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36 ABSTRACT

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38 A fundamental experiment involving the use of an ignition quality tester (IQT) was carried out to elucidate

39 the effects of lubricant oil composition which could lead to low speed pre-ignition (LSPI) processes in

40 direct injection spark ignition (DISI) engines. Prior to the IQT tests, lubricant base oils were analyzed using

41 ultra-high resolution mass spectrometry to reveal their molecular composition. High molecular-weight

42 hydrocarbons such as $nC_{16}H_{34}$, $nC_{17}H_{36}$, and $nC_{18}H_{38}$ were selected as surrogates of lubricant base oil

43 constituents, and then mixed with *iso*-octane (iC_8H_{18} -gasoline surrogate) in proportions of 1% vol. (iC_8H_{18}

44 = 99% vol.) and 10 % vol. (iC_8H_{18} = 90% vol.) for the IQT experiments. In addition, lubricant base oils

45 such as SN100 (Group I) and HC4 and HC6 (Group III) and a fully formulated lubricant (SAE 20W50)

46 were mixed with *iso*-octane in the same proportions. The IQT results were conducted at an ambient pressure

47 of 15 bar and a temperature range of 680 to 873 K. In the temperature range of 710 to 850K, the addition

48 of 10% vol. base oils surrogates, base oils, and lubricating oil to the 90% vol. iC_8H_{18} reduces the average

49 total ignition delay time by up to 54% for all mixtures, while the addition of 1% vol. to 99% vol. iC_8H_{18}

50 yielded a 7% reduction within the same temperature range. The shorter total ignition delay was attributed

51 to the higher reactivity of the lubricant base oil constituents in the fuel mixtures. A correlation between

52 reactivity of base oils and their molecular composition was tentatively established. These results suggest

53 that the lubricants have the propensity of initiating LSPI in DISI engines. Furthermore, similar results for

54 *n*-alkanes, lubricant base oils, and fully formulated commercial lubricants suggest that it is the hydrocarbon

55 fraction that contributes primarily to enhanced reactivity, and not the inorganic or organometallic additives.

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57 Keywords: Low Speed Pre-ignition (LSPI); Direct Injection Spark Ignition (DISI); Ignition Quality Tester

58 (IQT); Lubricant Base Oils; *iso*-octane; total ignition delay

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62 1.0 INTRODUCTION

63 Downsizing strategies are being employed in direct injection spark ignition (DISI) engines to improve fuel
64 economy and reduce emissions. Reducing engine displacement allows lower part-load operating conditions
65 to shift into positions of the operating map with higher efficiency and lower specific fuel consumption [1].
66 As a result maximum power in full-load operation decreases, so DISI engines are either supercharged or
67 turbocharged to achieve higher specific loading compared to naturally aspirated engines. This reduces
68 frictional losses, vehicle weight, and pumping losses, leading to an 12-16% improvement in fuel economy
69 compared to naturally aspirated engines [2]. Despite the benefits of downsizing, a major challenge is pre-
70 ignition occurring at low engine speeds (under 3000 rpm) and high loads in the BMEP range of 10 to 20
71 bar and above. According to Kalghatgi and Bradley [3], pre-ignition in DISI engines, which could be
72 related to fuel/air autoignition, is an abnormal phenomenon that causes the cylinder pressure to increase
73 above the compression pressure before the spark plug fires. If pre-ignition occurs in the end gas at high
74 pressure and temperature, it can lead to extremely heavy knock and subsequently damage the engine. The
75 causes of pre-ignition are numerous. Earlier studies in the 1950s reported that as a result of improvements
76 in octane numbers and increases in compression ratio, pre-ignition was initiated by hot combustion chamber
77 deposits on the spark plugs and/or valves [3]. Recently, Kalghatgi and Bradley [3] added that pre-ignition
78 could be caused by residual gases or particles creating hot spots, higher pressures, and/or higher
79 temperatures. Dahnz and Spicher [4] provided a comprehensive and exhaustive list of the factors that could
80 initiate pre-ignition in DISI engines. Of all the factors, it was reported that the main cause of pre-ignition is
81 the occurrence of highly ignitable droplets of lubricant oil in the combustion chamber, as opposed to only
82 surface ignition (i.e., hot spark plugs and valves). It was further reported that these droplets are released
83 during the deceleration phase before the piston reaches top dead center. Surface tension was found to be the
84 main factor influencing droplet release from the oil wiped off from the crank case liner during the
85 compression stroke. In a further work, using a similar set up as Dahnz and Spicher [4], Stefan et al. [5]
86 reported that spray/lubricant interactions can lead to pre-ignition. However, it was observed that engine

