A fundamental investigation into the relationship between lubricant composition and fuel ignition quality

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ABSTRACT

A fundamental experiment involving the use of an ignition quality tester (IQT) was carried out to elucidate the effects of lubricant oil composition which could lead to low speed pre-ignition (LSPI) processes in direct injection spark ignition (DISI) engines. Prior to the IQT tests, lubricant base oils were analyzed using ultra-high resolution mass spectrometry to reveal their molecular composition. High molecular-weight hydrocarbons such as \( nC_{16}H_{34}, nC_{17}H_{36}, \) and \( nC_{18}H_{38} \) were selected as surrogates of lubricant base oil constituents, and then mixed with \( iso\)-octane (\( iC_8H_{18} \)-gasoline surrogate) in proportions of 1% vol. (\( iC_8H_{18} = 99\% \) vol.) and 10% vol. (\( iC_8H_{18} = 90\% \) vol.) for the IQT experiments. In addition, lubricant base oils such as SN100 (Group I) and HC4 and HC6 (Group III) and a fully formulated lubricant (SAE 20W50) were mixed with \( iso\)-octane in the same proportions. The IQT results were conducted at an ambient pressure of 15 bar and a temperature range of 680 to 873 K. In the temperature range of 710 to 850K, the addition of 10% vol. base oils surrogates, base oils, and lubricating oil to the 90% vol. \( iC_8H_{18} \) reduces the average total ignition delay time by up to 54% for all mixtures, while the addition of 1% vol. to 99% vol. \( iC_8H_{18} \) yielded a 7% reduction within the same temperature range. The shorter total ignition delay was attributed to the higher reactivity of the lubricant base oil constituents in the fuel mixtures. A correlation between reactivity of base oils and their molecular composition was tentatively established. These results suggest that the lubricants have the propensity of initiating LSPI in DISI engines. Furthermore, similar results for \( n\)-alkanes, lubricant base oils, and fully formulated commercial lubricants suggest that it is the hydrocarbon fraction that contributes primarily to enhanced reactivity, and not the inorganic or organometallic additives.

Keywords: Low Speed Pre-ignition (LSPI); Direct Injection Spark Ignition (DISI); Ignition Quality Tester (IQT); Lubricant Base Oils; \( iso\)-octane; total ignition delay
1.0 INTRODUCTION

