



Title	Experimental Study on Evaporation Characteristics of Light Cycle Oil Droplet under Various Ambient Conditions
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1 Experimental study on evaporation characteristics of
2 light cycle oil (LCO) droplet under various ambient
3 conditions

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14 **KEYWORDS:** Droplet evaporation; Low ignitability fuel; Cetane index; Low sulfur fuel; Marine
15 fuel

16 ABSTRACT: The authors conducted droplet evaporation experiments of light cycle oil (LCO) at
17 various ambient temperatures and pressures. Five kinds of LCO and three kinds of arranged-fuels
18 were used. We investigated the evaporation characteristics of LCO and the relationships between
19 the evaporation characteristics and the cetane index. In addition to that, a surrogate fuel composed
20 of 4 chemical species, which can simulate the droplet evaporation characteristics of LCO, was
21 suggested. Experimental results show that the differences in droplet lifetime between fuel species
22 become larger with decreasing ambient temperature. This is because the low volatile component
23 made the evaporation rate outstandingly slow at a low ambient temperature. Second, it was found
24 that the relationship between droplet lifetime and the late-stage distillation temperature becomes
25 stronger at low ambient temperature and high ambient pressure. By an analysis employing the
26 properties of chemical species in LCO surrogate fuel, it is clarified that the mass evaporation rate
27 becomes smaller than the internal diffusion, which is the condition similar to that in the distillation
28 test. Finally, the relationship between the droplet lifetime and the cetane index was investigated.
29 It can be concluded that the droplet lifetime is independent of the cetane index under all conditions
30 tested in this study. The experimental data obtained by this research can be utilized for the
31 validation of multi-component fuel droplet evaporation models in the future.

32

33 1. INTRODUCTION

34 Spray combustion is widely employed in industrial applications such as internal combustion
35 engines, gas turbine engines, and rocket propulsion systems. However, the unstable combustion
36 phenomena which cause a malfunction of the combustor has been reported.^{1,2} For instance,
37 knocking has been recognized as one of major problems for the reciprocating engine. An ignition
38 delay of fuel is an important factor determining the occurrence of the knocking. To investigate the
39 relationship between the ignition delay and the knocking, a study for single droplet ignition was
40 conducted by some reserachers.³ Furthermore, the ignition delay and combustion characteristics
41 of biodiesel also have been studied because the practical usage of the next-generation fuel for an
42 internal combustion engine is attempted in recent years.^{4,5} Even though relationship between the
43 combustion characteristics and the ignition delay has been investigated a lot, dominant factors for
44 the ignition delay has not been clarified because the structure of spray combustion is much
45 complicated, which is including atomization, droplet evaporation, and chemical reactions.
46 Therefore, fundamental knowledge to clarify the dominant factors in the ignition delay is required.
47 To clarify the complex mechanism of spray combustion, a numerical simulation tool has been
48 strongly expanded. By employing the numerical simulation, not only the characteristics of spray⁶
49 and spray flame such as jet flame^{7,8} but also elements of spray flame such as atomization⁹ and
50 impingement¹⁰ have been investigated. In particular, the prediction of fuel droplet size
51 distributions and evaporation rate could affect the prediction of combustion properties including
52 efficiency, stability, and pollutant formation rate. Noh *et. al.*¹¹ compared the spray combustion
53 properties predicted by the different types of droplet evaporation models. As one of their findings,
54 the predicted flame lift-off height depends on the droplet evaporation rate. It was revealed that the
55 accuracy of a droplet evaporation model strongly influences the accuracy of the spray flame

56 structure predictions. Hence, the droplet evaporation model is one of the most important parts of
57 the numerical simulation technology for the prediction of the spray combustion fields of the
58 combustor. To develop the accurate droplet evaporation model, the experimental data for droplet
59 evaporation is necessary for its validation. Nomura *et al.* investigated the droplet effect of ambient
60 pressure on the evaporation characteristics of n-heptane¹² and n-hexadecane¹³.

61 The droplet evaporation experimental data for market fuels have been also obtained by some
62 researchers, while droplet combustion which is single droplet^{14,15} as well as droplet cloud¹⁶ have
63 been studied a lot. For example, Elkotb *et al.*¹⁷ studied the evaporation of commercial fuels (i.e.,
64 heavy diesel fuel, light diesel fuel, kerosene, gasoline, and their blends) at 400 °C and atmospheric
65 pressure. Morin *et al.*¹⁸ investigated the vaporization of vegetable oil droplets used as biofuels at
66 high ambient temperature. Ghassemi *et al.*¹⁹ investigated the vaporization of kerosene droplet at
67 high temperatures and high pressures. Hashimoto *et al.*²⁰ investigated the evaporation
68 characteristics of a palm methyl ester droplet at high ambient temperature. However, the
69 experimental data of multi-component market fuel droplet evaporation are still very limited. For
70 instance, the experimental data of droplet evaporation for light cycle oil (LCO) have not been
71 obtained. The following is the reason why the experimental data of droplet evaporation for LCO
72 is required.

73 As one of the significant environmental regulations, the International Maritime Organization
74 (IMO) decided to tighten the global regulations of sulfur content in maritime fuel used on-board
75 ships from 3.5% to 0.5% since 2020. To reduce the sulfur oxides in the exhaust gas, the fuel with
76 low sulfur contents could lead to finding a solution to the root cause. Therefore, the efficient use
77 of cracked middle distillates that contain fewer sulfur compositions is becoming important because
78 of the increasing demand for diesel fuel.²¹ As one of the cracked middle distillates, light cycle oil

79 (LCO) is a promising fuel of commercial diesel fuel, which is already mixed in maritime fuel as
80 the fuel oil base material.²² In response to the IMO regulations, some researchers investigated the
81 fuel properties of LCO for practical usage and market growth.^{23,24} Hence, to correspond to the
82 high market demand for LCO, the effect of using LCO on a combustor should be investigated.

83 Despite the advantages of LCO such as low sulfur compositions, LCO tend to contain a lot of
84 aromatic compositions and be characterized as low ignitability fuel. Therefore, considering the
85 increase of the situation that LCO is used as a part of a mixture product, the influence of using
86 LCO on the diesel engines should be clarified. Xu *et al.*^{25,26} investigated the combustion of LCO
87 single droplets in normal and microgravity conditions. Imhof *et al.*²⁷ investigated emissions of
88 LCO water-in-fuel emulsions with a test engine to reduce NO_x and unburned emission to follow
89 IMO regulation. Tashima *et. al.*²⁸ demonstrated computational fluid dynamics (CFD) simulation
90 including spray development and combustion process by using the fuel blending LCO.
91 Furthermore, to develop the high precision simulation technique for LCO spray combustion,
92 Takagi *et. al.*²⁹ developed a droplet evaporation model for multi-component fuel to investigate the
93 relationships between evaporation characteristics and ignition delay. They numerically clarified
94 that the effect of evaporation time on ignition delay become larger with increasing cetane index.
95 Furthermore, they compared the predicted droplet evaporation characteristics of 13 kinds of LCO
96 to clarify the relationship between the ignitability index and evaporation characteristics. However,
97 the accuracy of the droplet evaporation model for LCO has not been clarified yet because the
98 experimental data of LCO droplet evaporation have not been reported yet. To develop precise
99 numerical simulation technologies for LCO spray combustion, the accuracy of the droplet
100 evaporation model, which can affect the simulation results significantly, should be verified well
101 by using experimental data.

102 In this study, the droplet evaporation characteristics of LCO at various ambient temperatures
103 and pressures were investigated. The relationships between the evaporation characteristics and fuel
104 ignitability index are investigated. The experimental data obtained by this study can be utilized for
105 the future development of numerical simulation technology for LCO spray combustion as the
106 validation data.

