Proceedings of ICEF04
2004 Fall Technical Conference of the ASME Internal Combustion Engine Division
October 24-27, 2004, Long Beach, California USA

ICEF2004-889

NUMERICAL PREDICTION ON THE CHARACTERISTICS OF SPRAY-INDUCED MIXING AND THERMAL DECOMPOSITION OF UREA SOLUTION IN SCR SYSTEM

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ABSTRACT

The spray-induced mixing characteristics and thermal decomposition of aqueous urea solution into ammonia have been studied to design optimum sizes and geometries of the mixing chamber in SCR (Selective Catalytic Reduction) system. The cold flow tests about the urea-injection nozzle were performed to clarify the parameters of spray mixing characteristics such as mean diameter and velocity of drops and spray width determined from the interactions between incoming air and injected drops. Discrete particle model in Fluent code was adopted to simulate spray-induced mixing process and the experimental results on the spray characteristics were used as input data of numerical calculations. The simulation results on the spray-induced mixing were verified by comparing the spray width extracted from the digital images with the simulated particle tracks of injected drops. The single kinetic model was adopted to predict thermal decomposition of urea solution into ammonia and solved simultaneously along with the verified spray model. The hot air generator was designed to match the flow rate and temperature of the exhaust gas of the real engines. The measured ammonia productions in the hot air generator were compared with the numerical predictions and the comparison results showed good agreements. Finally, we concluded that the design capabilities for sizing optimum mixing chamber were established.

INTRODUCTION

Diesel engines are widely used in urban and marine environment. But many emission regulations such as Euro 4 have been proposed due to environment pollution by nitrogen oxides and particulate matters of diesel engines.

Since the early 1970s, the importance of selective catalytic reduction of nitrogen oxides (*NOx*) has grown in the economical and technological aspects. SCR is the leading after-treatment technology for NOx removal process in diesel engines for stationary and mobile applications.

SCR is the process in which nitrogen oxides in the exhaust gas of diesel engine is reduced to nitrogen and water by reacting with ammonia at the presence of oxygen, as follows.

$$4NO + 4NH_3 + 3O_2 \rightarrow 4N_2 + 6H_2O \tag{1}$$

The general reducing agent for SCR process is ammonia (NH_3), presented mainly in the gas state, with the property such as toxicity and explosiveness. Also, one of the disadvantages is that ammonia is served in the anhydrous gas state or liquid state melted in the water. To solve these problems, urea solution as a reducing agent has been studied and has been used practically for the ship applications.

When SCR system is adapted to mobile diesel engine such as the ship, the design of compact system has to be considered in order to install SCR system in the narrow space of the ship.

Our own SCR system in Fig.1 have been developed having higher efficiencies and economical advantages to meet the environmental requirements of marine industry. This is composed of four main parts (Fig.2); the inlet exhaust gas line, the mixing chamber, the reactor, and the outlet exhaust gas line. The mixing chamber is the space where aqueous urea solution is sprayed and then decomposed into ammonia by the heat of the exhaust gas.

When the exhaust gas meets the injected urea solution inside mixing chamber, the evaporation of water on the drop surface occurs first and then the remained urea which is in solid or molten state thermally decomposed into ammonia as illustrated in Fig. 3. These evaporation and reaction processes of urea solution are thought to be mainly affected by the spatial drop size and velocity distribution of injected urea solution and the temperature of exhaust gas.

