Elsevier required licence: ©2024. This manuscript version is made available under the CCBY-NC-ND 4.0 license http://creativecommons.org/licenses/by-nc-nd/4.0/ The definitive publisher version is available online at [https://doi.org/10.1016/j.fuel.2024.133249](https://doi.org/10.1016/j.jhazmat.2024.133491)



#### **Abstract**

 The cold start issue of methanol engines limits their wide application in cold seasons and regions. To explore the underlying mechanisms and propose effective improvement measures, the evaporation characteristics of methanol at 243-303 K were first investigated by the single droplet method in this study. The effects of ambient temperature, initial diameter, fuel temperature and intake air flow velocity on evaporation of methanol droplets were quantitatively analyzed and their guidance for improving the cold start performance of methanol engines were discussed. The results revealed that the evaporation process of methanol droplets in low temperature and humid environment showed two-stage feature due to its hygroscopicity, including pure methanol evaporation and water-dominated evaporation of methanol-water mixture, but it could be regarded as the evaporation of a pseudo single component and the same was true for other binary mixtures. The existence of water in methanol droplets not only led to their incomplete evaporation at temperatures below 263 K, but also caused the linear change of their evaporation rates with temperature, which was different from the exponential change of pure methanol evaporation rate with temperature. Increasing the ambient temperature from 243-283 K to 293 K was optimal for promoting methanol evaporation. Reducing droplet diameter inhibited the water absorption of methanol droplets, thus enhancing their evaporation rates. Increasing fuel temperature could not promote droplet evaporation, but mainly influenced water absorption of methanol droplets. The promotion effect of air flow on methanol evaporation became weaker with the increase of intake air flow velocity, especially when it exceeded 3 m/s. The findings

- of this study suggest that multiple methods should be combined to improve the cold
- start performance of methanol engines.
- *Keywords:* Cold start issues; Droplet evaporation; Low temperature; Initial diameter;
- Fuel temperature; Intake air flow velocity







# **Graphical abstract**

## **Nomenclature**

### *Abbreviations*



SI Spark ignition

### *Symbols*



- K<sup>a</sup> average evaporation rate of methanol droplets
- K<sup>w</sup> average evaporation rate of water droplets
- K<sub>c</sub> calculated value of average evaporation rate of methanol droplets
- $K_p$  evaporation rate constant of the pseudo single component
- $P_1$  proportion of the first stage
- $P_2$  proportion of the second stage
- $P_{K1}$  improved percent of  $K_1$
- $P_{K2}$  improved percent of  $K_2$
- $P_{Ka}$  improved percent of  $K_a$
- $P_{\tau}$  increased percent from  $\tau_i$  to  $\tau_a$
- $P_{\tau i}$  relative change (increased percent or decreased percent) of  $\tau_i$
- $P_{\tau a}$  relative change (increased percent or decreased percent) of  $\tau a$
- $\eta_{K1}$  improvement efficiency of  $K_1$
- $\eta_{K2}$  improvement efficiency of  $K_2$
- $\eta_{Ka}$  improvement efficiency of  $K_a$
- ΔT Value of increased ambient temperature
- ΔT' Value of increased fuel temperature
- V intake air flow velocity
- T<sub>d</sub> droplet temperature
- RH relative humidity
- AH absolute humidity

#### **1 Introduction**

 Automobiles are still predominately powered by traditional hydrocarbon fuels nowadays, inevitably leading to significant harmful pollutants such as particulate 62 matters (PM), nitrogen oxides  $(NO_x)$  and unburned hydrocarbons (UHC) [1]. Further, 63 the production of carbon dioxides  $(CO_2)$  also exacerbates the greenhouse effect [2]. The urgent need to achieve the carbon neutralization goal drives the engine industry to search for green, low-carbon and renewable alternative fuels [3]. Methanol has received extensive attention due to its unique advantages [4]. On the one hand, methanol can be produced by both fossil fuels (e.g., coal, biomass, natural gas and coke oven gas [5]) 68 and the synthesis of  $CO<sub>2</sub>$  captured in the air and hydrogen obtained by electrolysis of 69 water from renewable energies [6], so as to realize the green cycle of  $CO<sub>2</sub>$  to fuel. On the other hand, methanol has a high flame speed [7], and its low C/H ratio produces less  $CO<sub>2</sub>$  than gasoline. The high oxygen content reduces the formation of carbon monoxide (CO) [8]. The high latent heat of vaporization and more ternary molecules in the 73 combustion products lead to lower in-cylinder temperature [9], not only reducing  $NO<sub>x</sub>$  emissions and heat loss, but also providing better anti-knock performance [10]. The high-octane number allows higher compression ratios [11], thereby improving engine thermal efficiency [12]. Furthermore, methanol is liquid at standard temperature and pressure [13], making it easier to store and transport [14].

 Many scholars have studied the performance of methanol-fueled engines. Xu et al. [15] experimentally and numerically studied the engine performance and emission characteristics of methanol and iso-octane in a heavy-duty direct-injection compression



 coefficient of variation of the indicated mean effective pressure (IMEP) remained below 2% at EGR rate of 31%. In summary, the above studies showed that methanol engines have great advantages in energy saving and emission reduction. Combined with green production, methanol engines have broad application prospects.

