

# Dynamic behaviors of fuel droplets impacting on the wall surfaces with different wettability and temperatures

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## Abstract

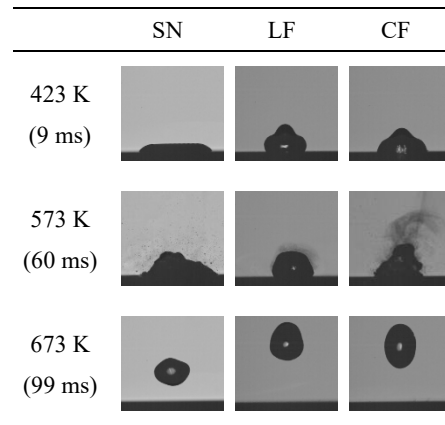
To improve the controllability of combustion and reduce the emissions of HC and CO of the newly developed combustion modes, such as the HCCI, PCCI and RCCI, the evaporation processes and morphological developments of diesel droplets impacting on the aluminum alloy surfaces with different wettability and temperatures are experimentally investigated. The results show that the oleophilic surface is conducive to evaporation of diesel droplets, while the oleophobic surface promotes the formation of the vapor film between the fuel droplets and the test surface at a high surface temperature and reduces the Leidenfrost temperature of the fuel droplets. Also, stronger oleophobicity of the surface is beneficial to the rebound and secondary breakup of the droplets, thereby promoting the evaporation of the droplets in the gas-phase space of the cylinder and improving the air-fuel mixing. Moreover, the stronger the surface oleophobicity, the smaller the spreading factor and the larger the rebound factor of the droplets. At a higher wall temperature, the ability for enhancing the surface oleophobicity of the convex domes, grooves and protrusions structures on the laser-etched surface is better than that of the boss/pits and needle-like structures on the chemically etched surface. Under the conditions of lower surface temperatures, the evaporation rate of the droplet after hitting the wall is closely related to the spreading area of the droplet. As the wall temperature increases, when the droplet is in transition boiling regime, the large heat transfer rate makes the diffusion width, height and diffusion area of the vapor phase region are

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24 obviously large.



25 Graphical abstract

26 **Keywords:** Fuel droplet; Surface wettability; Wall temperature; Evaporation process; Morphological  
27 development

## 28 1. Introduction

29 Higher fuel economy and lower emission levels are the motivations for the development of vehicle engines.  
30 New combustion modes such as homogeneous charge compression ignition (HCCI) [1], premixed charge  
31 compression ignition (PCCI) [2], reaction controlled compression ignition (RCCI) [3] and low temperature  
32 combustion (LTC) [4,5] are promising combustion modes for improving engine performance and reducing  
33 emissions. Premixed compression ignition modes such as HCCI and PCCI are mostly low temperature  
34 combustion modes that use lean mixtures, and often use the early injection, the high pressure injection and the  
35 multiple injections to improve atomization quality [6-9]. Due to the low temperature and gas density at the early  
36 injection timing, the phenomenon of wall-wetting is inevitable [10]. Wall-wetting is one of the important sources  
37 of the soot particles and unburned hydrocarbons. Therefore, it is necessary to conduct an in-depth study on the  
38 fluid-solid interactions between the fuels and the combustion chamber walls to actively control the spreading,  
39 bouncing and vaporization behaviors of the fuel droplets. Since spray-wall impingement is a multi-scale and  
40 strong transient process, and there are many influencing factors, the mechanism of spray-wall impingement  
41 cannot be explained in detail. The research of the droplet-wall impingement is the basis of the study of the spray-

42 wall impingement, and the wall-impinging droplet experiences dynamic behaviors (e.g. spreading, retraction,  
43 rebound, breakup, splashing) and thermodynamic behaviors (e.g. evaporation). Focusing on the droplet-wall  
44 impingement can highlight the influence of wall conditions, which is more conducive to exploring the fluid-  
45 solid coupling processes of droplet-wall impingement.

46 The research direction of the droplet-wall impingement has attracted attention for a long time. There are  
47 many factors that affect the dynamic processes of the wall-impinging droplets, and the influencing factors  
48 interact with each other [11]. With the development of material science and biomimetic science, specific  
49 wettability surfaces with micron-scale and nano-scale structures have been widely used [12], and the droplet  
50 behavior relates greatly to the apparent contact angle and the contact angle hysteresis [13]. Changing the  
51 geometrical sizes of the microstructures of the solid surfaces [14,15], adding coating [16-18] and modifying with  
52 low surface free energy material [19,20] can obtain surfaces with different wettability, such as  
53 superhydrophilicity, hydrophilicity, hydrophobicity and superhydrophobicity. Also, using a combination of  
54 masking, hydrophobic nanoparticle treatment and oxygen plasma treatment, the heterogeneous surfaces with  
55 moderate and extreme wettability contrasts are fabricated [21].

56 Many scholars have studied the movement and evaporation characteristics of the droplets after impacting  
57 on surfaces with different wettability and temperatures. At a room temperature, the wall wettability, physical and  
58 chemical properties of the droplets and Weber number have obvious effects on the spreading factor and apex  
59 height of the droplets impacting the walls with room temperature [22]. Similarly, the maximum spreading factor,  
60 spreading time and post-impact oscillation are also related to the above parameters [23]. The surface morphology  
61 could both suppress and facilitate drop splashing, and a method to predict splashing threshold on surfaces with  
62 different morphologies is presented [24]. When droplets hit the nano-textured superhydrophobic surfaces, the  
63 maximum spreading factor is related to  $We^{0.52}$ , and both of the contact time and non-dimensional contact time  
64 of bouncing droplets are independent of Weber number in the range of 1.5 to 121 [25]. When droplets impact

65 obliquely on microstructured superhydrophobic surfaces, the increase in the normal Weber number leads to a  
66 transition from conventional retracting bouncing, to incomplete-retracting bouncing, and then to impaled  
67 retracting bouncing. With the increase of Ohnesorge number, the contact time shows a trend of "decrease"-  
68 "increase"- "decrease" [26].

69 At higher temperatures, Liang et al [27] conducted a comprehensive review of published literatures  
70 concerning the fluid mechanics and heat transfer mechanisms of liquid drop impact on a heated wall. The surface  
71 wettability, wall temperature, physical and chemical properties of the droplets and Weber number have effects  
72 on the boiling and evaporation characteristics of droplets impacting on the walls [28-30]. For various  
73 applications in energy systems, advanced thermal management solutions promoted the developments of the  
74 graphene functionalized coatings [31] and the specially treated wicks [32] in the field of phase-change heat  
75 transfer. Compared to the pristine rectangular microgrooves, the rectangular microgrooves with superhydrophilic  
76 nano-textured surfaces increase the axial wetting lengths of the fluids, which have a critical influence on the  
77 evaporating heat transfer [33]. In addition, the four stages of the impingement process are identified: impact,  
78 boiling, near constant surface diameter evaporation and final dry-out. And the nano-structured surface has a  
79 lower dissipated energy during impact and enhances the heat transfer for evaporative cooling with a 20% shorter  
80 time to achieve final dry out [34]. With the increase of the wall temperatures, the fuel droplets are in four different  
81 regimes, including film evaporation ( $T_s \leq T_{sat}$ , where  $T_s$  is the surface temperature and  $T_{sat}$  is the liquid  
82 saturation temperature), nucleate boiling ( $T_{sat} \leq T_s \leq T_{chf}$ , where  $T_{chf}$  is the temperature corresponding to the  
83 maximum heat flux), transition boiling ( $T_{chf} \leq T_s \leq T_{Leid}$ , where  $T_{Leid}$  is the liquid Leidenfrost temperature)  
84 and film boiling ( $T_s \geq T_{Leid}$ ), respectively. When the droplets hit surfaces with the temperature higher than the  
85 Leidenfrost temperature of the droplets, the droplets are levitated upon the vapor layer resulting in a nonwetting  
86 state, which deteriorates the heat transfer [35-37]. This phenomenon is Leidenfrost phenomenon. However, water  
87 droplets can be suspended at the peaks of the roughness on a superhydrophobic interface, and vapor escapes