Fig.1 Installed SCR system in Hyundai HiMSEN engine

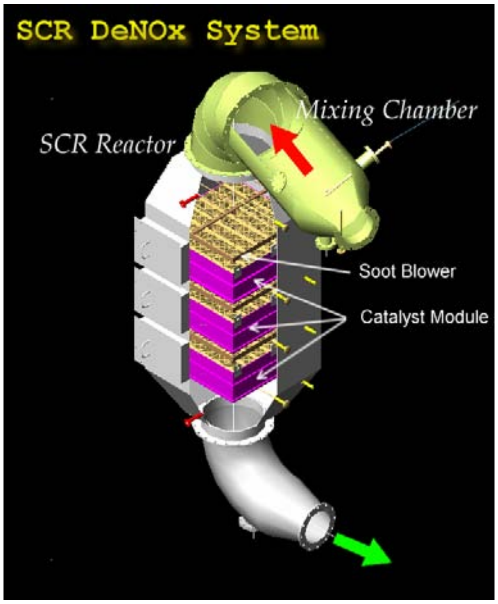


Fig.2 Schematic diagram of SCR system

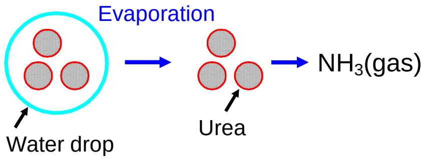


Fig.3 Thermal decomposition mechanism of urea solution into ammonia

In this study, the mixing characteristics of urea injection nozzle were first investigated with air and water at room temperature. The cone nozzle model was used to predict the spray characteristics and the results were verified with the experimental ones. Next, the experiments and calculations on the thermal decomposition of urea in the hot gas was investigated. Experiments were accomplished at the conditions of three different temperature and gas flow rate. The single reaction rate model for thermal decomposition of urea was adopted in numerical calculations and the model constants were properly adjusted with experimental data. Numerical results were verified by comparing to those of experiments. Above results were applied to the design of optimum mixing chamber of SCR system for our own medium-speed diesel engines.

EXPERIMENTAL SETUP

Figure 4 shows the installed urea-injection nozzle inside acrylic duct for the visualization of spray mixing characteristics and the detailed picture of the nozzle. The urea-injection nozzle used in this study is twin-fluid atomizer made in Spraying System Co. Aqueous urea solution is directly injected inside the duct through the six holes of nozzle exit with injection angle, 70°. The air at room temperature flows from left to right with three incoming velocities, 1.3, 5.4, 12.2 m/s. Circular duct having inside diameter, 300 mm and length, 3 m was made of acryl to visualize the mixing characteristics between injected drops and incoming air.

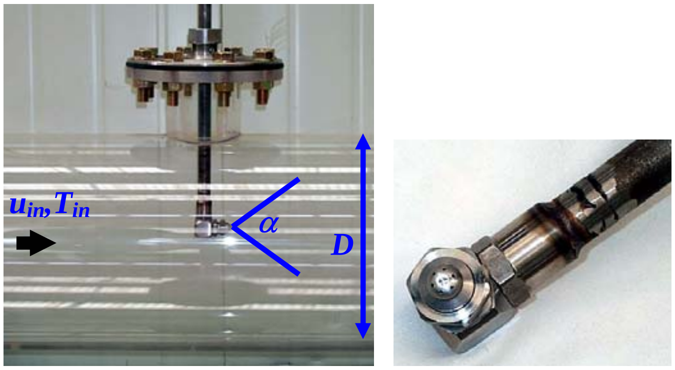


Fig.4 Acrylic duct for spray visualization and urea-injection nozzle

Table 1 shows the test conditions of urea-injection nozzles. As an indicator of the spray characteristics, the drop size distributions and velocity fields were measured using PDPA (Phase Doppler Particle Analyzer, Aerometrics Co.) and PIV (Particle Image Velocimetry, La Vision Inc.) system.