Downsizing strategies are being employed in direct injection spark ignition (DISI) engines to improve fuel economy and reduce emissions. Reducing engine displacement allows lower part-load operating conditions to shift into positions of the operating map with higher efficiency and lower specific fuel consumption [1]. As a result maximum power in full-load operation decreases, so DISI engines are either supercharged or turbocharged to achieve higher specific loading compared to naturally aspirated engines. This reduces frictional losses, vehicle weight, and pumping losses, leading to an 12-16% improvement in fuel economy compared to naturally aspirated engines [2]. Despite the benefits of downsizing, a major challenge is pre-ignition occurring at low engine speeds (under 3000 rpm) and high loads in the BMEP range of 10 to 20 bar and above. According to Kalghatgi and Bradley [3], pre-ignition in DISI engines, which could be related to fuel/air autoignition, is an abnormal phenomenon that causes the cylinder pressure to increase above the compression pressure before the spark plug fires. If pre-ignition occurs in the end gas at high pressure and temperature, it can lead to extremely heavy knock and subsequently damage the engine. The causes of pre-ignition are numerous. Earlier studies in the 1950s reported that as a result of improvements in octane numbers and increases in compression ratio, pre-ignition was initiated by hot combustion chamber deposits on the spark plugs and/or valves [3]. Recently, Kalghatgi and Bradley [3] added that pre-ignition could be caused by residual gases or particles creating hot spots, higher pressures, and/or higher temperatures. Dahnz and Spicher [4] provided a comprehensive and exhaustive list of the factors that could initiate pre-ignition in DISI engines. Of all the factors, it was reported that the main cause of pre-ignition is the occurrence of highly ignitable droplets of lubricant oil in the combustion chamber, as opposed to only surface ignition (i.e., hot spark plugs and valves). It was further reported that these droplets are released during the deceleration phase before the piston reaches top dead center. Surface tension was found to be the main factor influencing droplet release from the oil wiped off form the crank case liner during the compression stroke. In a further work, using a similar set up as Dahnz and Spicher [4], Stefan et al. [5] reported that spray/lubricant interactions can lead to pre-ignition. However, it was observed that engine
modifications enhancing chemical reactions have little or no influence on pre-ignition. Okada et al. [6] used optical techniques to visualize the in-cylinder state before the start of low speed pre-ignition combustion and observed the behavior of particles, which are thought to be the ignition source. They injected deposit flakes and other combustible particulate substances into the combustion chamber. It was observed that these particles require at least two combustion cycles to reach a glowing state that becomes an ignition source. Furthermore, deposits peeling form combustion chamber walls were identified as a new mechanism leading to pre-ignition. Their experiments further clarify the work done by Dahnz and Spicher [4] in explaining the low speed pre-ignition (LSPI), which could occur by dilution of lubricant oil in the bulk mixture composition in the DISI chamber. Takeuchi et al. [7] observed that engine oil formulations have significant effects on LSPI. It was found that the spontaneous ignition temperature of engine oil, as determined using high pressure differential scanning calorimetry (HP-DSC) correlates with LSPI frequency in a prototype turbocharged DISI engine. It was further observed that the oxidation reactions of the oil are an important factor for LSPI. Amann and Alger [8] performed a fundamental study using an ignition quality tester (IQT) to investigate the reactivity of different types of lubricants. By using an IQT, they observed that unconventional oil formulations and additives lowered the lubricant reactivity while maintaining lubricating properties. They further used a single cylinder variable compression ratio (VCR), naturally aspirated, spark ignition engine to further justify their claims. It was observed that lubricants with low combustion reactivity allowed the engine to be operated with improved combustion phasing and higher geometric compression ratio, and this further enabled the engine to operate at a higher efficiency without LSPI. From these previous findings, it is clear that lubricants play a vital role in the LSPI process in DISI engines. Amman and Alger [8] reported that the main constituents of lubricants are lubricant base stock (about 90% vol. and above) with various additives to reduce friction wear, decrease oxidation tendencies and modify viscosity. They further grouped lubricant base-stocks using the American Petroleum Institute (API) classification, as shown in Fig. 1
In order to develop upon previous research, this study involves carrying out fundamental experiments using an IQT to investigate the ignition propensity of selected base oil surrogates, real base oils, and real lubricants. Results from this fundamental research provide information on the effects of lubricant formulation on pre-ignition in DISI engines. To the knowledge of the authors, no systematic work has been done on the effect of the composition of lubricant base oils on pre-ignition, and the present work is intended to fill this gap.

2.0 EXPERIMENT

2.1 Ignition Quality Tester (IQT)

A fundamental experiment has been performed by using an ignition quality tester (IQT) to investigate the effect of lubricants on ignition propensity of gasoline-like fuels. The IQT machine can reasonably reproduce thermodynamic conditions in production DISI engines. Figure 2 shows the IQT (Advance Engine Technology Ltd.) used in the present study. Details on the IQT can be found in the American Society for Testing and Materials (ASTM) method D6890-08 [9], and has been reported by Bogin and co-workers [10] as a constant volume combustion system with a fuel injection system designed for the direct measurement of ignition delay of liquid fuel sprays.