107

108 2. EXPERIMENTAL METHOD

109 2.1 LCO properties

110 This study used five kinds of LCO with different properties. Table 1 shows the properties of the
111 LCO. L1, L2, L3, L12, and L13 are LCOs obtained at different oil refineries. L1, L2, L3 are the
112 combination to investigate the effect of the differences of distillation characteristics. L12 L13 is
113 the combination to have similar distillation characteristics. The fuels used in this study cover the
114 hydrocarbon compositions of LCO not only before but also after hydrogenation.³⁰ As one of the
115 remarkable characteristics of LCO, its cetane index is generally smaller than that of other
116 transportation fuels, such as light oil and A-type heavy oil, which is why LCO is generally well
117 known as a low-ignitibility fuel. The cetane index is applied instead of the cetane number when
118 the cetane number cannot be obtained by the prescribed test engine. In this study, two kinds of
119 cetane index are introduced. First on is the old cetane index (OCI) based on ASTM D976-66 or
120 JIS K 2204:1983, which is expressed as follows:

121

$$OCI = 0.49083 + 1.06577X - 0.0010552X^2 \quad (1)$$

$$X = 97.833(\log_{10}(A))^2 + 2.2088B_0 \log_{10}(A) + 0.0124B_0^2 - 423.51 \log_{10}(A) - 4.7808B_0 + 419.59 \quad (2)$$

$$A = \frac{9}{5}T_{50} + 32 \quad (3)$$

122

123 where B_0 is the API gravity (-), and T_{50} is 50% volume distillation temperature (°C). Only 50%
 124 volume distillation temperature is considered in the OCI. Second one is the new cetane index (NCI)
 125 based on ISO 4264:2007 or JIS K 2280-5:2013, which is expressed as follows:

126

$$\begin{aligned} \text{NCI} = & 45.2 + 0.0892(T_{10} - 215) + (0.131 + 0.901B)(T_{50} - 260) \\ & + (0.0523 - 0.42B)(T_{90} - 310) + 0.00049\{(T_{10} - 215)^2 \\ & - (T_{90} - 310)^2\} + 107B + 60B^2 \end{aligned} \quad (4)$$

$$B = \exp\{-0.0035(1000D - 850)\} - 1 \quad (5)$$

127

128 where T_{10} is the 10% volume distillation temperature (°C), T_{50} is the 50% volume distillation
 129 temperature (°C), T_{90} is the 90% volume distillation temperature (°C), and D is the density at 15 °C
 130 (g/cm³). In the NCI, 50%, 10%, and 90% volume distillation temperatures are considered, while
 131 only 50% volume distillation temperature is considered in the OCI. Note that in LCO, Takagi *et*
 132 *al.*³¹ clarified that the ignition delay of LCO, which has the equivalent OCI to standard fuel of
 133 cetane number, can be related to that of the standard fuel of cetane number. However, the
 134 relationship between CI and evaporation characteristics has not been clarified.

135 As the other characteristics of LCO, a large number of aromatic hydrocarbons are contained in
 136 comparison with the other transportation fuels. Table1 shows that L1, L2, and L3 contains
 137 significant amounts of aromatic hydrocarbons. L1 and L3 contain over 80vol% aromatic
 138 hydrocarbons. In particular, L3 has over 20vol% aromatic hydrocarbons with at least three rings,
 139 which is the largest amount in the present LCO. L2 contains the largest amount of olefin in the

140 present LCO. L12 and L13 contain a large
141 number of saturated hydrocarbons that are
142 over 50vol%. Figure 1 shows the distillation
143 curves of LCO and light oil ²⁰. According to
144 Figure 1, L1 has the minimum difference
145 between the initial boiling point (0%) and the
146 ending point (100%) in LCO. On the other
147 hands, L2 contains the largest number of the
148 component with a low boiling point in LCO.
149 Regarding the ending point of the distillation
150 curve, L3 contains components with the highest boiling point. On the contrary, L12 and L13 have
151 similar distillation characteristics. Note that the specific distillation temperatures in Figure 1 are
152 printed in Supporting Information.

153

154 2.2 Arranged-fuels (S30, S35 and S40)

155 Arranged-fuels (S30, S35, and S40) were used to investigate the effect of the differences between
156 the OCI and NCI on the evaporation characteristics of LCO. The arranged-fuels, are made to have
157 almost the same NCI, are the liquid mixtures of refinery feedstocks and solvents. LCO used in this
158 study has a variety of not only distillation characteristics but also cetane index. This makes it
159 difficult to clarify whether the distillation characteristics or the cetane index have related to the
160 evaporation characteristics. To clarify the relationship between the cetane index and droplet
161 evaporation characteristics, the authors made the arranged-fuels, which has different distillation

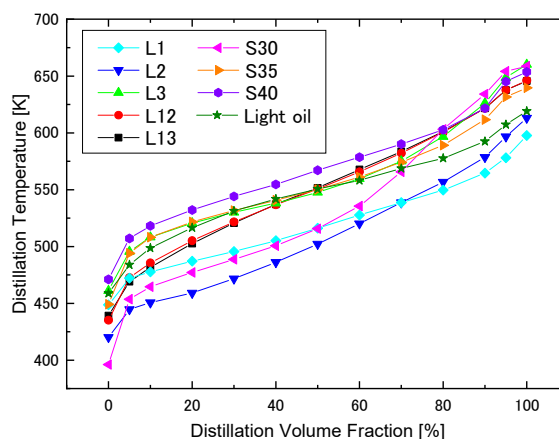


Figure 1. Distillation curves of LCO, arranged-fuels and light oil.

162 characteristics but almost the same cetane index. The properties of the arranged-fuels are shown
 163 in Table 1.

164

Table 1. Properties of light cycle oil and arranged-fuel used in this study

		Light Cycle Oil					Arranged-Fuel			
		L1	L2	L3	L12	L13	S30	S35	S40	
Density(15°C)	g/cm ³	0.9323	0.9266	0.9659	0.9018	0.8931	0.8834	0.8968	0.9028	
Flash point	°C	68	52	N/A	N/A	67	29	79	82	
Dynamic viscosity(30°C)	mm ² /s	2.169	2.097	N/A	N/A	3.425	2.454	3.844	4.582	
Dynamic viscosity(50°C)	mm ² /s	1.522	1.493	2.469	2.295	2.256	1.724	2.497	2.898	
Water content	wt%	0.00	0.00	N/A	N/A	0.00	0.00	0.00	0.00	
Pour point	°C	<-45	<-45	N/A	N/A	-2.5	-30.0	-22.5	-22.5	
CCAI	-	911	907	935	875	855	857	855	856	
Old cetane index (JIS K 2204)	-	15	13.0	13.5	33.0	36.0	30.0	34.5	36.5	
New cetane index (ISO 4264)	-	19.8	22.5	23.1	32.5	34.5	35.5	35.2	35.3	
10%carbon residue	wt%	0.1	0.11	N/A	N/A	0.05	0.02	0.46	0.05	
Sulfur	wt%	0.14	0.13	0.39	0.049	0.058	0.047	0.14	0.073	
Nitrogen	wt%	0.011	0.012	N/A	N/A	0.016	0.008	0.04	0.024	
Carbon	wt%	90.2	89.9	N/A	N/A	88.6	88.8	88.4	88.8	
Hydrogen	wt%	9.6	9.9	N/A	N/A	11.3	11.1	11.4	11.1	
Molecular structures	Saturated molecule	vol%	14.3	16.7	14.6	35.0	39.8	39.2	45.4	44.8
	Olefin	vol%	1.5	16.8	0.8	7.0	6.2	4.5	3.0	7.4
	Aromatics	vol%	84.2	66.5	84.6	58.0	54.0	56.3	51.6	47.8
	1ring aromatics	vol%	36.6	33.2	16.5	21.8	20.7	34.1	17.9	12.8
	2ring aromatics over 2 ring aromatics	vol%	43.6	27.8	47.4	24.6	22.8	17.9	23.9	18.5

165

166 2.3 Experimental setup and test conditions

167 Figure 2 shows the experimental setup²⁰ and the droplet suspend holder used in this study. The
 168 pressure vessel (inner diameter: 100 mm; inner height; 229 mm) was made by extra-super
 169 duralumin (JIS: A7075). The pressure vessel was filled with N₂ before the experiment to observe