Table 1 Test conditions for the measurement of spray characteristics

	Air injection pressure [bar]	Liquid injection pressure [bar]	Liquid flow rate [l/hr]
case1	0.6	0.7	5.3
case2	1.1	1.2	6.2
case3	1.9	2.0	6.6

The hot gas generator (Fig.5) was designed to provide the same conditions of gas flow rate and temperature in diesel engines. The combustion gases of temperature 1200 °C are produced by LNG burner and mixed with the cold air to set the gas flow rate and temperature as listed in Table 2. The urea-injection nozzle is installed at 1.5 m downstream from burner outlet. The ammonia production was measured by FTIR (Model No.I1200 MIDAC Co.). The sampling part of FTIR was purged utilizing nitrogen gas every five minutes to minimize its contamination by impurities such as residues and by-products during urea decomposition. Three sampling positions are located 3 m apart from the injection nozzle. At each sampling position, six point samples from bottom to top are averaged to calculate the ammonia production. Aqueous urea solution (40 wt% solution) is sprayed from the nozzle at injection pressure, 2 bar and urea flow rate, $18\,cc/min$. If all injected urea solution is converted to ammonia gas, the flow rate of ammonia will be 6 l/min.

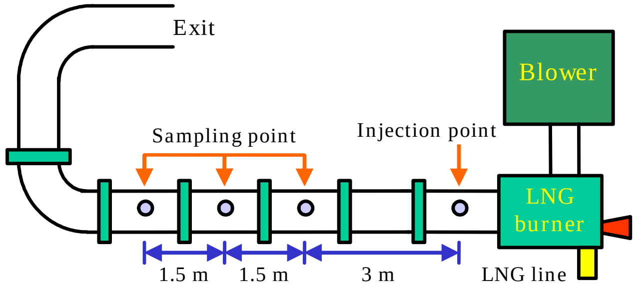


Fig.5 Schematic diagram for thermal decomposition experiments of urea solution

Table 2 Test conditions of the combustion gases

Gas Temp. [°C]	Avg. Velocity [m/s]	Gas Density [kg/m^3]	Volume Flow Rate [m^3/min]	NH$_3$ 100% conversion [ppm]
300	6.55	0.616	27.78	454.7
	9.04		38.35	329.5
	10.99		46.59	271.2
350	6.39	0.567	27.08	507.2
	9.08		38.49	356.9
	10.77		45.69	300.6
400	6.03	0.524	25.55	580.7
	8.33		35.33	420.0
	10.84		45.97	322.8

NUMERICAL PROCEDURES

Fluent code v6.0 was used for spray and urea reaction calculations. The spray behavior is modeled by discrete phase model (DPM) which can simulate a discrete second phase in a Lagrangian frame of reference. This second phase consists of spherical particles (which may be taken to represent droplets or bubbles) dispersed in the continuous phase. FLUENT computes the trajectories of these discrete phase entities, as well as heat and mass transfer to/from them. The coupling between the phases and its impact on both the discrete phase trajectories and the continuous phase flow can be included. The cone injection type was selected to model the urea-injection nozzle in which a hollow spray cone of particle streams can be conveniently defined in 3D problems.

To model thermal decomposition of urea solution, the single kinetic rate devolatilization model in Eq. (2) and (3) was adopted which is originally for the simulation of coal combustion. This model assumes that the rate of reaction is first-order dependent on the amount of reactants remaining in the particle. The kinetic rate, k is defined by input of an Arrhenius type pre-exponential factor, A_1 and an activation energy, E.

$$m_p(t) = m_{p,0}\left(1 - f_{w,0}\right) \cdot exp\left(-k \cdot t\right) \tag{2}$$

$$k = A_1\, exp\left(-\frac{E}{RT}\right) \tag{3}$$

RESULTS AND DISCUSSIONS

Drop sizes of urea-injection nozzle were first measured at 100 mm downstream from nozzle exit using PDPA system and Fig.6 shows the measured drop size distribution in case 3.

