8th U. S. National Combustion Meeting
Organized by the Western States Section of the Combustion Institute
and hosted by the University of Utah
May 19-22, 2013

Numerical Modeling of Urea Injection and NO Emission in a Stoker Boiler

Mohsen Ghamari[1]   *Samarth Vats*[2]   *Albert Ratner*[1]

[1]*Department of Mechanical and Industrial Engineering, University of Iowa, 3131 SC, Iowa City, Iowa, 52242, USA*
[2]*Department of Mechanical Engineering, Delhi Technological University, Shahbad Daulatpur, Main Bawana Road, Delhi-110042,India*

The Selective Non-Catalytic Reduction (SNCR) of NO emission was investigated for a coal stoker boiler using ANSYS FLUENT. For this purpose, first a combustion model was applied to simulate coal combustion in a three dimensional full scale boiler. In order to assess the accuracy of heat sink and heat transfer model a series of temperature measurements were carried out at different locations of stoker boiler. To verify the model accuracy in predicting pollutants' emission, the emission of NO was investigated using FLUENT post-processing module and compared to measured data. The post-processing results of NO emission showed good agreement with stack emissions reported to EPA by the University of Iowa Power Plant. Once a good accuracy of comprehensive model was achieved, FLUENT Discrete Phase Modeling (DPM) was considered to simulate urea solution injection into the boiler. For this purpose, several injection rates as well as different injection arrangements and velocities were examined to characterize SNCR process. Results revealed the importance of temperature zone to which urea is injected. A temperature window to have maximum NO reduction while keeping the ammonia slip at its low levels was found to be about 1250-1420 K. It was also found that the nozzles closer to the corners of the wall are more likely to be in this temperature zone and would provide more satisfactory result than injection through middle ones or the innermost. The results showed that injection from higher elevation could provide better result in terms of higher NO reduction and lower ammonia slip by means of more even temperature profile and being closer to the flue gases. It was also found that for the case of injection through middle nozzles and at the elevation of secondary air, urea should have high momentum in order to penetrate into right temperature window and prevent from high amount of ammonia slip. This could be done by means of injecting urea into air pipe and take the advantage of air momentum to carry the urea solution.
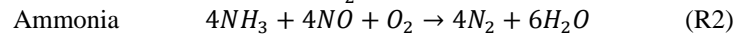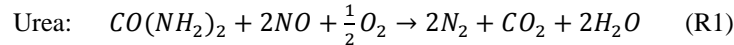
1.   Introduction

Nitrogen oxides (NO_x) are a group of combustion products that contribute in variety of environmental problems such as acid rains and acidification of aquatic systems, ozone layer depletion and ground level ozone. Different processes might be involved in their formation based on their combustion origin; in power plant boilers, which are of interest in this study, high temperature and chemically bound nitrogen in the coal count as the main sources of NO_x formation. Based on the main routes of NO_x formation and the environmental criteria, different reduction technologies such as combustion modification and post-combustion NO_x removal have been developed (Comparato, 2001). Selective Non-Catalytic Reduction (SNCR) is a post-combustion method to reduce NO_x emission by injecting a selective reductant such as ammonia (NH_3) or urea ($CO(NH_2)_2$) into a furnace, where it reacts with NO to form N_2 and consequently reduce emission. However, the reductant can be oxidized into NO_x at specific operating conditions and increase pollutant emission. In spite of large number of researches in this area, there are still many unknowns because of the volatile behavior of combustion and diversity of industrial facilities that benefit mainly from combustion. Farzan et al. showed that improved NO_x reduction performance is attained by injection of urea at full load, and via a convective nozzle lance in front of the superheater tubes, which proves the importance of the injection location (Farzan, 2003, Farzan, Sivy, Boyle, Xu, & Lani, 2006). Cremer et al. studied the application of Rich Reagent Injection (RRI) in a 138 MW cyclone-fired boiler (Cremer, Adams, O'Connor, Bhamidipati, & Broderick, 2001). They showed that utilizing SNCR combined with Over Fire Air could increase NO_x reduction from 25-30% to 50-55%. Kim et al. developed a numerical simulation to investigate implementation of SNCR in afterburner region of a full-scale incinerator (Kim, Shin, Jang, & Ohm, 2004). Another study which deals with the

