

EVAPORATION CHARACTERISTICS OF A SINGLE AQUEOUS UREA SOLUTION DROPLET

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ABSTRACT Selective catalytic reduction of NO_x using an ammonia compound as reductant is known as one of the technology capable of reducing diesel NO_x emissions to levels required by future emissions standards. Aqueous urea solution injected in this system may exhibit varieties of phenomena by the heating of each spray droplets. This study was undertaken to investigate the evaporation characteristics of a single aqueous urea solution droplet. Data are presented for experiments using two different apparatus, which were, a heated surface and an electric furnace. Evaporation behavior of urea solution was differed from water in both experiments. In experiment using a heated surface, urea evaporation behavior was classified into two patterns when temperature exceeded the maximum evaporation point. These patterns are short lifetime evaporation and long lifetime evaporation. In experiment using an electric furnace where droplet was suspended at the end of a quartz fiber, evaporation behavior was divided into three stages. Urea solution droplet showed similar behavior as water only at the first stage, where the square of droplet diameter decreased linearly with time, following the *d-square law* (*d² law*). In the second stage, formation of bubbles and foams, and expansion of droplet size were observed. The last stage was crystallization stage. The differences between water and urea droplet evaporation characteristics were assumed to be caused by the thermal decomposition of the urea.

Keywords: SCR System, Aqueous Urea solution, Thermal Decomposition, Leidenfrost Phenomenon, *d-square Law*

1. INTRODUCTION

For many years, air pollution has been the worldwide problem. Air pollutants such as carbon monoxide, nitrogen oxides and hydrocarbon are dispersed throughout the world's atmosphere in concentrations gradually hazardous to cause serious health problem. Diesel engine has been recognized as one of the dominant source that contributes toward the growing air pollution problem. As one of the solution for this problem, Selective Catalytic Reduction (SCR) systems are widely used to reduce nitrogen oxides (NO_x) from combustion exhaust gases. SCR system might be used to treat the exhaust emissions from small and large reciprocating engines, as well as turbine and thermal fired power generation equipment. This system is a cost effective way to reduce NO_x when used in conjunction with ammonia or urea-based reducing agent.

Since pure anhydrous ammonia requires extreme caution in handling, urea solution is more preferable. In this system, an aqueous urea solution is injected into exhaust gas stream where it evaporates and decomposes to ammonia and mixes with the exhaust gas before passing a catalyst. As the injected urea solution travel through the exhaust stream, size and composition of the urea spray may have change, and some of the droplets may have touched the exhaust pipe. Consequently, efficiency of this system is depends on the droplet evaporation which is influenced by several effects such as convection of surrounding gas flow and hot surface.

For a basic understanding of urea spray evaporation, it is necessary to investigate the evaporation characteristics of

a single urea solution droplet. This study was undertaken to investigate the evaporation characteristics of a single urea solution droplet on a heated surface and the evaporation of a suspended urea solution droplet in an electric furnace.

2. EXPERIMENTAL APPARATUS AND METHOD

Two different experimental apparatus were used for the investigation of urea droplet evaporation. The schematic diagram of apparatus used to study evaporation behavior of urea droplet on a heated surface (Experiment 1) is shown in Fig.1. A steel block with 100mm diameter was used as the heated surface. Using a dispenser, a 10 μl droplet was dropped to the surface at a height of 15~20mm.

An electric furnace was used to study the evaporation characteristics of a single urea solution droplet suspended in a quiescent atmosphere (Experiment 2). The schematic of experimental apparatus is shown in Fig.2. Rollers were placed at the bottom of the electronic furnace so that it can be moved to and fro. Droplet was suspended at the end of a thin quartz fiber, and evaporation behavior of the droplet was observed through a quartz glass window which was placed at one side of the furnace. Evaporation behavior was recorded using a digital video camera (Canon, FMV 200). Droplet shape was distorted by the quartz fiber, but since the liquid droplet was very small, suspended droplet was assumed to be a symmetry elliptical droplet. Droplet diameter, *d*, was calculated using following equation;