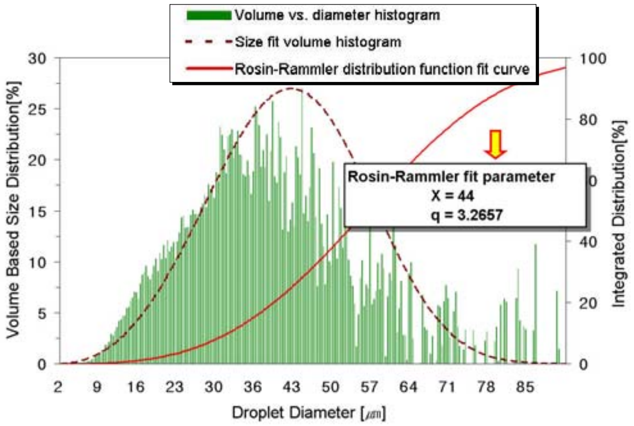


Fig.6 Measured drop size distribution in case 3

When a liquid is injected through the nozzle, it is atomized into many drops. Except special cases, these drops have the spatial and temporal distributions. Even though there are many representative mean diameters to characterize the spray, these single values of drop diameter are not enough to fully describe the interactions between incoming air and injected drops. So, in this study, Rosin-Rammler distribution function as shown in Eq. (4) was adopted to fit the measured drop size distribution and the results are listed in Table 3 and Fig.7. These drop size distributions were used as an input data for the spray model in numerical calculations.

$$1 - v(d) = exp\left[-\left(\frac{d}{X}\right)^q\right] \tag{4}$$

Table 3 Experimental data of urea-injection nozzle

	case1	case2	case3
X	62.3	45.6	44
Q	2.5357	2.7491	3.2657
$u_d\,[m/s]$	6.7	9.5	10.6

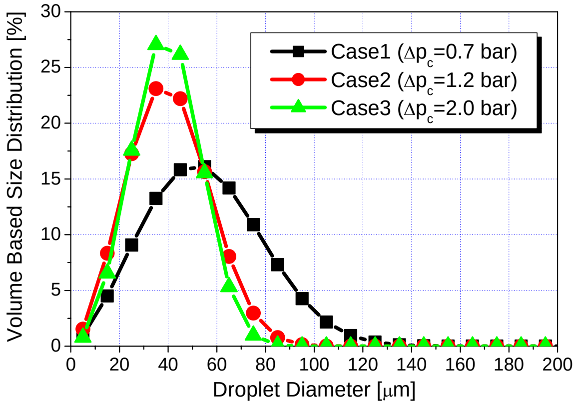
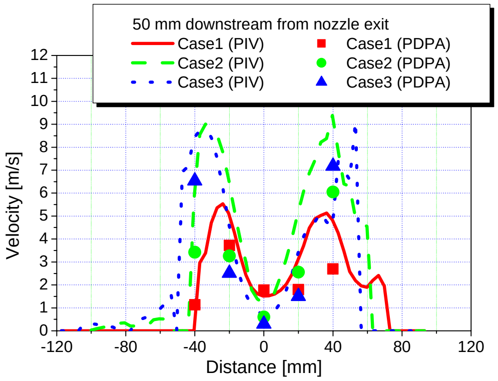


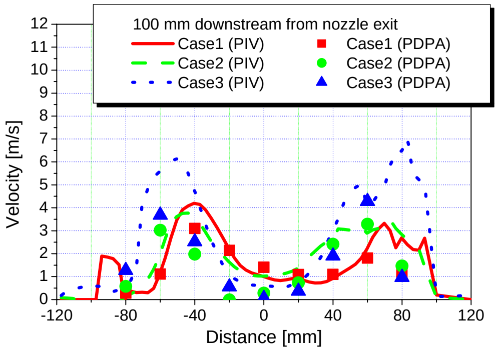
Fig.7 Drop size distribution used as an input data for numerical calculation

Drop velocities were also measured at 50, 100 mm downstream from nozzle exit using PDPA and PIV system and the results are shown in Fig.8. There are some differences due to the different measuring method between local point ensemble averaged velocities of PDPA and velocity fields of PIV at specified instance, but the spatial distributions have similar shapes. The measured velocities were extrapolated near the nozzle exit and the results are also listed in Table 3. The drop velocity data at the nozzle exit are also required for the spray model.