The IQT has a volume capacity of 0.21 liters and variable experimental parameters, such as the initial charge air temperature and pressure, chamber wall temperature, and mass of fuel injected. The inner part of the IQT chamber is heated by electrical heaters embedded in the outer wall of the steel combustion chamber. An initial charge temperature of about 818 K close to the nozzle tip and 873 K near the middle of the chamber can be maintained. An ambient pressure of 1.5 MPa was maintained in the IQT, which is similar to the pressure achieved in a typical turbocharged DISI engine. After initial heating, a temperature range of 680 to 873 K was achieved in the IQT by switching off the electrical heater. This was done in order to obtain ignition delay data over a wider range of temperature. For the fuel injection system, a pneumatically driven mechanical fuel pump and a single-hole S-type delayed inward opening pintle nozzle injector was utilized, which has an orifice diameter of about 700 μm. The fuel was injected by a variable displacement
pump, which has a capability of injecting fuel at a wider range of temperatures. A pressure transducer is installed at the end of the combustion chamber to measure the pressure rise during a combustion event. The high speed needle lift and pressure signals were simultaneously measured at a sampling rate of 50 kHz. Three thermocouples were used to measure the skin, air-back, and air-front temperatures inside the IQT chamber. The air-front temperature is regarded as the test temperature, and is measured near the injector nozzle assembly containing a coolant system. The air-front temperature is generally maintained between the skin and air back temperatures. Details about the experimental conditions are presented in Table 1. Typical IQT time histories of chamber pressure and needle lift are shown in Fig. 4. As the fuel is injected and atomized into the hot ambient air in the chamber, droplet vaporization occurs and the vaporization time depends on droplet size distribution and the fuel’s volatility characteristics. As vaporization proceeds, the mixture temperature decreases and subsequently the chamber pressure decreases. As heat is added by conduction from the heated walls and by chemical reactions, the pressure recovers and then rises rapidly at the ignition event. In defining the ignition delay, as shown in Fig. 4, two tangents were drawn; one at the pressure recovery point to the initial point (slope I) and the other at the point where pressure has a maximum slope ((dP/dt)_{max}) (slope II). The time at which slopes I and II intersect defines the start of ignition (SoIgn). The ignition delay time is the duration from the start of injection (SoInj), as obtained from the needle lift timing, to the SoIgn.

2.2 Sample Selection and Preparation

Typical motor oils consist of hydrocarbon base oils (~90% vol.) blended with various organo-metallic additives (~10% vol.). The ignition propensity and ignition kinetics of a lubricant oil will depend on its specific chemical composition. In this study, five base oil samples were analyzed: a group I (G I) base oil SN100; and two group III (G III) base oils HC4 and HC6. Typical bulk content assays of the selected base oils are given in Table 2. G III base oils contain less sulfur and higher levels of saturated hydrocarbons than G I base oils. In addition, a commercial lubricant oil with SAE 20W50 high performance specifications for
spark ignition engines was selected. In this research, the authors were not privy to information regarding the specific composition of the commercially purchased SAE 20W50 lubricant oil. Experiments were also performed with $n$-hexadecane ($n$C$_{16}$H$_{34}$), $n$-heptadecane ($n$C$_{17}$H$_{36}$), and $n$-octadecane ($n$C$_{18}$H$_{38}$) as lubricant base oil surrogates. The lubricant surrogates, base oils, and SAE 20W50 lubricant were mixed thoroughly with iso-octane ($i$C$_{8}$H$_{18}$-gasoline surrogate) in proportions of 1% vol. ($i$C$_{8}$H$_{18}$ = 99% vol.) and 10% vol. ($i$C$_{8}$H$_{18}$ = 90% vol.). The fuel temperature is 35±3°C, as it flows through the pump and in the lines to the injector. The injector nozzle is cooled by water, as it is exposed to the hot combustion chamber gases. This maintains the fuel temperature at 50±4°C prior to injection. The boiling point of iso-octane is 99°C, so the fuel is not expected to undergo distillation or pyrolysis in the injector nozzle.