application of urea-based SNCR to a municipal incinerator was carried out by Nguyen et al. (Nguyen et al., 2009). They observed 66% in their CFD simulation which met with 70% reduction obtained from on-site experiments. They also reported that non-uniform urea solution droplet size enhances mixing with the flu gas and increases NO reduction efficiency. In a series of on-site experiments, Heider combined Acoustic Gas Temperature Measurement and SNCR at 5 levels to optimize the NO reduction at different boiler loads (Heide, 2010). He reported 36.7% reduction for 100% boiler load and a maximum reduction of 57.9% for 75% load. His study underlines the fact that location and rate of injection has crucial impact on reduction efficiency. Notwithstanding all of researches, the performance of SNCR for full scale coal-fired boilers and at full load is not completely known. This becomes more complicated when it comes down to extensive range of coal properties and compositions in the market that makes each case to be studied separately for optimum design and performance.

The University of Iowa Power Plant is seeking available NO_x reducing technologies that are yet easy to be incorporated into current boiler facilities (Boiler 10 for this study). Because of space limitation both around the boilers and on the boiler walls for injection ports, a study on the different aspects of reductant injection such as injection location, rate and injection characteristics (velocity, angle, etc.) seems to be crucial before stepping into any experiment or full scale test. In this paper, first a review of SNCR mechanism and the way it works for urea is carried out and then several injection scenarios are considered.

2. Methods

The objective of all NO_x control technologies is to reach the highest level of NO_x reduction with the minimum amount of reagent while keeping the ammonia slip at the lowest possible level. What is used in SNCR as reductant is an aqueous solution (ammonia or urea in water) or gaseous form (ammonia) of reagent that breaks down NO through the following overall reactions:

Urea: $\quad CO(NH_2)_2 + 2NO + \frac{1}{2}O_2 \rightarrow 2N_2 + CO_2 + 2H_2O \quad$ (R1)

Ammonia $\quad 4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad$ (R2)

The key point in the SNCR method is that there is only a narrow temperature window in which the reagent injection is optimum in terms of reducing NO_x and generating the least carbon dioxide and ammonia, depending on the flue gas composition. Different ranges have been reported in the literature for different applications (incinerator, coal fired boiler, natural gas fired boilers, etc.), but what all of them have in common is that ammonia works in a lower range (1140K-1250K), while urea effectiveness range is higher (1250K-1420K). Above this temperature range, ammonia is oxidized to nitrogen oxides and the effectiveness of reagent injection decreases dramatically. On the other hand, at lower temperatures the reaction rate is considerably slowed, causing ammonia slip which itself could result in the formation of ammonia salt in the downstream of flow of the boiler.

Since the only available option for reagent injection is a set of secondary air nozzles on the front wall of boiler 10, an examination of the temperature profile in the zones closest to these potential injection locations seems to be necessary. Although no experimental data is available at the secondary air injection level, the measurements conducted in winter 2011 at the elevation of the observation windows could be used as an estimate (Zhang, 2011). Figures 1 (a) and (b) show that the temperature above the grate is more within the temperature range of urea. In addition, since the maximum temperature occurs on the grate, lower temperatures are expected higher in the boiler. Fig. 1(c) (based on CFD modeling) verifies this expectation and indicates that the maximum temperature profile at the level of the secondary air injectors is 1580K. Since urea will most likely break down into ammonia and isocyanic acid in the environment of interest (reaction R3 and R4), the SNCR process can be described using urea as a combination of SNCR with ammonia and SNCR using cyanuric acid (that under heating sublimes and decomposes into isocyanic acid). The two-step mechanism for urea breakdown and seven-step mechanism for NO_x reduction along with their corresponding coefficients for Arrhenius equation have been listed in Tables 1 and 2 respectively. Table 2 simply shows that if the proper conditions for SNCR are not provided, reactions R5 through R10 do not take place completely and high amount of NH_3 remains unused and leaves with flue gases (ammonia slip). The other problems involved in SNCR using urea are slow decay of HNCO (through R7) and negative activation energy of reaction channels leading to N_2O and CO which can significantly increase the emission of pollutants other than NO such as CO and HNCO.