 However, methanol evaporates slowly at low ambient temperatures due to its low vapor pressure and high latent heat of vaporization [10], resulting in cold start issues of methanol engines. Li et al. [19] concluded that methanol engines cannot start reliably without auxiliary devices under an ambient temperature below 289 K even when a large amount of methanol is injected, which limits the use of methanol engines in cold seasons and regions. Therefore, to promote the application of methanol engines, it is of great significance to explore the evaporation characteristics of methanol at low temperatures and find ways to improve its evaporation rate.

 In real engines, the fuel is injected into combustion chamber through high pressure injectors and evaporates in the form of spray droplets to produce an ignitable mixture before combustion and power output [20]. As a result, the engine performance is closely related to the evaporation of droplets. Thus, it is a common and necessary method to investigate the fuel evaporation characteristics from the perspective of a single droplet [21]. Many scholars have used this method to study the evaporation characteristics of methanol fuel. Yuan et al. [22] studied the evaporation characteristics of methanol droplets at ambient temperatures of 323-473 K. They found that methanol droplets evaporated linearly when the ambient temperature was higher than 373 K, while the evaporation process of methanol droplets was divided into two linear evaporation

 stages at temperatures below 373 K, which was caused by the hygroscopicity of methanol. Wang et al. [23] studied the evaporation characteristics of methanol droplets at ambient temperatures of 473-1087 K and reported a similar conclusion: the normalized square diameter of methanol droplets decreased linearly with time. The evaporation of methanol droplets in different humidity environments at an ambient temperature of 297 K was investigated by Law [24]. The results showed that methanol droplets evaporated linearly when the humidity was 0%. As the humidity increased, the droplet normalized diameter curve became a downwards concave and the droplet lifetime prolonged. Hegseth et al. [25] studied the evaporation characteristics of methanol droplets at an atmospheric pressure and an ambient temperature of 293 K. They found a convection driven by surface tension gradient inside the droplets during evaporation. Kosasih et al. [26] investigated the heat and mass transfer of methanol droplets at ambient temperatures of 308-328 K and air flow rates of 0.1-0.7 m/s. However, the ambient temperatures in above studies were all over 293 K. There is a research gap in the evaporation of methanol droplets at temperatures below 293 K, which is of great significance for the cold start of methanol engines. Depending on the seasons and regions, the start-up temperature of an engine usually changes between 243 and 303 K. Therefore, this study investigated the evaporation characteristics of methanol droplets at a wide range of ambient temperatures between 243-303 K. The effects of ambient temperature, initial droplet diameter, fuel temperature and intake air flow velocity on the evaporation of methanol droplets were quantitatively analyzed, and their implications for designing methanol engines were discussed. The findings of  this research are expected to provide great theoretical and practical guidance for tackling the cold start issues of methanol engines and thus promote their applications in cold seasons and regions.

#### **2 Material and methods**

#### **2.1 Experimental setup**

 **Fig. 1** shows the schematic of the experimental setup for the evaporation of methanol droplets at low temperatures. It consisted of a droplet generation and transport system, a temperature control system, a fuel heating system, an inlet air flow system and an image acquisition system. In the droplet generation and transport system, as the stepper motor Ⅰ runs, a given volume of liquid was squeezed out by a microliter syringe and then a droplet with the specific diameter was formed on the K-type thermocouple with the diameter of 0.08 mm, which was sent to the constant volume chamber (CVC) by stepper motor Ⅲ. According to the conclusion of Rehman et al. [27], the effect of thermocouple was ignorable when the ratio of the square of thermocouple diameter to the square of initial droplet diameter was less than 0.01. Considering that the diameter of the thermocouple was 0.08 mm and the diameters of the droplets in the experiment exceeded 0.8 mm, the effect of heat conduction by thermocouple on droplet evaporation could be negligible. The temperature control was achieved by the environmental chamber which could change between 233 and 353 K. Three K-type thermocouples were evenly arranged in the CVC to ensure uniform ambient temperature. The accuracy 168 of temperature control was  $\pm 1$  K. The fuel heating system was used to change the

 methanol temperature before the evaporation, which was reached by the heating plate pasted on the baffle below the droplet. Since the heating plate was exposed to the cold environment, a large amount of heat generated by the heating plate was dissipated to the environment and only a small part of the heat was used to improve the fuel temperature, which ultimately led to a smaller increase in fuel temperature. The maximum value of increased fuel temperature was only 8.5 K in this experiment. After the baffle was removed by the stepper motor Ⅱ, the droplets with different fuel temperatures were sent to the CVC. The inlet air flow system mainly included an intake port manufactured by three-dimensional printing, a flowmeter (1.5% accuracy) and a blower, which could vary the intake air flow velocity. In the image acquisition system, a LED lamp, an industrial camera (MV-CS060-10GM) and a tele-macro lens (Nikon Micro-ED 200 mm f/4) were combined to get the droplet images with the resolution of 1072×1548 pixels. Due to the slow evaporation of methanol droplets at low temperatures, the sampling frequency was changed between 1 and 18 frames per second (fps).



#### **2.2 Test conditions**

 The evaporation characteristics of methanol droplets with various initial diameters were first investigated at ambient temperatures of 243-303 K. Then the fuel temperature and intake air flow velocity were increased to study their promotion effects on the evaporation of methanol droplets at 273 K. The specific experimental conditions were presented in **Table 1**.