The base oil samples were analyzed using a solariX Fourier transform ion cyclotron resonance mass spectrometer (FTICR-MS) (Bruker Daltonik GmbH) equipped with a 12 Tesla refrigerated actively shielded superconducting magnet (Bruker Biospin). The FTICR-MS was coupled with an atmospheric pressure chemical ionization (APCI) in a direct infusion methodology. The detailed analytical method can be found elsewhere [11]. Data was collected and processed using Data Analysis software (Bruker Daltonics) for peak picking and assigning the elemental composition based on accurate mass. The elemental compositions were then categorized according to the number and type of heteroatoms. The physical properties of the $i$C$_{8}$H$_{18}$/lubricant mixtures were also measured. Mixture densities were measured using the density meter (Anton Paar DSA 5000M). Viscosities were measured using the Stabinger viscometer (Anton Paar SVM 3000). Distillation curves of the mixtures were carried out using the Minidis ADXpert distillation machine (Grabner Instruments). Prior to the experiments, mass calibration of the fuel was performed using the IQT variable displacement pump. The mass calibration was done to ensure that the same mass of samples at all mixture compositions were injected into the IQT chamber. As shown in Fig. 2, these processes involve varying the gap between the pneumatically controlled IQT fuel pump piston rod and a plunger connected the fuel reservoir. The fuel pump piston rod is connected to the plunger via a spring, which compresses during the injection processes. The fuel reservoir has a piston that is pressurized using Nitrogen gas. A
The stylus gauge is placed in between the piston and the plunger to regulate the gap length required to control the quantity of fuel injected to the IQT chamber. The pneumatics consist of a charged accumulator, an AC solenoid valve, and a pneumatic actuator. In the event of an injection, the charge air of the accumulator is released by a digital signal to the solid state relay board. The AC relay completes the solenoid valve circuit and opens the solenoid valve. High-pressure air produces a force on the pneumatic actuator, which is connected to the plunger. The actuator forces the plunger into the barrel causing a rapid increase in fuel pressure. Fuel pressure in the injector sac increases to the point where the nozzle opening pressure is reached. Depending on the pressure generated at the actuator, the gap length determines the quantity of fuel injected into the IQT chamber. The wider the gap length, the more the mass of fuel injected. This method has the advantage of reducing the time required to collect ignition data. For the mass calibration, the prepared fuel/lubricant mixtures were injected into a receptacle at varying gap lengths. At each gap length displayed on the stylus gauge, the mass of fuel injected is measured using a sensitive digital scale. For consistency and replicability, triplicate sessions each consisting of 10 fuel injections were carried out. Figure 3 shows how the mass of the 99% vol. \(iC_8H_{18} + 1\% \text{ vol. } nC_{16}H_{34}\) mixture was calibrated. There is an inverse linear relationship \((R^2 = 0.99)\) between the mass of fuel injected and the distance moved by the pump piston rod. With the relationship derived in Fig. 3, the quantity of fuel injected is specified based on the distance moved by the pump piston. For example as stated in Table 1, injecting 83 ± 0.1 mg of the 99% vol. \(iC_8H_{18} + 1\% \text{ vol. } nC_{16}H_{34}\) mixture requires the IQT pump piston rod to be set at 0.28 inches.

3.0 RESULTS AND DISCUSSION

3.1 Physical Properties and Chemical Characterization

The results from the FTICR-MS data in Fig. 5 showed the intensity versus mass range of m/z (mass to charge ratio) for each base oil. For example SN100 had a mass range of m/z of 200-500. Carbon number ranges of C\text{15-C50}, C\text{20-C60}, C\text{20-C90}, C\text{15-C55} and C\text{15-C60} were found in SN100, HC4 and HC6, respectively. The carbon number ranges are similar between G I and G III base oils with higher viscosity index base oils in each class having higher carbon number constituents.
The class distributions shown in Fig. 6 indicate that the major hydrocarbon classes present in the samples are HC (hydrocarbons), S1 (one sulfur-containing hydrocarbons), N1 (one nitrogen-containing hydrocarbons) and S2 (two sulfur-containing hydrocarbons). This shows that in addition to major saturated hydrocarbon groups (based on Table 2), other sulfur-containing hydrocarbons are present. For HC4 and HC6, S class species are relatively negligible, which agrees with their elemental sulfur content of < 0.003% shown in Table 2. Low to negligible levels of N1 class components were observed, which suggests these species were removed during the refining process. Based on the classification of the base stock oil components presented in Table 2, the three n-alkanes were chosen to represent the large saturated hydrocarbon fractions present in lubricant oils. Previous base oil analyses [12] reported a significant presence of C20-C34 normal alkanes (n-paraffins) with other iso-alkanes and cycloalkanes. As will be shown later, fundamental chemical kinetic modeling studies have shown that alkanes larger than C14 exhibit nearly identical fuel/air gas-phase ignition delay times across a range of operating temperatures [13, 14]. Thus, surrogate components comprising linear alkanes of carbon number range of C15-C20 can represent the ignition propensity and ignition kinetics of lubricant base oils. The lubricant surrogates, base oils, and SAE 20W50 lubricant were mixed with iso-octane (iC8H18-gasoline surrogate) in proportions of 1% vol. (iC8H18 = 99% vol.) and 10% vol. (iC8H18= 90% vol.) for IQT experiments. As reported by Wellings and co-authors [15], the quantity of contaminant (i.e., lubricant entering the cylinder bulk gas that can initiate LSPI) is not consistent. This has been attributed to the variability combined with other stochastic engine processes like mixing, which can likely contribute to the unpredictable nature of LSPI. Based on this, it is believed that the quantity of the lubricant surrogates, base stock oils, and SAE 20W50 added to iso-octane in this study could be realized in a real engine undergoing LSPI. It should be noted that the global equivalence ratio varies as the temperature changes from 873 to 680 K. For brevity, the lubricant surrogates, base oils, and SAE 20W50 lubricant are referred to as lubricant additives in this research. Table 3 presents the physical properties of the mixtures in terms of density and viscosity. The addition of 1% of the lubricant additive into 99% iC8H18 minimally affects the density of the mixture, while 10% of the lubricant additive into 90%...
iC_{8}H_{18} increases the density. The viscosity does not change much with the addition of the 1% lubricant additive into 99% iC_{8}H_{18}. While the addition of 10% of the lubricant additive into 90% iC_{8}H_{18} led to an increase in the viscosity of the mixtures. The increase in both density and viscosity can be attributed to the increase in average molecular weight of the mixtures since the lubricant additives are heavier than pure iso-octane. The distillation curves for the mixtures of iso-octane and lubricant oils are shown in Fig. 7. The temperature corresponding to the 0% recovered distillate signifies the initial boiling point while that for the 100% recovered distillate is the final boiling point. For pure iso-octane, the initial boiling point (0% recovered distillate) was attained at a temperature of 96.3°C. Note that for 100% iso-octane, the initial boiling point and final boiling are identical since it is a single component sample.