3. Results and Discussion

Overall results are shown in Table 3. This table summarizes 11 cases that best describe the behavior of urea injection and the parameters influencing its performance and effectiveness. The first row, denoted as case 0 (or base case), reports NO emission before urea injection for the case of pure coal combustion. This case will be considered as the reference point

to calculate NO reduction. Through these simulations, 4 different injection rates, 1cc/s, 3cc/s, 10cc/s and 15cc/s, of commercial 32% urea-water solution were examined.

The effect of urea injection rate has also been mirrored in Fig. 2. In this diagram, all the cases that had been set up with the same injection properties and are different only by their injection rates have been compared. From this figure, it is obvious that by increasing urea injection rate, NO emission decreases significantly (from 177 ppm at 1cc/s to 131 ppm at 15cc/s).

Fig. 3, which will be referred to during future discussions, shows that SNCR using urea is most beneficial within the desired temperature window (Heide, 2010). Below this window, the temperature is not high enough to provide the required activation energy for reactions R5 and R6. As a result, NH_3 fails to react with NO and O2 and to dissociate into other products, so a high amount of ammonia slip is observed for this zone. On the other hand, above the temperature window, reaction R6 predominates through which NH_3 is oxidized to an increasing extent and nitrogen oxide is formed.

3.1. Base case study

The first case is Case 0 (or base case) which is the modeling of NO emission from boiler 10 under normal conditions and before any NO_x control measures are undertaken. The NO emission for this case was observed to be 88.85 lb/hr which is in agreement with the numbers reported through actual measurement (varying between 85 and 105 lb/hr through several measurements). The only problem with the solution of base case is the higher ammonia slip (0.89 mg/Nm^3) than most of the urea injection cases. The reason could be the activation of SNCR reactions in the case of urea injection which considers NH_3 depletion. Those reaction which take place in real combustion cases, are included under SNCR option and not in normal NO_x model of ANSYS FLUENT. It is worth noting that during the combustion processes in which ammonia is formed as a combustion product, the SNCR process might still occur if NH_3 is in the right temperature window and there is sufficient local NO_x. Thus, the predicted ammonia slip for base case is probably higher than its real value and should not be considered as a reference. Instead, all ammonia slips will be compared with the value of case 1.

For case 1, 1cc/s of urea-water solution is injected from secondary air nozzle N6 (on the front wall) into the boiler. Looking back at Fig. 1(c), it is evident that the temperature at most of the points is higher than 1300K, but the key fact is that this plane is not the best location to see the effect of urea. For this purpose, we need to see injection of urea and then its distribution in the boiler. Fig. 4(a) shows the injection of liquid droplets into the boiler and the paths they travel. The particles have been colored by their temperature to make more sense and provide insight into understanding their disappearance due to sublimation.

This figure shows that particles exist between the range of injection temperature and 650K. Fig. 4(b) shows the change in particles' diameter because of the sublimation. As it was mentioned before and by comparing Fig. 4(a) and (b), we see that the size reduction starts immediately and as a result of evaporation of water enclosing urea particles. Unfortunately it is not possible to determine the exact point at which the sublimation process starts due to the fact that size reduction is because of both evaporation and sublimation. In contrast, we could determine the zone after which no particle exists. That is the location where particles have their minimum diameter and the sublimation of urea is complete. Fig. 4(a) shows this point having temperature of around 650K which is in agreement with before mentioned temperature of 380℃ for maximum decomposition of urea. These points are about 8 feet higher than injection plane and are the area of maximum mass fraction of gaseous urea (the product of sublimation) in Fig. 4(c).

Figures 5(a) and (b) show the NO profiles of base case and 1cc/s urea injection respectively. The reduction of NO as a result of SNCR process is completely evident in this figure. Fig. 6 shows the temperature profiles of both injection plane and plane of maximum urea mass fraction. From this figure we could find the zone on the temperature window of Fig. 3 in which urea acts. According to the diagram of Fig. 3, the reduction for case 1 should be in the range of 30%-40%. Ammonia slip should also be very small. However, this diagram is just a schematic diagram and should be used as a reference for validation; a problem which is evident from large difference in ammonia slips of model and diagram.