170 a pure evaporation phenomenon without combustion. A charge-coupled device (CCD) video
 171 camera and a high-speed camera (DITECT, HAS-X) was used to observe the inside of the pressure
 172 vessel. The CCD video camera observed the droplet generating process. A fuel droplet with a
 173 diameter in the range of $0.5 \pm 15\%$ mm was suspended on the intersection point of two $\text{Al}_2\text{O}_3/\text{SiO}_2$
 174 fibers with $7 \mu\text{m}$ diameter. The fuel was pumped with a microflow pump to the tip of the glass
 175 needle (outer diameter: $40 \mu\text{m}$) of the droplet generator. After the fuel droplet was suspended at
 176 the intersection point of the droplet suspender, the glass needle was evacuated in preparation for
 177 the droplet insertion of the droplet into the hot chamber. A linear slider-crank mechanism was
 178 applied to the fuel droplet elevator to reduce the impact on the suspended droplet during the droplet
 179 insertion process. The traveling time of the droplet during the insertion into the hot chamber was
 180 0.26 s , whose traveling distance is 6 mm . We compared the measured droplet diameter before and

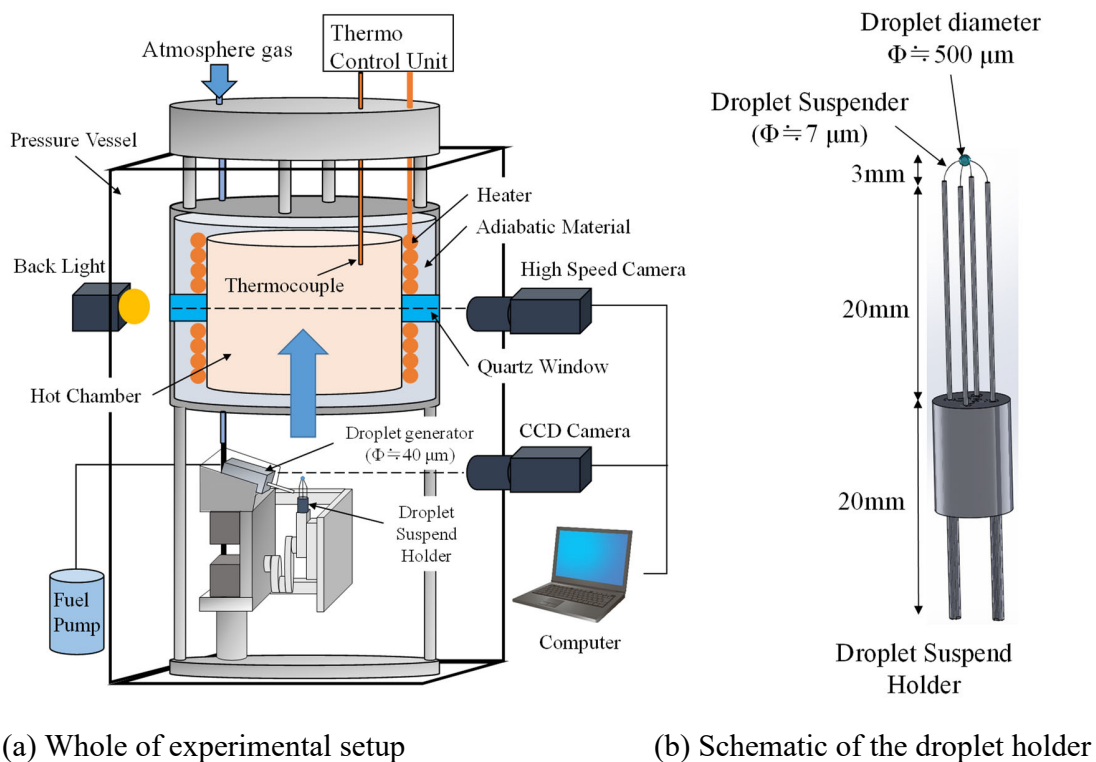


Figure 2. Schematic of the experimental setup for the droplet evaporation experiment

181 after droplet insertion for all measured
 182 experimental data in the case of L1 to clarify
 183 the effect of the linear slider-crank mechanism
 184 on the evaporation characteristics. As a result,
 185 the average error of diameter difference is less
 186 than 5%. The ambient temperature (T_{amb})
 187 inside the hot chamber was arbitrarily
 188 controlled in the range of 473-873 K by a
 189 thermal control unit. The images of an
 190 evaporating droplet were taken with a high-

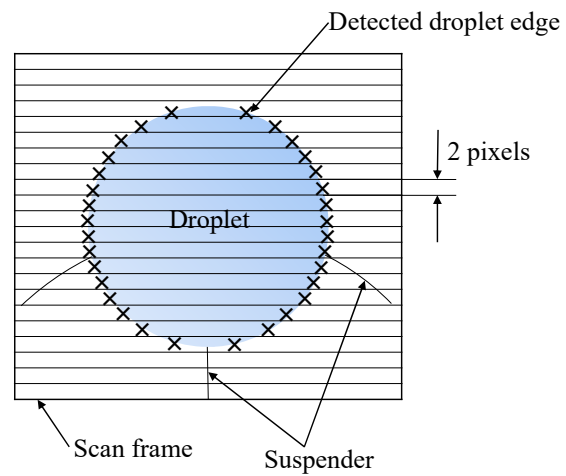


Figure 3. Schematic of the image analysis used to measure the droplet diameter

191 speed camera with backlit photography. The recorded backlit image of an evaporating fuel droplet
 192 was analyzed by using a self-made image analyzer program ³². Figure 3 shows the details of the
 193 image analysis in this study. Each backlit image of a fuel droplet was divided into horizontal line
 194 sections with a vertical thickness of 2 pixels. The average horizontal intensity profiles were
 195 calculated for each section. The edge of a droplet was determined as the farthest position from the
 196 suspender at which the intensity was less than $(I_A + 2I_B)/3$, where I_A and I_B were the average
 197 intensities of the background and droplet, respectively. The droplet volume was calculated by an
 198 ellipsoidal approximation using the determined edge. Finally, the droplet diameter was defined as
 199 the diameter of a sphere with the same volume. The measurement limit of the droplet diameter
 200 using the image analyzer was under 0.078 mm, which corresponded to D^2/D_0^2 of 0.025.

201 Figure 4 describes the definition of the periods during the droplet evaporation. The squared
 202 diameter was normalized by the squared initial diameter. Note that the droplet diameter when the
 203 fuel droplet was inserted in the hot chamber was defined as the initial droplet diameter in this study.

204 In the droplet evaporation experiments, the
 205 droplet diameter initially increases because of
 206 the thermal expansion effect caused by
 207 momentarily increasing the inner droplet
 208 temperature, which is shown as an initial
 209 heating period (τ_i/D_0^2). In the initial heating
 210 period, most of the heat energy from the
 211 ambient gas into the droplet is consumed to
 212 heat up the droplet. Therefore, decreasing the
 213 droplet density leads to an increase in the droplet diameter until the droplet evaporation rate
 214 becomes equal to the thermal expansion rate. The droplet diameter decreases monotonically after
 215 the droplet diameter reaches the maximum. As the indicator of the droplet lifetime, the 95vol%
 216 lifetime (τ_{95}/D_0^2) was defined as the period between the time when the fuel droplet was inserted
 217 into the hot chamber and the time when the droplet volume decreased to 5% of the initial volume
 218 equivalent to a relative diameter square of 13.6%. The droplet lifetime was also normalized by the
 219 second power of the initial droplet diameter because the initial droplet diameter strongly affects
 220 the droplet lifetime. The period obtained by removing the initial heating period from the 95vol%
 221 lifetime is defined as the main evaporation period (τ_{evap}/D_0^2).