The overall mixing behavior between the incoming air and spray was examined using the acrylic duct (Fig.4). The inlet velocities of air were varied from 1.3 to 12.2 m/s and the cross-sectional spray images were taken for three cases of injection pressure (Table 1) using CCD camera, light sheet optics and Nd-Yag laser. Figure 9 (a) shows the example of captured spray image at 100 mm downstream from the nozzle exit with inlet velocity, 5.4 m/s. The spray widths from these images were measured by image processing technique as illustrated in Fig.3 (b) and the results are shown in Fig.10. The spray width is a function of injection pressure, drop size and velocity, injection angle, and incoming air velocity. It indicates how the air and spray interacts in the confined duct. So, this parameter was compared with the numerical results as shown in Fig.10 to verify the reliability of the spray models in numerical calculations. The calculated spray width agrees well with the measured one and this means the adjusted spray model properly predicts the mixing characteristics between incoming air and injected drops.

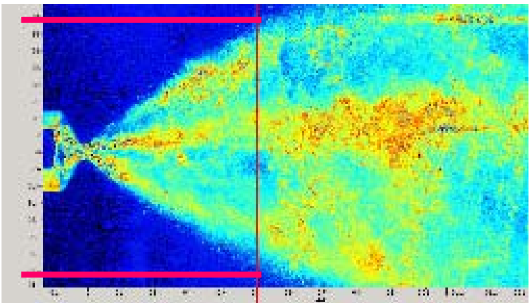


(a) 50 mm downstream from nozzle exit

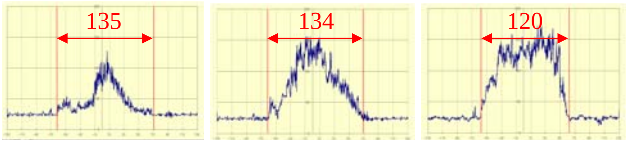


(b) 100 mm downstream from nozzle exit

Fig.8 Comparison of drop velocity measurement using PDPA and PIV system



(a) Example of captured spray image



Case 1 Case 2 Case 3

(b) Image processing examples of spray width measurement at 100 mm downstream from the nozzle exit with inlet air velocity, $u_{in} = 5.4\,m/s$

Fig.9 Examples of captured spray image and image processing of spray width measurement

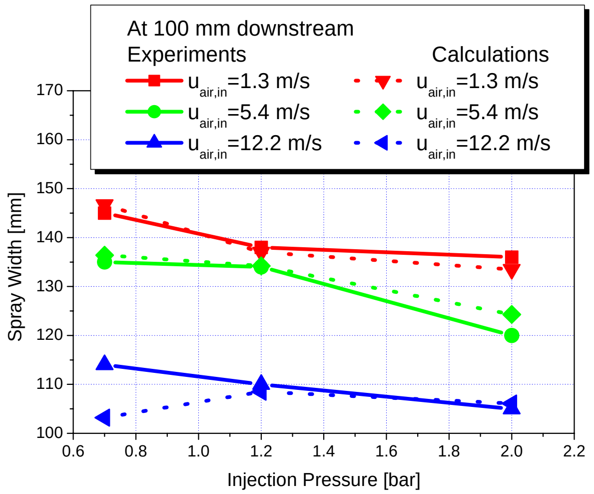
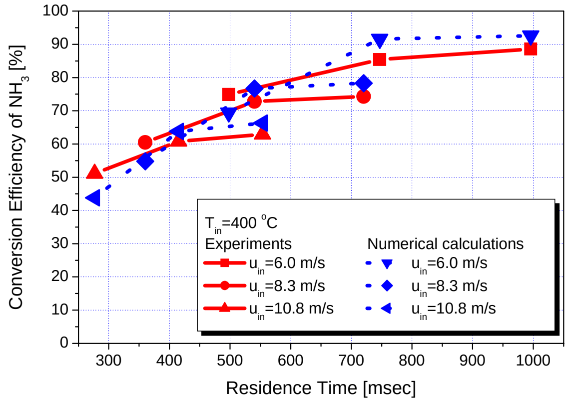
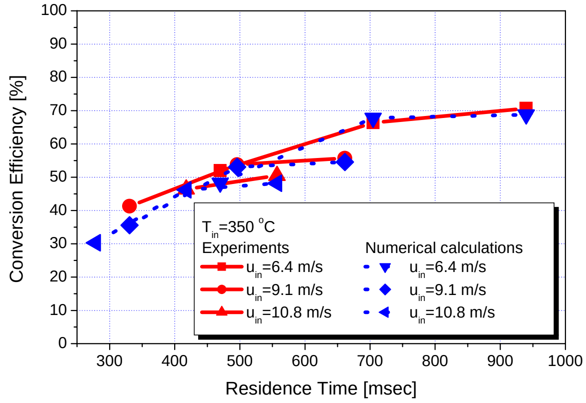