The addition of 1% lubricant additive to iC_{8}H_{18} did not change the distillation characteristics until the point corresponding to 95% recovery. From the 95 to 100% (final boiling point), there is a notable change in the distillation temperature, which can be triggered by the lubricant additive remaining after iso-octane has been vaporized. For the 90% iC_{8}H_{18} with 10% lubricant additive, the distillation features did not change until the distillate recovered reaches 90%. However, from the 90 to 100% there is an appreciable change in the distillation as the final boiling point is reached. This implies that at the 90% distillate recovery stage, iso-octane is almost totally vaporized while the remaining distillate (i.e. lubricant additive) has a high boiling point causing a rapid rise in the distillation temperature up to the final boiling point.

The results obtained from the 90% iC_{8}H_{18} with 10% lubricant additive show that the base oils have higher boiling points compared to the lubricant surrogates (i.e., \(n\)-alkanes). This is an indication that the lubricant base oils contain larger molecules of saturates having higher boiling points compared to the C_{16}-C_{18} \(n\)-alkane lubricant surrogates. In addition, the initial boiling point temperature was lower compared to pure iC_{8}H_{18}, suggesting some synergistic effects of suppressing boiling point in the mixtures or the presence of lighter molecules in the mixtures. The actual cause of lower initial boiling point in the mixtures requires further investigation, and is beyond the scope of the present work. The influence of the aforementioned distillation curve features will be correlated with ignition delay in the following section.
3.2 Effect of Lubricant Surrogates on Ignition

In analyzing IQT data, the ignition event was identified by the rapid rise in ambient pressure, as shown in Fig. 4. The chamber pressure fluctuates immediately after the initial pressure rise due to the resonance near a cavity in front of the pressure transducer. A MATLAB-based code was written to process the pressure data by incorporating a filtering design tool to smoothen the pressure data.

The variation of ignition delay time with temperature for the lubricant surrogate/iso-octane mixtures is presented in Fig 8, which presents the effect of the addition of 1 and 10% of the lubricant surrogates into 99% and 90% iso-octane, respectively. The results show that adding 1% of the lubricant surrogates into 99% of iso-octane shortens the ignition delays by about 15%. Further increase in the quantity of lubricant surrogates to 10% in the mixtures led to an appreciable shortening in the ignition delay time. The shortening in ignition delay time is an indication of the propensity of these surrogates to pre-ignition, if they are used to formulate engine lubricants. The reduction in ignition delay time can be attributed to the high reactivity of the surrogate n-alkanes in the mixtures. One of the major factors reported in [16] affecting the reactivity of fuel is the cetane number (CN). The cetane numbers of these lubricant surrogates are well documented and have been reported in [17] as 100, 105, and 110 for n-hexadecane (n-C$_{16}$H$_{34}$), n-heptadecane (n-C$_{17}$H$_{36}$) and n-octadecane (n-C$_{18}$H$_{36}$), respectively. The cetane number values for these fuels are much higher than that of iso-octane (CN=17.5). The similar reactivity amongst the mixtures with 10% addition of C$_{16}$-C$_{18}$ n-alkanes confirms that a C$_{16}$ structure is a suitable surrogate for larger n-alkanes. The difference in n-alkanes is smaller at high temperatures than at lower temperatures; variations in physical properties with varying carbon number become more evident at lower temperatures where physical processes (e.g., spray vaporization) play a more important role in the ignition process.