87 modifications enhancing chemical reactions have little or no influence on pre-ignition. Okada et al. [6]
88 used optical techniques to visualize the in-cylinder state before the start of low speed pre-ignition
89 combustion and observed the behavior of particles, which are thought to be the ignition source. They
90 injected deposit flakes and other combustible particulate substances into the combustion chamber. It was
91 observed that these particles require at least two combustion cycles to reach a glowing state that becomes
92 an ignition source. Furthermore, deposits peeling from combustion chamber walls were identified as a new
93 mechanism leading to pre-ignition. Their experiments further clarify the work done by Dahnz and Spicher
94 [4] in explaining the low speed pre-ignition (LSPI), which could occur by dilution of lubricant oil in the
95 bulk mixture composition in the DISI chamber. Takeuchi et al. [7] observed that engine oil formulations
96 have significant effects on LSPI. It was found that the spontaneous ignition temperature of engine oil, as
97 determined using high pressure differential scanning calorimetry (HP-DSC) correlates with LSPI frequency
98 in a prototype turbocharged DISI engine. It was further observed that the oxidation reactions of the oil are
99 an important factor for LSPI. Amann and Alger [8] performed a fundamental study using an ignition quality
100 tester (IQT) to investigate the reactivity of different types of lubricants. By using an IQT, they observed
101 that unconventional oil formulations and additives lowered the lubricant reactivity while maintaining
102 lubricating properties. They further used a single cylinder variable compression ratio (VCR), naturally
103 aspirated, spark ignition engine to further justify their claims. It was observed that lubricants with low
104 combustion reactivity allowed the engine to be operated with improved combustion phasing and higher
105 geometric compression ratio, and this further enabled the engine to operate at a higher efficiency without
106 LSPI. From these previous findings, it is clear that lubricants play a vital role in the LSPI process in DISI
107 engines. Amman and Alger [8] reported that the main constituents of lubricants are lubricant base stock
108 (about 90% vol. and above) with various additives to reduce friction wear, decrease oxidation tendencies
109 and modify viscosity. They further grouped lubricant base-stocks using the American Petroleum Institute
110 (API) classification, as shown in Fig. 1

111 In order to develop upon previous research, this study involves carrying out fundamental experiments using
112 an IQT to investigate the ignition propensity of selected base oil surrogates, real base oils, and real lubricants.
113 Results from this fundamental research provide information on the effects of lubricant formulation on pre-
114 ignition in DISI engines. To the knowledge of the authors, no systematic work has been done on the effect
115 of the composition of lubricant base oils on pre-ignition, and the present work is intended to fill this gap.