$$d = \sqrt[3]{([d_s^2 \cdot d_L] - [d_s'^2 \cdot d_L'])} \quad (1)$$

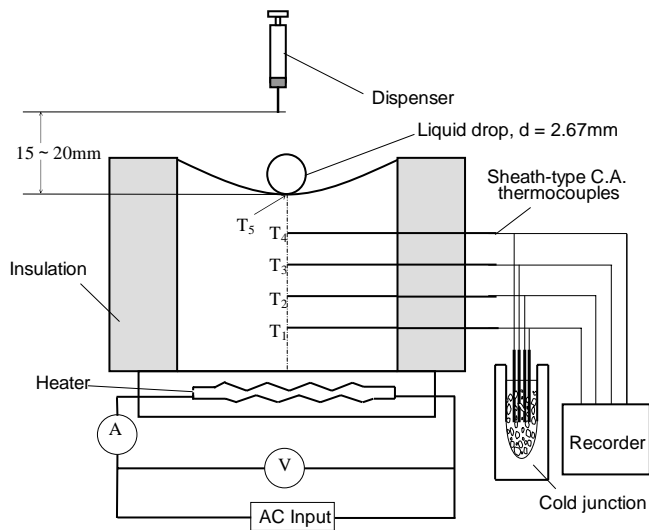


Fig.1 Schematic of experimental apparatus for Experiment 1

where d_s is minor diameter of urea droplet, d_L is major diameter of urea droplet, d_s' is minor diameter of fiber head and d_L' is major diameter of fiber head.

In Experiment 1, water, 10wt% urea solution and 30wt% urea solution were used, and in Experiment 2 was undertaken using water and 30wt% urea solution. As for a reference solution, a 17wt% NaCl solution with molar concentration equal to 30wt% urea solution was also used in both experiments.

3. RESULTS AND DISCUSSION

3.1 Evaporation on a Heated Surface

Variety of interesting phenomena was observed when a droplet is impinged on a hot surface. When a droplet is impinged on hot surface maintained at a temperature higher than the saturation temperature of the liquid, forced-convection boiling may occur, causing a few distinct boiling phenomena known as “Leidenfrost phenomenon” [4], [5], [8].

Figures 4, 5 and 6 show the relations between droplet lifetime and surface temperature of water, 10wt% urea solution and 30wt% urea solution respectively. Numbers in Fig.4 represent the boiling phenomenon that occurred during the heating period, and the three vertical dotted lines at the temperature of 140°C, 190°C and 300°C denote the boundary of each phenomenon region [2], [4], [5], [8]. Boiling phenomena of urea solution can be classified into these four regions.

Evaporation behavior of 10wt% and 30wt% urea solutions was almost same in each region. In region ①, a few seconds after a single droplet of urea solution was impinged onto the hot surface, a very thin film formed on the droplet surface and the liquid droplet turned into a sticky substance. Since thermal decomposition of urea does not occur in low temperature [3], [19], the sticky substance is speculated to be an aqueous urea solution with high concentration of urea.

In region ②, urea droplet sizzled and danced around at once when the droplet touched the hot surface. This phenomenon was same as the phenomenon observed in experiment using distilled water except that a