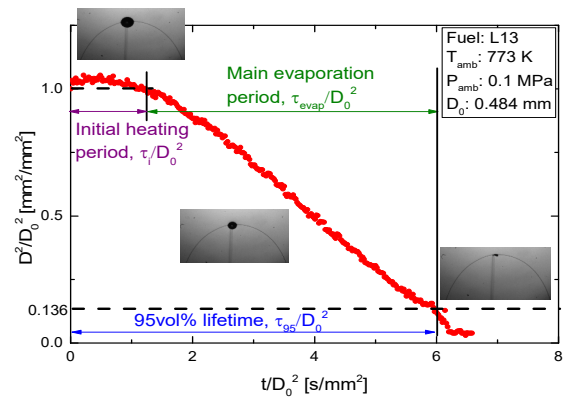


Figure 4. Definition of periods during the droplet evaporation

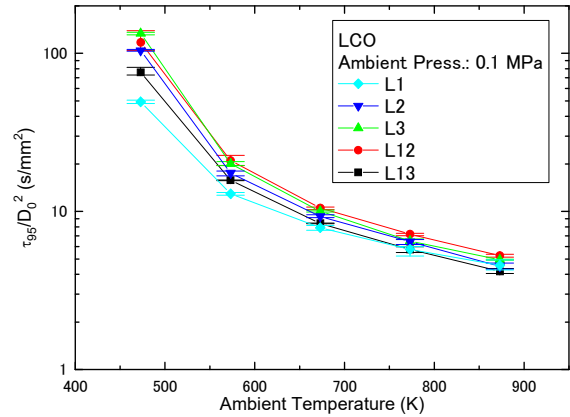
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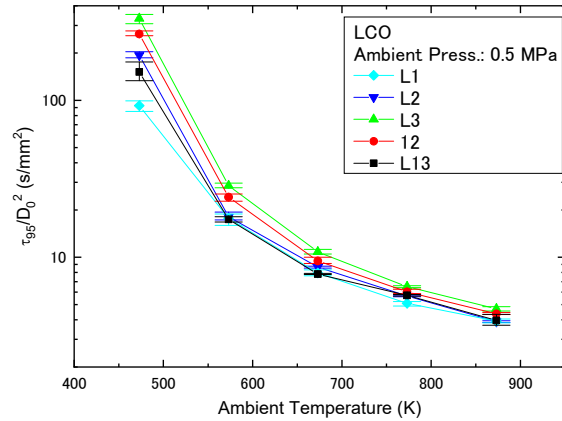
228 3. RESULTS AND DISCUSSIONS

229 3.1 Effect of the ambient temperature on the
230 evaporation characteristics for LCO and
231 arranged-fuels

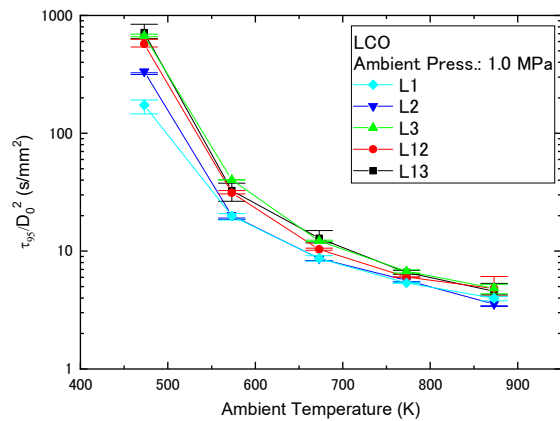
232 Figure 5 shows the τ_{95}/D_0^2 of LCO in the
233 ambient temperature range of 473-873 K at the
234 ambient pressures (P_{amb}) of 0.1, 0.5, and 1.0
235 MPa. The differences of τ_{95}/D_0^2 between each
236 LCO clearly become large with decreasing
237 ambient temperature at all ambient pressures.
238 In particular, at $T_{amb} = 473$ K, L1 has the
239 smallest τ_{95}/D_0^2 at all ambient pressures.
240 Subsequently, τ_{95}/D_0^2 become large in the
241 order of L2, L12, and L3. The reason for the
242 pressure dependence of L13 becoming
243 different from the other LCO at the lower
244 ambient temperature will be discussed in
245 Section 3.2. Figure 6 shows the τ_{95}/D_0^2 of the
246 arranged-fuels in the ambient temperature
247 range of 473-873 K at the ambient pressures of
248 0.1, 0.5, and 1.0 MPa. Similar to LCO, the
249 trend that the differences of τ_{95}/D_0^2 become



(a) $P_{amb} = 0.1$ MPa



(b) $P_{amb} = 0.5$ MPa



(c) $P_{amb} = 1.0$ MPa

Figure 5. Normalized 95vol% lifetime (τ_{95}/D_0^2) as a function of the ambient temperature for LCO

250 large with decreasing ambient temperature can
 251 be seen at all ambient pressures. On the other
 252 hands, the differences of τ_{95}/D_0^2 between S30
 253 and S40 become much small at various
 254 ambient temperatures, except 473 K, at all
 255 ambient pressures.

256 The reason that the differences of τ_{95}/D_0^2
 257 between the fuels become large at the low
 258 ambient temperature will be discussed in the
 259 parts that follow. Figure 7 shows the histories
 260 of the D^2/D_0^2 of LCO and the arranged-fuels
 261 at various ambient temperatures and $P_{amb} =$
 262 0.1 MPa. Note that the detailed law data for all
 263 histories of the D^2/D_0^2 obtained in this study
 264 are provided in the Supporting Information
 265 section of this paper. These D^2/D_0^2 history
 266 data will be directly used for the future
 267 validation for the multi-component droplet
 268 evaporation model development. In particular,
 269 the sensitivity of the components in fuel for the
 270 models can be validated in detail, because the
 271 D^2/D_0^2 histories significantly differ each other
 272 when the components are different as

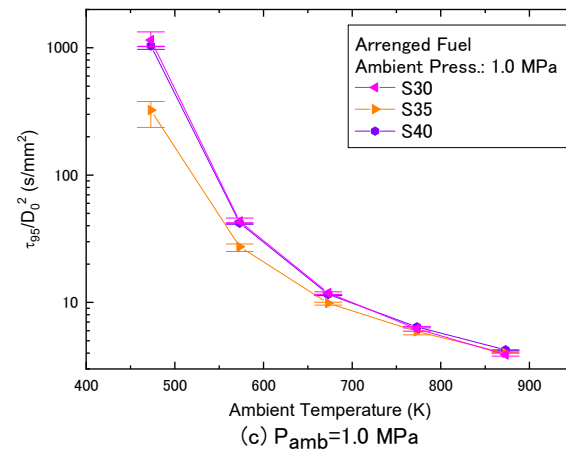
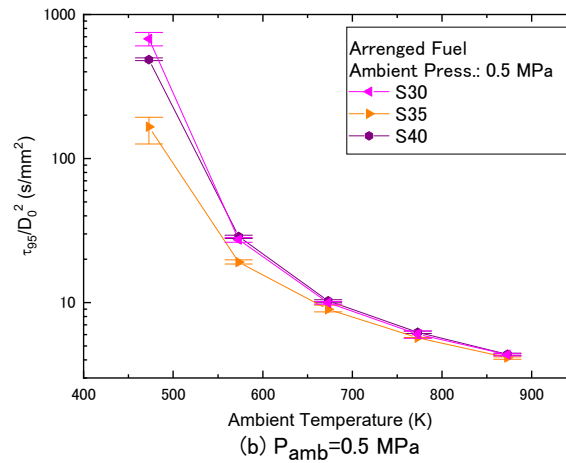
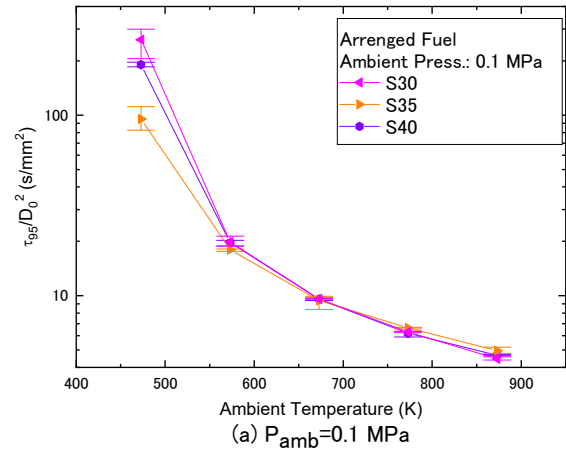


Figure 6. Normalized 95vol% lifetime (τ_{95}/D_0^2) as a function of the ambient temperature for the arranged-fuel