#### **2.3 Data processing**

 Droplet diameter was a key parameter in the evaporation process, which was obtained by a MATLAB code. The procedures of image processing were shown in **Fig. 2**. Firstly, a region of 300\*300 with the droplet at the center was cut out from the raw image (1072\*1548). Secondly, the image was binarized by a proper threshold. Then thermocouple wire on both sides of the droplet was removed. Finally, the droplet boundary was extracted from the image and the pixel number (*N*) of the droplet was obtained. The droplet diameter (*d*) was calculated by Eq. (1) where *l* was the image spatial resolution:



**Fig. 2.** The procedures of image processing.

 Droplet lifetime and evaporation rate were also significant parameters to evaluate the evaporation, which were described in **Fig. 3**. The evaporation process of methanol droplets included two linear stages and the demarcation point between them was 210 determined by the maximum value of the second derivative of the concave part of 211 droplet diameter curve. The average evaporation rates of the first and second stages 212 were defined as  $K_1$  and  $K_2$ , respectively which were obtained by linear fitting for each 213 stage. The times of two stages were defined as  $\tau_1$  and  $\tau_2$ , respectively, and their sum 214 was the actual normalized lifetime  $\tau_a$ . The ideal normalized lifetime,  $\tau_i$ , was defined by 215 Eq. (2), where  $\sigma$  was the corresponding normalized squared diameter at the end of 216 evaporation, which represented the lifetime of methanol droplets without the 217 disturbance of water vapor. The difference between  $\tau_a$  and  $\tau_i$  indicated the effect of water 218 vapor on the evaporation of methanol droplets. In addition, the average evaporation rate 219 of methanol droplets in the entire evaporation process,  $K_a$ , was calculated by the Eq. 220 (3), where  $d_0$  was the initial droplet diameter,  $d_1$  was the droplet diameter when the 221 evaporation was completed and t was the evaporation time.

$$
\tau_i = (1 - \sigma) / K_1 \tag{2}
$$

$$
K_a = (d_0^2 - d_1^2)/t \tag{3}
$$



224

225 **Fig. 3.** The parameters characterizing the evaporation of methanol droplets.

226

#### 227 **2.4 Experimental errors and uncertainties**

228 The errors of droplet characteristic parameters were mainly caused by the random 229 error of experiment and the error of droplet boundary identification. Experiment was 230 repeated five times to minimize the random error  $(\delta)$  which was calculated by Eq. (4):

231 
$$
\delta = \sqrt{(x_1 - \bar{x})^2 + ((x_2 - \bar{x})^2) + \dots + ((x_n - \bar{x})^2)/(n - 1)}
$$
(4)

232 where  $x_1, x_2 \cdots x_n$  were the values of repeated experiments,  $\bar{x}$  was the average 233 value, and *n* was the number of experiment.

234 Regarding the error of droplet boundary identification, if the experimental result 235 *R* satisfied Eq. (5) [28], [29] [30], the relative uncertainty of *R* was calculated by Eq. 236 (6):

237 
$$
R = Y_1^{a_1} * Y_2^{a_2} * \cdots * Y_n^{a_n}
$$
 (5)

238 
$$
\frac{\Delta R}{R} = \sqrt{(a_1 * \frac{\Delta Y_1}{Y_1})^2 + (a_2 * \frac{\Delta Y_2}{Y_2})^2 + \dots + (a_n * \frac{\Delta Y_n}{Y_n})^2}
$$
(6)

239 where  $Y_i$  was the variable, and  $\Delta R$  and  $\Delta Y_i$  were the uncertainties of *R* and  $Y_i$ , 240 respectively. Assuming that a pixel was a square, then the droplet area could be 241 calculated by Eq. (7) where *L* was the side length of pixel,  $D_0$  was the diameter of 242 alundum tube for calibration, *M* was the pixel number of alundum tube diameter, and 243 *N* was the pixel number of the droplet.

244 
$$
S = L^2 * N = \left(\frac{D_0}{M}\right)^2 * N = D_0^2 * M^{-2} * N \tag{7}
$$

245 Assuming that the droplet was a sphere, then the relative uncertainty of square of 246 droplet diameter could be calculated by Eq. (8) where *ΔN*, *ΔD<sup>0</sup>* and *ΔM* were the 247 uncertainties of the pixel number of the droplet, the diameter and pixel number of  alundum tube, respectively. In this study, the droplet diameter varied from 0.816 mm to 1.604 mm and *D<sup>0</sup>* was 2.5 mm (measured by a vernier caliper whose accuracy was 0.02 250 mm, so  $\Delta D_0$  was 0.02 mm). It was assumed that there was an error of two pixels when measuring alundum tube diameter, so *ΔM* was 2. According to Morin et al. [31], the pixels on the droplet boundary were regarded as errors. For the droplet with diameter of 0.816 mm, *M*, *N* and *ΔN* were 290, 6512 and 260, respectively, so  $\Delta D^2/D^2$  was 4.52%. For the droplet with diameter of 1.604 mm, *M*, *N* and *ΔN* were 290, 25149 and 255 562, respectively, so  $\Delta D^2/D^2$  was 3.08%. Overall, it could be concluded that the uncertainty of the droplet diameter was less than 5%.