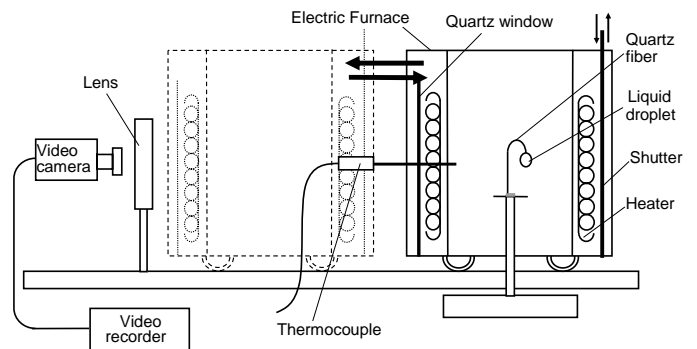


Fig.2 Schematic of experimental apparatus for Experiment 2

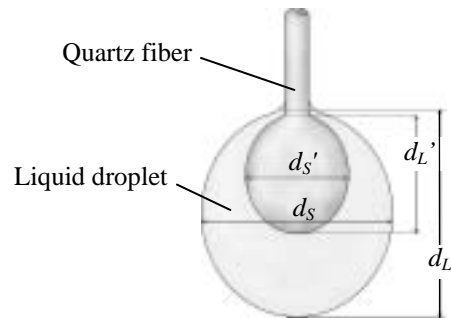
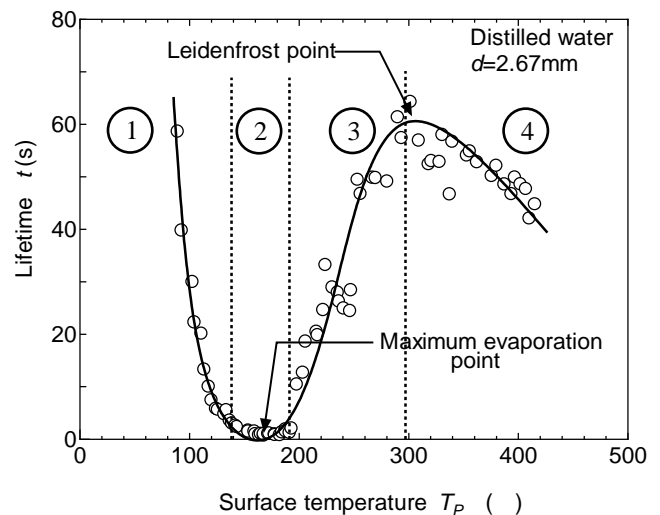


Fig.3 Parameters in Experiment 2



- ① : Natural convection
- ② : Nucleate boiling
- ③ : Transient boiling
- ④ : Film boiling

Fig.4 Evaporation characteristics of distilled water on a heated surface

white-brownish solid substance remained on the surface for urea solution.

When surface temperature exceeds the maximum evaporation point, two different evaporation patterns which can be classified as evaporation with a short lifetime, indicated by the lower curve line (Pattern 1), and evaporation with a long lifetime indicated by the upper curve line (Pattern 2) were observed. Illustrations of Pattern 1 and Pattern 2 evaporation behavior are shown in Fig.7.

In Pattern 1, impinged droplet was first danced around as in a spherical ball for moments before suddenly split into several tiny droplets and finally evaporated. In Pattern 2,