88 from underneath the droplet, so a “pseudo-Leidenfrost” state appears for all excess temperatures [38]. The  
89 second fast spreading of the droplet resulting from vigorous boiling on the micro/nanostructured surfaces (ZnO  
90 nanowire surface and copper inverse opal surface) could enhance the heat transfer between the droplet and the  
91 surface and promote the Leidenfrost temperature of the impact droplet [39]. The Leidenfrost effect is closely  
92 related to practical applications. Recent studies with designed micropatterned surfaces were able to control the  
93 movement and evaporation of the Leidenfrost drop and change the drag [40-42]. For such applications, there are  
94 more efforts that focus on how to change the Leidenfrost temperature. Compared to smooth surfaces, surfaces  
95 with different textures can achieve a Leidenfrost temperature shift [43]. Micro/nano multiscale texture is the  
96 essential component in significantly increasing Leidenfrost temperature by inducing capillary wicking [44].  
97 Some authors have reported that changing the surface roughness [45], the porous structure [46] and the nanofiber  
98 mats [47] could increase the Leidenfrost temperature. Also, as the hydrophilic surface causes vigorous nucleate  
99 boiling and large viscous dissipation during the droplet contact, higher the Leidenfrost temperature is required  
100 for stable film boiling state [48]. For rib-patterned superhydrophobic substrates, as the cavity fraction (relative  
101 projected cavity area of substrate to total projected surface area) increases, the heat transfer rate decreases,  
102 nucleate boiling is delayed to higher substrate temperatures and the Leidenfrost temperature reduces [49]. Other  
103 studies have found that enhancing surface hydrophobicity [50,51] could reduce the Leidenfrost temperature.  
104 Also, the dependence of the Leidenfrost temperature on the ambient conditions was investigated [52]. The  
105 increasing (decreasing) the ambient pressure lead to an increase (decrease) in Leidenfrost temperature.  
106 Increasing the ambient temperature stabilized meta-stable, levitating drops at increasingly lower temperatures  
107 below the Leidenfrost temperature. Besides the aforementioned experimental studies, some numerical researches  
108 on the processes of droplet-wall impingement are also performed to description of the complex problem  
109 involving both fluid mechanics and coupled heat and mass transfer [53-55].

110 So far, many researches related to the development processes of water droplets impacting on the surfaces

111 have been reported. However, there are very few researches on the effects of the surface wettability on the  
 112 behavioral development of fuel droplets hitting surfaces with high temperatures. Especially, the evaporation  
 113 processes and morphological development processes of the wall-impinging fuel droplets containing multiple  
 114 components at different wall temperatures have not been thoroughly explored. Aiming at the problem of wall-  
 115 wetting during cold start of internal combustion engines, to realize the active control of the evaporation processes  
 116 of the wall-wetting fuels under different wall conditions and improve the heat transfer efficiency in the heat  
 117 transfer process, this research uses physical and chemical methods to reconstruct the microstructures of the  
 118 aluminum alloy surfaces and fabricate surfaces with special wettability. High-speed photography and schlieren  
 119 methods are used to study the evaporation processes and the morphological development processes of the liquid  
 120 phase and the vapor phase after fuel droplets impact walls with special wettability under different wall  
 121 temperature conditions. The comprehensive effects of surface wettability and wall temperature on heat exchange  
 122 rates and evaporation processes of the droplets are analyzed. To improve heat transfer performance and reduce  
 123 soot particles and unburned hydrocarbons, the results of this study will lay an experimental foundation for  
 124 establishing active control methods of fuel evaporation, fuel-air mixture formation and combustion.

## 125 **2. Experimental materials and methods**

### 126 *2.1. Experimental fuels and platforms*

127 Diesel is selected as the test fuel. Diesel is mixtures of certain hydrocarbon compounds, and its physical  
 128 and chemical properties are shown in **Table 1**.

129 **Table 1** Characteristics of the tested fuel.

Properties	Diesel
Density $/(kg \cdot m^{-3})$	821.9
Latent heat of vaporization $/(kJ \cdot kg^{-1})$	251.2
Surface tension at 293 K $/(mN \cdot m^{-1})$	29.3
Viscosity at 293 K $/(mm^2 \cdot s^{-1})$	4.07
Boiling point $/(K)$	453-623

130 Aluminum alloy is selected as the material of the test surface. The chemical compositions of the aluminum  
 131 alloy used in the experiments are shown in the **Table 2**.

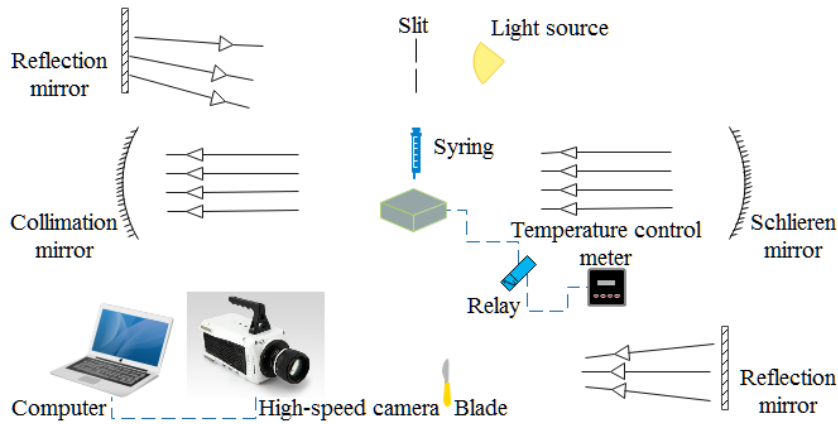
132 **Table 2** Chemical compositions of aluminum alloy.

Element	Cu	Mn	Mg	Zn	Cr	Ti	Si	Fe	Al
Content /(%)	0.15-0.4	0.15	0.8-1.2	0.25	0.04-0.35	0.15	0.4-0.8	0.7	Margin

133 The microscopic morphologies of the metal surfaces are measured and recorded using Scanning Electron  
 134 Microscope (SEM). The variations of the contact angles of the diesel droplets on the surfaces with time are  
 135 recorded with the contact angle measuring instrument. A self-developed high-speed photography platform and a  
 136 schlieren optical test platform are used to record the evaporation processes and morphological developments of  
 137 the fuel droplets after impacting the surfaces. The evaporation times of the fuel droplets on the heated surfaces  
 138 are recorded by a timer. The "z-type" layout scheme is selected for the schlieren optical test platform. The  
 139 schematic diagrams of the above test platforms are shown in **Fig. 1**. The high-speed camera used in the  
 140 experiments is a Phantom V611 high-speed camera. The practical resolution and shooting frequency selected for  
 141 the present experiments are 512 pixels  $\times$  512 pixels and 1000 fps, respectively. The metal surface temperature is  
 142 regulated and controlled with a self-developed temperature feedback measurement and control system. After  
 143 calibration, the accuracy of the surface temperature is within 1 K. With a precise control knob, the droplet volume  
 144 of each titration is controlled to 5  $\mu$ L, with an error of no more than 1%.



145  
 146 (a) The high-speed photography platform



(b) The schlieren optical test platform

**Fig. 1.** Schematic diagrams of the test platforms.

## 2.2. Experimental surfaces

For the study of the contact angles and morphological developments of the liquid phase and gas phase of the droplets on the different surfaces, the sizes of the metal blocks are selected as  $30 \text{ mm} \times 30 \text{ mm} \times 10 \text{ mm}$ . However, to determine the evaporation times of the droplets, the sizes of the metal blocks are selected as  $100 \text{ mm} \times 100 \text{ mm} \times 15 \text{ mm}$ . A droplet in the Leidenfrost state tends to move around on the surface in a nearly frictionless manner. Therefore, a conical depression is machined with a  $1^\circ$  slope and a depth of  $0.52 \text{ mm}$  at the center of the test surface to keep the droplet from rolling off the test area.