Fuel structures have been reported to play a major role on reactivity. Chevalier et al. [18] investigated the role of the C-H bonds in n-heptane and iso-heptane. It was observed that methyl substituted heptane isomers are less reactive than n-heptane. Iso-octane is highly branched compared to the lubricant surrogates, so it
has a low ignition propensity. Thus, the addition of $n$-C$_{16}H_{34}$, $n$-C$_{17}H_{36}$ and $n$-C$_{18}H_{38}$, which have straight carbon chains, tends to increase the reactivity of the mixtures.

3.3 Effect of Lubricant Base oils on Ignition

Figure 9 shows the effect of the lubricant base stock oil on ignition. The addition of 1% of HC4, HC6 (Group III), and SN100 (Group I) in the mixtures reduces the ignition delay time similar to what was observed for the lubricant surrogates. Increasing the quantity of the base stock oil to 10% shows an appreciable decrease in the total ignition delay. This result suggests that the base stock oil used in formulating lubricant oil may initiate LSPI in spark ignition engines. The reduction in ignition delay in the mixtures can be attributed to the reactivity of the HC4, HC6, and SN100 in the mixtures. Since the base stock oils are mainly composed of saturated alkanes, similar reactivity trends as exhibited by the lubricant surrogates in the mixtures are observed.

The effect of the lubricant types (surrogates or base oils) on the total ignition delay can be partially reasoned based on the previous distillation curves of the mixtures. When the iso-octane in the mixtures vaporizes (at about 98°C), the remaining lubricant vaporizes and accelerates ignition chemistry due their straight chain saturated hydrocarbon content. The mixtures with the Group III (i.e. HC4 and HC6) base oil are more reactive (decreasing the total ignition delay time more) compared to iso-octane/SN100 (Group I) base oil mixtures. This is attributed to the high quantity of saturates (>95%) in the Group III base oils, which are mainly alkanes. The use of the Group III base oils could favor the formulation of engine lubricants in terms of corrosiveness and emission profiles since it contains less sulfur and aromatics compared to the Group I lubricants. However, the issue of its reactivity favoring pre-ignition processes in DISI engines needs to be taken into consideration.