257 
$$
\frac{\Delta D^2}{D^2} = \frac{\Delta S}{S} = \sqrt{(2 * \frac{\Delta D_0}{D_0})^2 + (-2 * \frac{\Delta M}{M})^2 + (\frac{\Delta N}{N})^2}
$$
(8)

258

#### 259 **3. Results and discussion**

#### 260 **3.1 Evaporation characteristics of methanol droplets at low temperatures**

 **Fig. 4(a)** plots the normalized squared diameters and temperatures of methanol droplets at temperatures of 243-303 K. The droplet diameter and the time are normalized to eliminate the effect of different initial diameters between repeated experiments caused by surface tension [32]. As shown in **Fig. 4(a),** the evaporation process of methanol droplets at 253-303 K is divided into two stages by the two linear parts of the diameter curves and the two quasi-steady parts of the droplet temperature curves, which is similar to the evaporation of binary mixture. It is because the first stage is the evaporation of pure methanol and the second stage is the water-dominated 269 evaporation of methanol-water mixture [33]. The  $d^2$  law is obeyed in each stage, which  is consistent with the evaporation of methanol droplets at ambient temperature of 323- 373 K [22]. This is also the result of the hygroscopicity of methanol in humid environment, because there is always water vapor in the air even when the ambient temperature is extremely low. The normalized squared diameter corresponding to the turning point between the first and second stages gradually decreases with the decrease of ambient temperature, which suggests that more methanol is evaporated in the first stage and the concentration of water in the mixture is increased. The reason is that less water vapor is absorbed by the methanol droplets, which is attributed to the reduction of number of water molecule in the environment caused by the lower saturation vapor pressure and slower evaporation of water. **Fig. 4(b)** describes the relative humidity and absolute humidity at various temperatures. It can be seen from **Fig. 4(b)** that the relative humidity is gradually reduced when ambient temperature increases, which is due to the simultaneous increase of the partial pressure and saturation vapor pressure of water vapor in the air. To better evaluate the content of water vapor in the air, absolute humidity is used to represent the mass of water vapor per unit volume of air. According to **Fig. 4(b)**, absolute humidity increases with temperature and reaches the maximum 286 value of 3.76  $g/m^3$  at 303 K, which is far less than the absolute humidity at temperature of 298 K and relative humidity of 50%. This proves that the content of water vapor in the air is low and its increase is limited when ambient temperature increases from 243 K to 303 K, leading to the little change of turning point between the first and second stages. Owing to the relatively low humidity, the droplets are evaporated by over 85 % in the first stage. Surprisingly, the absorbed water can still evaporate at 263 K when it  is mixed with methanol. Maybe it is the result of the hydrogen bonding interaction between the hydroxyl of methanol and water [34], which promotes the water evaporation. However, the methanol droplets cannot completely evaporate at 253 K, and even the second stage is missing at 243 K, as presented in **Fig. 4(a)**. The experimental images show that the absorbed water is attached on the thermocouple and basically not evaporated. This is due to the separation of methanol and water caused by the low temperature and reduced concentration of methanol in the mixture, and the residual methanol continues to evaporate, while the water freezes on the thermocouple. Then the schematic of evaporation for methanol droplets is concluded in **Fig. 4(c)**. It can be inferred that the freezing phenomenon of water can also occur on the wall once the spray impinges on the engine wall in the cold start process of methanol engines, whose effect on engine performance is needed to consider. With the decrease of ambient temperature, the difference in the droplet diameter curves is more obvious, which implies the slower evaporation of methanol at lower temperatures.





**Fig. 4.** (a) Temporal evolution of the normalized squared diameters  $(d/d_0)^2$  and 313 temperatures  $(T_d)$  of methanol droplets at temperatures of 243-303 K. (b) The change of the relative humidity (RH) and absolute humidity (AH) with ambient temperature. (c) The schematic of evaporation for methanol droplets.

 The average evaporation rates of the first and second stages, methanol droplets 317 and pure water at various ambient temperatures,  $K_1$ ,  $K_2$ ,  $K_a$  and  $K_w$  are shown in **Fig.** 318 **5**. Apparently, the trends of  $K_1$ ,  $K_2$  and  $K_w$  are similar, that is, the average evaporation





 **Fig. 5.** Variation of the average evaporation rates of the first and second stages (K<sup>1</sup> 342 and K<sub>2</sub>), methanol droplets  $(K_a)$  and pure water  $(K_w)$  with ambient temperature.  $K_c$  is 343 the calculated value of  $K_a$  by another method.

