Experimental study on the evaporation performance of suspended CeO$_2$ nano-fuel droplets

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Abstract

In order to study the influence of nanoparticles on the evaporation of nano-fuel and reveal the mechanism of heterogeneous heat and mass transfer induced by the dispersion of nanoparticles, CeO$_2$ nano-fuels with different mass concentration and particle size were prepared based on the two-step method. The visualized evaporation apparatus for single suspended droplets was utilized to investigate the evaporation performance of diesel and nano-fuels at 673K and 973K using image processing technology. The results show that at 673K, evaporation of diesel and nano-fuel droplets accorded with classical D^2-law and can be divided into a constant-volume evaporation stage and a quasi-steady evaporation stage. The addition of nanoparticles suppressed the evaporation of diesel droplets while increasing concentration or particle size can intensify the extent of suppression. At 973K, however, micro-explosions of droplets occurred, and the variation of droplet diameter did not conform with classical D^2-law. Evaporation was divided into a constant-volume evaporation stage and a fluctuating evaporation stage. Nanoparticles as heterogeneous nucleation sites enhanced the expansion intensity and micro-explosion intensity of droplets, in turn promoting the evaporation of fuel. With the increase of mass concentration or decrease of nanoparticle size, the promotion effect of nanoparticles on evaporation was more significant.

Keywords
nano-fuel; droplet evaporation; nanoparticles; micro-explosion

1 Introduction
In recent years, with the promulgation of increasingly stringent emission regulations for commercial vehicles, fuel quality as a crucial factor impacting the engine power, fuel economy and emission performance is being gradually improved in varying methods [1], examples include reforming extraction technology, optimizing preparation formula and adding fuel additive. Nano-fuel, which is prepared by dispersing various nanoparticles into fuel, is regarded as a new generation of high energy density fuel and has the potential to substitute gasoline/diesel fuels since the suspended nanoparticles can serve as secondary energy carriers [2]. Additionally, owing to high surface to volume ratio and thermodynamic characteristics of nanoparticles, the physical properties of nano-fuel are known to be varied in contrast to the base fuel, such as thermal conductivity, surface tension, vapor pressure, viscosity, wettability, etc., which further lead to the excellent performance of engine fuelled with nano-fuel. Numerous studies have revealed that the nano-fuel can not only promote thermal efficiency, but also reduces fuel consumption and pollutant emissions [3, 4]. Spray and combustion in internal combustion engines is a complex process involving two-phase flow, phase transition, heat and mass transfer, chemical reaction and so on, and the evaporation of fuel droplets plays a crucial role [5, 6]. However, the addition of nanoparticles not only changes the mechanism of fuel droplet evaporation, it also enhances the radiation heat transfer during

evaporation [7]. Therefore, a study on the evaporation of nano-fuel droplets is the foundation of the future application.

A mass of literatures related to the evaporation performance of suspended nanofluid droplets has been published. Dai et al. [8] revealed that the evaporation of diesel/ceria nano-fuel was subjected to transient heating stage and equilibrium evaporation stage obeying classical D^2-law at 673K, in which the nano-fuel droplet has not visible difference from a diesel droplet during evaporation, but it underwent a transient heating stage, a fluctuating evaporation stage and an equilibrium evaporation stage at 773K and 873K, wherein the evaporation time of nano-fuel was greatly reduced compared with that of pure diesel. Javed et al. [9] classified the evaporation behavior of kerosene based nano-fuel containing dense concentration of Al nanoparticles into a heating up stage, a D^2-law stage and a micro-explosion stage at the temperature ranging from 673K to 1073K. Micro-explosions solely occurred in the presence of Al nanoparticles and intense micro-explosions can bring a tremendous growth in the evaporation of kerosene droplets via swiftly shattering the droplet into small-sized ones. However, Jiang et al. [10] did not observe the occurrence of micro-explosions in the evaporation of Jatropha methyl ester-diesel blend at 873K and 973K, and they confirmed that low nanoparticle concentration was conducive to the evaporation of nano-fuel while high concentration did the opposite.

In summary, due to the difference in experimental conditions and research methods, a substantial divergence on how nanoparticles affect droplet evaporation has not be resolved. In this study, CeO_2 nano-fuel, in which diesel worked as base fuel and Cetyl Trimethyl Ammonium Bromide (CTAB) served as surfactant, was prepared based on two-step method, and the evaporation performance of suspended nano-fuel droplets was investigated using image processing technology at the ambient temperature of 673K and 973K to provide a basis for the future development and application of nano-fuel.