The surface microstructures are reconstructed through laser etching and chemical etching. To avoid the influence of surface oxidation to the preparation of chemical etching, the in total six metal surfaces are pretreated with mechanical grinding and chemical cleaning. After mechanical grinding, the roughness of all the test surfaces is kept at  $0.5 \text{ }\mu\text{m}$ . The test substrates are further chemically cleaned using the ultrasonic cleaner with acetone, rectified ethanol and deionized water in sequence. After the pretreatment, different fabrication methods are used for different metal surfaces to complete the reconstruction of the surface microstructures. After micro fabrication, the metal surfaces with different microstructures are cleaned again with deionized water and rectified ethanol. To reduce the surface free energy, three of the metal surfaces are modified through surface free energy reduction method by immersing the test blocks into the ethanol solution of perfluorooctanoic acid (ESF) with a

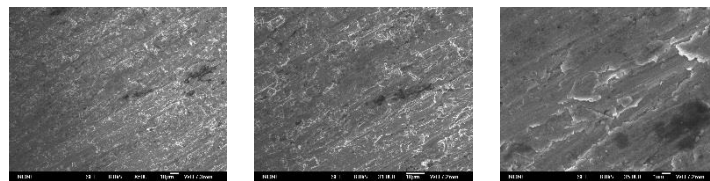


166 concentration of 0.03 mol/L, for an immersing time of 24 hours. The detailed information of the fabrication  
 167 methods, together with the surface codes used in the experiments are given in **Table 3**.

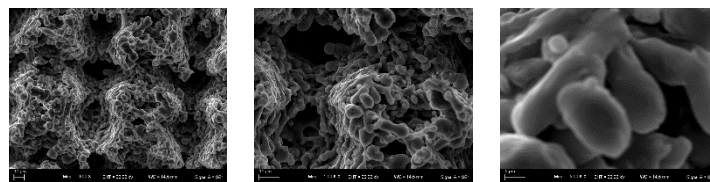
168 **Table 3** Fabrication methods of the metal surfaces.

Fabrication methods		Modified with the ESF	Surface codes
Smooth surface	Not etched by other methods after pretreatment	No	SN
		Yes	SF
Laser etching	Pretreatment + laser etching	No	LN
		Yes	LF
Chemical etching	Pretreatment + 2.5 mol/L hydrochloric acid solution (10 min), boiling water (40 min)	No	CN
		Yes	CF

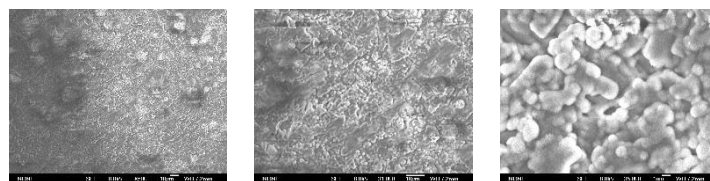
169 From a macro perspective, the orthogonal grid structure is seen on the laser-etched surface, and the labyrinth  
 170 structure is observed on the chemically etched surface. To determine the microstructures of the surfaces obtained  
 171 through different fabrication methods, the SEM photos of the test metal surfaces are taken as shown in **Fig. 2**.



172 (a) Smooth surface (500× & 1000× & 5000×)



173 (b) Laser-etched surface (500× & 1000× & 5000×)



174 (c) Chemically etched surface (500× & 1000× & 5000×)

175 **Fig. 2.** SEM photos of the test surfaces.

176 Among the photos, **Fig. 2(b)** shows the SEM photos of the laser-etched surface. It can be seen from the  
 177 figures that the micron-scale convex domes and grooves and the nano-scale protrusions are orderly formed by  
 180

181 molten metal after laser etching. The size of a convex dome is about  $80\ \mu\text{m} \times 100\ \mu\text{m}$ . **Fig. 2(c)** shows the SEM  
182 photos of the chemically etched surface. After being etched by means of the hydrochloric acid solution  
183 immersion, the rectangular-shaped staggered cuboid boss/pits with a length and width of about  $1\text{-}3\ \mu\text{m}$  are  
184 formed upon the aluminum alloy surface. In addition, needle-like structures are formed through reaction between  
185 the aluminum alloy and the boiling water. The above two structures together form a good micro-nano interlaced  
186 structure on the aluminum alloy surface.

### 187 2.3. Data processing

188 To facilitate the analysis, the parameters relevant to morphological developments of both liquid phase and  
189 vapor phase of diesel droplets before and after it impacting on the walls are preliminarily defined, including the  
190 liquid phase spreading factor ( $d$ ), the liquid phase rebound factor ( $h$ ), the vapor phase diffusion width ( $W$ ), the  
191 vapor phase diffusion height ( $H$ ) and the vapor phase diffusion area ( $A$ ). Among the parameters,  $d$  and  $h$  can  
192 be expressed as Eqs. (1) and (2).

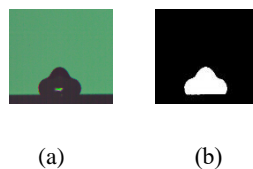
$$193 \quad d = d_i/d_0 \quad (1)$$

$$194 \quad h = h_i/h_0 \quad (2)$$

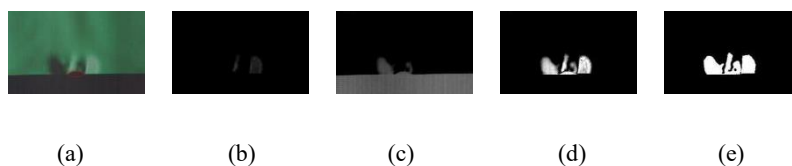
195 Where,  $d_i$  is the spreading width of the droplet at the moment  $i$  after the diesel droplet impacts the wall.  
196  $h_i$  is the vertical height between the highest point of the droplet and the wall at the moment  $i$  after the diesel  
197 droplet hits the wall.  $d_0$  and  $h_0$  are the droplet width (horizontal diameter) and height (vertical diameter),  
198 which are measured just before the first impact of the droplet, at the moment when the lower edge of the droplet  
199 is tangent to the wall. When the droplet rebounds against the surface without touching the surface, the spreading  
200 factor is 0.  $W$  is the width of the vapor phase diffusion along the wall surface after the impact.  $H$  is the height of  
201 the vapor phase diffusion in the direction perpendicular to the wall after the impact.  $A$  is the sum of the pixel  
202 area values included in the vapor phase measured from the schlieren images.

203 In order to make the measured droplet related physical parameters of this research have a higher accuracy,

204 all the test results of the measured parameters are the averaged value of at least three measurements. All the  
 205 calculated parameters are obtained from a self-developed image processing and calculation code. For the images  
 206 obtained by high-speed photography, the parameters of the liquid phase of the wall-impinging droplets can be  
 207 obtained through the steps of image reading, grayscale processing, background elimination, filtering, noise  
 208 reduction, binarization and edge detection, etc. The schematic diagram of the process of the image processing  
 209 of the liquid phase of droplets is shown in **Fig. 3**. The relevant parameters of the vapor phase after the fuel  
 210 droplets hit the walls can be obtained by processing the images captured by the schlieren method. The schematic  
 211 diagram of the image processing of vapor phase of the droplets is shown in **Fig. 4**. **Fig. 4(a)** is the original image  
 212 of a single droplet hitting the wall obtained by schlieren method. Due to the opposite direction of the  
 213 concentration gradient, it can be seen from the figure that there are obvious bright and dark areas on both sides  
 214 of the droplet. The bright and dark areas are the vapor phase formed by the evaporation of the droplet. The area  
 215 in the red circle in the middle of the image is the liquid phase of the droplet. According to different grayscale  
 216 ranges, the bright and dark areas of the original image are extracted respectively. **Fig. 4(b)** is the extracted bright  
 217 area and **Fig. 4(c)** is the extracted dark area. **Fig. 4(d)** is obtained by superimposing two grayscale images of **Fig.**  
 218 **4(b)** and **Fig. 4(c)**, removing background, and enhancing brightness. After filtering, noise reduction, binarization  
 219 and other steps to obtain the final image **Fig. 4(e)**. In addition, according to the calibration, the relevant  
 220 parameters of the vapor phase of the wall-impinging droplets can be calculated.



223 **Fig. 3.** Schematic diagram of the image processing of liquid phase of the droplets.