116 2.0 EXPERIMENT

117 2.1 Ignition Quality Tester (IQT)

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

125 The IQT has a volume capacity of 0.21 liters and variable experimental parameters, such as the initial charge
126 air temperature and pressure, chamber wall temperature, and mass of fuel injected. The inner part of the
127 IQT chamber is heated by electrical heaters embedded in the outer wall of the steel combustion chamber.
128 An initial charge temperature of about 818 K close to the nozzle tip and 873 K near the middle of the
129 chamber can be maintained. An ambient pressure of 1.5 MPa was maintained in the IQT, which is similar
130 to the pressure achieved in a typical turbocharged DISI engine. After initial heating, a temperature range
131 of 680 to 873 K was achieved in the IQT by switching off the electrical heater. This was done in order to
132 obtain ignition delay data over a wider range of temperature. For the fuel injection system, a pneumatically
133 driven mechanical fuel pump and a single-hole S-type delayed inward opening pintle nozzle injector was
134 utilized, which has an orifice diameter of about 700 μm . The fuel was injected by a variable displacement

135 pump, which has a capability of injecting fuel at a wider range of temperatures. A pressure transducer is
136 installed at the end of the combustion chamber to measure the pressure rise during a combustion event. The
137 high speed needle lift and pressure signals were simultaneously measured at a sampling rate of 50 kHz.
138 Three thermocouples were used to measure the skin, air-back, and air-front temperatures inside the IQT
139 chamber. The air-front temperature is regarded as the test temperature, and is measured near the injector
140 nozzle assembly containing a coolant system. The air-front temperature is generally maintained between
141 the skin and air back temperatures. Details about the experimental conditions are presented in Table 1.
142 Typical IQT time histories of chamber pressure and needle lift are shown in Fig. 4. As the fuel is injected
143 and atomized into the hot ambient air in the chamber, droplet vaporization occurs and the vaporization time
144 depends on droplet size distribution and the fuel's volatility characteristics. As vaporization proceeds, the
145 mixture temperature decreases and subsequently the chamber pressure decreases. As heat is added by
146 conduction from the heated walls and by chemical reactions, the pressure recovers and then rises rapidly at
147 the ignition event. In defining the ignition delay, as shown in Fig. 4, two tangents were drawn; one at the
148 pressure recovery point to the initial point (slope I) and the other at the point where pressure has a maximum
149 slope ($(dP/dt)_{\max}$) (slope II). The time at which slopes I and II intersect defines the start of ignition (SoIgn).
150 The ignition delay time is the duration from the start of injection (SoInj), as obtained from the needle lift
151 timing, to the SoIgn.

152 2.2 Sample Selection and Preparation

153 Typical motor oils consist of hydrocarbon base oils (~90% vol.) blended with various organo-metallic
154 additives (~10% vol.). The ignition propensity and ignition kinetics of a lubricant oil will depend on its
155 specific chemical composition. In this study, five base oil samples were analyzed: a group I (G I) base oil
156 SN100; and two group III (G III) base oils HC4 and HC6. Typical bulk content assays of the selected base
157 oils are given in Table 2. G III base oils contain less sulfur and higher levels of saturated hydrocarbons than
158 G I base oils. In addition, a commercial lubricant oil with SAE 20W50 high performance specifications for

159 spark ignition engines was selected. In this this research, the authors were not privy to information regarding
160 the specific composition of the commercially purchased SAE 20W50 lubricant oil. Experiments were also
161 performed with *n*-hexadecane ($nC_{16}H_{34}$), *n*-heptadecane ($nC_{17}H_{36}$), and *n*-octadecane ($nC_{18}H_{38}$) as lubricant
162 base oil surrogates. The lubricant surrogates, base oils, and SAE 20W50 lubricant were mixed thoroughly
163 with *iso*-octane (iC_8H_{18} -gasoline surrogate) in proportions of 1% vol. (iC_8H_{18} = 99% vol.) and 10% vol.
164 (iC_8H_{18} = 90% vol.). The fuel temperature is $35\pm 3^\circ C$, as it flows through the pump and in the lines to the
165 injector. The injector nozzle is cooled by water, as it is exposed to the hot combustion chamber gases. This
166 maintains the fuel temperature at $50\pm 4^\circ C$ prior to injection. The boiling point of *iso*-octane is $99^\circ C$, so the
167 fuel is not expected to undergo distillation or pyrolysis in the injector nozzle.