2 Material and Methods

Two types of CeO_2 nanoparticles (20 and 50 nm), with the purity of 98%, were purchased from Beijing DK Nano Technology Co., Ltd., China. The micromorphology of the nanoparticles was inspected using a Thermal Field Emission Scanning Electron Microscope (JEOL JSM-7001F) under magnification of 100k×, as shown in **Figure 1**. It is obvious that CeO_2 nanoparticles were almost spherical, and slight agglomeration occurred in nanoparticles owing to the Van der Waals force and Coulomb force. Long-term stability of nanofluids is a fundamental requirement for maintaining thermophysical properties, so that combined chemical and physical methods are often utilized to achieve homogeneity and stability of the nanofluid. As a surfactant, CTAB is to increase the Zeta potential and form a coating on the surface of nanoparticles, which enhances the repulsive force and hinders them from aggregating. For this reason, the nanoparticles were mixed with the same mass of CTAB and the mixture was poured into neat diesel to obtain nano-fuel blend. After being stirred, the blend was oscillated in an ultrasonic bath (KQ3200V) at a power of 150 W and a frequency of 40 kHz for 2 hours to improve stability. Nano-fuels with the mass concentrations of 50, 100 and 150 mg/L were prepared. There were no discernible sediments in nano-fuels after 3 days of storage by visual inspection, which demonstrates the satisfactory dispersity and stability of the prepared nano-fuels. The presence of CTAB has been confirmed to marginally alter some physical properties impacting the evaporation of the base fluid, including surface tension, viscosity, vapor pressure etc., therefore, 100 mg/L of CTAB was added to neat diesel as reference samples to verify that the variation of evaporation performance is induced by the nanoparticles rather than surfactant. For the purpose of clarity and convenience, CeO_2 nano-fuel with the particle size

of 20 nm and the mass concentration of 100 mg/L was abbreviated as Ce_{20}^{100}. Other samples were abbreviated in the same way.
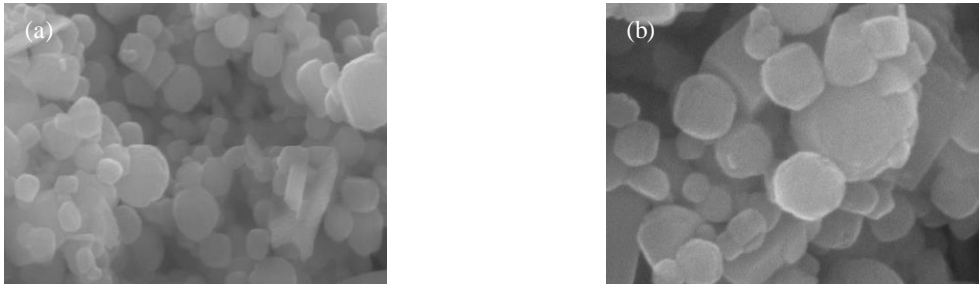

Figure 1. TFESEM images of (a) 20 nm CeO_2 and (b) 50 nm CeO_2

The apparatus for recoding evaporation process of single droplet, as shown in **Figure 2**, are mainly comprised of a heating vessel, a thermostat, a droplet transmission system, a high-speed camera, a nitrogen cylinder etc. The heating vessel of which the inner wall is made of two-layer ceramic material and the shell is made of stainless steel possesses excellent thermal insulation characteristic. A thermostat controls the vessel in a temperature range of 25-1198K with a deviation of ±5K by adjusting the current of resistance wire embedded between two ceramic layers. A K-type thermocouple is responsible for measuring the temperature. There are two opposite observation windows with the diameter of 50 mm in the front and rear of heating vessel for imaging. Before experimentation, the heating vessel was filled with nitrogen to 1 atm in order to prevent droplet combustion during evaporation. A 0.5 μL droplet was located on a cross-shaped quartz fibre by a micro-syringe and placed (including quartz fibre) in a closed quartz tube that is covered with heat insulation coating to avoid droplet evaporation in the process of entering the vessel. Afterwards this quartz tube was transmitted vertically via a stepper motor with a speed of 300 mm/s. The time required for the droplet to reach the focus was less than 0.5 s, so that heat convection and radiation during this period had negligible effect on evaporation of droplet. When the in-vessel temperature reached a predetermined value, the shell of quartz tube was detached from its bottom cover through a controller and then the droplet was exposed to the high temperature environment. At the same time, the high-speed camera (FASTCAM SA-X2) with a resolution of 1024×1024 pixels and an exposure time of 0.001 ms captured the evaporation evolution of droplet at a frequency of 1000 fps.
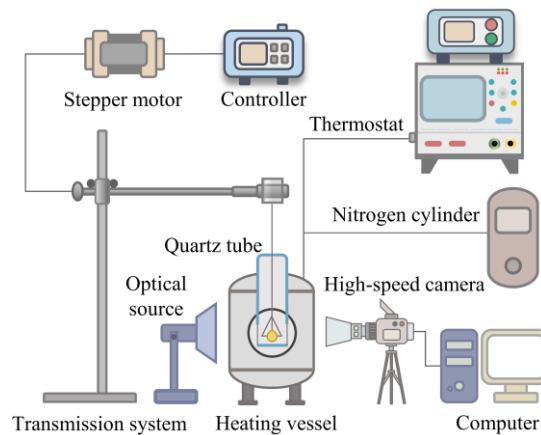