 In the actual methanol engines, the larger injection quantity and higher latent heat of vaporization of methanol as compared to gasoline can reduce the combustion chamber temperature [10]. This reduces the evaporation rate of methanol, which is the main reason for the cold start difficulty of methanol engines. Therefore, the promotion of methanol evaporation brought by increasing temperature at different initial ambient temperatures is quantitively analyzed. **Fig. 6(a)** illustrates that the improved percent of the average evaporation rates of the first and second stages and methanol droplets, 351 P<sub>K1</sub>, P<sub>K2</sub> and P<sub>Ka</sub>, both increases with the increased temperature  $\Delta T$  for each initial ambient temperature, but gradually weakens at higher initial ambient temperature. For 353 instance,  $P_{K1}$  is 106.13% at an initial temperature of 243 K, but only 19.41% at an initial temperature of 293 K when ΔT is 10 K, as demonstrated in **Fig. 5**. On the other hand, the improvement efficiency of the average evaporation rates of the first and







372 **Fig. 6.** (a) Variation of the improved percent  $(P_{K1}, P_{K2}$  and  $P_{K4})$  of  $K_1, K_2$  and  $K_3$  with 373 the increased temperature  $\Delta T$ .  $K^{\Delta T}$  is the K after the ambient temperature increases by 374  $\Delta T$  and  $K^0$  is the K at initial ambient temperature. (b) Variation of the improvement 375 efficiency ( $\eta_{K1}$ ,  $\eta_{K2}$  and  $\eta_{Ka}$ ) of K<sub>1</sub>, K<sub>2</sub> and K<sub>a</sub> with the increased temperature  $\Delta T$ .

 **Fig. 7** shows the ideal and actual normalized lifetimes, the time of the first and second stages, and their proportion in the entire lifetime. With the increase of ambient temperature, the ideal and actual normalized lifetimes both decrease exponentially and the latter is always greater than the former due to the presence of the second stage caused by water vapor in the environment. The difference between them is related to the ambient temperature and humidity. As shown in **Fig. 7**, the increased percent from 382 the ideal to the actual normalized lifetime,  $P_{\tau}$ , has little change at 283-303 K due to similar low humidity, but rise quickly due to the extremely slow evaporation of methanol-water mixture in the second stage when the ambient temperature is below 273 K. This can be also proved by the rapidly increased proportion of the second stage with  a value of 39.62% at 263 K. Since the methanol droplets cannot completely evaporate at 253 and 243 K owing to the freezing of absorbed water, their lifetimes and the time of the first and second stages are missing.



390 **Fig. 7.** Variations of the ideal and actual droplet normalized lifetimes ( $\tau_i$  and  $\tau_a$ ), times 391 of the first and second stages ( $\tau_1$  and  $\tau_2$ ), proportion of the first and second stages ( $P_1$ 392 and P<sub>2</sub>), and the increased percent of lifetime  $(P<sub>\tau</sub>)$  with ambient temperature.

#### **3.2 Effect of initial droplet diameter on methanol evaporation**

 With the decrease of ambient temperature, the size of spray droplets in methanol engines become larger [35], which affects the evaporation of methanol droplets and further the cold start performance. Hence, the effect of initial droplet diameter on the evaporation characteristics of methanol droplets is discussed in this section. **Fig. 8** shows temporal evolution of the normalized squared diameters of methanol droplets with different initial diameters at temperatures of 243-303 K. It is noticed that the pure methanol evaporation of the first stage of methanol droplets has weak dependence on  initial droplet diameter. According to the conclusion of Verwey and Birouk [36], the droplet evaporation in quiescent environment is related to molecular diffusion and natural convection. The former is determined by fuel volatility and mainly affected by vapor concentration gradient on the droplet surface, while the latter is proportional to 406 the square of pressure and the cube of droplet diameter. For high volatile droplets, such as methanol, the relative importance of the molecular diffusion appears to govern the entire evaporation process at low temperatures and atmospheric pressure as compared to natural convection, leading to the little effect of initial droplet diameter on pure methanol evaporation. Similarly, Verwey and Birouk [37] also found that the change of the evaporation rate of n-heptane with initial droplet size in quiescent environment at room temperature and atmospheric pressure is insignificant due to its high volatility. However, the effect of initial droplet diameter on the methanol-water mixture evaporation of the second stage is more obvious as compared to the first stage.



416 **Fig. 8.** Temporal evolution of the normalized squared diameters  $(d/d_0)^2$  of methanol

droplets with different initial diameters at temperature of 243-303 K.

 **Fig. 9** demonstrates the average evaporation rates of the first and second stages 419 and methanol droplets with various initial diameters at 243-303 K,  $K_1$ ,  $K_2$  and  $K_a$ . As 420 demonstrated in Fig. ,  $K_1$  is almost a constant and do not change with the initial droplet 421 diameter, while  $K_2$  shows relatively large fluctuation, especially at 293 and 303 K. And K<sub>a</sub> also shows a different trend, which decreases with the increase of the initial droplet diameter. This can be explained by the fact that the larger the methanol droplet, the more water vapor it absorbs, and the longer time of the second stage is, which can be validated by the increased proportion of the second stage in **Fig. 10(a)**. Then the lifetime 426 of methanol droplets is prolonged and  $K_a$  is reduced.



**Fig. 9.** Variation of the average evaporation rates of the first and second stages (K<sup>1</sup>

429 and  $K_2$ ) and methanol droplets  $(K_a)$  with initial droplet diameter at ambient

temperatures of 243-303 K.