Fig.10 Comparison of measured spray width with numerical one at 100 mm downstream from the nozzle exit

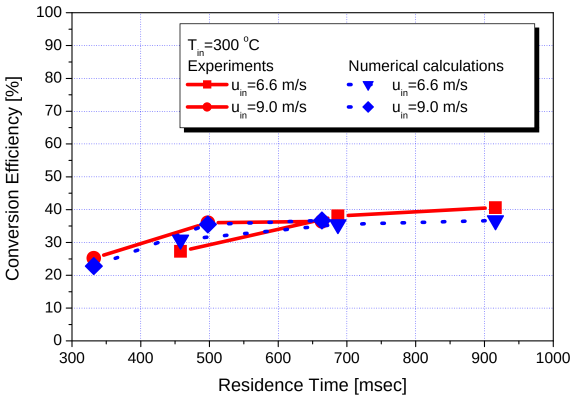
The productions of ammonia from aqueous urea solution were measured in the hot gas generator and all the results are summarized in Fig.11.



(a) Gas Inlet temperature T_{in}=400℃



(b) Gas Inlet temperature T_{in}=350℃



(c) Gas Inlet temperature T_{in}=300℃

Fig.11 Experimental results of conversion efficiency of urea decomposition to ammonia

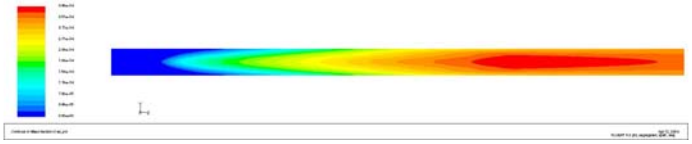
The measurement results of ammonia production were rearranged with the residence time and conversion efficiency. The residence time of injected urea solution has the meanings that how much time urea reaction is processed and is related to both the incoming exhaust gas velocity and length of mixing chamber. The values of measured ammonia production are converted to the conversion efficiency since the maximum amount of ammonia when 100 % urea is converted is different with respect to the gas flow rate and injected urea solutions. So, the measured results were divided by the maximum amount of ammonia and this is the definition of conversion efficiency. In Fig.11, as the temperatures of incoming gas are increased, the productions of ammonia are increased. On the other hand, as the incoming gas velocities are increased which mean the decrease of residence time, the amount of ammonia is decreased at the same temperature. Also, with the given gas velocity and temperature, all results show the tendencies of the steep increases of ammonia production at initial entrance and slow down at downstream. Of course, this involves the fact that there exists the optimum length of mixing chamber.

To solve the thermal decomposition of numerically, the single kinetic model was adopted with the adjusted model constants as in Eq. (5) and solved simultaneously along with the verified spray model.

$$k = 382 \cdot exp\left(-\frac{2.94\times10^{7}}{RT}\right) \qquad (5)$$

Figure 12 shows the example of the calculated temperature and ammonia distributions at the condition of $u_{in} = 6.4\ m/s$, $T_{in} = 350\,^{\circ}C$.