3.4 Effect of SAE 20W50 Lubricant on Ignition

The addition of 1 and 10% of SAE 20W50 lubricating oil to iso-octane reduces the ignition delay time, as shown in Fig. 10. This implies that the SAE 20W50 has the propensity to initiate pre-ignition if its droplets/vapor escape into the bulk gas mixtures in the engine chamber. The ignition delay of the iso-
octane/SAE 20W50 mixture followed similar trends observed in the lubricant surrogates and base oils. Thus, one can conclude that the saturated alkanes predominant in the SAE20W50 contribute to its shorter ignition delay time. At lower temperature, the reactivity of mixtures with SAE 20W50 is closer to the mixtures G III base oils (HC4 and HC6) than those with G I SN100 base oil. This suggests that the fully formulated lubricant has a base oil molecular composition similar to HC4 and HC6. Note that the SAE 20W50 lubricant oil is not only made of base oils, but also contains organo-metallic additives such as anti-oxidant, anti-friction and anti-wear agents. There is a need to carry out an isolated investigation of the effect of representative additives on ignition delay, which could have an effect on LSPI. However, by comparing the present results of the SAE 20W50 to those of the base oils, the role of the additives on ignition delay does not appear to be significant. This result is contrary to that obtained by [7], wherein a Calcium detergent was mixed with a G III base oil. The addition of Calcium detergent was found to increase the LSPI occurrence in DISI engines. Similar observations were made by [19-21] on the effect of Calcium detergents on the propensity of LSPI in DISI engines when added to G III base oils. However it was reported that the addition of additives such as Zinc Di-Alkyl-Dithio-Phosphate (ZnDTP) and Molybdenum Di-Thio Carbamate (MoDTC) to G III and high quality G IV base oils suppressed the occurrence of LSPI since they act as antioxidants. It was further stated by [20-21] that in formulating lubricants, reducing the quantity of Calcium detergents while increasing the quantity of MoDTC and ZnDTP tends to reduce LSPI by 10 %. In the present work, similar ignition delays observed for SAE 20W50 lubricant compared to the other base oils may be attributed to the presence additives such as MoDTC and ZnDTP. If these substances are present in larger quantities than Calcium detergents in the SAE 20W50 lubricant, then ignition delay will not be significantly affected when compared to the base oils. It should be noted that the authors do not have information about the specific additives present in the commercially purchased SAE 20W50 used herein. As part of future work, through spectroscopy techniques, the authors will measure the concentration of these additives in the SAE 20W50. Information from these will be useful to elucidate the role played by each additives on the ignition delay of the fuel. In addition, a fundamental experiment on the propensities
of these additives in lubricant base oils to initiate auto-ignition of surrogate fuel for spark ignition engines. i.e. *iso*-octane will be investigated as part of future work.

It is interesting to note that the *iso*-octane mixtures with addition of 1% of various additives display similar reactivity. However, 10% addition of G III base oils and SAE 20W50 display similar ignition delay times (e.g., < 5% difference), while 10% addition of base oil surrogates (C$_{16}$-C$_{18}$ *n*-alkanes) display slightly longer ignition delay times (up to 25% difference). This may be due to the longer *n*-alkane chains (higher carbon number) in the base oils and real lubricants, which have higher reactivity when blended with *iso*-octane in larger amounts.

3.5 Chemical Ignition Delay

As reported in [22], the total ignition delay used to explain the onset of lubricant ignition comprises a physical ignition delay and chemical ignition delay. The physical delay starts with the fuel spray leaving the injector and includes the induction period for droplet formation, hot air entrainment, and vaporization. On the other hand, the chemical delay is the period that a gaseous fuel/air mixture at a specified temperature and mixture ratio undergoes chemical reactions leading to ignition. Both physical and chemical delays have been reported to occur simultaneously [23]. In this work, a zero dimensional (0-D) closed homogeneous reactor simulation was carried out using CHEMKIN-PRO [24] to further analyze the chemical ignition delay of *iso*-octane blended with large alkanes.