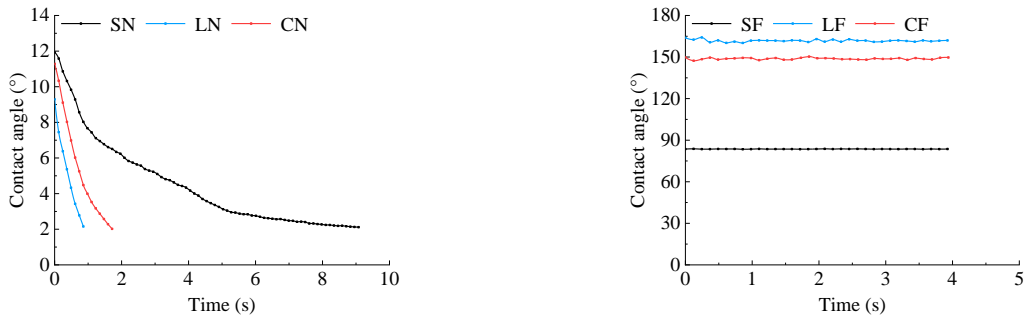


**Fig. 4.** Schematic diagram of the image processing of vapor phase of the droplets.

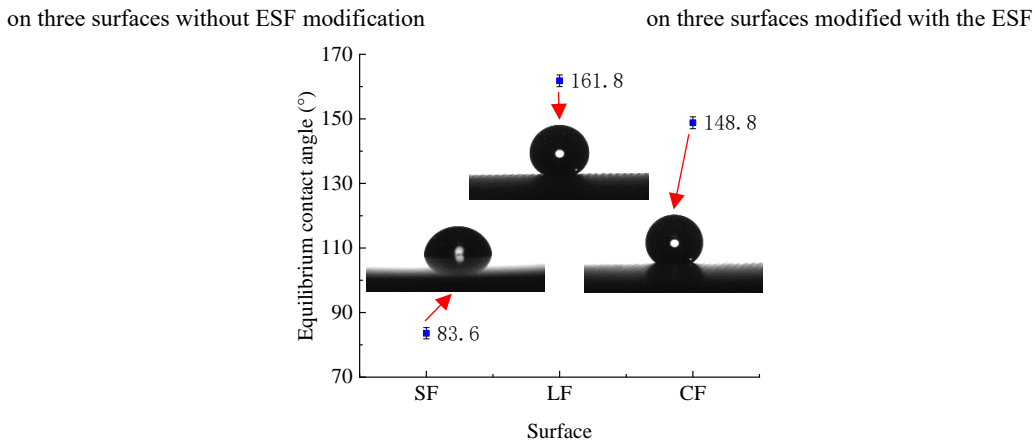
227 **3. Results and discussion**

228 *3.1. Effects of the surface microstructures and surface free energy on the wettability*

229 The contact angle is one of the most important parameters in characterizing the wettability of a surface. **Fig.**  
230 **5** shows the variations of the contact angles of diesel droplets on the six surfaces over time and the static  
231 visualization results of the droplets on the three surfaces modified with the ESF.



(a) Variations of the contact angles over time of the droplets (b) Variations of the contact angles over time of the droplets



(c) Static visualization results of the droplets on the three surfaces modified with the ESF

**Fig. 5.** Contact angles of the diesel droplets on the surfaces with different wettability.

235 **Fig. 5(a)** shows the changing trends of the contact angles on the three different surfaces without surface  
236 free energy modification. It can be seen that all the three surfaces including the surfaces SN, LN and CN are  
237 oleophilic to diesel droplets. Compared with the smooth surface, the microstructures of the laser-etched surface  
238 and the chemically etched surface increase the surface roughness, and therefore, the oleophilicity of both the  
239 surface LN and the surface CN increase. The reduction rates of the contact angles of the diesel droplets on the  
240 surface LN and the surface CN are larger. Compared with the sizes of the cuboid boss/pits on the chemically

241 etched surface, the sizes of the convex domes and grooves on the laser-etched surface are larger, and the  
242 interconnection between the intersecting grooves has an effect of promoting diversion of the fuel droplet, which  
243 makes the reduction rate of the contact angles of diesel droplet on the surface LN larger than that on the surface  
244 CN.

245 **Fig. 5(b)** shows the changing trends of the contact angles of diesel droplets on the three surfaces with  
246 different microstructures that are modified with ESF. It can be seen from **Fig. 5(b)** that the surface LF and the  
247 surface CF are more oleophobic to diesel droplets, compared with the smooth surface. After being modified with  
248 the ESF, the oleophobicity of the surface is found increasing with the increase of the surface roughness. As a  
249 result, the contact angle of the diesel droplet on the surface LF is largest among all the three ESF modified  
250 surfaces.

251 **Fig. 5(c)** shows the static visualization results of diesel droplets on the surfaces SF, LF and CF. Depending  
252 on the surface wettability, the equilibrium shapes of droplets vary. The intrinsic contact angles obtained on the  
253 surface SF is  $83.6^\circ$ , and the apparent contact angles obtained on the surface LF and the surface CF are  $161.8^\circ$   
254 and  $148.8^\circ$ , respectively, which are determined by the characteristics of the solid-liquid-gas three-phase  
255 composite contact surface formed between the liquid and the solid surface. The Cassie-Baxter equation is as  
256 follows:

$$257 \quad \cos \theta_c = f_1 \cos \theta - f_2 \quad (3)$$

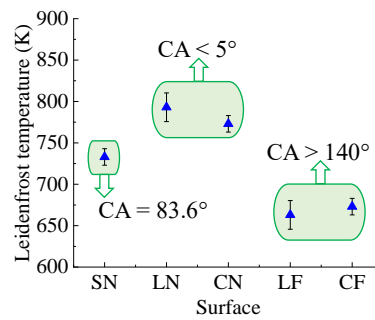
$$258 \quad f_1 + f_2 = 1 \quad (4)$$

259 Where,  $\theta_c$  is the apparent contact angle of the droplet on the rough surface.  $\theta$  is the intrinsic contact angle  
260 of the drop on the smooth surface.  $f_1$ ,  $f_2$  are the proportions of the solid-liquid contact surface and the gas-  
261 liquid contact surface in the composite contact surface, respectively. According to the results calculated with the  
262 Cassie-Baxter equation, the proportions of the solid-liquid contact surface in the composite contact surface are  
263 4.5% and 13.0% for the surface LF and the surface CF, respectively. That is, the convex domes, grooves and

264 protrusions structures on the laser-etched surface have a stronger ability to trap the air than the boss/pits and  
265 needle-like structures on the chemically etched surface.

### 266 3.2. Effects of the surface wettability on the Leidenfrost temperature of the droplets

267 For internal combustion engines, the wall temperatures of the combustion chamber could vary over a wide  
268 range under different operating conditions. To study the effects of the surface wettability on the Leidenfrost  
269 temperature of the wall-impinging fuel droplets, the evaporation times of the diesel droplets after impacting the  
270 different surfaces are investigated. The evaporation times of diesel droplets hitting surfaces with different  
271 wettability and temperatures are recorded. The Leidenfrost temperature of the droplet is determined by the  
272 method of droplet evaporation time. **Fig. 6** shows the Leidenfrost temperature of diesel droplets on the different  
273 surfaces. In the figure, CA is the abbreviation of contact angle.



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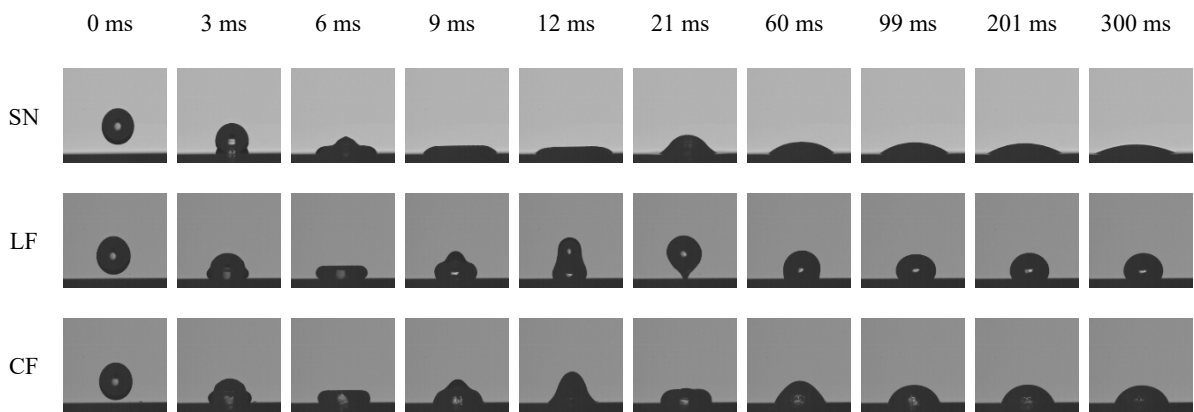
275 **Fig. 6.** Leidenfrost temperature of the droplets on different surfaces.