Figure 2. Schematic diagram of experimental apparatus

Since the boiling point of light diesel oil is about 453-643K and the bulk temperature in combustion chamber of diesel engine before injection is around 773-973K, ambient

temperatures of 673K and 973K were selected as the working conditions in this study to explore the evaporation evolution of nano-fuel droplets. **Figure 3** exhibits serial images of evaporation evolution for Ce_{20}^{150} droplet. As can be seen, evaporation was relatively steady at 673K, wherein the volume of the droplet decreased uniformly. At 973K, however, the droplet repeatedly underwent three stages: bubble generation, bubble expansion and bubble collapse, which results in micro-explosions and the fluctuation of droplet shape.
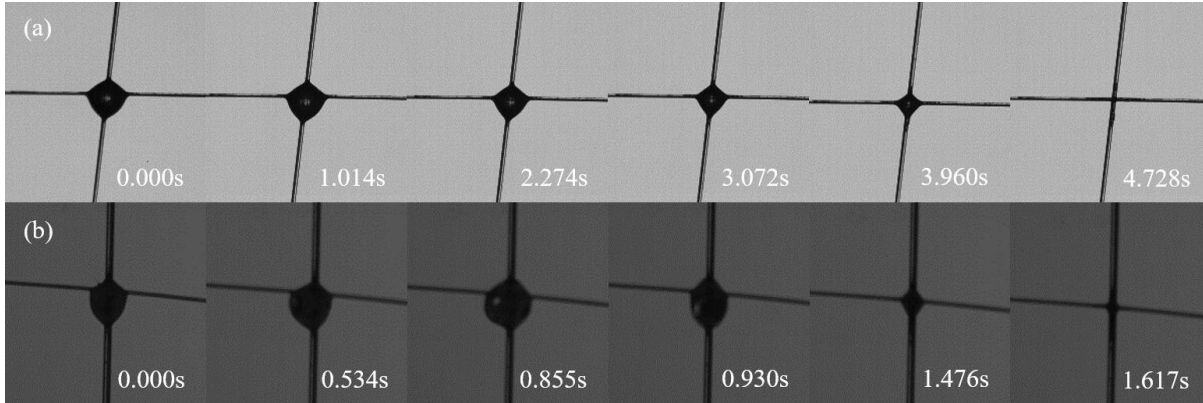

Figure 3. Time serial images of evaporation evolution for Ce_{20}^{150} droplet: (a) 673K, (b)973K