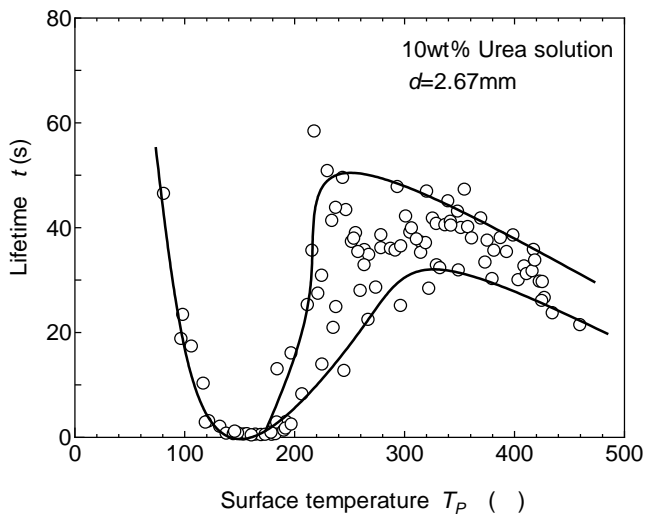


Fig.5 Evaporation characteristics of 10wt% urea solution on a heated surface

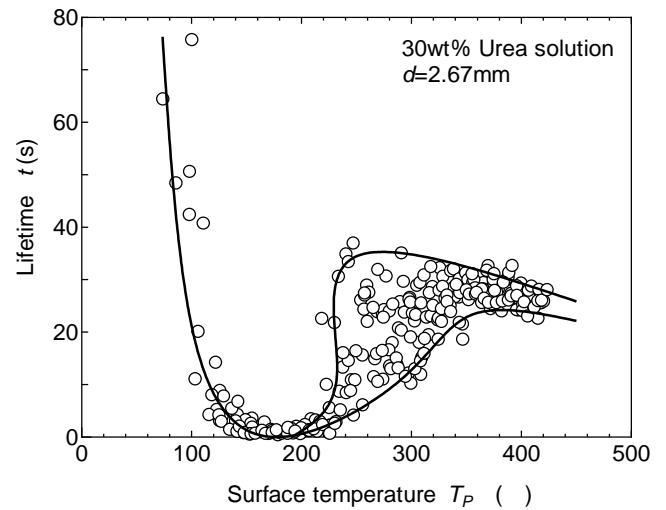


Fig.6 Evaporation characteristics of a 30wt% urea solution on a heated surface

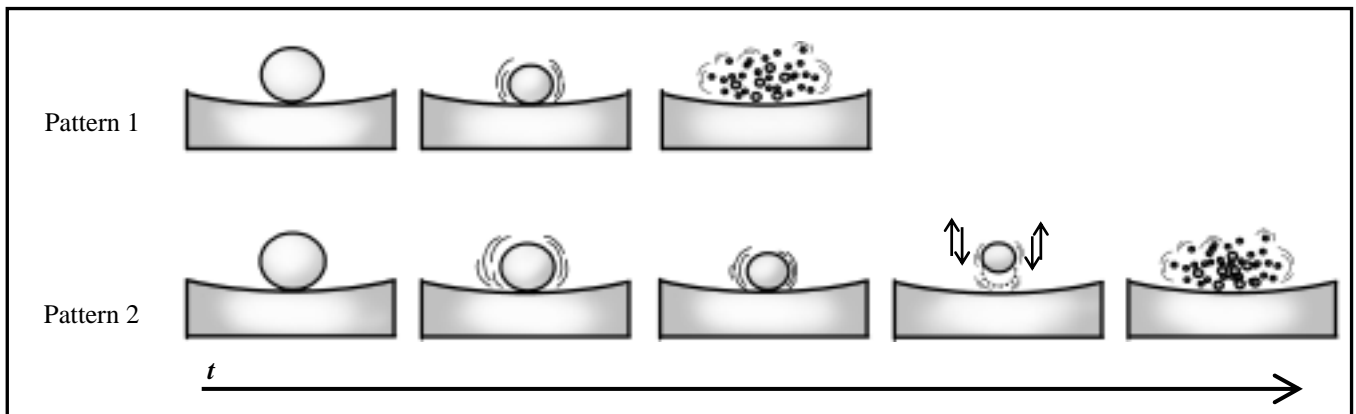


Fig.7 Illustrations of evaporation behavior in Pattern 1 and Pattern 2

spherical small droplet was first skittered around the hot surface for moments, just like Pattern 1, however this skittering time lasted much longer than Pattern 1, before suddenly hastily vibrates up and down for a few seconds and split into very tiny drops and finally evaporated.

The difference in evaporation behavior of Pattern 1 and Pattern 2 is considered to be caused by the very complex and diverse process of urea thermal decomposition^[3]. Several studies have reported that the complete decomposition of urea takes place in three steps^{[9],[11]}, but there are also ample possibilities that non-ideal behavior can occur during the decomposition process^[9]. Urea thermal decomposition was reported^[3] to be unstable when the heating temperature exceeds 190°C.