276 It can be seen from **Fig. 6** that diesel droplets have the highest Leidenfrost temperature on the surface LN  
277 among the three oleophilic surfaces. This is mainly because the roughness of the surface LN is the largest, and  
278 the microstructures are easier to pierce the vapor film formed between the droplets and the solid surfaces.  
279 Therefore, the droplets are in direct contact with the surfaces, and due to the rapid heat exchange, the droplets  
280 are disturbed by the fuel vapor escaped from three-phase contact surfaces. That is, when a droplet hits an  
281 oleophilic surface with a larger roughness, a higher surface temperature is required to produce a sufficiently  
282 stable vapor layer to make the droplets are in film boiling regime. The formation of the vapor layer is related to  
283 the nucleation, growth and merging of vapor bubbles. The Leidenfrost temperature of fuel droplets on the

284 oleophilic and oleophobic surfaces is different, which can be attributed to the following aspects. On the  
 285 oleophilic surfaces, the spreading areas of the droplets are larger and the liquid films are thinner. At the same  
 286 time, isolated bubbles are difficult to merge and the bubbles easily penetrate the free surfaces of the liquid films.  
 287 However, on the oleophobic surfaces, the bubbles are easy to merge, which facilitates the formation of the vapor  
 288 layer. Furthermore, when droplets hit oleophobic surfaces, the potential barrier for the transition to film boiling  
 289 is smaller, which makes it easier for droplets to enter film boiling regime on oleophobic surfaces. It suggests that  
 290 the stronger oleophobic the surfaces, the lower the Leidenfrost temperature of the droplets. As a result, the  
 291 Leidenfrost temperature of the droplets on the surface LF with the strongest oleophobicity is the lowest.

292 *3.3. Effects of the surface wettability on the morphological development of the liquid phase of the droplets at*  
 293 *different wall temperatures*

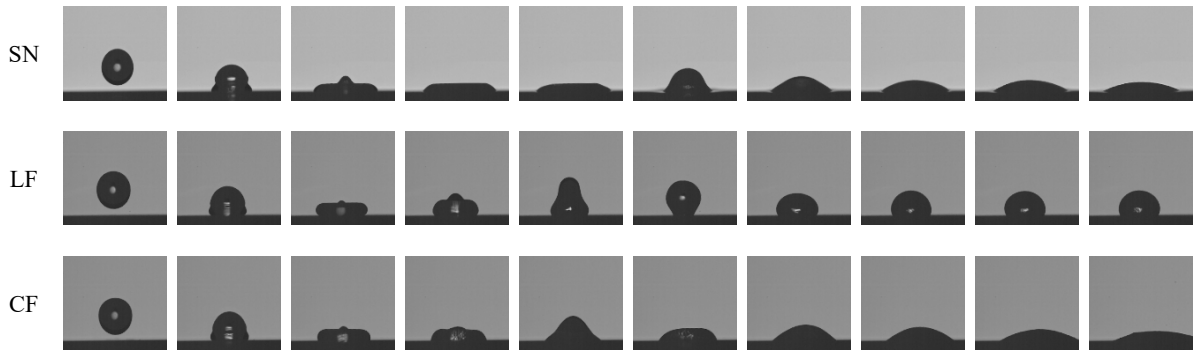
294 To deeply understand the influence mechanisms of the surface wettability and wall temperature on the  
 295 morphological developments of the liquid phase of the wall-impinging fuel droplets in four different regimes,  
 296 the development characteristics of the diesel droplets after impacting the different surfaces are investigated. The  
 297 surfaces SN, LF and CF shown in **Table 3** are used as the surfaces for the test. Four typical wall temperatures of  
 298 423 K, 473 K, 573 K and 673 K are investigated. The morphological development of the liquid phase of the  
 299 droplets are studied with a droplet titration height of 10 mm. The visualization results are shown in **Fig. 7**.



(a) 423 K

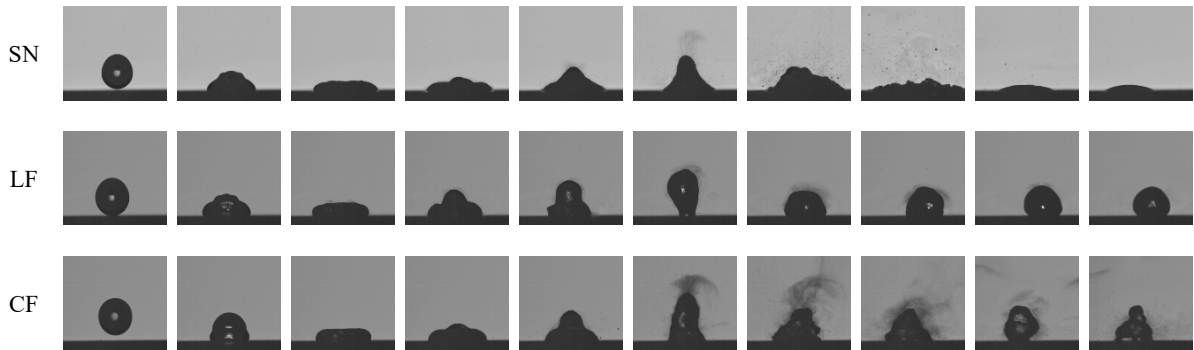
300

0 ms 3 ms 6 ms 9 ms 12 ms 21 ms 60 ms 99 ms 201 ms 300 ms



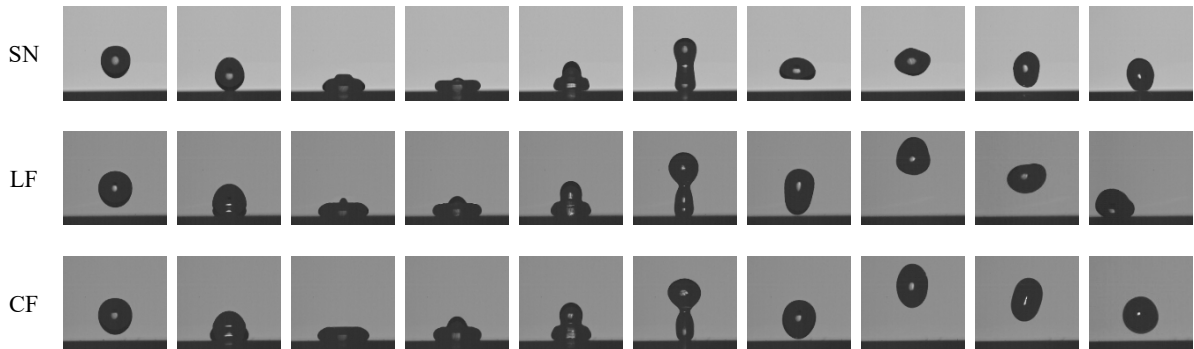
(b) 473 K

0 ms 3 ms 6 ms 9 ms 12 ms 21 ms 60 ms 99 ms 201 ms 300 ms



(c) 573 K

0 ms 3 ms 6 ms 9 ms 12 ms 21 ms 60 ms 99 ms 201 ms 300 ms



(d) 673 K

**Fig. 7.** Morphological developments of the liquid phase of the droplets after impacting on the different surfaces.

It can be seen in **Fig. 7** that the morphological developments of the fuel droplets after impacting on the oleophobic surfaces are significantly different, due to the different surface temperatures. At the wall temperature of 423 K, as seen in **Fig. 7(a)**, the diesel droplet is in the film evaporation regime. At 9 ms, the heat transfer performance is better on the surface SN with thinner liquid film than that on the surfaces LF and CF. Interestingly, at 12 ms, when the droplet shows the "disc-like" appearance on the surface SN, they appear as "gourd-like" and



310 "mountain-like" shapes on the other two surfaces, LF and CF, respectively. Among the three surfaces, the  
311 oleophobicity of the surface LF is the strongest one. As it can be seen, at about 21 ms after collision, the droplet  
312 rebounds against the surface LF.