3 Results and Discussion

3.1 Effect of nanoparticles concentration on evaporation

The average evaporation rate (K_{ave}), one of assessment criterion for evaporation characteristics of droplet, is defined as the ratio of initial drop volume to evaporation time. The average evaporation rate of diesel and nano-fuels with different mass concentrations is depicted in **Figure 4**. Results show that Ce_{20}^{50}, Ce_{20}^{100} and Ce_{20}^{150} had the K_{ave} of 0.1161, 0.1129 and 0.1048 mm^3/s at 673K, which decreased by 3.27%, 5.97% and 12.76% in comparison with that of diesel. It is obvious that at 673K, the higher nanoparticle concentration of nano-fuel is, the lower K_{ave} is, and then the slower droplet evaporation is. On the contrast, at 973K, the K_{ave} values of Ce_{20}^{50}, Ce_{20}^{100} and Ce_{20}^{150} were 0.2590, 0.2717 and 0.3027 mm^3/s, respectively, which were 9.02%, 14.38% and 27.42% higher than that of diesel. In other words, nanoparticles had a promotion effect on droplet evaporation and increasing nanoparticle concentration would give a considerable rise in evaporation of nano-fuel at 973K.
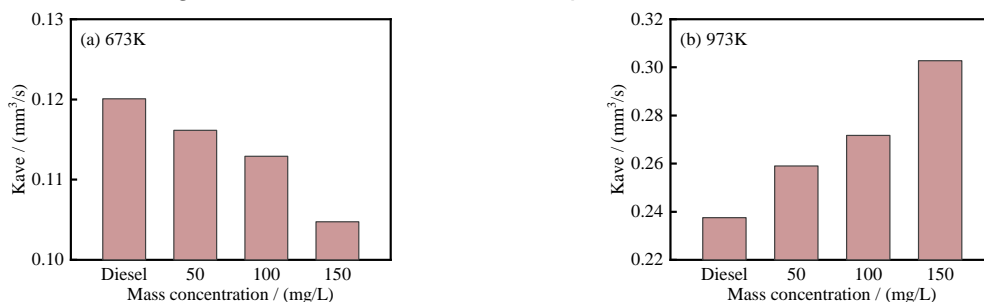

Figure 4. Average evaporation rate of diesel and nano-fuel with different mass concentration

The temporal variation of the normalized squared diameter of diesel and nano-fuel droplets is shown in **Figure 5.** Apparently, the droplet experienced a relatively stable evaporation at 673K while it went through a volatile evaporation at 973K. The evaporation process at 673K can be divided into two stages: a constant-volume evaporation stage (hereinafter abbreviated as CV stage) in which normalized squared diameter of droplet remained roughly constant and

a quasi-steady evaporation stage (hereinafter abbreviated as QS stage) where the variation of droplet diameter conformed to D^2-law. At 973K, diesel droplets also underwent a CV stage at initial time, but its duration was extremely short due to the larger difference of heat transfer temperature. Afterward the normalized squared diameter fluctuated significantly instead of coinciding with D^2-law, whereupon this period was called as fluctuation evaporation stage (hereinafter abbreviated as FE stage). As shown in **Figure 5(a)**, nano-fuel had a similar trend as diesel with respect to the variation of normalized squared diameter with time at 673K, though the evaporation time of all nano-fuels exceeded that of diesel in different degrees. Increasing nanoparticle concentration prolonged the evaporation time of nano-fuel droplet slightly. It may be resulted from the formation of a more compact spherical shell near the droplet surface and much higher surface tension of the nano-fuel droplet. Additionally, there was some small fluctuation in the evaporation process of Ce_{20}^{150}, which may be caused by a increase of local overheat hotspots generated by nanoparticles. In contrast, it is revealed form **Figure 5(b)** that nanoparticles induced a stimulation in evaporation of nano-fuel at 973K, and the stimulation intensified considerably with an increase in nanoparticle concentration. The reason may be that the higher the mass concentration, the more nanoparticles in fuel, which generated more nucleation sites in droplet and gasified diesel molecules rapidly.
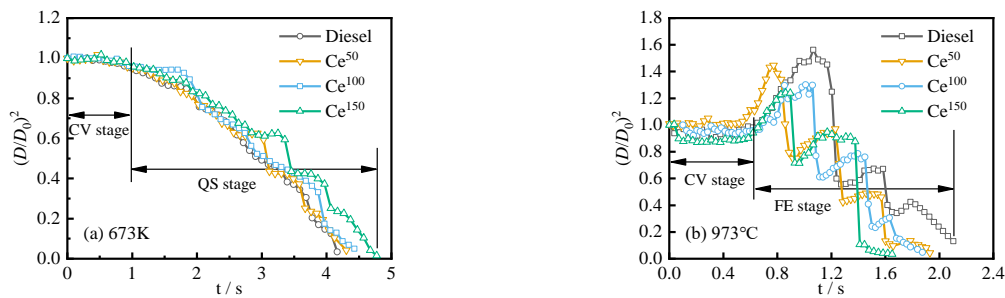

Figure 5. Temporal variation of normalized squared diameter of diesel and nano-fuel