The simulations were conducted using a detailed chemical kinetic model for *n*-alkanes up to C$_{16}$ and 2-methylalkanes up to C$_{20}$ [14]. This mechanism was merged with the *iso*-octane mechanism presented by Mehl et al. [25] to simulate mixtures of large alkanes with *iso*-octane. Parametric studies of the chemical ignition delay at global equivalence ratios of 0.975 and 1.95 were carried out to have an overview of the reactivity of the *iso*-octane/alkanes mixtures at wider range of conditions. It should be noted that real lubricant oils comprise various large *n*-alkanes and *iso*-alkanes with one, two, or more methyl substitutions. Simulations are presented for blends of *iso*-octane with large *n*-alkanes and 2-methylalkanes to better understand the effects of lubricant oil’s alkane composition on chemical ignition delay. Fig. 11 (a) shows
the variation of the chemical ignition delay of the iso-octane mixtures with large alkanes at a global equivalence ratio of 0.975. In the temperature range of 900 to 1000 K (1 < 1000/T < 1.1), the reactivity of pure iso-octane and iso-octane (99% vol.)/alkanes (1% vol.) mixtures are similar. The chemical ignition delay further increases as temperature decreases to 800 K for both pure iso-octane and iso-octane (99% vol.)/alkanes (1% vol.) mixtures. As temperature decreases from 900 to 800K, the chemical ignition delay of the iso-octane (99% vol.)/alkanes (1% vol.) mixtures tend to be shorter than the pure iso-octane. This is an indication of the impact of large alkanes on the reactivity of the mixtures. As obtained in the experimental results, the reactivity of the iso-octane/alkane mixtures increased significantly when the quantity of large alkanes in the iso-octane mixtures increases to 10%. At the temperature range of 920 to 1000 K, there is less significant difference in the chemical ignition delay of the iso-octane with 10% vol. large alkanes compared to the mixtures with 1% vol. alkanes. However a remarkable difference exists in the chemical ignition delay of iso-octane with 10% vol. large alkanes compared and the mixtures with 1% vol. alkane as temperature decreases from 925 to 600 K. By doubling the equivalence ratio, the variation of the chemical ignition delay of the fuels with temperature is presented in Fig. 11 (b). The result obtained follow similar trend to that obtained at leaner conditions except that the mixture with 10% alkanes shows a greater difference in reactivity compared to other mixtures. When the equivalence ratio increases, the reactivity is enhanced thus decreasing the chemical ignition delay. This is in line with the work done by Darcy and et al. [26] and Healy et al. [27], in which it was observed that at low temperatures and high ambient pressure conditions chain branching reactions accelerate as fuel concentration increases. Fig. 10 indicates that the presence of 1% larger n-alkanes and 2-methylalkanes in the iso-octane yielded no significant difference in reactivity. This is in agreement with the experimental measurements presented earlier for mixtures of iso-octane with 1% of various lubricant additives. Therefore, the chemical ignition delay of large alkanes present in lubricant oils can be adequately reproduced with n-hexadecane as surrogate, further supporting the experimental approach presented herein.
Finally, considering the physical properties such as density, distillation temperature, and viscosity, the addition of the lubricant surrogates, base oils, and engine oils have the tendency of increasing the physical delay part of the total ignition delay. On the other hand the chemical ignition delay is shortened with the addition of the large \( n \)-alkanes and \( iso \)-alkanes that are found in the base oils and real lubricants. Since the total measured ignition delay for all the mixtures are shortened as a result of the addition of the lubricant surrogates, base oils, and engine oils, it can be assumed that the chemical ignition delay is more rate controlling than the physical ignition delay. This suggests that the propensity of a lubricant to initiate pre-ignition in DISI engines can be attributed to the chemical kinetic properties of the base oil used in the formulation. The results presented herein showed that base oils with high percentage of long chain hydrocarbons, such as HC4, have the tendency to ignite faster than base oils with lower amounts of long chain hydrocarbons (e.g., SN 100 and SN 500).

4.0 CONCLUSIONS

In this research the ignition propensities of selected lubricant oil surrogates, lubricant base oils, and a fully formulated lubricant oil were investigated using an ignition quality tester. These lubricant additives were blended with \( iso \)-octane, a gasoline surrogate, to study their effects on pre-ignition. The results obtained show that:

1. Compared to 100\% \( iso \)-octane, the addition of 1 \% vol. of the lubricant additives into 99\% vol. of \( iso \)-octane resulted in ignition delays being shortened by 15\%. Further increase in the quantity of lubricant surrogate to 10\% in the mixture led to a drastic shortening in the ignition delay time.

2. The previous points suggest that \( C_{16} - C_{18} \) \( n \)-alkanes are adequate surrogates for capturing the ignition characteristics of real base oils and fully formulated lubricants. Additional studies with organo-metallic additives are needed to ascertain their role in ignition delay; however, the present work suggests that their effects are negligible compared to the hydrocarbon components in the base oil.

3. Simulations indicate that the presence of the higher \( n \)-alkanes and 2-methylalkanes in \( iso \)-octane mixtures leads to a reduction in chemical ignition delay.
4. The chemical ignition delay plays a greater role than the physical ignition delay in the reduction of the total ignition delay.

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ABBREVIATIONS

API American Petroleum Institute

CN cetane number

DISI direct injection spark ignition

FTICR-MS Fourier transform ion cyclotron resonance mass spectrometer

HP-DSC high pressure differential scanning calorimetry

IQT ignition quality tester

LSPI low speed pre-ignition

SoIgn start of ignition

SoInj start of injection

iC_8H_{18} iso-octane

max (dP/dt) maximum change in pressure with time

m/z mass to charge ratio

nC_{16}H_{34} n-hexadecane

nC_{17}H_{36} n-heptadecane

nC_{18}H_{38} n-octadecane