3.2. Effect of urea injection rate

Next cases are 3cc/s, 10cc/s and 15cc/s which correspond to cases 7, 9 and 11 respectively. Fig. 2 shows the increase both in NO reduction and ammonia slip. This diagram proves that by increasing only urea injection rate into the boiler from 1cc/s to 15cc/s, NO reduction increases up to 57%. However, the reduction does not appear to be linearly proportional to the injection rate and it is expected that under current situation and without applying any other change to our injection settings, adding more urea into the boiler will not probably result in big changes in NO reduction. In contrast, ammonia slip at 15cc/s is twice the slip of 3cc/s and it is anticipated that by increasing urea injection, the ammonia slip would go up significantly. Considering the local cooling effect of high injection rates, this could also be anticipated from Fig. 3.

3.3. Effect of different injection location/arrangements in the plane of secondary air

Since the distribution of urea in the right temperature zone is very crucial to efficient urea injection and optimum reduction, a series of cases were designed to study the nozzles arrangement. Cases 8 and 10 are both for simultaneous injection of urea through nozzles N1, N6 and N11 (first, middle and last nozzles) but for different rates of 3cc/s and 10cc/s respectively. From previous cases it seems obvious to have higher reduction for case 10 in comparison to case 8 by virtue of higher urea as the reducing reagent. What is of more importance in this part of study is the difference we get by switching from one nozzle (N1) to three nozzles which seems completely promising. Comparison of cases 8 and 7 that differ only in their nozzle arrangements shows that higher reduction is achieved both in NO emission and NH_3 slip by using new arrangement of three nozzles. The reason for having less ammonia slip could be due to the higher temperatures zones into which the urea from N1 and N11 is injected. Fig 7 shows the faster sublimation (smaller zone) for the urea particles being injected from N1 and N11. Table 3 shows that NO reduction using 3cc/s through three nozzles (~50%) is almost the same as using 10cc/s with one nozzle (~52%). Even better result could be achieved at higher injection rates (~76% at 10cc/s).

Because of the importance of temperature window for effectiveness of urea injection, it is necessary to investigate other possible injection points. Basically, it is expected that there are colder areas close to the side walls of boiler. Therefore, nozzle N1 was considered as urea injection port for case 3. The results show that the reduction for this case is higher than case 1 (injection through N6) but not because of being located in a colder area. Fig. 1(c) shows that in contrast to our expectation of having lower temperature, the temperature is higher close to N1. The reason of having such higher temperature could be local recirculations at the corners of boiler which result in intensified local temperature. Figures 8(a) and (b) verify this condition by showing very high temperature gradient and fast sublimation respectively. Though urea should be completely sublimed below 650K, but due to the high temperature gradient close to the injection nozzle and considering initial momentum of particles and the minimum required residence time for being completely sublimed, this process continues to exist until about 1000K. Yet, the sublimation occurs even faster and sooner than for case 1 as is shown in Fig. 8 (b). This figure shows that fast sublimation and low velocity regime in the area close to the wall helps the gaseous urea to move along the wall and successfully disperse into the right temperature region in the flue gases. The location of this point has been specified on Fig. 3 and could be compared with case 1.

3.4. Effect of injection velocity / momentum

Case 2 shows the effect of injection velocity. The reason behind this strategy is to send urea particles deeper into the hot zones which are more likely to produce thermal NO. Results in Table 3 validate this strategy by showing 77% reduction. However, more study is required to assess the energy required to produce this velocity and the possible technological costs.

3.5. Effect of injection elevation

By looking at Fig.6 we see that as we go higher in the furnace, the temperature becomes less and its distribution becomes more even. This even distribution of temperature could provide an opportunity for NO_x reduction if it is in the right temperature window. Therefore, a series of other interesting cases were designed to investigate the effect of injection at higher elevations. For this purpose it was assumed that we have a same line of nozzles similar to secondary air nozzles but 11 feet higher on the front wall. Three cases were considered for this part: In case 4, 1cc/s was injected through N6 (similar to case 1). Case 5 was considered to inject the same amount of urea as case 4 but with higher velocity, i.e. 30m/s (similar to case 3). Finally, the effect of utilizing multiple injectors was investigated by injecting total amount of 1cc/s from three nozzles N1, N6 and N11.