 **Fig. 10(a)** shows the evolution of ideal and actual lifetimes with the square of initial droplet diameter at 243-303 K. As presented in **Fig. 10(a)**, the ideal lifetime of methanol droplets without the disturbance of water vapor increases linearly with the  increase of the square of droplet diameter. And the relation between droplet lifetime t 435 and square of droplet diameter  $d_0^2$  is obtained:  $t = A * d_0^2$ . According to the classical 436 d<sup>2</sup> law of single component evaporation:  $d^2 = d_0^2 - K * t$ , where K is evaporation rate constant, A is 1/K. Notably, the same trend occurs in the actual lifetime. This suggests that the actual two-stage and binary component evaporation process of methanol droplets can be regarded as the evaporation of a pseudo single component, whose evaporation rate constant can be acquired by the reciprocal of the linear fitting slope of 441 actual lifetime curves, that is,  $K_p = 1/A$ , where  $K_p$  is the evaporation rate constant of 442 the pseudo single component. The variation of  $K_p$  with ambient temperature is shown 443 in Fig. 10(b). It can be found that  $K_p$  increases linearly rather than exponentially with the increase of ambient temperature, meaning that the pseudo single component is various at each ambient temperature. Base on the above analysis, the lifetime of 446 methanol droplets will be  $n^2$  times of the original if the initial droplet diameter increases by n times. Due to the larger size of spray droplet during the cold start process of methanol engines, the evaporation of methanol droplets is greatly prolonged, resulting in less combustible mixture of methanol vapor and air in a short time, whose combustion is not enough to start the engine. Therefore, in order to enhance the average evaporation rate of methanol droplets and shorten the entire evaporation time of methanol, the size of spray droplets in the cold start process of methanol engines should be reduced by improving injection pressure or other methods. For example, when the droplet diameter is reduced by half, the droplet lifetime can be reduced to 1/4 of the original according to the above formula, which greatly promotes the complete



evaporation of injected methanol in a short time.

 **Fig. 10.** (a) The ideal and actual droplet lifetimes (t<sup>i</sup> and ta) and the proportions of the 462 first and second stages  $(P_1 \text{ and } P_2)$  under different initial droplet diameter at 243-303 K. (b) The effect of ambient temperature on evaporation rate constant of the pseudo

464 single component  $(K_p)$ .

**3.3 Effect of fuel temperature on methanol evaporation**

 Fuel temperature plays an important role on its physical properties, such as density, viscosity and surface tension [38], thus affecting the spray droplets [39]. Consequently, 469 the effect of fuel temperature on the evaporation characteristics of methanol droplets at 273 K is investigated to reveal the underlying mechanism, which can provide guidance for practical methanol engine application. **Fig. 11** shows the temporal evolution of the normalized squared diameters and temperatures of methanol droplets with various fuel temperatures. As shown in **Fig. 11**, there is little difference in the evaporation process of droplets when methanol temperature changes. However, the relatively large difference can be found for droplet temperature curves. When the droplet is not heated, its temperature rises rapidly first, namely transient heating stage, and then rises slowly, reaching quasi-steady state, which is called equilibrium evaporation stage [40]. This occurs again in the late stage of evaporation due to the existence the second stage of methanol droplets. Adversely, the temperature of droplets with higher fuel temperature experiences first a process of rapid decline and then rising again before equilibrium evaporation. The reason may be that the hot droplets releases heat rapidly until it reaches a relatively equilibrium state with the surrounding cold environment due to their enormous temperature difference. Therefore, there is an additional transient cooling stage in the evaporation process of methanol droplets when the fuel temperature rises. And the higher fuel temperature, the longer transient cooling stage and the shorter transient heating stage. The effect of fuel temperature on the first equilibrium evaporation stage is negligible, but mainly reflects in the second equilibrium

 evaporation stage. Due to the test methanol droplets is in a large space, the effect of heat transfer to the environment on the ambient temperature can be neglected, while the humidity around the droplets is changed. This means that the fuel temperature has little influence on pure methanol evaporation, but mainly affects the evaporation of methanol-water mixture.



494 **Fig. 11.** Temporal evolution of the normalized squared diameters  $(d/d_0)^2$  and 495 temperatures  $(T_d)$  of methanol droplets with various fuel temperatures at ambient

temperature of 273 K.

 **Fig. 12** illustrates the effect of fuel temperature on the average evaporation rates. As presented in **Fig. 12**, although the fuel temperature of droplets has increased by 8.5 499 K, the average evaporation rate of the first stage,  $K_1$ , is almost unchanged and the 500 improved percent of  $K_1$ ,  $P_{K1}$ , is around 0 % due to considerable droplet temperature rise rate in the first equilibrium evaporation stage according to **Fig. 11**. On the contrary, the 502 average evaporation rate and its improved percent of the second stage,  $K_2$  and  $P_{K2}$ , show remarkable fluctuation when the fuel temperature rises. It is because that the water  absorption in the second stage is influenced by the changed humidity around the 505 methanol droplets. Ultimately, the average evaporation rate of methanol droplets,  $K_a$ , gradually decreases with the increase of fuel temperature owing to the increased proportion of the second stage shown in **Fig. 13**.



(a)



 **Fig. 12.** Variation of the average evaporation rate of the first and second stages (K<sup>1</sup> 513 and K<sub>2</sub>) and methanol droplets  $(K_a)$  (a) and their improved percent  $(P_{K1}, P_{K2}$  and  $P_{Ka})$ 





**Fig. 13.** Variation of the ideal and actual normalized droplet lifetimes (τ<sub>i</sub> and τ<sub>a</sub>) and 533 their increased percent ( $P_{\tau i}$  and  $P_{\tau a}$ ) and the proportions of the first and second stages 534 (P<sub>1</sub> and P<sub>2</sub>) with the increased fuel temperature  $\Delta T'$ . τ<sup> $\Delta T'$ </sup> is the τ after the fuel 535 temperature increases by  $ΔT'$ ,  $τ<sup>0</sup>$  is the τ under initial fuel temperature.