273 observed in Figure 7 (a). According to
 274 Figure 7-(a), the rate of decrease in D^2/D_0^2
 275 become obviously slow as time goes by. The
 276 rate of decrease in D^2/D_0^2 approaches to a
 277 constant rate during τ_{evap}/D_0^2 with
 278 increasing ambient temperature (Figure 7).
 279 To evaluate the rate of decrease in D^2/D_0^2 ,
 280 this study defined the instantaneous
 281 evaporation coefficient (K_{inst}) to
 282 quantitatively evaluate the rate of decrease in
 283 D^2/D_0^2 . K_{inst} was calculated by the
 284 following procedures: first, the original data
 285 plots during τ_{evap}/D_0^2 consisting of 200-
 286 3000 plots were thinned to 40-50 plots.
 287 Second, the smoothing differentiation
 288 method, called as the SG method³³, was
 289 applied to the thinned data plots. The
 290 absolute value of the differential coefficient
 291 calculated by the SG method gave K_{inst} .
 292 Figure 8 shows the K_{inst} of LCO and the
 293 arranged-fuels in various ambient
 294 temperatures at $P_{amb} = 0.1$ MPa. The
 295 fluctuation of K_{inst} history shown in Figure

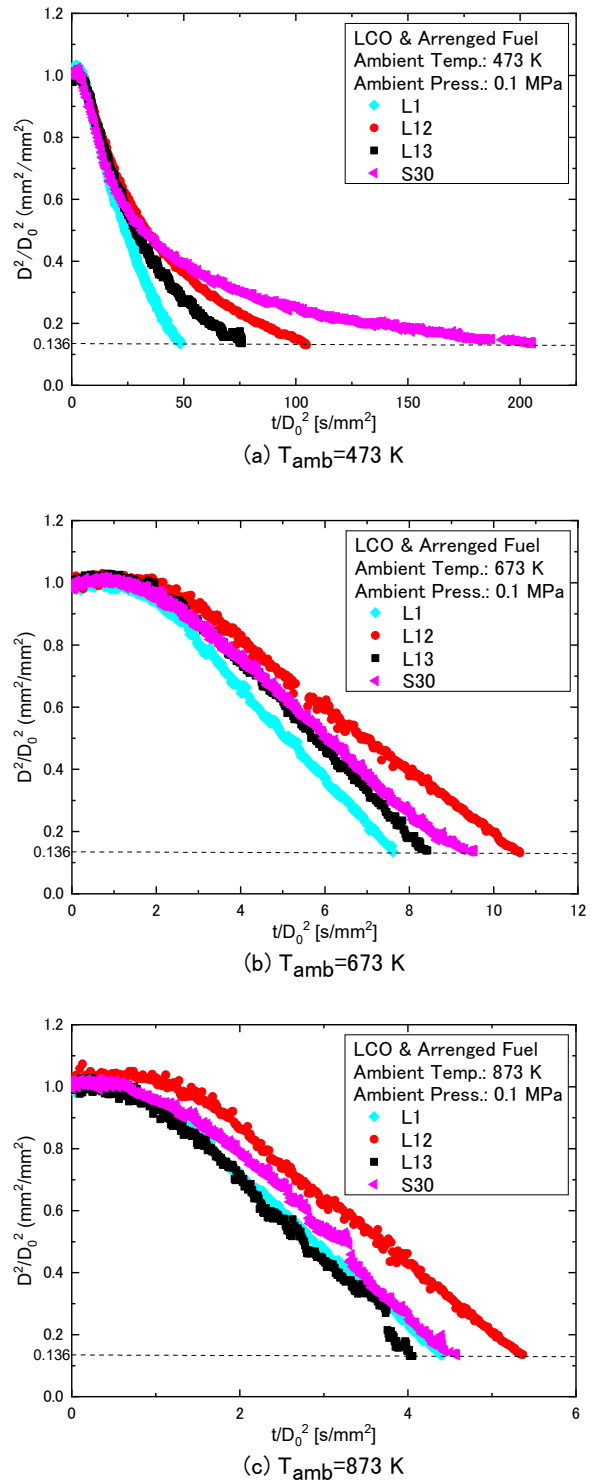


Figure 7. Examples of the histories of normalized D^2 for LCO

296 8 is caused by image analysis error. A
 297 decreasing of K_{inst} indicates that the rate of
 298 decrease in D^2/D_0^2 shown in Figure 7 is not
 299 constant as time goes by at $T_{amb}=473$ K. The
 300 gradient shown in Figure 8-(a) become steep
 301 in the order of S30, L12, L13, and L1. This
 302 order matches the order of the highest boiling
 303 point component in the fuel. Hence, it is
 304 considered that the end point of distillation
 305 curve may make the rate of decrease in
 306 D^2/D_0^2 slower even though LCO contain the
 307 various chemical species having the various
 308 boiling point. Note that there is an obvious
 309 difference of K_{inst} between L12 and L13
 310 even though the difference of the highest
 311 boiling point component between L12 and
 312 L13 is much small. To clarify this reason,
 313 much fundamental experimental data based
 314 on the single component are necessary.
 315 However, Figure 8-(b) and (c) shows that the
 316 difference of K_{inst} between the fuels
 317 decrease, and the absolute value of K_{inst}
 318 reaches an almost constant value with

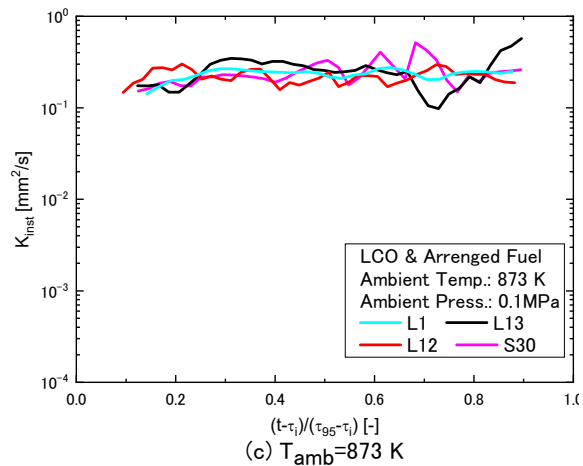
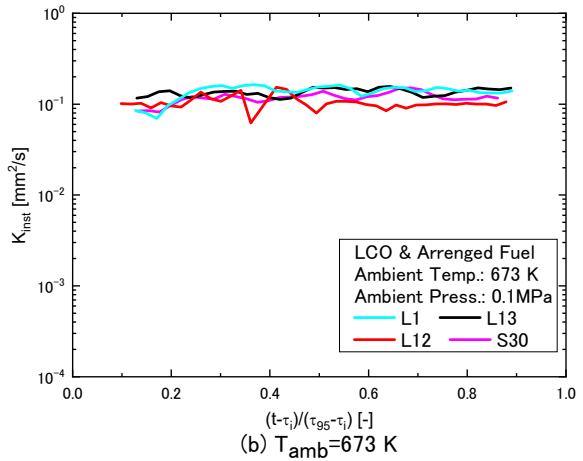
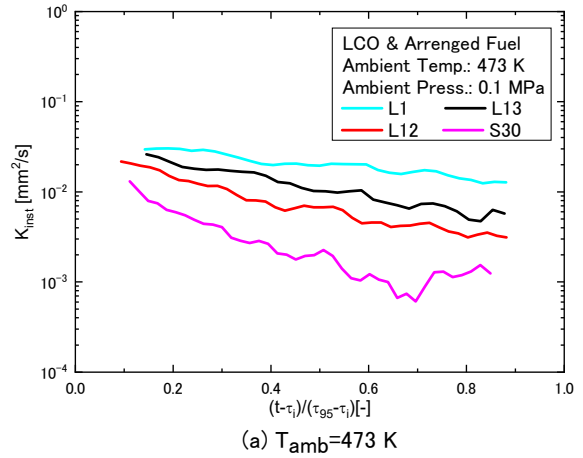


Figure 8. Instantaneous evaporation coefficient (K_{inst}) for LCO and the arranged-fuels

319 increasing ambient temperature. These findings confirm that the rate of decrease in D^2/D_0^2 is
 320 almost constant at the higher ambient temperature. On the other hand, the ambient pressure
 321 dependence on the evaporation characteristics will be discussed in section 3.3.
 322

Table 2. Compositions and properties of L1 surrogate fuel

Molecular Formula		C ₁₀ H ₁₄	C ₁₁ H ₁₀	C ₁₆ H ₃₄	C ₂₀ H ₄₂
Molecular Weight	g/mol	134	142	226	282
Mass Fraction	-	0.3116	0.4402	0.1753	0.0729
Boiling Point	°C	169.1	244.6	286.9	344.1
Density (15°C)	g/cm ³	0.8708	1.027	0.7773	0.7908

323 3.2 Development and validation of the surrogate fuel for LCO

324 In the numerical simulation, a surrogate fuel is usually used. A surrogate fuel consists of distinct
 325 fuel to simulate a certain characteristic of physical phenomena. By using a surrogate fuel in
 326 combustion simulation, we are able to utilize the detailed chemical reaction mechanism. However,
 327 the surrogate fuel of LCO has not been developed. To conduct the precise combustion simulation
 328 using LCO in future works, the surrogate fuel of LCO should be developed.