By comparing cases 1 and 4 in Table 3, it is understood that putting the injection lance at higher elevation could provide about 15% more reduction (~57% for case 7 vs. ~42% for case 1) while keeping ammonia slip at a very low level. As a result recirculation due to heat exchanger lower wall, the urea particle cannot penetrate deep into the furnace and sublime in the area close to the wall. It was anticipated that by increasing injection velocity to 30 m/s we could increase the depth of penetration similar to what happened for case 2, but ending up with less reduction is not in compliance with this idea. In addition, using three injectors in a row, as in case 6, did not show a considerable boost in NO reduction (only 3% more than case 7). All of the results in this part of the study imply that the temperature profile and flow field of injection zone are crucial to the effectiveness of injection and call for different measures.

4. Conclusions

In this study, the effect of urea injection on NO_x reduction and NH_3 slip were investigated. For this purpose, several injection rates as well as different injection arrangements and velocities were examined to understand how SNCR process

works. By analyzing results, it was revealed that the temperature of the zone to which urea is injected is very important. The best temperature window to have maximum NO reduction while keeping the ammonia slip at its lowest levels is about 1250K-1420K (~980℃-1150℃). It was found that the nozzles closer to the corners of the wall are more likely to be in this temperature zone and would provide more satisfactory result than injection through middle ones or the innermost. The result showed that if possible, injection from higher elevation could provide better results in terms of higher NO reduction and lower ammonia slip by means of more even temperature profile and being closer to the flue gases.

Acknowledgements

References

Comparato, J. R. (2001). NO$_X$ Control Technologies: Focus SNCR. *Western Coal Council, Burning PRB Coal Seminar, Birmingham* (pp. 24–26).

Cremer, M. A., Adams, B. R., O'Connor, D. C., Bhamidipati, V. & Broderick, R. G. (2001). Design and demonstration of rich reagent injection (RRI) for NO$_x$ reduction at Conectiv's BL England Station. *Proceedings of the EPRI-DOE-EPA Combined Power Plant Air Pollutant Control Symposium: The MEGA Symposium* (pp. 20–23).

Farzan, H. (2003). NO$_x$ Control for Utility Boiler OTR Compliance.

Farzan, H., Sivy, J. L., Boyle, J., Xu, H. & Lani, B. (2006). NO$_x$ Control for Utility Boiler Ozone Transport Rule Compliance. *31st International Technical Conference on Coal Utilization & Fuel Systems*.

Heide, B. V. D. (2010). NO$_x$ Reduction for the Future with the SNCR Technology for Medium and Large Combustion Plants. *Power Engineering and Environment*. Essen, Germany.

Kim, H. S., Shin, M. S., Jang, D. S. & Ohm, T. I. (2004). Numerical study of SNCR application to a full-scale stoker incinerator at Daejon 4th industrial complex. *Applied thermal engineering*, *24*(14), 2117–2129. Elsevier.

Nguyen, T. D. B., Kang, T. H., Lim, Y. I., Eom, W. H., Kim, S. J. & Yoo, K. S. (2009). Application of urea-based SNCR to a municipal incinerator: On-site test and CFD simulation. *Chemical Engineering Journal*, *152*(1), 36–43. Elsevier.

Zhang, X. (2011). *Numerical modeling of biomass combustion in a stoker boiler*. University of Iowa.
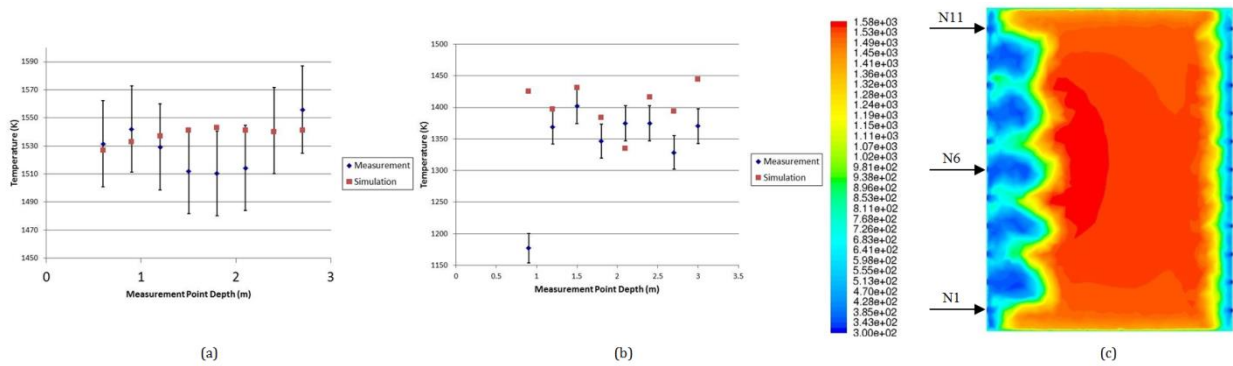
1. Figures and Tables

