

Paper SOMCHE 2005

The Importance of Rate and Time Dependence on Conversion of NO_x in the Cleaning of NO_x in Exhaust Gases Using Ozone.

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ABSTRACT

The reactions involved in the ozonation of NO_x present in the exhaust gases are discussed. The equations of reaction rate are formulated and the kinetic model analysis is presented to describe the reaction rate of removal NO_x from simulated exhaust gases. The model is analyzed based on the already published reaction rate equations. The orders of magnitudes of the rates of important reactions in the model are discussed. The results from simulation showed that conversion of NO to NO₂ takes place at a fast rate and achieved completely in a short time of a few hundred of seconds. The resulting mixture of NO₂ seemed to be slow in conversion to NO₃ in order of time magnitude of several hundreds and thousands seconds. The respective conversions in the time scales of 10s, 100s, and 1000s are analyzed and presented. The study shows the importance of rates of treatment times for cleaning of NO_x in the exhaust gases.

Keywords: Exhaust gases, Ozone, NO_x rate cleaning..

1. INTRODUCTION

Internal combustion (IC) engines usually consume liquid or gas petroleum products of varying compositions of carbon, hydrogen, oxygen, nitrogen and sulphur. The combustion reactions within engine produce carbon dioxide, oxides of nitrogen, water vapor, carbon monoxide, traces of hydrocarbons elemental carbon in the form of soot and excess inert nitrogen. (Bond et. al., 1972).

Oxides of nitrogen are released into the atmosphere mainly in the form of nitric oxide

and some nitrogen dioxide (Fernando et.al., 2003), as a result of fossil fuel combustion. Nitric oxide is readily oxidized to nitrogen dioxide by reaction with ozone. Elevated levels of nitrogen oxides are generally observed in urban environments under stable meteorological conditions, when the air mass is unable to disperse (website www.columbia.edu/itc 2005). Together with hydrocarbons, they play an important role in the formation of ozone in the atmosphere, as described below. Nitrogen oxides have a lifetime of approximately 1 day with respect to conversion to nitric acid, which is removed from the atmosphere by direct deposition to the ground, or transfer to aqueous droplets (e.g. cloud or rainwater), thereby contributing to acid deposition.

Oxidation technologies for flue gas NO_x control developed in recent years have become commercially successful and economically viable as an alternative to ammonia and urea based technologies using reduction chemistry to remove NO_x. Older commercial technologies such as 'Selective Catalytic Reduction' (Jiménez M. 2002) and 'Selective Non-Catalytic Reduction' (Nakanishi Y. et. Al. 2000), which reduce NO_x to nitrogen using ammonia or urea as an active chemical, are limited in their use for high particulate and sulfur containing NO_x streams such as from coal-fired combustors, or are unable to achieve sufficient NO_x removal to meet new NO_x regulation levels (Sexton J. et.al 2004). In contrast, oxidation technologies convert lower nitrogen oxides such as nitric oxide (NO) and nitrogen dioxide (NO₂) to higher nitrogen oxides such as nitrogen sesquioxide (N₂O₃) and nitrogen pentoxide (N₂O₅).

In this study, a kinetic model to predict the behavior of NO removal by oxidation with

ozone is proposed. The process is analyzed for low temperature ranges such as 300K to 500K.

2. OZONATION REACTIONS.

The removal of NO_x using the ozonation process is based on the excellent solubility of higher order nitrogen oxides. Typical combustion processes produce NO_x streams that are approximately 95% NO and 5% NO_2 . Both NO and NO_2 are relatively insoluble in aqueous streams. Therefore, wet scrubbers will only remove a small fraction of NO_x from the flue gas stream. Species solubility in water at 25°C and 1atm 0.063g/l and 1.260g/l for NO and NO_2 respective (Sexton et.al. 2004).