329 To simulate the evaporation characteristics of LCO (L1), we choose the chemical species and
 330 determine their fractions so that the distillation characteristics of LCO can be reproduced by the
 331 surrogate fuel. Table 2 shows the compositions and properties of the developed surrogate fuel.
 332 LCO surrogate fuel, which is treated as a mixture composed of tert-butylbenzene (C₁₀H₁₄), 1-
 333 methylnaphthalene (C₁₁H₁₀), n-hexadecane (C₁₆H₃₄) and n-eicosane (C₂₀H₄₂) with mass fraction
 334 of 0.3116, 0.4402, 0.1753, and 0.0729, respectively, was developed. The boiling point with volume

Table 3. Properties of L1 surrogate fuel

Fuel		L1	Surrogate Fuel
Density (15°C)	g/cm ³	0.9323	0.9173
Cetane Index [JIS K 2280]		19.8	19.7
Sulfur	wt%	0.14	0
Nitrogen	wt%	0.011	0
Carbon	wt%	90.3	89.9
Hydrogen	wt%	9.6	10.1
C/H ratio	-	9.4	8.9
Saturated molecule	vol%	14.3	16
Olefin	vol%	1.5	0
Aromatics	vol%	84.2	84
1ring aromatics	vol%	36.6	36
2ring aromatics	vol%	43.6	48
over 2 ring aromatics	vol%	4	0

335 fraction for each chemical species was compared with the distillation curve of L1. The boiling
336 temperature width of the surrogate fuel stays within the boiling temperature range of LCO,
337 especially the first drop point and ending point of L1 distillation curve is in good agreement with
338 the boiling point of components in the
339 surrogate fuel. Second, the properties of the
340 surrogate fuel are compared with that of LCO.
341 According to table 3, the surrogate fuel
342 emulates the density at 15 °C, the NCI
343 calculated by eq 4, the C/H ratio, and the
344 molecular types of L1. Hence, the
345 thermodynamic properties and the ratio of
346 molecular structure types of the surrogate fuel

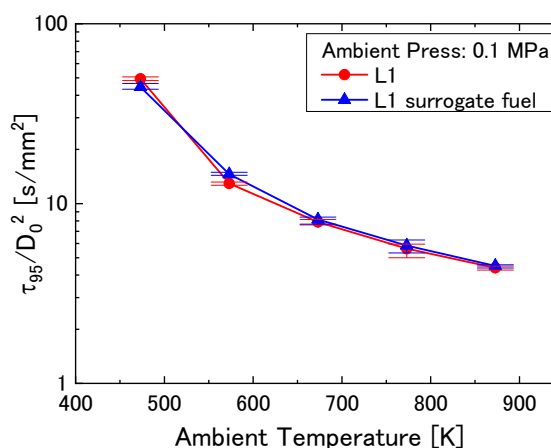


Figure 9. Validation of LCO surrogate fuel at various ambient temperature.

347 are in good agreement with those of L1. Finally, the droplet evaporation experiments of the
 348 surrogate fuel were conducted in the present set-up to validate the evaporation characteristics.
 349 Figure 9 shows the comparison of droplet lifetimes between the surrogate fuel and L1 at various
 350 ambient temperatures. It is found that the droplet lifetimes of the surrogate fuel are in good
 351 agreement with that of L1 at various ambient temperatures. Especially, the difference of droplet
 352 lifetime between L1 and the surrogate fuel was less than 5% in higher ambient temperature. It can
 353 be concluded that we succeeded to develop the LCO surrogate fuel, which well simulates the
 354 droplet evaporation characteristics of LCO.

355

356 3.3 Effect of the ambient pressure on the evaporation characteristics for LCO and arranged-fuels.

357 Figure 10 shows the pressure dependence of

358 τ_{95}/D_0^2 for L1, L2, and L13 at $T_{amb} =$

359 473 and 873 K. When $T_{amb} = 873$ K, the

360 difference of τ_{95}/D_0^2 between the fuels

361 become smaller at all ambient pressure. On the

362 other hands, when $T_{amb} = 473$ K, the

363 difference of τ_{95}/D_0^2 between the fuels

364 become large at all ambient pressures.

365 Accordingly, the τ_{95}/D_0^2 of L13 is larger than

366 that of L1 and smaller than that of L2 at

367 $T_{amb} = 473$ K and $P_{amb} = 0.1$ MPa. However, the τ_{95}/D_0^2 of L13 steeply increase with increasing

368 ambient pressure (Figure 10). Eventually, the τ_{95}/D_0^2 of L13 becomes the largest among LCO at

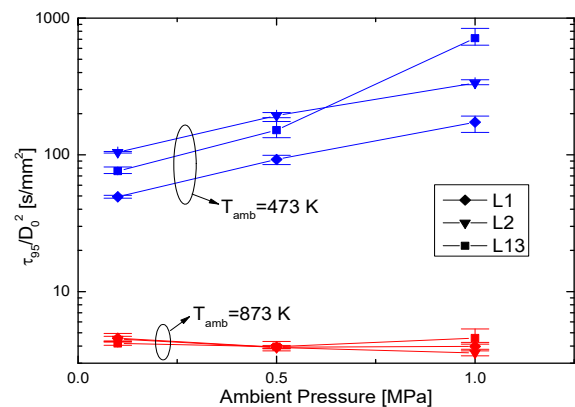


Figure 10. Normalized 95vol% lifetime (τ_{95}/D_0^2) as a function of the ambient pressure for LCO

369 $P_{amb} = 1.0$ MPa. Figure 10 depicts the τ_{95}/D_0^2
 370 become large in the order of increasing the
 371 ending point of the distillation curve shown in
 372 Figure 1.

373 Figure 11 shows the relationships between
 374 the distillation temperature and τ_{95}/D_0^2 at
 375 various ambient temperature at $P_{amb} = 0.1$ and
 376 1.0 MPa. In both figures (Figure 11), the left
 377 region shows the range of 10vol% distillation
 378 temperature for all species, whereas the right
 379 region illustrates the range of 90vol%
 380 distillation temperature for all species. The
 381 scattering of τ_{95}/D_0^2 is smaller at the high
 382 ambient temperature at various ambient
 383 pressures. In other words, the droplet lifetimes
 384 are independent of the distillation
 385 temperatures at the high ambient temperature
 386 at various ambient pressures. However, $\tau_{95}/$

387 D_0^2 become longer with increasing 90vol% distillation temperatures in low ambient temperatures.
 388 In Figure 11, linear least-squares fitting equations for $T_{amb} = 473$ K are shown. Apparently, the
 389 gradient of the fitting line becomes steeper in higher ambient pressure. This means that the
 390 relationships between 90vol% distillation temperature and droplet lifetime become strong in low

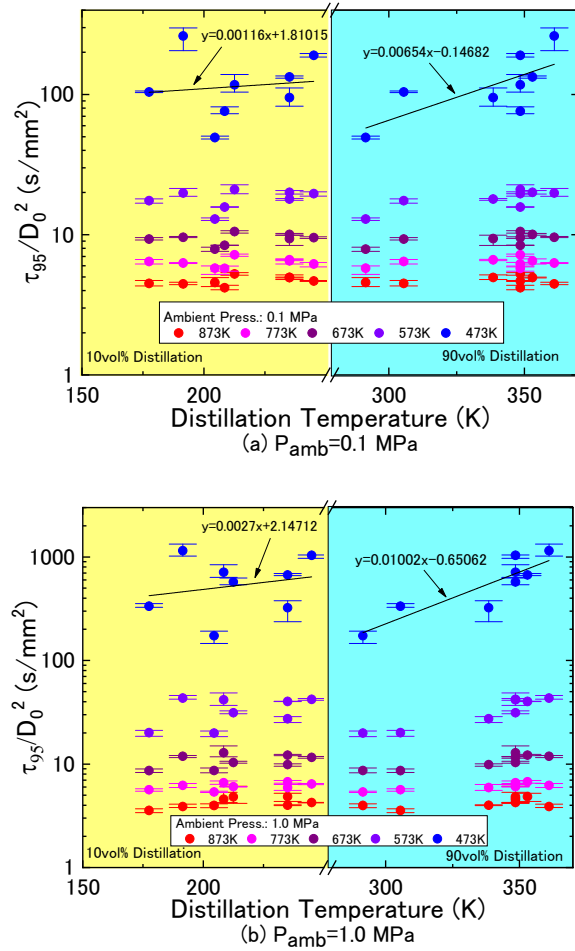


Figure 11. Normalized 95vol% lifetime (τ_{95}/D_0^2) as a function of the distillation temperature for the fuels used in this study

391 ambient temperature and high ambient pressure. The reason for this relationship will be discussed
392 in the paragraphs that follow.