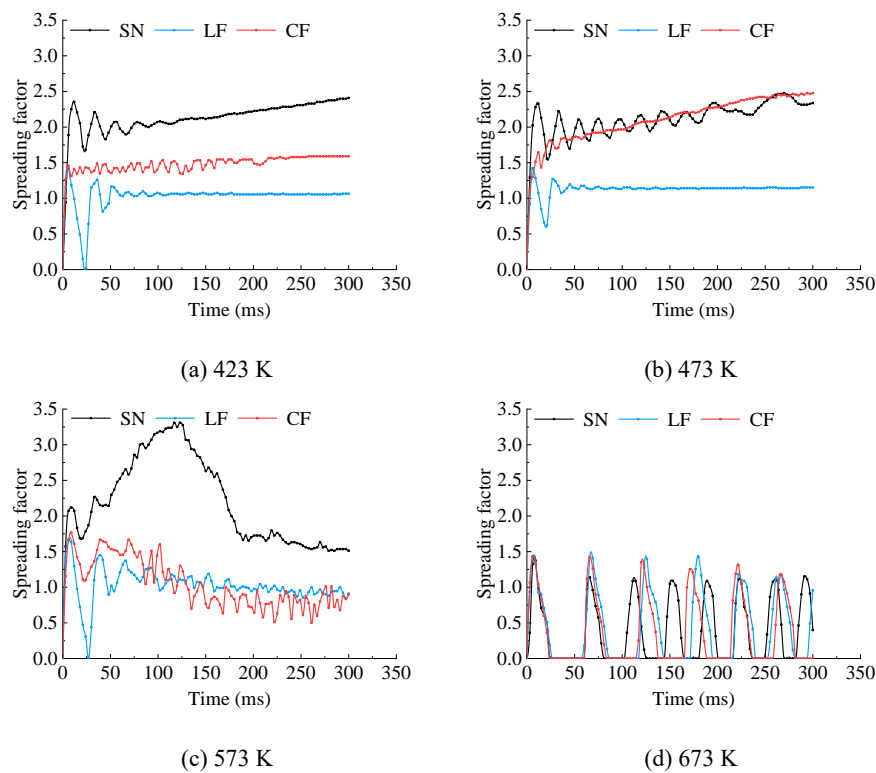
313 At the wall temperature of 473 K, the wall temperature reaches the boiling temperature of some components  
314 of the fuel that have a low boiling point, such as alkanes, cycloalkanes and aromatics with low carbon numbers.  
315 At the same time, the viscosity and the surface tension of the droplets decrease with the increased surface  
316 temperature. It can be seen from **Fig. 7(b)** that at 9 ms, compared with the photos taken at the wall temperature  
317 of 423 K, the spreading widths of droplets on the surface LF and the surface CF are larger under the wall  
318 temperature of 473 K, particularly on the surface CF after 21 ms of collision.

319 At the wall temperature of 573 K, steam appeared above the droplets can be seen clearly in **Fig. 7(c)**, that is  
320 generated due to the high surface temperature, especially at and after 21 ms of collision to the surface LF and the  
321 surface CF. Remarkably, the behaviors of the droplets impacting on the surfaces with different wettability are  
322 various. On the oleophilic surface, small splashes of liquid are clearly observed on the upper surface of the liquid  
323 after the collision. This is mainly due to the venting of the vapor bubbles. After the droplets hit the oleophobic  
324 surfaces, the droplets are disturbed by the fuel vapor escaped from three-phase contact surface, which makes the  
325 shapes of the droplets complex. The contours of the droplets are irregular and jagged, as shown in **Fig. 7(c)**. The  
326 surfaces with a stronger oleophobicity promotes the rebound of the droplets against the surface and makes it  
327 easier for the droplets to be in film boiling regime, which is consistent with the previous conclusions.

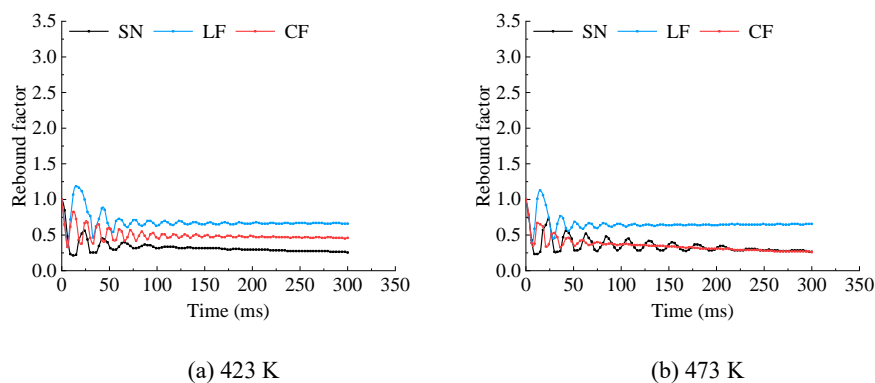
328 At the wall temperature of 673 K, as seen in **Fig. 7(d)**, due to the unstable vapor film, the droplet on the  
329 surface SN has a tendency to rebound off the surface, and when the vapor film becomes more stable as the wall  
330 temperature rises, the droplet will be in film boiling regime. However, on the two oleophobic surfaces, due to the  
331 metal surface temperatures is much higher than the boiling point of all the diesel components, and the stable  
332 vapor films prevent the direct liquid-solid contact, the diesel droplets are in film boiling regime. The droplets on

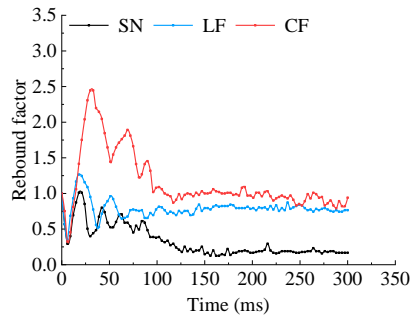
333 the above two surfaces are supported by the vapor films, so the heat flux significantly reduce. As a result, the fuel  
 334 droplets will no longer wet the walls after hitting them, but will behave as periodic beating until they are  
 335 completely evaporated.

336 The behaviors related to the morphological development process of the fuel droplets due to injection within  
 337 the internal combustion engines mainly include spreading, rebounding, splashing and secondary breakup. To  
 338 quantify and compare the effects of surface wettability and wall temperature on the behavioral developments of  
 339 the droplets, such as spreading and rebound, after hitting the walls, the spreading factor and rebound factor of the  
 340 droplets under different wall conditions are measured and compared to each other, as shown in **Fig. 8** and **Fig. 9**.

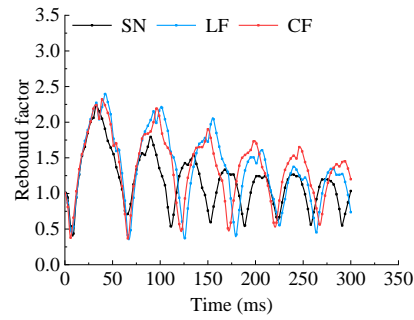


345 **Fig. 8.** Effects of the surface wettability and wall temperature and on the spreading factor of the droplets.





(c) 573 K



(d) 673 K

**Fig. 9.** Effects of the surface wettability and wall temperature on the rebound factor of the droplets.

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Generally, at lower surface temperatures, e.g. 423 K and 473 K, the smooth surface SN presents a higher spreading factor and a lower rebound factor compared to the surface LF and the surface CF. While, the laser etched surface with a surface free energy modification shows a lower spreading factor but a higher rebound factor compared to the other two surfaces. The above results are attributed to the smaller energy required for rebounding on the oleophobic surfaces. At the surface temperature of 423 K, the maximum rebound factor of the fuel droplets on the surface LF reaches 1.18, and the spreading factor is 0.72 at this moment. These results indicate that at a lower surface temperature condition, the oleophobic surface is more conducive to the rebound rather than spreading of the fuel droplets.

When the surface temperature is 473 K, comparing to the surface temperature of 423 K, it can be seen that the variations of both the spreading factor and rebound factor on the surface SN are more significant. At the same time, the spreading factor and the rebound factor on the surface CF are found to be increased and decreased, respectively, due to the increase in the surface temperature. It makes the value of these two parameters on the surface CF closer to that of the surface SN. The changes in spreading factor and rebound factor are mainly the results of the decrease in the viscosity and surface tension of the fuel droplets caused by the increased surface temperature. In addition, the result indicates that the ability of convex domes/grooves and protrusions structures on the laser-etched surface for enhancing the oleophobicity is better than that of the boss/pits and needle-like structures of the chemically etched surface.