In this study, evaporation behavior of a 17wt% NaCl solution droplet was also studied in order to confirm the speculation that differences in urea evaporation behaviors in region ③ were caused by the thermal decomposition of the urea itself. Figure 8 shows the evaporation characteristics of 30wt% urea solution and 17wt% NaCl solution. It is apparent from this figure that the evaporation curve of Pattern 1 is very similar to 17wt% NaCl solution. The similarity of these curves shows that, there is possibility that the urea droplet was hardly decomposed and only water was evaporated in Pattern 1. In Pattern 2, as the contact time taken by the droplet to

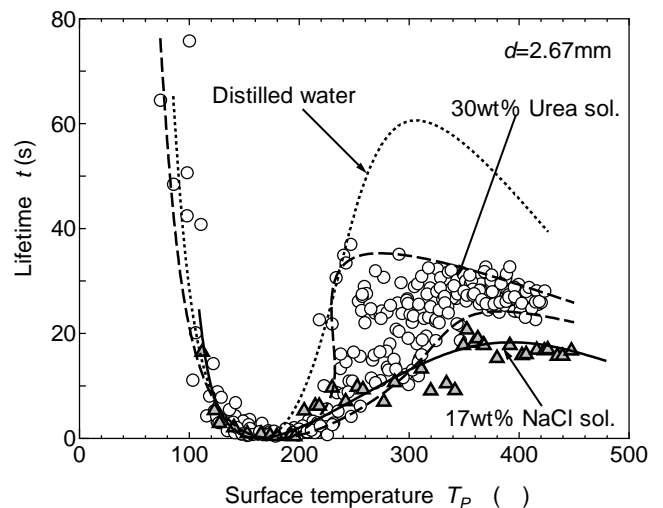


Fig.8 Evaporation characteristics between distilled water, 30wt% urea solution and 17wt% NaCl solution

directly touch the surface was much longer than in Pattern 1, contact area between droplet and hot surface increased and simultaneously improved the heat transfer^{[4],[8]}.

3.2 Evaporation in an Electric Furnace

Several studies have reported that the diameter of a

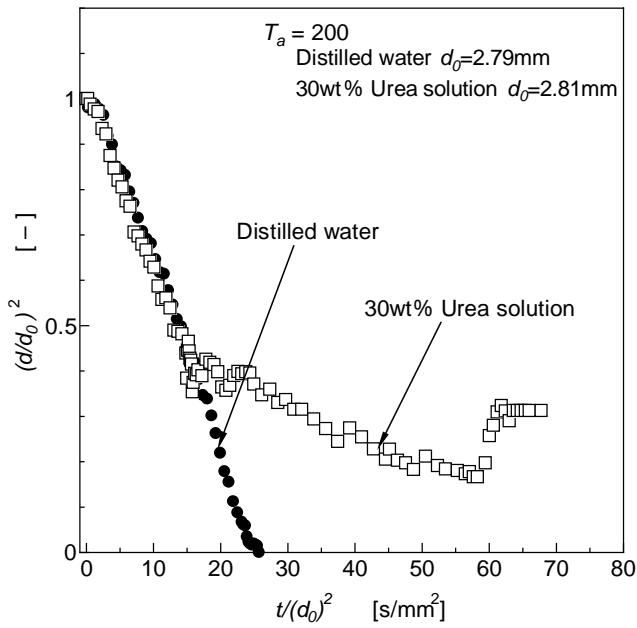


Fig.9 Evaporation characteristics of water and 30wt% urea solution at $T_a = 200^\circ\text{C}$