(a) Temperature distribution



(b) Ammonia distribution

Fig.12 Computational results on the temperature and ammonia distributions

At first thought, the evaporation of water vapor is crucial to the reaction rate of thermal decomposition of urea solution since this reaction occurs after the evaporation of water is finished and the water vaporization has much impact on the resulting temperature filed due to high enthalpy of vaporization. This is of course true in this study but, as shown in Fig.12 (a), the temperature drop for all cases is small about 15 °C and the temperature field is almost uniform except for near nozzle region. This is because the total amount of injected water is small (about 10 ppm) in comparison to the gas flow rate and the evaporation occurs too fast near the nozzle due to high gas temperature. So, the effect of temperature drop caused by water evaporation is not significant in this study, but, this effect will not be neglected when the energy of water evaporation is comparable to that of incoming gas. Figure 12 (b) confirms again numerically the steep increase of ammonia production near nozzle region since the ammonia distribution profile is changing very rapidly at upstream but almost unchanging at downstream.

All results of numerical predictions on the ammonia production are also plotted in Fig.11 for the verification of reliability. Even though there are still some differences between measurements and calculations, the overall comparison results show reasonable agreements both in magnitude and tendency especially when considering the effect of temperature and residence time. It is thought that some differences between measurements and calculations are mainly due to the simplified reaction model and the input data in the spray model because the question still arises that the input data on the drop size and velocity distributions do really represent the spatially and temporally changing real spray behaviors. Nevertheless, it was concluded from the discussions so far that the reliability of the numerical predictions was acquired and the design capabilities for sizing optimum mixing chamber were established in engineering sense.

CONCLUSIONS

The spray-induced mixing characteristics and thermal decomposition of aqueous urea solution into ammonia have been studied to design optimum sizes and geometries of the mixing chamber in SCR system. For this purposes, both the experiments and calculations were done to clarify the spray characteristics at room temperature and thermally decomposed ammonia productions at the exhaust gas conditions of diesel engines. From this study, we concluded as follows.

- The cold flow tests about the urea-injection nozzle were performed to clarify the spray mixing characteristics such as mean diameter and velocity of drops and spray width determined from the interactions between incoming air and injected drops.
- The simulation results on the spray-induced mixing characteristics were verified by comparing the spray width extracted from the digital images with the simulated particle tracks of injected drops.
- The single kinetic model was adopted to predict thermal decomposition of urea solution into ammonia and solved simultaneously along with the verified spray model.
- The measured ammonia productions in the hot air generator were compared to the numerical predictions with adjusted model constants and the comparison results showed good agreements. Finally, we concluded that the design capabilities for sizing optimum mixing chamber were established.

NOMENCLATURE

A_1 :	Model constant	
E :	Activation energy	$[\,kJ/kmol\,]$
$f_{w,0}$:	Initial mass fraction of water contained in urea solution	
k :	Kinetic rate	$[\,s^{-1}\,]$
$m_{p,0}$:	Initial particle mass of urea solution	$[\,kg\,]$
$m_p(t)$:	Particle mass of urea solution	$[\,kg\,]$
$v(d)$:	Fraction of the total volume contained in drops of diameter less than d	
d :	Drop diameter	$[\,\mu m\,]$
u_d :	Droplet velocity	$[\,m/s\,]$
u_{in} :	Incoming air velocity	$[\,m/s\,]$
T_{in} :	Temperature of incoming air	$[\,°C\,]$
t :	Time	$[\,s\,]$
X :	Model constant of Rosin-Rammler function	
q :	Model constant of Rosin-Rammler function	

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[1] S. Y. Lee, “Atomization of Liquids,” in Korean, 1996.

[2] Fluent v6.0 user manual.

[3] H. L. Fang, H.F. DaCosta, “Urea Thermolysis and NOx Reduction with and without SCR Catalysts,” Applied Catalysis B, Article in press.