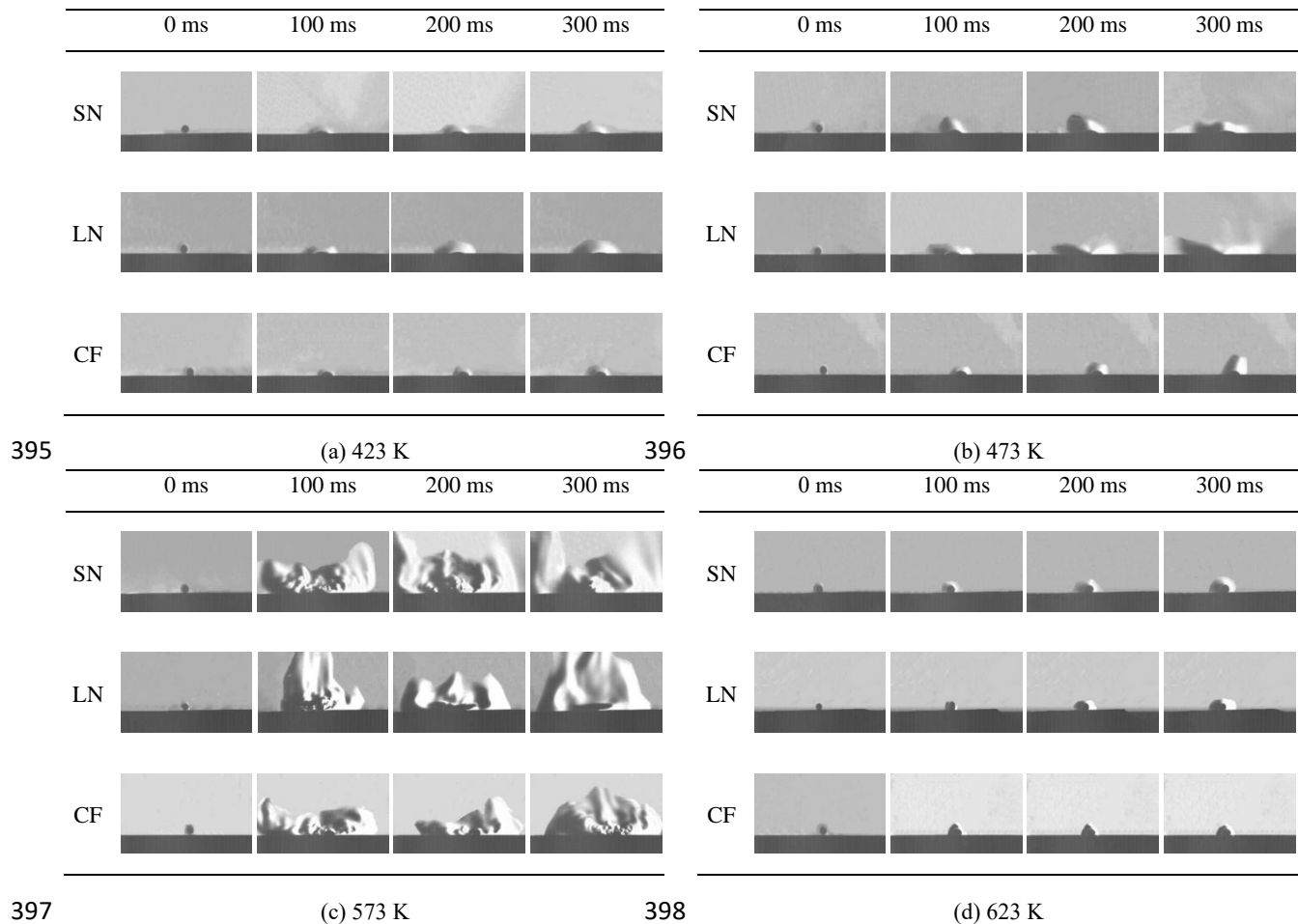
368 With a further increase of surface temperature to 573 K, the variation amplitude of both the spreading factor  
369 and the rebound factor on all the three surfaces become higher, especially in the short period right after hitting  
370 the walls. As mentioned in the previous section, the surface LF and the surface CF has stronger oleophobicity  
371 than the surface SN, and the high oleophobicity of the both surfaces can be kept at a higher surface temperature.  
372 As a result, after hitting the surface LF and the surface CF, the droplets can still keep a very small spreading area  
373 which is also the evaporation area. Although both viscosity and surface tension of the droplets are decreased after  
374 impacting on the high temperature surfaces, it seems that the wettability of the surface is not influenced  
375 significantly by the surface temperature when it is 573 K.

376 At the surface temperature of 673 K, as shown in **Fig. 8(d)** and **Fig. 9(d)**, it can be seen that both the  
377 spreading factor and rebound factor of the droplets present clear changes compared with that on the three surfaces  
378 with lower temperatures. The most important change is that under the surface temperature of 673 K, the two  
379 factors both show periodic fluctuations with obvious regularity. This is mainly because at the excessively high  
380 surface temperature, the vapor film formed between the hot surface and the droplet lifts the droplet periodically  
381 and prevents the direct contact between the droplet and the surface. As a result, the fuel droplets on all the surfaces  
382 exhibit similar behaviors, that is, the droplets are not able to spread stably on the surface when the surface  
383 temperature is about the Leidenfrost temperature. It indicates that when the wall temperature is higher than the  
384 Leidenfrost temperature of the droplets, the effects of the surface wettability on the morphological development  
385 of the wall-impinging droplets are significantly weakened.

#### 386 *3.4. Effects of the surface wettability on the morphological development of the vapor phase of the droplets at* 387 *different wall temperatures*

388 To further understand the performance of wettability and wall temperature in improving the fuel evaporation,  
389 the morphological development processes of both liquid and vapor phases of diesel droplets impacting on the  
390 different surfaces are investigated with schlieren method. The wall temperatures used for the experiment are 423

391 K, 473 K, 573 K and 623 K, respectively. The surfaces SN, LN and CF are used as the test surfaces. The titration  
 392 height of 15 mm for the droplet is used which is higher than that of the experiment introduced in last section. The  
 393 schlieren visualization results of the morphological development of the both liquid and vapor phases are shown  
 394 in **Fig. 10**.



397 **Fig. 10.** Morphological developments of the liquid and the vapor phases.

400 **Fig. 10(a)** shows the imaging results of the droplets hitting the surfaces with different wettability at a wall  
 401 temperature of 423 K. Compared to the images obtained at higher wall temperatures as shown in **Fig. 10(b)** and  
 402 **Fig. 10(c)**, it can be found that at a wall temperature of 423 K, the diffusion rates of the vapor phase of diesel on  
 403 all the three surfaces are slower. It can also be seen that among all the three surfaces, the smallest vapor diffusion  
 404 area appears on the surface CF which has strongest oleophobicity, while the largest vapor diffusion area appears  
 405 on the surface LN of which the oleophilicity is strongest among all the surfaces. It suggests that under the

406 conditions of lower surface temperatures, the vapor phase diffusion area of the droplet after hitting the wall is  
407 closely related to the spreading area of the droplet. The larger the spreading area, the faster the evaporation rate  
408 of the fuel.