#### **3.4 Effect of intake air flow velocity on methanol evaporation**

 It is commonly accepted that fuel droplet evaporation can be enhanced by flow. On the one hand, flow can take away the fuel vapor on the droplet surface, which promotes the diffusion of methanol molecules into the environment [42]. Furthermore, the heat transfer between the droplet and the environment is also strengthened [37]. Thus, the effect of intake air flow velocity on the improvement of methanol droplets evaporation at low temperatures is quantitively evaluated at ambient temperature of 273 K. **Fig. 14** shows temporal evolution of the normalized squared diameters and temperatures of methanol droplets at various intake air flow velocities. It is clear that the two-part feature of methanol droplets evaporation still exists, meaning that the  $d^2$ 

 law is not influenced by turbulence, which is consistent with the conclusion of Birouk and Fabbro [43]. And the evaporation is accelerated as expected. This promotion effect is more noticeable at low intake air flow velocity, but become weaker at higher velocity. It can be also seen from the time history of the droplet temperature that temperature rise rate of methanol droplets gradually increases with the increase of intake air flow velocity due to the enhanced heat transfer by flow.



554 **Fig. 14.** Temporal evolution of the normalized squared diameters  $(d/d_0)^2$  and 555 temperatures  $(T_d)$  of methanol droplets at various intake air flow velocities and ambient temperature of 273 K.

 **Fig. 15** illustrates that average evaporation rates of the first and second stages and 558 methanol droplets,  $K_1$ ,  $K_2$  and  $K_a$ , both are enhanced with the increase of intake air flow 559 velocity. For example,  $K_1$  is increased by 182 %,  $K_2$  is increased by 145 % and  $K_a$  is increased by 163 % at intake air flow velocity of 2.92 m/s as compared to stationary methanol droplets, respectively. However, this enhancement is gradually weakened, because there are limits on the ability of vapor molecules to follow the fluid and the





 **Fig. 15.** Variation of the average evaporation rates of the first and second stages (K<sup>1</sup> 578 and  $K_2$ ) and methanol droplets ( $K_a$ ) and their improved percent ( $P_{K1}$ ,  $P_{K2}$  and  $P_{Ka}$ ) and

579 improvement efficiency ( $η_{K1}$ ,  $η_{K2}$  and  $η_{K4}$ ) with intake air flow velocity V. K<sup>V</sup> is the K 580 at intake air flow velocity of V,  $K^0$  is the K in the quiescent state.

 According to the **Fig. 16**, the proportion of the first stage, P1, decreases and the 582 proportion of the second stage,  $P_2$ , increases as compared to the droplets in the quiescent environment. It indicates that the flow also affects the water absorption of methanol droplets while enhancing the evaporation rate. Moreover, the effect of intake air flow on the lifetime of methanol droplets is shown in **Fig. 16**. The ideal and actual normalized lifetimes of droplets both decrease exponentially with intake air flow 587 velocity. But their decreased percent,  $P_{\tau i}$  and  $P_{\tau a}$ , are gradually leveling off with the increase of intake air velocity, meaning that degree of the decrease of droplet lifetime gradually decreases, e.g., the ideal and actual normalized lifetimes decrease by 50.44 % and 48.07 %, respectively, when the intake air flow velocity increases from 0 m/s to 1.17 m/s, while only 21.56 % and 21.99 %, respectively, when it increases from 1.17 m/s to 2.34 m/s. Based on the above analysis, it implies that the intake air velocity should not seemingly continue to increase when it reaches to a certain value. Considering that there is already flow in the cylinder caused by inlet stroke of methanol engines, the improvement of droplet evaporation rate caused by further increasing intake air flow velocity can be limited based on the above analysis. However, from another point of view, the flow is beneficial to spray breakup [45], thereby reducing the droplet size, which can reduce the entire evaporation time of methanol. Besides, the spatial distribution of methanol droplets can be more uniform under the action of flow. This avoids the extreme descent of temperature in the local area caused by the  concentrated evaporation of methanol to absorb a large amount of heat, then the reduction of evaporation rate of methanol droplets due to the descent of surrounding temperature can be alleviated. Therefore, high intensity turbulence is useful for improving the evaporation of methanol in the cold start process of methanol engines.



606 **Fig. 16.** Variation of the ideal and actual normalized droplet lifetimes ( $\tau_i$  and  $\tau_a$ ), their 607 decreased percent ( $P_{\tau i}$  and  $P_{\tau a}$ ) and the proportions of the first and second stages ( $P_1$ 

608 and  $P_2$ ) with intake air flow velocity V.