168 The base oil samples were analyzed using a solariX Fourier transform ion cyclotron resonance mass
169 spectrometer (FTICR-MS) (Bruker Daltonik GmbH) equipped with a 12 Tesla refrigerated actively shielded
170 superconducting magnet (Bruker Biospin). The FTICR-MS was coupled with an atmospheric pressure
171 chemical ionization (APCI) in a direct infusion methodology. The detailed analytical method can be found
172 elsewhere [11]. Data was collected and processed using Data Analysis software (Bruker Daltonics) for peak
173 picking and assigning the elemental composition based on accurate mass. The elemental compositions were
174 then categorized according to the number and type of heteroatoms. The physical properties of the
175 iC_8H_{18} /lubricant mixtures were also measured. Mixture densities were measured using the density meter
176 (Anton Paar DSA 5000M). Viscosities were measured using the Stabinger viscometer (Anton Paar SVM
177 3000). Distillation curves of the mixtures were carried out using the Minidis ADXpert distillation machine
178 (Grabner Instruments). Prior to the experiments, mass calibration of the fuel was performed using the IQT
179 variable displacement pump. The mass calibration was done to ensure that the same mass of samples at all
180 mixture compositions were injected into the IQT chamber. As shown in Fig. 2, these processes involve
181 varying the gap between the pneumatically controlled IQT fuel pump piston rod and a plunger connected
182 the fuel reservoir. The fuel pump piston rod is connected to the plunger via a spring, which compresses
183 during the injection processes. The fuel reservoir has a piston that is pressurized using Nitrogen gas. A

184 stylus gauge is placed in between the piston and the plunger to regulate the gap length required to control
185 the quantity of fuel injected to the IQT chamber. The pneumatics consist of a charged accumulator, an AC
186 solenoid valve, and a pneumatic actuator. In the event of an injection, the charge air of the accumulator is
187 released by a digital signal to the solid state relay board. The AC relay completes the solenoid valve circuit
188 and opens the solenoid valve. High-pressure air produces a force on the pneumatic actuator, which is
189 connected to the plunger. The actuator forces the plunger into the barrel causing a rapid increase in fuel
190 pressure. Fuel pressure in the injector sac increases to the point where the nozzle opening pressure is reached.
191 Depending on the pressure generated at the actuator, the gap length determines the quantity of fuel injected
192 into the IQT chamber. The wider the gap length, the more the mass of fuel injected. This method has the
193 advantage of reducing the time required to collect ignition data. For the mass calibration, the prepared
194 fuel/lubricant mixtures were injected into a receptacle at varying gap lengths. At each gap length displayed
195 on the stylus gauge, the mass of fuel injected is measured using a sensitive digital scale. For consistency
196 and replicability, triplicate sessions each consisting of 10 fuel injections were carried out. Figure 3 shows
197 how the mass of the 99% vol. *i*C₈H₁₈ + 1% vol. *n*C₁₆H₃₄ mixture was calibrated. There is an inverse linear
198 relationship ($R^2 = 0.99$) between the mass of fuel injected and the distance moved by the pump piston rod.
199 With the relationship derived in Fig. 3, the quantity of fuel injected is specified based on the distance moved
200 by the pump piston. For example as stated in Table 1, injecting 83 ± 0.1 mg of the 99% vol. *i*C₈H₁₈ + 1%
201 vol. *n*C₁₆H₃₄ mixture requires the IQT pump piston rod to be set at 0.28 inches.

202 3.0 RESULTS AND DISCUSSION

203 3.1 Physical Properties and Chemical Characterization

204 The results from the FTICR-MS data in Fig. 5 showed the intensity versus mass range of m/z (mass to
205 charge ratio) for each base oil. For example SN100 had a mass range of m/z of 200-500. Carbon number
206 ranges of C₁₅-C₅₀, C₂₀-C₆₀, C₂₀-C₉₀, C₁₅-C₅₅ and C₁₅-C₆₀ were found in SN100, HC4 and HC6, respectively.
207 The carbon number ranges are similar between G I and G III base oils with higher viscosity index base oils
208 in each class having higher carbon number constituents.