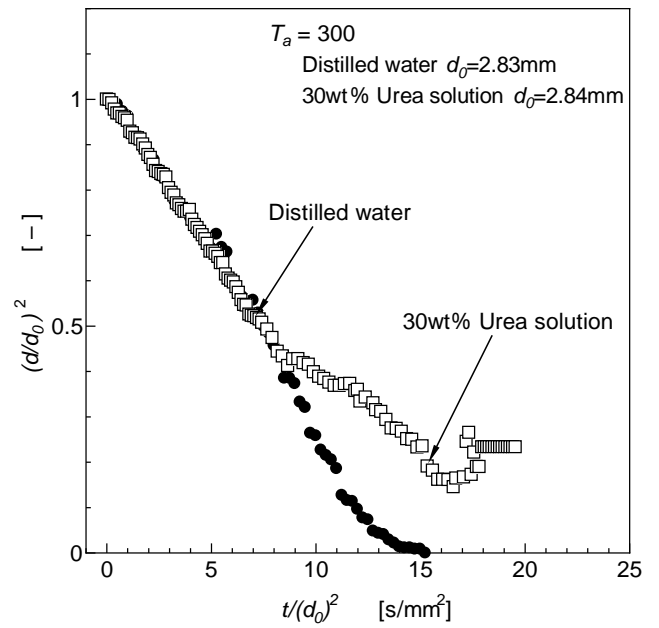


Fig.10 Evaporation characteristics of water and 30wt% urea solution at $T_a = 300^\circ\text{C}$

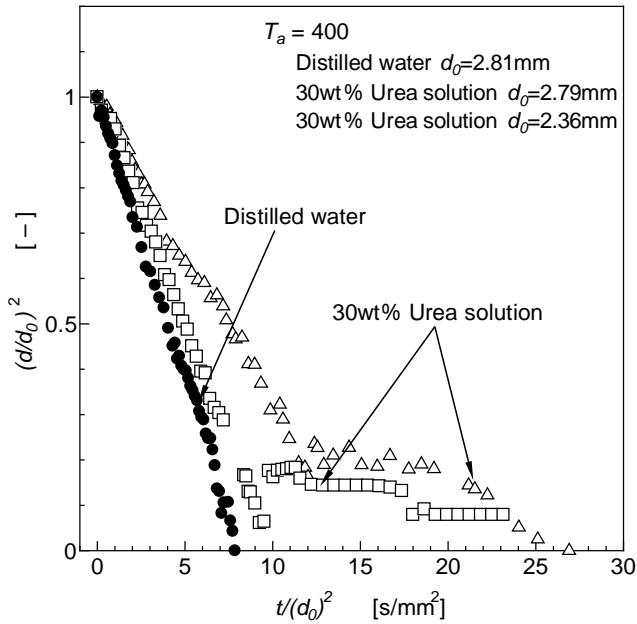


Fig.11 Evaporation characteristics of water and 30wt% urea solution at $T_a = 400^\circ\text{C}$

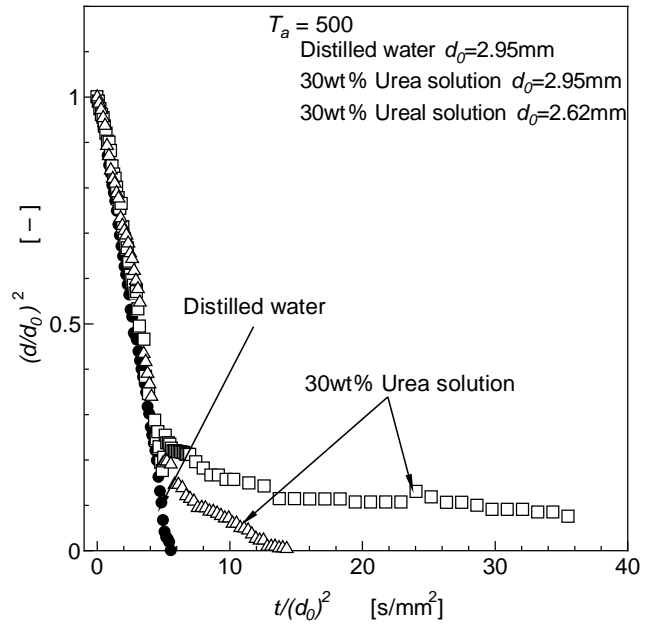


Fig.12 Evaporation characteristics of water and 30wt% urea solution at $T_a = 500^\circ\text{C}$

single component droplet in a quiescent atmosphere diminishes with time^{[6], [7]}. This evaporation behavior is called *d-square law* (d^2 law), where the square of droplet diameter decreases linearly with time^{[1], [10]}. Equation 2 shows the fundamental equation of this law^{[1], [7], [10]},

$$d^2 = d_0^2 - K_e t \quad (2)$$

where d is droplet diameter, d_0 is initial droplet diameter, K_e is evaporation rate constant and t is time.