Figure 1. Comparison of predicted results with measurement data of window (a):N2, (b): N3, (c): injection plane (2.14 kg/s coal).
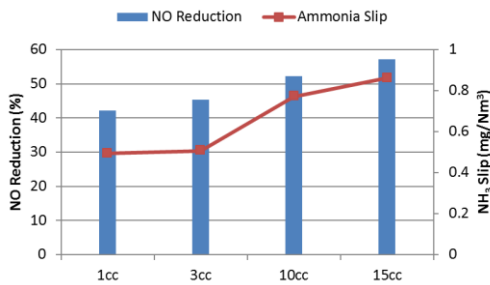

Figure 2. The effect of urea injection rate on NO reduction and ammonia slip.
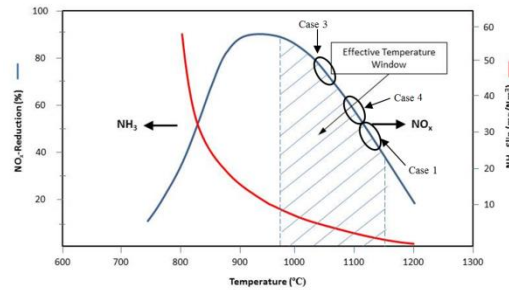
Figure 3. Schematic of NO reduction and ammonia slip as a function of temperature.
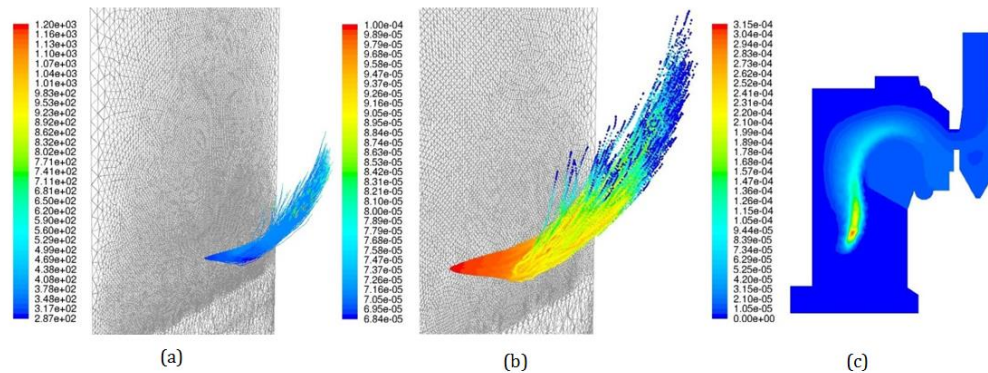

Figure 4. Urea injection through secondary air nozzle N6; (a): change in particles' temperature in Kelvin, (b): change in particle's diameter in meter and (c): mass fraction of gaseous urea.
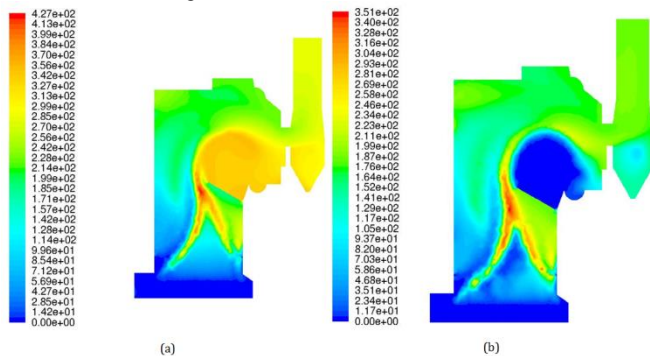