#### **4. Conclusions**

 This study investigated the cold start issues of methanol engines and their improvement methods from the perspective of droplet evaporation. A wide range of fuel temperatures of 243-303 K was investigated. In particular, the low temperatures below 293 K were rarely studied in existing studies, which are of great importance for understanding the cold start issues of methanol engines and proposing effective improvement measures. The key conclusions are as follows:

 (1) The evaporation process of methanol droplets with hygroscopicity consists of two stages. The first stage is the evaporation of pure methanol and the second stage is the water-dominated evaporation of methanol-water mixture, which shows noticeable difference in their evaporation rates. The droplets are evaporated by over 85% in the first stage and freeze in the second stage at temperatures below 263 K. The proportion of the second stage and the normalized droplet lifetime increase greatly when the ambient temperature is below 273 K. The empirical formulas describing the relationship between evaporation rate and ambient temperature for single-component and binary-component droplets are obtained. The average evaporation rates of methanol droplets are enhanced by increasing ambient temperature, but this promotion effect becomes weaker at higher initial ambient temperature. Increasing the ambient temperature from 243-283 to 293 K has the largest improvement efficiency of evaporation rate.

 (2) The initial droplet diameter has little effect on the pure methanol evaporation, but mainly influences the evaporation of methanol-water mixture. The increase of absorbed water in methanol droplets leads to the decrease of their evaporation rates with initial droplet diameter. The proportion of the second stage increases with the increase of initial diameter and the droplet lifetime increases linearly with the square of initial diameter. The two-stage and binary-component evaporation process of methanol droplets in humid environment can be regarded as the evaporation of a pseudo single component and the same is true for other binary mixtures. The size of spray droplets should be reduced by improving injection pressure or other methods to shorten the

 entire evaporation time of methanol, so that more combustible fuel/air mixture can be produced in a short time for cold start of methanol engines.

 (3) The fuel temperature has little effect on the pure methanol evaporation, but mainly influences the evaporation of methanol-water mixture. There is an additional transient cooling stage before the evaporation of methanol droplets when the fuel temperature rises. With the increase of fuel temperature, the average evaporation rate of methanol droplets in humid environment decreases, while both the proportion of the second stage and the normalized droplet lifetime increase. A higher fuel temperature promotes methanol evaporation mainly through the reduced droplet size in real methanol engines when the increase of fuel temperature is insufficient.

 (4) The intake air flow enhances the evaporation rate, but does not affect the two- stage feature of methanol droplet evaporation. This promotion effect is more noticeable at low intake air flow velocities and becomes weaker at higher velocity, especially when intake air flow velocity exceeds 3 m/s. With the increase of intake air flow velocity, the normalized droplet lifetime decreases exponentially, while the proportion of the second stage increases. High intensity turbulence is needed to reduce the size of spray droplets and make the descent of overall ambient temperature in the cylinder relatively small, thus improving cold start performance of methanol engines.

 To sum up, multiple methods should be combined to improve the cold start performance of methanol engines efficiently. For example, to avoid a significant decrease in droplet evaporation rate caused by the massive heat absorption, the environment in the cylinder should be heated and the intake air flow velocity should be increased. To shorten the evaporation time of methanol, the injection pressure and fuel

temperature can be also increased to reduce the size of spray droplets. In the future

work, molecular dynamics simulation method can be applied to investigate the

behaviors of water vapor in the process of methanol evaporation and further understand

the interaction between methanol and water.

**Acknowledgements**

The assistance from the Geely Royal Engine Components Co., Ltd is greatly

appreciated.

#### **References**

- [1] Huang Y, Lei C, Liu CH, Perez P, Forehead H, Kong S, et al. A review of strategies for mitigating roadside air pollution in urban street canyons. Environ Pollut 2021; 280:116971. [https://doi.org/10.1016/j.envpol.2021.116971.](https://doi.org/10.1016/j.envpol.2021.116971)
- [2] Sacchi R, Bauer C, Cox B, Mutel C. When, where and how can the electrification of passenger cars reduce greenhouse gas emissions? Renew Sust Energ Rev 2022; 162:112475. [https://doi.org/10.1016/j.rser.2022.112475.](https://doi.org/10.1016/j.rser.2022.112475)
- [3] García-Olivares A, Solé J, Osychenko O. Transportation in a 100% renewable energy system. Energ Convers Manage 2018; 158:266-85. [https://doi.org/10.1016/j.enconman.2017.12.053.](https://doi.org/10.1016/j.enconman.2017.12.053)
- [4] Chen Z, Wang L, Zeng K. A comparative study on the combustion and emissions of dual-fuel engine fueled with natural gas/methanol, natural gas/ethanol, and natural gas/n-butanol. Energ Convers Manage 2019; 192:11-9. [https://doi.org/10.1016/j.enconman.2019.04.011.](https://doi.org/10.1016/j.enconman.2019.04.011)
- [5] Zhen X, Wang Y. An overview of methanol as an internal combustion engine fuel. Renew Sust Energ Rev 2015; 52:477-93. [https://doi.org/10.1016/j.rser.2015.07.083.](https://doi.org/10.1016/j.rser.2015.07.083)
- [6] Eisavi B, Ranjbar F, Nami H, Chitsaz A. Low-carbon biomass-fueled integrated system for power, methane and methanol production. Energ Convers Manage 2022; 253:115163. [https://doi.org/10.1016/j.enconman.2021.115163.](https://doi.org/10.1016/j.enconman.2021.115163)
- [7] Chen Z, Chen H, Wang L, Geng L, Zeng K. Parametric study on effects of excess air/fuel ratio, spark timing, and methanol injection timing on combustion characteristics and performance of natural gas/methanol dual-fuel engine at low