393 We conducted a Peclet number analysis to discuss the above relationship. According to ref. ³⁴,
394 the molar weight variation has a decisive influence on the ratio of the characteristics time scales
395 of the droplet lifetime and the mass diffusion. The gasification Peclet number ³⁵ shown in eq 6 can
396 assess the relative dominance of the diffusion limit versus distillation behavior.

397

$$Pe = \frac{\dot{m}_{vap}}{2\pi D_d \Gamma_l \rho_l} \quad (6)$$

398

399 where Pe is the Peclet number ($-$), \dot{m}_{vap} is the mass evaporation rate (kg/s), D_d is the droplet
400 diameter (m), Γ_l is the diffusion coefficient inside the droplet (m^2/s), and ρ_l is the droplet density
401 (kg/m^3). However, the Peclet number given by eq 6 is not considering the multi-component
402 interaction effect. Therefore, the Peclet number on droplet evaporation was estimated in this paper
403 by rearranging eq 6 to multi-component fuel.

404 The Peclet number shown in eq 6 can be rearranged by using the Spalding model ³⁴. Mass
405 evaporation rate (\dot{m}_{vap}) and evaporation constant (K) is described as the following.

406

$$\dot{m}_{vap} = \frac{4\pi k_g r_s}{c_{p,g}} \ln(B_q + 1) \quad (7)$$

$$K = \frac{8k_g}{\rho_l c_{p,g}} \ln(B_q + 1) \quad (8)$$

407

408 Where k_g is the thermal conductivity of ambient gas (W/m-K), $c_{p,g}$ is the specific heat of gas
 409 (J/kg-K), r_s is droplet radius (m), ρ_l is fuel density (kg/m³), B_q is Spalding number (-).
 410 Substituting eq 8 into eq 7, the mass evaporation rate can be expressed as a function of evaporation
 411 constant (K), and the Peclet number shown in eq 6 can be rearranged as the following.

412

$$Pe = \frac{\dot{m}_{vap}}{2\pi D_d \Gamma_l \rho_l} = \frac{1}{4\pi r_s \Gamma_l \rho_l} \frac{\pi r_s \rho_l}{2} K = \frac{K}{8\Gamma_l} \quad (9)$$

413

414 Note that the surrogate fuel developed in section 3.2 was used to calculate the diffusion coefficient
 415 inside the droplet (Γ_l). In, our analysis, K was replaced by instantaneous evaporation coefficient,
 416 K_{inst} , which was obtained from experimental results shown in Figure 8.

417 Figure 12 shows the history of estimated Peclet number at two ambient conditions, (1) $T_{amb} =$
 418 473 K and $P_{amb} = 1.0$ MPa (2) $T_{amb} = 873$ K and $P_{amb} = 0.1$ MPa. Pe shown in Figure 12 are
 419 calculated by eq 9. Furthermore, K_{inst} used in eq 9 was obtained from experimental results. This
 420 is why Pe shown in Figure 12 is renewed moment by moment. Note that the diffusion coefficient
 421 inside the droplet (Γ_l) is a function of droplet temperature (Appendix). As a droplet temperature,
 422 473 K which is the same temperature with ambient temperature was applied in case (1), and 617
 423 K which is the same temperature with the boiling point of n-eicosane was applied in case (2).
 424 According to Figure 12, the Peclet number in case (1) decreases as time goes by although the Peclet
 425 number in case (2) shows almost constant value, and the Peclet number in case (1) becomes much
 426 smaller than that in case (2). When the Peclet number becomes larger, the internal diffusion is not
 427 able to catch up with the mass evaporation rate. Therefore, the droplet composition remains
 428 unchanged³⁴, thus indicating that evaporation characteristics approach the evaporation
 429 characteristics of the single component described by the D² law. This is why the correlation

430 between the droplet evaporation
 431 characteristics and the distillation process is
 432 weak at high ambient temperatures. On the
 433 other hand, when the Peclet number becomes
 434 smaller, the mass evaporation rate becomes
 435 sufficiently slow compared with the internal
 436 diffusion. This result implies that the
 437 relationship between the droplet evaporation
 438 characteristics and the distillation curve is
 439 strong. This is why the D^2 law cannot be
 440 applied to the evaporation of multi-component
 441 fuel droplet at the low ambient temperature.
 442 Moreover, the evaporation rate is further
 443 reduced at high pressure ambient. Therefore,
 444 the tendency of droplet lifetime lengthening
 445 with increasing the ending point of the fuel
 446 distillation temperature become strong under
 447 the low ambient temperature and high ambient
 448 pressure.

449 The relationships between the different ways of calculating the cetane index and droplet
 450 evaporation characteristics were investigated. Figure 13 shows the pressure dependence of τ_{95}/D_0^2

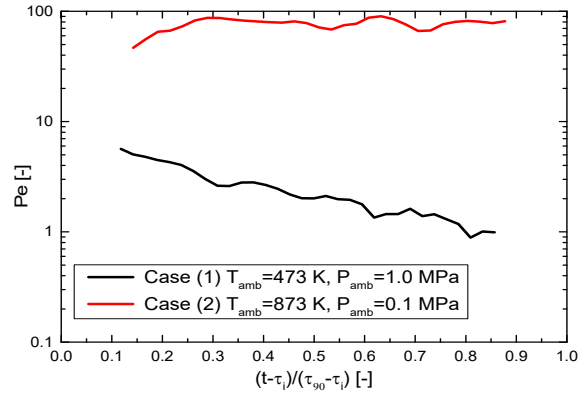


Figure 12. Histories of estimated Peclet number during main evaporation term

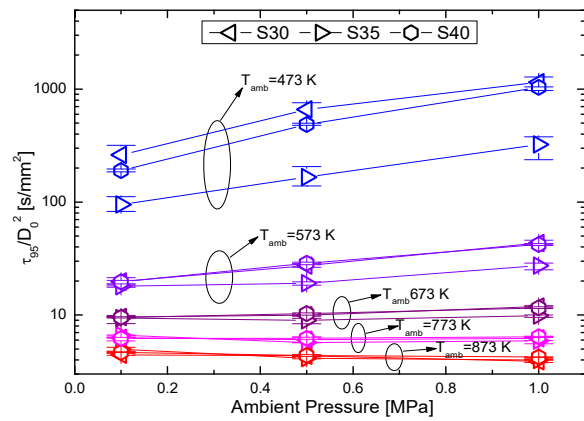


Figure 13. Normalized 95vol% lifetime (τ_{95}/D_0^2) as a function of the ambient pressure for the arranged-fuels

451 for the arranged-fuels. As mentioned in
 452 Section 2.2, the arranged-fuels were made
 453 such that their NCI is 35. Figure 13 shows that
 454 the difference of τ_{95}/D_0^2 between the fuels
 455 became small at $T_{amb} = 673, 773$, and
 456 873 K. However, the difference of τ_{95}/D_0^2
 457 between the fuels became large at $T_{amb} =$
 458 473 and 573 K. As discussed in Section 3.1,
 459 this behavior is caused by components with a
 460 high boiling point, which make the rate of
 461 decrease in D^2/D_0^2 slower. By contrast, the
 462 OCI of S30, S35, and S40 are increased in the
 463 order of S30, S35, and S40. However, the
 464 τ_{95}/D_0^2 of S30, S35, and S40 is increased in
 465 the order of S30, S40, and S35. These results
 466 implied that the τ_{95}/D_0^2 is independent of the
 467 OCI. Simultaneously, the τ_{95}/D_0^2 of S30, S35,
 468 and S40 increased in the order of S30, S40,
 469 and S35, although all the arranged-fuels have
 470 the almost same new cetane index that is 35.
 471 In conclusion, τ_{95}/D_0^2 cannot be associated
 472 with the cetane index when the cetane index is
 473 35.