Figures 9, 10, 11 and 12 show the relations between diminishment rate of droplet diameter with time at furnace temperature of $T_a = 200, 300, 400$ and 500°C . The vertical axis of the graphs indicates dimensionless droplet diameter, while the horizontal axis indicates the elapsed time divided

by the square of the droplet initial diameter. From these figures, the evaporation rate of droplet, which can be defined as the magnitude of the negative slope of the curves, can be obtained easily. In this study, since the droplet was suspended at the end of thin fiber, the effect of heat transfer between droplet and fiber could not be avoided.

In all cases, the water droplet diameter decreases linearly with time, following the d^2 law. During the heating process, the droplet size diminished slowly with time until there was nothing left on the quartz fiber surface at the end of heating process. The evaporation rate constant, K_e , of water at each temperature was found to be constant.

Contrary to water, diameter of urea droplet was linearly decreased with time only at the early stage of the heating process, showing that the primary evaporation rate was

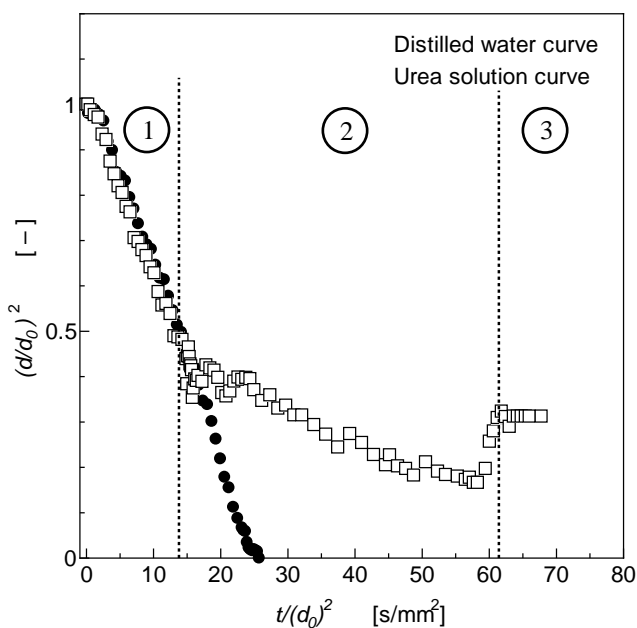


Fig.13 Evaporation stage of urea solution droplet in an electric furnace

constant. After this time interval, data began to curved, showing that the evaporation rate had decreased, as shown in Figs.9-12. During this time interval, the urea droplet showed different evaporation behavior from the early-stage behavior. Formation of bubbles inside the droplet, boiling, expansion and crystallization were observed in this stage. Based on these observations, evaporation behavior of a single urea solution droplet in a furnace were divided into three stages^[1] as shown in Fig.13. Numbers in the figure indicates the evaporation stage.

Stage ①: Primary evaporation stage. In stage ①, the evaporation behavior of urea droplet was very similar to water, where the droplet size diminished slowly with time. The temperatures of droplet and quartz fiber were relatively low during this stage. Thus, it is speculated that the decrease in urea solution droplet diameter was caused only by the evaporation of water, since pyrolysis of solid urea does not occurred between room temperature and 133°C^{[3],[11]}. Consequently, urea concentration in the droplet increases gradually with time as water in the solution evaporates slowly.

Stage ②: Transition stage. When the urea solution droplet entered this stage, urea concentration was already high, and the quartz fiber and the droplet itself had been heated up to temperature high enough to allow thermal decomposition of urea to occur. Thus, formation of bubbles and foams, expansion of droplet size and boiling were observed in this stage. During the thermal decomposition of urea, urea decomposes and other substances, for instance, iso-cyanic acid (HNCO [gas]) were released^{[3],[9],[11]}. This suggests that the featured evaporation behavior mentioned above might be caused by the formation and expansion of the entrapped gas inside the droplet.