Figure 5. ppm of NO distribution; (a): no urea injection, (b): after 1cc/s injection of urea through N6.
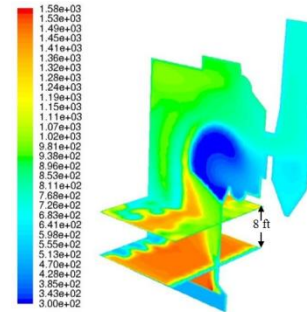
Figure 6. Temperature profile at the plane of injection and plane of maximum gaseous urea mass fraction.
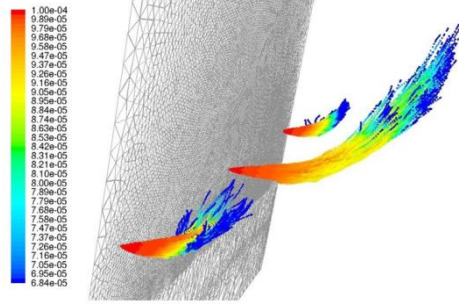
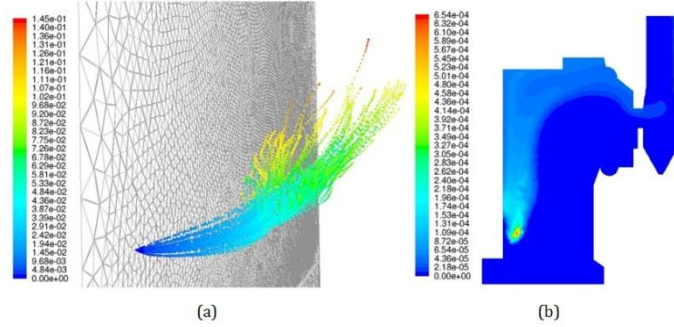Figure 7. Change in particle's diameter in meter (case 10).

(a)   (b)

Figure 8. Urea injection through secondary air nozzle N1 (case 3); (a): change in particle's diameter in meter, (b): mass fraction of gaseous urea

Table 1. Two-step urea breakdown process.

Reaction	A	b	E_a	Reaction No.
$CO(NH_2)_2 \rightarrow NH_3 + HNCO$	1.27E+04	0	65048.109	(R3)
$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$	6.13E+04	0	87819.133	(R4)

Table 2. Seven-step reduced mechanism for SNCR with urea.

Reaction	A	b	E_a	Reaction No.
$NH_3 + NO \rightarrow N_2 + H_2O + H$	4.24E+02	5.30	349937.06	(R5)
$NH_3 + O_2 \rightarrow NO + H_2O + H$	3.500E-01	7.65	524487.005	(R6)
$HNCO + M \rightarrow H + NCO + M$	2.400E+08	0.85	284637.8	(R7)
$NCO + NO \rightarrow N_2O + CO$	1.000E+07	0.00	-1632.4815	(R8)
$NCO + OH \rightarrow NO + CO + H$	1.000E+07	0.00	0	(R9)
$N_2O + H \rightarrow N_2 + O_2 + H$	2.000E+06	0.00	41858.5	(R10)
$N_2O + M \rightarrow N_2 + O + M$	6.900E+17	-2.5	271075.646	(R11)
Arrhenius equation: $\qquad k = AT^b \exp(-\frac{E_a}{RT})$				

Table 3. Test cases.

Case No.	Inj. Rate (cc/s)	Inj. Vel. (m/s)	Elevation (ft)	NO Emission		NH₃ Slip (mg/Nm³)	Injection Nozzles
				(ppm)	(lb/hr)		
0 (Base)	-	-	-	306	88.85	0.89	-
1	1	15	6	177	51.41	0.49	N6
2	1	30	6	69	20.04	0.35	N6
3	1	15	6	154	44.85	0.67	N1
4	1	15	17	132	38.34	0.21	N6
5	1	30	17	171	49.77	0.66	N6
6	1	15	17	123	35.47	0.54	N1, N6, N11
7	3	15	6	168	48.77	0.51	N6
8	3	15	6	156	45.45	0.97	N1, N6, N11
9	10	15	6	146	42.50	0.77	N6
10	10	15	6	71	20.84	0.21	N1, N6, N11
11	15	15	6	131	38.22	0.86	N6