209 The class distributions shown in Fig. 6 indicate that the major hydrocarbon classes present in the samples
210 are HC (hydrocarbons), S1 (one sulfur-containing hydrocarbons), N1 (one nitrogen-containing
211 hydrocarbons) and S2 (two sulfur-containing hydrocarbons). This shows that in addition to major saturated
212 hydrocarbon groups (based on Table 2), other sulfur-containing hydrocarbons are present. For HC4 and
213 HC6, S class species are relatively negligible, which agrees with their elemental sulfur content of $< 0.003\%$
214 shown in Table 2. Low to negligible levels of N1 class components were observed, which suggests these
215 species were removed during the refining process. Based on the classification of the base stock oil
216 components presented in Table 2, the three *n*-alkanes were chosen to represent the large saturated
217 hydrocarbon fractions present in lubricant oils. Previous base oil analyses [12] reported a significant
218 presence of C₂₀-C₃₄ normal alkanes (*n*-paraffins) with other iso-alkanes and cycloalkanes. As will be shown
219 later, fundamental chemical kinetic modeling studies have shown that alkanes larger than C₁₄ exhibit nearly
220 identical fuel/air gas-phase ignition delay times across a range of operating temperatures [13, 14]. Thus,
221 surrogate components comprising linear alkanes of carbon number range of C₁₅-C₂₀ can represent the
222 ignition propensity and ignition kinetics of lubricant base oils. The lubricant surrogates, base oils, and SAE
223 20W50 lubricant were mixed with *iso*-octane (*i*C₈H₁₈-gasoline surrogate) in proportions of 1% vol. (*i*C₈H₁₈
224 = 99% vol.) and 10% vol. (*i*C₈H₁₈= 90% vol.) for IQT experiments. As reported by Wellings and co-authors
225 [15], the quantity of contaminant (i.e., lubricant entering the cylinder bulk gas that can initiate LSPI) is not
226 consistent. This has been attributed to the variability combined with other stochastic engine processes like
227 mixing, which can likely contribute to the unpredictable nature of LSPI. Based on this, it is believed that
228 the quantity of the lubricant surrogates, base stock oils, and SAE 20W50 added to *iso*-octane in this study
229 could be realized in a real engine undergoing LSPI. It should be noted that the global equivalence ratio
230 varies as the temperature changes from 873 to 680 K. For brevity, the lubricant surrogates, base oils, and
231 SAE 20W50 lubricant are referred to as lubricant additives in this research. Table 3 presents the physical
232 properties of the mixtures in terms of density and viscosity. The addition of 1% of the lubricant additive
233 into 99% *i*C₈H₁₈ minimally affects the density of the mixture, while 10% of the lubricant additive into 90%

234 iC_8H_{18} increases the density. The viscosity does not change much with the addition of the 1% lubricant
235 additive into 99% iC_8H_{18} . While the addition of 10% of the lubricant additive into 90% iC_8H_{18} led to an
236 increase in the viscosity of the mixtures. The increase in both density and viscosity can be attributed to the
237 increase in average molecular weight of the mixtures since the lubricant additives are heavier than pure *iso*-
238 octane. The distillation curves for the mixtures of *iso*-octane and lubricant oils are shown in Fig. 7. The
239 temperature corresponding to the 0% recovered distillate signifies the initial boiling point while that for the
240 100% recovered distillate is the final boiling point. For pure *iso*-octane, the initial boiling point (0%
241 recovered distillate) was attained at a temperature of 96.3°C. Note that for 100 % *iso*-octane, the initial
242 boiling point and final boiling are identical since it is a single component sample.

