in Table 7, the value of “ a ” varies with the RON, while “ b ” is invariant. By carrying out the exponential fit

Figure 8. Line fit of the TI data in the log scale.

to the data of “ a ” against the RON of the mixture (Figure 9), the correlation between “ a ” and the RON can be expressed as

$$a = 2 + 18,000 \times e^{0.05(RO\text{N})} \quad (5)$$

By substituting eq 5 into eq 4, the final empirical model for showing $TI^* = f(RO\text{N}, P^*)$ can be presented as follows:

$$TI^* = 2 \times e^{-0.14(P^*)} [1 + 9000 \times e^{0.05(RO\text{N})}] \quad (6)$$

Figure 7. TI^* distribution of hexadecane-fuel mixtures against P^* (a) 75% hexadecane + 25% FACE-I, (b) 75% hexadecane + 25% PRF-91, (c) 75% hexadecane + 25% PRF-95, and (d) 75% hexadecane + 25% toluene.

Table 7. Tabulation of the Values of a and b from eq 4 for each RON of the Mixture

mixtures	RON	DCN (calculated using eq 2)	a	b
100% hexadecane	−263.50	105.00	2.3	−0.14
75% hexadecane + 25% FACE-I	−180.13	91.73	3.5	−0.14
75% hexadecane + 25% PRF-91	−174.88	90.83	4.4	−0.14
75% hexadecane + 25% PRF-95	−173.88	90.66	5.5	−0.14
75% hexadecane + 25% toluene	−167.63	89.58	7.5	−0.14

Figure 9. Data plotting of a parameter versus RON.

By plotting the TI^* data obtained at the vessel pressures of 462 4, 10, and 22 bar against the empirical line fit (Figure 11), it is 463 f11

Figure 11. Plot of the TI^* as a function of the RON at the vessel pressures of 4, 10, and 22 bar.

evident that the TI of the mixture increases exponentially with 464 increasing the mixture's RON. A plausible explanation of this 465 phenomenon is based on the fact that the RON is a measure of 466 auto-ignition or anti-knock quality of a fuel, which affect the 467 ignition delay time. Therefore, in the current study, the auto- 468 ignition or anti-knock quality of the mixture has been 469 improved as the fuel's RON of the fuel mixed with hexadecane 470 is increased. It results in an increase in TI as the fuel's RON 471 increases. These results agree with those reported by 472 Kalghatgi²⁹ who studied the auto-ignition of practical fuels 473 and found that fuels in the gasoline auto-ignition range, RON 474 > 60 and DCN < 30, have relatively long ignition delay. 475

It is also demonstrated in Figure 11 that the empirical model 476 agrees very well with the experimental data at pressures of 10 477 and 22 bar, while at a pressure of 4 bar, the empirical model 478 slightly overestimated the TI . Nevertheless, the empirical 479 model can show the trend of the data at 4 bar. It is also shown 480 that, as the pressure increases, the difference of the TI for 481 different RONs becomes smaller. This suggests that the effect 482 of the fuel's RON in delaying the auto-ignition of lubricating 483 oil-fuel droplets diminishes with increasing pressure. In other 484 words, the current study shows that in the high-pressure 485 regime (>20 bar), the dilution of lubricating oil surrogate due 486 to the mixing with different fuels (and hence different RONs), 487 at a 25% volume fraction, does not delay the auto-ignition of 488 the droplet significantly. 489

To show the correlation between the mixture DCN and TI^* , 490 data have been plotted to initially find the correlation between 491 the DCN and the constant " a ". As presented in Figure 12, the 492 correlation between the DCN and " a " can be expressed as 493

$$a = 2.25 \times \{1 + 5 \times 10^{23} \times e^{(-0.6 \times DCN)}\} \quad (7) \quad 494$$

It is very obvious that the empirical function presented in eq 495 7 shows good agreement with the experimental data. By 496 substituting this equation into eq 4, the correlation between 497 the TI^* and DCN can be expressed as: 498

$$TI^* = 2.25 \times e^{(-0.4 \times P^*)} \times \{1 + 5 \times 10^{23} \times e^{(-0.6 \times DCN)}\} \quad (8) \quad 499$$

451 This empirical model shows the dependence of the TI^* of 452 the mixtures to P^* and its RON for a 25% volume fraction of 453 fuels mixed with a 75% volume fraction of hexadecane 454 (lubricating oil surrogate). To visualize this correlation, a 3D 455 plot of this equation model is presented in Figure 10. TI^*

Figure 10. 3D plot of $TI^* = f(RON, P^*)$.