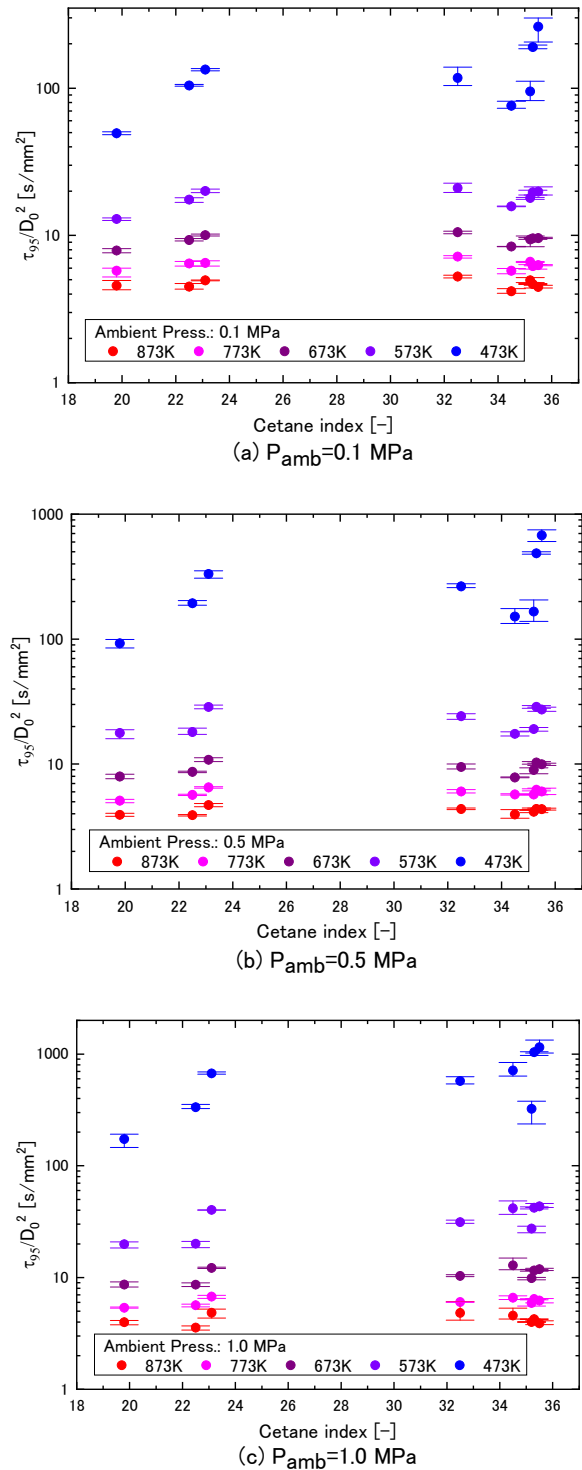


Figure 14. Normalized 95vol% lifetime (τ_{95}/D_0^2) as a function of the cetane index for the fuels used in this study

474 Finally, the relationships between the droplet lifetime and the cetane index were investigated.
475 Figure 14 shows the relationships between the cetane index calculated by eq 4 and τ_{95}/D_0^2 at the
476 various ambient pressures (0.1, 0.5, and 1.0 MPa) and temperatures. It was found that there is no
477 correlation between the cetane index and τ_{95}/D_0^2 . It can be concluded that the droplet lifetime is
478 independent of the cetane index introduced in this paper under the conditions tested. Furthermore,
479 the correction coefficient between the droplet evaporation lifetime and the mole fraction of mono-,
480 di-, and 3+ cyclic aromatic compounds at all experimental conditions were investigated. However,
481 we found that there is little correlation between the evaporation characteristics and aromatic
482 compositions. In actuality, fuel droplets will continuously evaporate at higher temperature and
483 pressure conditions after the ignition. Therefore, the clarification of droplet evaporation
484 characteristics in such conditions is also necessary as the future research.

485

486 4. CONCLUSIONS

487 In this study, LCO single droplet evaporation experiments were conducted at various ambient
488 temperature and pressure to obtain the validation data. The detailed droplet evaporation history
489 data of fuels with various composition ratios were obtained by this study. The data can be utilized
490 for the validation of the sensitivity of the components for multi-component droplet evaporation
491 models in the future. In addition, development and validation of the surrogate fuel for LCO (L1)
492 were conducted. Finally, the relationships between the evaporation characteristics and cetane index,
493 which is one of the indicators for fuel ignitability, were investigated. The main findings are as
494 follows:

- 495 1. The droplet lifetime decreases with increasing ambient temperature for all fuel species. The
496 differences of droplet lifetime between the fuels become larger with decreasing ambient

497 temperature. This is because the low volatile component made the evaporation rate
498 outstandingly slow at low ambient temperature.

499 2. The evaporation characteristics of the surrogate fuel are in good agreement with that of LCO
500 at various ambient temperatures. Especially, the difference of droplet lifetime between L1 and
501 the surrogate fuel is less than 5% in higher ambient temperature.

502 3. The droplet evaporation lifetime can be characterized by the late stage distillation temperature
503 at a low ambient temperature. The correlation between the droplet lifetime and the late-stage
504 distillation temperature becomes stronger with increasing ambient pressure because the mass
505 evaporation rate becomes smaller than the internal diffusion, which is a condition similar to
506 that in the distillation test. Hence, the tendency of the droplet lifetime to increase with
507 increasing the end point of the fuel distillation temperature become strong at low ambient
508 temperature and high ambient pressure.

509 4. The droplet lifetime of LCO and the arranged-fuels is independent of the cetane index under
510 experimental conditions shown in this paper.

511

512 Appendix Diffusion coefficient inside a droplet

513 The diffusion coefficients used in the Peclet number were estimated as the following. First, the
514 binary diffusion coefficient can be calculated from ref. ³⁶ as

515

516
$$D_{i,j} = 8.93 \times 10^{-8} \frac{V_j^{0.267} T}{V_i^{0.433} \eta_j}$$

517

518 where $D_{i,j}$ is the binary diffusion coefficient of species i and j in the droplet; V is the molar
519 volume of species i ; T is droplet temperature; η_j Pearson's the viscosity of species i . For multi-
520 component fuels, the mixture of all the species except i is assumed as the second species m . Then,
521 the diffusion coefficient of species i for the mixture can be described as

522

$$523 \quad D_{i,m}\eta_m^{0.8} = \sum_{\substack{j=1 \\ j \neq i}}^{N_l} x_j D_{i,j} \eta_j^{0.8}$$

524

525 where x_j is the mole fraction of species j and N_l is the number of species. Hence, the binary
526 diffusion coefficient (Γ_l) used for Peclet number in eq 9 can be averaged as the following.

$$527 \quad \Gamma_l = \sum_{i=1}^{N_l} x_i D_{i,m}$$

528

529

530 ■ ASSOCIATED CONTENT

531 **Supporting Information.**

532 The following files are available free of charge.

533 Experimental data_LCO (xlsx)

534

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538 **Notes**

539 The authors declare no competing financial interest.

540

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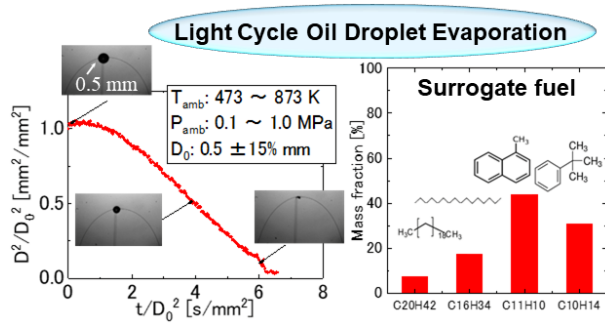
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662 TOC graphic



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