243 The addition of 1% lubricant additive to iC_8H_{18} did not change the distillation characteristics until the point
244 corresponding to 95% recovery. From the 95 to 100% (final boiling point), there is a notable change in the
245 distillation temperature, which can be triggered by the lubricant additive remaining after *iso*-octane has
246 been vaporized. For the 90% iC_8H_{18} with 10% lubricant additive, the distillation features did not change
247 until the distillate recovered reaches 90%. However, from the 90 to 100% there is an appreciable change in
248 the distillation as the final boiling point is reached. This implies that at the 90% distillate recovery stage,
249 *iso*-octane is almost totally vaporized while the remaining distillate (i.e. lubricant additive) has a high
250 boiling point causing a rapid rise in the distillation temperature up to the final boiling point.

251 The results obtained from the 90% iC_8H_{18} with 10% lubricant additive show that the base oils have higher
252 boiling points compared to the lubricant surrogates (i.e., *n*-alkanes). This is an indication that the lubricant
253 base oils contain larger molecules of saturates having higher boiling points compared to the C_{16} - C_{18} *n*-
254 alkane lubricant surrogates. In addition, the initial boiling point temperature was lower compared to pure
255 iC_8H_{18} , suggesting some synergistic effects of suppressing boiling point in the mixtures or the presence of
256 lighter molecules in the mixtures. The actual cause of lower initial boiling point in the mixtures requires
257 further investigation, and is beyond the scope of the present work. The influence of the aforementioned
258 distillation curve features will be correlated with ignition delay in the following section.

259 3.2 Effect of Lubricant Surrogates on Ignition

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

264 The variation of ignition delay time with temperature for the lubricant surrogate/*iso*-octane mixtures is
265 presented in Fig 8, which presents the effect of the addition of 1 and 10% of the lubricant surrogates into
266 99% and 90% *iso*-octane, respectively. The results show that adding 1% of the lubricant surrogates into
267 99% of *iso*-octane shortens the ignition delays by about 15%. Further increase in the quantity of lubricant
268 surrogates to 10% in the mixtures led to an appreciable shortening in the ignition delay time. The shortening
269 in ignition delay time is an indication of the propensity of these surrogates to pre-ignition, if they are used
270 to formulate engine lubricants. The reduction in ignition delay time can be attributed to the high reactivity
271 of the surrogate *n*-alkanes in the mixtures. One of the major factors reported in [16] affecting the reactivity
272 of fuel is the cetane number (CN). The cetane numbers of these lubricant surrogates are well documented
273 and have been reported in [17] as 100, 105, and 110 for *n*-hexadecane ($n\text{-C}_{16}\text{H}_{34}$), *n*-heptadecane ($n\text{-C}_{17}\text{H}_{36}$)
274 and *n*-octadecane ($n\text{-C}_{18}\text{H}_{36}$), respectively. The cetane number values for these fuels are much higher than
275 that of *iso*-octane (CN=17.5). The similar reactivity amongst the mixtures with 10% addition of C₁₆-C₁₈
276 *n*-alkanes confirms that a C₁₆ structure is a suitable surrogate for larger *n*-alkanes. The difference in *n*-
277 alkanes is smaller at high temperatures than at lower temperatures; variations in physical properties with
278 varying carbon number become more evident at lower temperatures where physical processes (e.g., spray
279 vaporization) play a more important role in the ignition process.

280 Fuel structures have been reported to play a major role on reactivity. Chevalier et al. [18] investigated the
281 role of the C-H bonds in *n*-heptane and *iso*-heptane. It was observed that methyl substituted heptane isomers
282 are less reactive than *n*-heptane. *Iso*-octane is highly branched compared to the lubricant surrogates, so it

283 has a low ignition propensity. Thus, the addition of $n\text{-C}_{16}\text{H}_{34}$, $n\text{-C}_{17}\text{H}_{36}$ and $n\text{-C}_{18}\text{H}_{38}$, which have straight
284 carbon chains, tends to increase the reactivity of the mixtures.