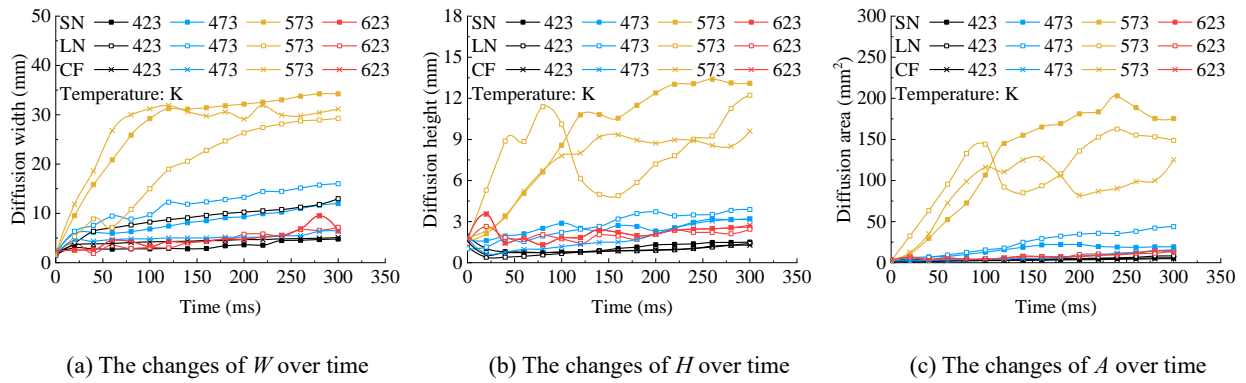
409 At a wall temperature of 473 K, after the droplets impact on all the three surfaces the walls, the heat transfer  
410 modes between surfaces and droplets are heat conduction. The evaporation rate is seen higher than that at the  
411 wall temperature of 423 K. It can be seen from **Fig. 10(b)** that during the development of the vapor phase, the  
412 maximum diffusion width of vapor phase of diesel appears on the surface LN. This is mainly because, on the one  
413 hand, the increase in surface temperature reduces the viscosity of the fuel and makes it easier to obtain a greater  
414 spreading area. On the other hand, the laser-etched orthogonal groove structure on the surface has a strong  
415 diversion effect on the fuel droplet, so that after hitting the wall, a larger spreading area and a thinner fuel film  
416 thickness can be obtained, which is conducive to the escape of bubbles from the surface of the fuel film and  
417 promote heat transfer. For the surface CF, it has been verified from the test results that the oleophobicity of the  
418 surface can be well maintained at a wall temperature of 473 K. Because of the smaller spreading area as well as  
419 the smaller heat exchange area of the droplet on the surface CF, the heat transfer to the droplet and evaporation  
420 rate of it will also be smaller.

421 As is evident in above images, when the wall temperature rises to 573 K, the degree of the vapor phase  
422 diffusion is significantly enhanced, and the diffusion area is obviously larger than that of the results obtained at  
423 the other three wall temperatures. This is mainly because at 573 K, the wall temperature has reached the boiling  
424 temperature of most components of the fuel components, but has not yet reached the Leidenfrost temperature of  
425 them. Under such condition that the stable vapor film has not yet formed, the droplet will not detach from the  
426 surface after hitting the wall, but the heat transfer rate between the surface and the droplet is larger due to the  
427 increased temperature difference between the two, leading to the immediately boiling and quick evaporation of  
428 the fuel droplet right after it hits the wall. It implies that, compared with the surface temperature, the wall

429 wettability has little effect on the droplet evaporation rate at the condition that the droplet is in the transient  
 430 boiling regime.

431 **Fig. 10(d)** shows that when the wall temperature reaches 623 K, due to combined effect of the lift force of  
 432 the vapor film and the wall reaction force, the fuel droplets partially wet the metal surfaces after hitting the walls.  
 433 Also, the partial nonwetting results in less energy dissipation, which causes the droplets to gain more kinetic  
 434 energy to retract and tend to rebound and fall periodically. Furthermore, as the temperature rises from 573 K to  
 435 623 K, the low thermal conductivity of the vapor film inhibits heat transfer between the hot surface and the  
 436 droplet. As a result, when the wall temperature rises to 623 K, the evaporation amount of droplets on all the three  
 437 surfaces are reduced compared with that at the surface temperature of 573 K, for all the time intervals after hitting  
 438 the walls.

439 Based on the imaging results, the width, height and the two-dimensional area value of the vapor phase region  
 440 perpendicular to the camera direction are quantified at different moments after droplet-wall impingement through  
 441 the method of pixel point progressive scanning, as shown in the **Fig. 11**.



442 (a) The changes of  $W$  over time      (b) The changes of  $H$  over time      (c) The changes of  $A$  over time  
 443  
 444 **Fig. 11.** Effects of the surface wettability and wall temperature on  $W$ ,  $H$ ,  $A$ .

445 It can be seen from **Fig. 11** that when the wall temperature is 573 K, the diffusion width, height and area of  
 446 the vapor phase region are obviously larger than those under the other three wall temperature conditions. This is  
 447 mainly because the larger heat transfer rate at 573 K makes the evaporation rate of the droplet at this surface  
 448 temperature is clearly larger than the results obtained under other surface temperature conditions.

449 At the surface temperature of 473 K, it is noted that the maximum values of the three geometric parameters  
450 of the evaporation region are all contributed by the surface LN, as seen in **Fig.11**. At the wall temperature of 473  
451 K, the evaporation rate is closely related to the spreading area of the droplet. Referring to the imaging results of  
452 **Fig. 10**, it can be seen that after impacting the wall, affected by the wettability and micro-morphology of the  
453 surfaces, the spreading area of the droplet on the surface LN is largest among all the three surfaces, resulting in  
454 a greater evaporation rate of the surface LN, comparing to that of the other two surfaces.

455 In addition, **Fig. 11** shows that at the wall temperature of 423 K and 623 K, the width, height and area of  
456 the evaporation region in different time intervals after droplet-wall impingement are significantly smaller than  
457 those obtained at the other two surface temperatures. However, the reasons for the small evaporation rates under  
458 the surface temperatures of 423 K and 623 K are different. When the wall temperature is 423 K, the main reason  
459 for the small evaporation rate is the small temperature difference between the surfaces and the droplets. Although  
460 the surface wettability has a notable effect on spreading area of the droplets after hitting the walls, it has less  
461 influence on the evaporation rate of the droplets due to the low heat transfer rate between the surfaces and the  
462 droplets which is caused by the low wall temperature of all the three test surfaces. While on the surfaces of 623  
463 K, the vapor film between the droplets and the wall surfaces is the main reason that affects the evaporation rate  
464 of the droplets, indicating that when the wall temperature is near the Leidenfrost temperature of the fuel, the  
465 vapor film causes a significant drop in fuel evaporation rate. However, in the actual application of the engines, if  
466 the droplets hit vertically a surface such as the cylinder wall, the film boiling caused by the high surface  
467 temperature could be beneficial to the rebound and secondary breakup of the fuel droplets, thereby promoting  
468 the evaporation of the droplets in the gas-phase space of the cylinder and improving the air-fuel mixing.

#### 469 **4. Conclusions**

470 The aluminum alloy surfaces with different microstructures and special wettability are fabricated with the  
471 methods of laser etching, chemical etching and surface free energy modification. Using the high-speed



472 photography and the schlieren methods, the morphological development process of both liquid phase and vapor  
473 phase of the diesel droplets together with the evaporation process after the droplets impact on the surfaces with  
474 different wettability and temperatures are experimentally investigated. The main conclusions can be summarized  
475 as follows:

476 (1) Depending on the surface microstructures and surface free energy, the contact angle of diesel droplets  
477 on the laser-etched oleophilic surface is the smallest, and the contact angle on the laser-etched oleophobic surface  
478 modified with the ESF is the largest among the all test surfaces.

479 (2) When the droplets hit oleophilic surfaces, the larger the roughness, the faster the evaporation rate at low  
480 wall temperatures. Stronger oleophobicity of the surface reduces the Leidenfrost temperature of the fuel droplets,  
481 and makes it easier for the droplets to be transferred to the film boiling regime, thereby promoting the evaporation  
482 of the droplets in the gas-phase space of the cylinder and improving the air-fuel mixing.

483 (3) Compared with the spreading behavior, the oleophobic surface facilitates the rebound of the droplets.  
484 When the wall temperature exceeds the Leidenfrost temperature of the droplet, the influence of the surface  
485 wettability on the morphological development of the droplet after the droplet-wall impingement is significantly  
486 weakened.

487 (4) Under the lower surface temperatures, the vapor phase diffusion area of the droplet after collision is  
488 closely related to the spreading area of the droplet. The larger the spreading area, the better the heat transfer  
489 performance and the faster the evaporation rate of the fuel. When the droplet is in transition boiling regime, the  
490 large heat transfer rate makes the diffusion width, height and diffusion area of the vapor phase region are  
491 obviously large.

## 492 **Notes**

493 The authors declare no competing financial interest.

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