Duration of each stage for Ce_{20} nano-fuel at 673K and 973K are shown in **Figure 6**. At 673K, compared with diesel, both CV stage and QS stage of nano-fuel were increased, and the duration of each stage was prolonged as the mass concentration rose. Quantitively, Ce_{20}^{50}, Ce_{20}^{100} and Ce_{20}^{150} increased by 19.32%, 23.88% and 32.30% in duration of CV stage, and increased by 3.38%, 6.35% and 14.62% in the QS stage, compared with diesel. In general, along with the rise of mass concentration, the surface tension of nano-fuel increases and the number of nanoparticles per unit volume increases as well, which can reduce the evaporation area and increase heat transfer from the surface molecules to inner molecules. In addition, more of heat that should be used for droplet evaporation is absorbed by nanoparticles to elevate their own temperature due to their lower specific heat, whereupon the CV stage of nano-fuel is prolonged. Of course, nanoparticles that have absorbed a lot of heat, as hotspots, can promote evaporation in subsequent QS stage. Regrettably, quantitative analysis indicated that this promotion effect was too weak, thereby the total evaporation time of nano-fuel with higher concentration was still longer than that with lower concentration. At 973K, however, increasing nanoparticle concentration induced an inverse tendency in the evaporation behavior of nano-fuel droplet. The total evaporation time and duration of FE stage for nano-fuel decreased while the duration of the CV stage increased as mass concentration rose. Ce_{20}^{50}, Ce_{20}^{100} and Ce_{20}^{150} had a CV stage duration of 0.54, 0.57 and 0.59 s, which decreased by 12.46%, 8.30% and 5.60% in comparison to that of diesel. For the duration of the FE stage, however, Ce_{20}^{50}, Ce_{20}^{100} and Ce_{20}^{150} were shorter than that of diesel by 8.27%, 10.89% and 21.52%, respectively. Visibly, although the nanoparticles can reduce the evaporation time of nano-fuel, the two stages

produce the opposite trend with the rise of mass concentration. It may be caused by the more compact spherical shell formed on the droplet surface due to increased number of nanoparticles, further reducing the evaporation area in CV stage. Subsequently, these nanoparticles absorb a lot of heat, as nucleation sites, vaporizing more diesel molecules and stimulating the micro-explosion of droplet.
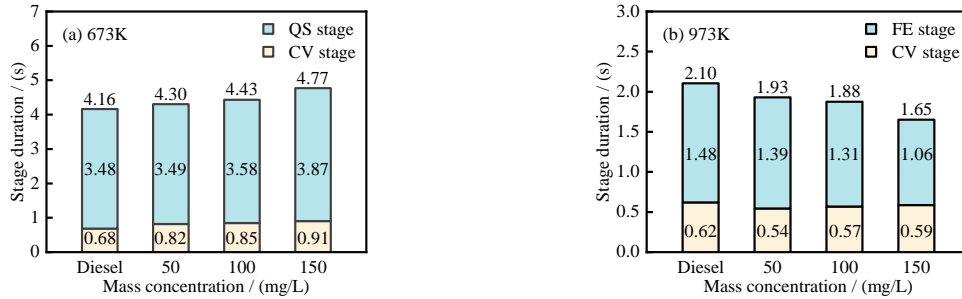
Figure 6. Duration of each stage for nano-fuel with different mass concentration

3.2 Effect of nanoparticle size on evaporation

Nanoparticle size is one of the essential factors impacting the thermophysical properties of a nano-fuel, therefore, it is inevitable that changing particle size of nanoparticles in fuel will affect evaporation performance. As shown in **Figure 7**, nano-fuel had a decrease trend in K_{ave} at two temperatures when particle size increased. Compared with diesel, K_{ave} of Ce_{20}^{50}, Ce_{20}^{100} and Ce_{20}^{150} were reduced by 12.76% and 14.46% at 673K, and increased by 27.42% and 23.08% at 973K, which means the evaporation process of nano-fuel was sensitive to the nanoparticle size.
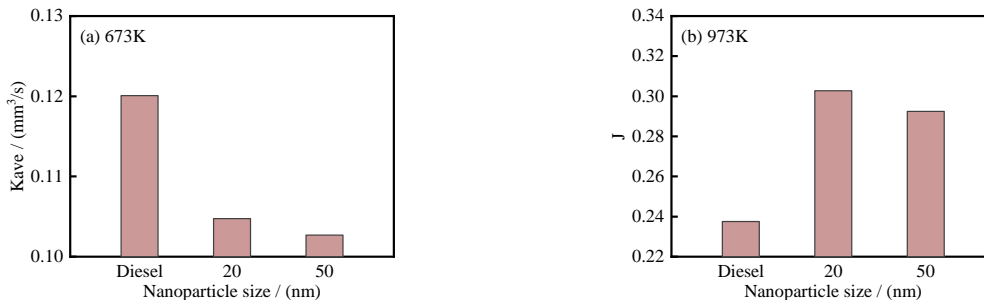
Figure 7. Average evaporation rate of nano-fuel with different nanoparticles size