285 3.3 Effect of Lubricant Base oils on Ignition

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

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

304 3.4 Effect of SAE 20W50 Lubricant on Ignition

305 The addition of 1 and 10% of SAE 20W50 lubricating oil to *iso*-octane reduces the ignition delay time, as
306 shown in Fig. 10. This implies that the SAE 20W50 has the propensity to initiate pre-ignition if its
307 droplets/vapor escape into the bulk gas mixtures in the engine chamber. The ignition delay of the *iso*-

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

333 of these additives in lubricant base oils to initiate auto-ignition of surrogate fuel for spark ignition engines
334 i.e. *iso*-octane will be investigated as part of future work.

335 It is interesting to note that the *iso*-octane mixtures with addition of 1% of various additives display similar
336 reactivity. However, 10% addition of G III base oils and SAE 20W50 display similar ignition delay times
337 (e.g., < 5% difference), while 10% addition of base oil surrogates (C₁₆-C₁₈ *n*-alkanes) display slightly longer
338 ignition delay times (up to 25% difference). This may be due to the longer *n*-alkane chains (higher carbon
339 number) in the base oils and real lubricants, which have higher reactivity when blended with *iso*-octane in
340 larger amounts.

341 3.5 Chemical Ignition Delay

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

350 The simulations were conducted using a detailed chemical kinetic model for *n*-alkanes up to C₁₆ and 2-
351 methylalkanes up to C₂₀ [14]. This mechanism was merged with the *iso*-octane mechanism presented by
352 Mehl et al. [25] to simulate mixtures of large alkanes with *iso*-octane. Parametric studies of the chemical
353 ignition delay at global equivalence ratios of 0.975 and 1.95 were carried out to have an overview of the
354 reactivity of the *iso*-octane/alkanes mixtures at wider range of conditions. It should be noted that real
355 lubricant oils comprise various large *n*-alkanes and *iso*-alkanes with one, two, or more methyl substitutions.
356 Simulations are presented for blends of *iso*-octane with large *n*-alkanes and 2-methylalkanes to better
357 understand the effects of lubricant oil's alkane composition on chemical ignition delay. Fig. 11 (a) shows

358 the variation of the chemical ignition delay of the *iso*-octane mixtures with large alkanes at a global
359 equivalence ratio of 0.975. In the temperature range of 900 to 1000 K ($1 < 1000/T < 1.1$), the reactivity of
360 pure *iso*-octane and *iso*-octane (99% vol.)/alkanes (1% vol.) mixtures are similar. The chemical ignition
361 delay further increases as temperature decreases to 800 K for both pure *iso*-octane and *iso*-octane (99%
362 vol.)/alkanes (1% vol.) mixtures. As temperature decreases from 900 to 800K, the chemical ignition delay
363 of the *iso*-octane (99% vol.)/alkanes (1% vol.) mixtures tend to be shorter than the pure *iso*-octane. This is
364 an indication of the impact of large alkanes on the reactivity of the mixtures. As obtained in the experimental
365 results, the reactivity of the *iso*-octane/alkane mixtures increased significantly when the quantity of large
366 alkanes in the *iso*-octane mixtures increases to 10%. At the temperature range of 920 to 1000 K, there is
367 less significant difference in the chemical ignition delay of the *iso*-octane with 10% vol. large alkanes
368 compared to the mixtures with 1% vol. alkanes. However a remarkable difference exists in the chemical
369 ignition delay of *iso*-octane with 10% vol. large alkanes compared and the mixtures with 1% vol. alkane as
370 temperature decreases from 925 to 600 K. By doubling the equivalence ratio, the variation of the chemical
371 ignition delay of the fuels with temperature is presented in Fig. 11 (b). The result obtained follow similar
372 trend to that obtained at leaner conditions except that the mixture with 10% alkanes shows a greater
373 difference in reactivity compared to other mixtures. When the equivalence ratio increases, the reactivity is
374 enhanced thus decreasing the chemical ignition delay. This is in line with the work done by Darcy and et
375 al. [26] and Healy et al. [27], in which it was observed that at low temperatures and high ambient pressure
376 conditions chain branching reactions accelerate as fuel concentration increases. Fig. 10 indicates that the
377 presence of 1% larger n-alkanes and 2-methylalkanes in the *iso*-octane yielded no significant difference in
378 reactivity. This is in agreement with the experimental measurements presented earlier for mixtures of *iso*-
379 octane with 1% of various lubricant additives. Therefore, the chemical ignition delay of large alkanes
380 present in lubricant oils can be adequately reproduced with *n*-hexadecane as surrogate, further supporting
381 the experimental approach presented herein.