456 contours presented in Figure 10 suggest that the use of a high 457 RON fuel at the pressure range higher than 20 bar has an 458 insignificant effect on enhancing or suppressing the auto- 459 ignition of hexadecane-fuel mixture's droplet. This is indicated 460 by the TI , which is invariant with increasing the RON of the 461 fuels.

Figure 12. Data plotting of a parameter versus DCN.

Figure 13 shows that the empirical function presented in eq 8 agrees well with the experimental data from the current study.

Figure 13. Plot of the TI^* as the function of the DCN at the vessel pressures of 4, 10, and 22 bar.

CONCLUSIONS

A study of the auto-ignition of a single droplet of a lubricating oil surrogate (hexadecane) diluted with different fuels at a mixture ratio of 3:1 at an ambient temperature of 300 ± 4 °C has been carried out over a range of initial pressures. The temperature difference between the “cold” droplet and the hot ambient air results in heat transfer into the droplet. Some hexadecane-fuel mixture will evaporate and mix with the ambient air to form a gaseous combustible mixture surrounding the droplet. As a result, the ignition of the droplet is found to be triggered by a region just off the droplet surface. This phenomenon is attributed to the occurrence of the Stefan flow of fuel vapor from the droplet surface that is slow as a consequence of the increase in boiling temperature and a decrease in diffusion coefficient. The current study also shows that the entrapment of a more volatile component within the heated droplet results in the fragmentation of the droplet due to internal pressure build up. The following concluding remarks can be drawn:

- The temperature history of the droplet ignition shows that the rate increase in temperature ($\frac{dT}{dt}$), which represents the evaporation rate of the droplet, increases as the pressure of the vessel is increased. Since, for all liquids, the coefficient of the thermal conductivity increases with pressure, it suggests that the heat transfer in the current work is dominated by conduction.
- At constant pressure, the rate of evaporation of the mixture's droplet increases with increasing RON. Since the RON is a measure of auto-ignition or anti-knock quality of the fuel, therefore, increasing the RON of the fuel mixed with hexadecane has improved the auto-ignition or anti-knock quality of the mixture. As a result, although the evaporation rate of the mixture is increased, the TI of the mixture increases exponentially as the fuel's RON used in the mixture increases.
- On the other hand, for a given fuel RON, the TI decreases with increasing ambient pressure.
- An empirical model is proposed, which shows the dependency of the TI to the mixture's RON and vessel pressure for the mixture ratio used in the current work. It shows that, in the pressure range above 20 bar, the mix with a 25% volume fraction of fuel having different RON fuels does not delay the auto-ignition of the droplet. The effect of fuel's RON to the droplet auto-ignition is diminished at pressures above 20 bar. In other words, the presence of the fuel in the lubricating oil surrogate droplet does not affect the auto-ignition characteristics of pure hexadecane droplets significantly at the pressure range above 20 bar.

FUTURE WORK

The future studies are planned for a wider range of hexadecane-fuel mixture's RON to be conducted at constant and elevated pressures of the vessel, which includes the test that will be carried out using the Rapid Compression Machine (RCM) and Ignition Quality Tester (IQT).

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Notes

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NOMENCLATURE

CN = cetane number
CVCC = constant volume combustion chamber
DCN = derived cetane number
FACE-I = fuels for advanced combustion engines type I with the octane number of 70

579 IQT = Ignition Quality Tester
 580 P = pressure inside the chamber [bar]
 581 P^* = pressure inside the chamber normalized by
 582 atmospheric pressure ($P^* = \frac{P}{P_{\text{atm}}}$)
 583 P_{atm} = atmospheric pressure [bar]
 584 PRF = primary reference fuels
 585 PRF-91 = primary reference fuels with an octane number of
 586 91
 587 PRF-95 = primary reference fuels with an octane number of
 588 95
 589 RCM = rapid compression machine
 590 RON = research octane number
 591 T = temperature [$^{\circ}\text{C}$]
 592 t = time [s]
 593 TI = time to ignition [s]
 594 TI^* = TI of the mixture normalized by TI of hexadecane at
 595 4 bar ($\text{TI}^* = \frac{\text{TI}_i}{\text{TI}_{\text{Hex-4bar}}}$)

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