Figure 8 displays the variation of normalized squared diameter versus time for diesel and Ce^{150}. It is apparently that the total evaporation time was lengthened with an increase in nanoparticle size at two temperatures. At 673K, the evaporation process can still be divided into CV stage and QS stage, and all cases were consistent with D^2-law. At 973K, CV stage became relatively longer but duration of FE stage declined obviously for nano-fuel. Earlier micro-explosion can be seen and the micro-explosion delay time was shorter for nano-fuel with smaller nanoparticles. It is interesting that the much greater micro-explosion took place in the evaporation of Ce_{20}^{150} although the micro-explosion just occurred twice, indicating that adding smaller nanoparticles to traditional fuel to improve evaporation performance is an appealing method for highly efficient and clean combustion of engine.
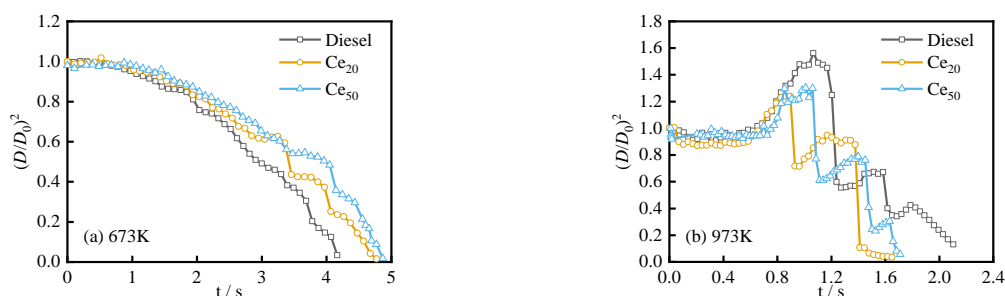
Figure 8. Variation of normalized squared diameter versus time for diesel and nano-fuel

As shown in **Figure 9**, at 673K, both CV stage and QS stage were prolonged with the increase of nanoparticle size. Compared with diesel, the increase of 14.62% and 16.90% appeared in CV stage and the increase of 11.14% and 12.03% occurred in QS stage for Ce_{20}^{150} and Ce_{50}^{150}. Larger nanoparticles, with lower charge density and higher surface absorption energy, have weaker repulsive force to diesel molecules, which results in the higher surface tension of nano-fuel. In addition, specific surface area is inversely proportional to nanoparticle size, so that the total heat transfer area is smaller for larger nanoparticles than smaller ones under the same mass concentration. Since the environment temperature (673K) is close to the boiling point of diesel, the effects of surface tension and heat transfer area are relative important on droplet evaporation. Thereby the evaporation of nano-fuel was suppressed with an increase in nanoparticle size. It is corroborated that the presence of nanoparticles in fuel can reduce the vapor pressure of fuel and increase the activation energy required for molecules evaporation. The larger the nanoparticle size is, the lower the vapor pressure of nano-fuel is and the greater the activation energy is, so the more appreciable suppression in the evaporation of nano-fuel. At 973k, however, adding nanoparticles can stimulate the evaporation of fuel droplet, but the promoting effect reduced when particle size enlarged. Under the same mass concentration, there are more nanoparticles in the nano-fuel containing small nanoparticles, which in turn forms more nucleation sites. Additionally, small nanoparticles have bigger specific surface area, attributing to rapid formation of nucleation sites under the same temperature difference. As a result, small nanoparticles are more conducive to the evaporation of fuel droplet.
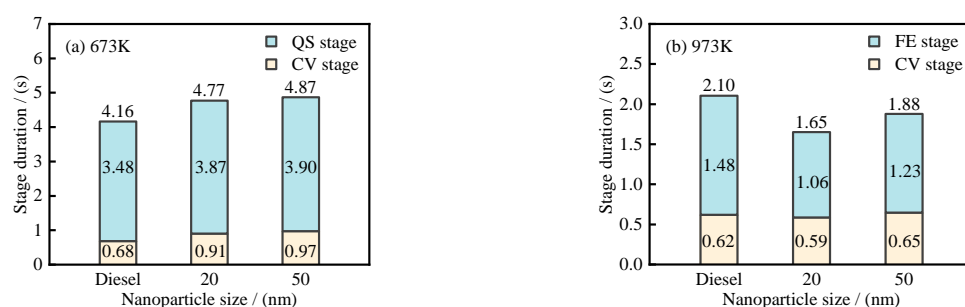