382 Finally, considering the physical properties such as density, distillation temperature, and viscosity, the
383 addition of the lubricant surrogates, base oils, and engine oils have the tendency of increasing the physical
384 delay part of the total ignition delay. On the other hand the chemical ignition delay is shortened with the
385 addition of the large *n*-alkanes and *iso*-alkanes that are found in the base oils and real lubricants. Since the
386 total measured ignition delay for all the mixtures are shortened as a result of the addition of the lubricant
387 surrogates, base oils, and engine oils, it can be assumed that the chemical ignition delay is more rate
388 controlling than the physical ignition delay. This suggests that the propensity of a lubricant to initiate pre-
389 ignition in DISI engines can be attributed to the chemical kinetic properties of the base oil used in the
390 formulation. The results presented herein showed that base oils with high percentage of long chain
391 hydrocarbons, such as HC4, have the tendency to ignite faster than base oils with lower amounts of long
392 chain hydrocarbons (e.g., SN 100 and SN 500).

393 4.0 CONCLUSIONS

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

- 398 1. Compared to 100% *iso*-octane, the addition of 1 % vol. of the lubricant additives into 99% vol. of *iso*-
399 octane resulted in ignition delays being shortened by 15 %. Further increase in the quantity of lubricant
400 surrogate to 10% in the mixture led to a drastic shortening in the ignition delay time.
- 401 2. The previous points suggest that C₁₆-C₁₈ *n*-alkanes are adequate surrogates for capturing the ignition
402 characteristics of real base oils and fully formulated lubricants. Additional studies with organo-metallic
403 additives are needed to ascertain their role in **ignition delay**; however, the present work suggests that
404 their effects are negligible compared to the hydrocarbon components in the base oil.
- 405 3. Simulations indicate that the presence of the higher *n*-alkanes and 2-methylalkanes in *iso*-octane
406 mixtures leads to a reduction in chemical ignition delay.

407 4. The chemical ignition delay plays a greater role than the physical ignition delay in the reduction of the
408 total ignition delay.

409

410 5.0 ACKNOWLEDGEMENTS

411 The authors thank Saudi Aramco for sponsoring this research under the FUELCOM theme. We thank Tunde
412 Gasper of the Clean Combustion Research Center for her assistance in measuring the physical properties of
413 the *iso*-octane-lubricant mixtures.

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506 ABBREVIATIONS

507	API	American Petroleum Institute
508	CN	cetane number
509	DISI	direct injection spark ignition
510	FTICR-MS	Fourier transform ion cyclotron resonance mass spectrometer
511	HP-DSC	high pressure differential scanning calorimetry
512	IQT	ignition quality tester
513	LSPI	low speed pre-ignition
514	SoIgn	start of ignition
515	SoInj	start of injection
516	<i>i</i> C ₈ H ₁₈	<i>iso</i> -octane
517	max (dP/dt)	maximum change in pressure with time
518	m/z	mass to charge ratio
519	<i>n</i> C ₁₆ H ₃₄	<i>n</i> -hexadecane
520	<i>n</i> C ₁₇ H ₃₆	<i>n</i> -heptadecane
521	<i>n</i> C ₁₈ H ₃₈	<i>n</i> -octadecane

522