The rate of bubbles formation and growth were different with temperature. At $T_a = 200^\circ\text{C}$, only formation of tiny bubbles inside the droplet, foams on the droplet surface and small expansion in droplet size were observed. At elevated temperature, $T_a = 300, 400, 500^\circ\text{C}$, bubbles and

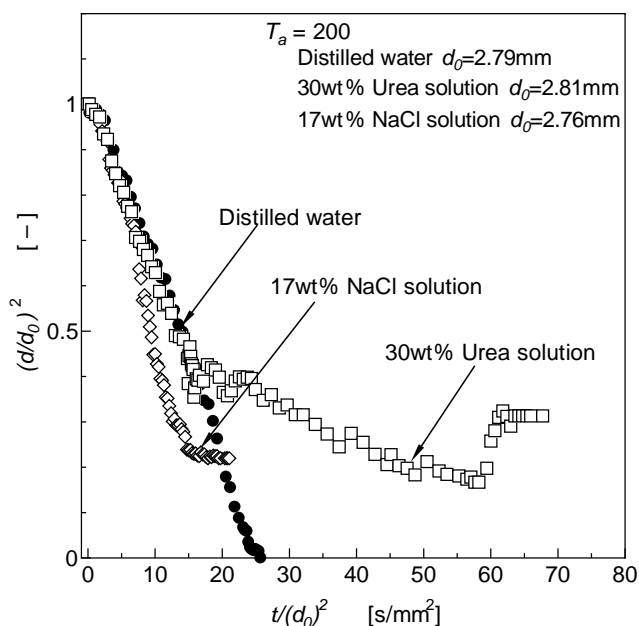


Fig.14 Evaporation characteristics of distilled water, 30wt% urea solution and 17wt% NaCl solution

foams formation were faster than when the temperature was much lower, leading to boiling and bigger expansion. The evaporation behavior of urea solution observed in this experiment was also corresponded to the boiling phenomena of Experiment 1.

Stage ③: Crystallization stage. At the end of the heating process, white solid substance remained on the quartz fiber surface. At $T_a = 400, 500^\circ\text{C}$, there was also a case that, after the droplet crystallized to white solid substance, it turned back to sticky substance before completely evaporates until nothing was left on the fiber surface at the end of heating process.

Figure 14 shows the evaporation behavior of water, 30wt% urea solution and 17wt% NaCl solution. Contrary with 30wt% urea solution, transient stage was not observed in the evaporation process of 17wt% NaCl solution. 17wt% NaCl solution droplet diminished slowly with time until it entered the crystallization stage. This result strongly supports the assumption that transient stage observed in 30wt% urea solution was caused by the thermal decomposition of the urea solution itself.

4. CONCLUSIONS

Evaporation characteristics of a single aqueous urea solution droplet under different circumstances were investigated. Lifetimes of urea droplet when being heated directly on a hot surface and when being suspended in an electric furnace were measured, and the data were compared with distilled water. Main conclusions from the data gathered from this study are as follows:

- (1) Boiling phenomena of urea solution droplet on a heated surface can be classified into four region same as water. These regions are natural convection, nucleate boiling, transient boiling and film boiling.
- (2) Urea evaporation behavior on a heated surface was classified into two patterns, which are fast evaporation and slow evaporation, when surface temperature

- exceeded the maximum evaporation point.
- (3) Evaporation stage of a single urea solution droplet suspended at the end of a fiber in an electric furnace can be divided into following three stages.
 - (4) In stage ①, urea droplet evaporation behavior was very similar to water and follows the d^2 law. Evaporation rate constant, K_e , was constant in this stage.
 - (5) In stage ②, formation of bubbles and foams, expansion and boiling were observed. Bubble formation and its growth were influenced by surrounding temperature.
 - (6) Crystallization of urea droplet began in stage ③. At elevated temperature, droplet that was once turned into white solid substance, turned back into sticky substance and evaporated until nothing was left on the fiber at the end of heating process.

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