Figure 9. Duration of each stage for nano-fuel with different particle size

Conclusions

CeO_2 nanoparticles with different particle size (20 and 50 nm) were dispersed into pure diesel to prepare various concentration of nano-fuels (50, 100 and 150 mg/L), in which the CTAB was applied to stabilize the nano-fuel. Evaporation experiments for diesel and nano-fuel were carried out at 673K and 973K. At 673K, the evaporation of diesel and nano-fuel was relatively stable and can be divided into constant-volume evaporation stage and quasi-steady evaporation stage. In the process of evaporation, the variation of droplet diameter conformed to the classical D^2-law. Owing to the rise of surface tension and the formation of porous spherical shell near droplet surface for nano-fuel, the evaporation was suppressed compared with that of diesel and the extend of suppression intensified with the increase in mass

concentration and nanoparticle size. At 973K, the occurrence of micro-explosion brought about the drastic fluctuation in droplet volume during evaporation, which further caused droplet evaporation to deviate the D^2-law. The evaporation was comprised of constant-volume evaporation stage and fluctuation evaporation stage. Nanoparticles as the heterogeneous nucleation sites accelerated the evaporation of diesel droplet and the higher evaporation rate was observed for nano-fuel with higher concentration or smaller particle size.

References

[1] Nanthagopal, K., Kishna, R. S., Atabani, A. E., Al-Muhtaseb, A. a. H., Kumar, G., and Ashok, B., 2020, "A compressive review on the effects of alcohols and nanoparticles as an oxygenated enhancer in compression ignition engine," Energy Conversion and Management, 203, p. 112244.

[2] Murugesan, A., Avinash, A., Gunasekaran, E. J., and Murugaganesan, A., 2020, "Multivariate analysis of nano additives on biodiesel fuelled engine characteristics," Fuel, 275, p. 117922.

[3] Soudagar, M. E. M., Nik-Ghazali, N. N., Kalam, M. A., Badruddin, I. A., and Akram, N., 2019, "An investigation on the influence of aluminium oxide nano-additive and honge oil methyl ester on engine performance, combustion and emission characteristics," Renewable Energy, 146, pp. 2291-2307.

[4] Gowtham, M., and Prakash, R., 2020, "Control of regulated and unregulated emissions from a CI engine using reformulated nano fuel emulsions," Fuel, 271, p. 117596.

[5] Hinrichs, J., Shastry, V., Junk, M., Hemberger, Y., and Pitsch, H., 2020, "An experimental and computational study on multicomponent evaporation of diesel fuel droplets," Fuel, 275, p. 117727.

[6] Wang, J., Huang, X., Qiao, X., Ju, D., and Sun, C., 2020, "Experimental study on evaporation characteristics of single and multiple fuel droplets," Journal of the Energy Institute, 93(4), pp. 1473-1480.

[7] Gan, Y., and Qiao, L., 2012, "Radiation-enhanced evaporation of ethanol fuel containing suspended metal nanoparticles," International Journal of Heat & Mass Transfer, 55, pp. 5777-5782.

[8] Dai, M., Wang, J., Wei, N., Wang, X., and Xu, C., 2019, "Experimental study on evaporation characteristics of diesel/cerium oxide nanofluid fuel droplets," Fuel, 254, p. 115633.

[9] Javed, I., Baek, S. W., and Waheed, K., 2014, "Effects of dense concentrations of aluminum nanoparticles on the evaporation behavior of kerosene droplet at elevated temperatures: The phenomenon of microexplosion," Experimental Thermal and Fluid Science, 56, pp. 33-34.

[10] Jiang, G., Yan, J., Wang, G., Dai, M., and Wang, J., 2019, "Effect of nanoparticles concentration on the evaporation characteristics of biodiesel," Appl Surf Sci, 492, pp. 150-156.