The ozonation process uses ozone to oxidize NO and NO_2 to N_2O_5 , which is highly soluble, and by wet scrubbing N_2O_5 , is easily and quickly converted to HNO_3 , based on the following reactions (R. Atkinson et.al. 2005):

1. $\text{O} + \text{O}_3 \rightarrow \text{M} \rightarrow \text{O}_3 + \text{M}$
2. $\text{O} + \text{O}_3 \rightarrow \text{O}_3 + \text{O}_2$
3. $\text{H} + \text{HO}_2 \rightarrow \text{H}_2 + \text{O}_2$
4. $\text{H} + \text{HO}_2 \rightarrow \text{OH} + \text{OH}$
5. $\text{H} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}$
6. $\text{H} + \text{O}_3 \rightarrow \text{M} \rightarrow \text{HO}_2 + \text{M}$
7. $\text{H} + \text{O}_3 \rightarrow \text{HO}_2$
8. $\text{H} + \text{O}_3 \rightarrow \text{OH} + \text{O}_2$
9. $\text{O} + \text{H}_2 \rightarrow \text{HO} + \text{H}$
10. $\text{O} + \text{OH} \rightarrow \text{O}_2 + \text{H}$
11. $\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$
12. $\text{O} + \text{H}_2\text{O}_2 \rightarrow \text{OH} + \text{HO}_2$
13. $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$
14. $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$
15. $\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$
16. $\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O}_2$
17. $\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$
18. $\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{HO}_2$
19. $\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$
20. $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$
21. $\text{HO}_2 + \text{HO}_2 + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 + \text{M}$
22. $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2$
23. $\text{O} + \text{NO} + \text{M} \rightarrow \text{NO}_2 + \text{M}$
24. $\text{O} + \text{NO} \rightarrow \text{NO}_2$
25. $\text{O} + \text{NO}_2 \rightarrow \text{O}_3 + \text{NO}$
26. $\text{O} + \text{NO}_2 + \text{M} \rightarrow \text{NO}_3 + \text{M}$
27. $\text{O} + \text{NO}_2 \rightarrow \text{NO}_3$
28. $\text{O} + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}$
29. $\text{OH} + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2$
30. $\text{OH} + \text{HNO}_2 \rightarrow \text{H}_2\text{O} + \text{NO}_2$
31. $\text{OH} + \text{NO} + \text{M} \rightarrow \text{HNO}_2 + \text{M}$
32. $\text{OH} + \text{NO} + \text{M} \rightarrow \text{HNO}_2$
33. $\text{OH} + \text{NO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$
34. $\text{OH} + \text{NO}_2 \rightarrow \text{HNO}_3$
35. $\text{OH} + \text{NO}_2 \rightarrow \text{HO}_2 + \text{NO}$
36. $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$
37. $\text{HO}_2 + \text{NO}_2 \rightarrow \text{O}_2 + \text{HNO}_3$
38. $\text{NO} + \text{NO}_3 \rightarrow \text{NO}_2 + \text{NO}_2$
39. $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{NO}_2$
40. $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
41. $\text{NO}_2 + \text{NO}_2 + \text{M} \rightarrow \text{N}_2\text{O}_4 + \text{M}$

Both N_2O_5 and HNO_3 are extremely soluble in water. N_2O_5 reacts instantaneously with water forming HNO_3 . In the presence of caustics, the nitric acid is converted to nitrates. Ozone is injected into the process gas stream. The reaction zone provides uniform distribution of the ozone and adequate mixing to effect rapid reaction. The residence time in the reaction zone allows complete reaction of ozone to oxidize insoluble NO and NO_2 to highly soluble N_2O_5 . The N_2O_5 is then absorbed from the gas phase into the liquid phase by water in an aqueous scrubber. The oxidation of NO_x with ozone that creates the N_2O_5 and the subsequently produced dilute nitric acid is a similar process that occurs in the atmosphere, when smog reacts with moisture, resulting in acid rain. Scrubber systems are highly efficient in scrubbing N_2O_5 and the reaction into the liquid phase is irreversible.

The time dependency of the ozonation process was examined using the simulated exhaust gas composition. The process is studied at temperatures 300K to 500K and at atmospheric pressure. The initial OH concentration used for this process was assumed at 10^4 ppm.

Fig. 1 shows the graph of concentration of NO, NO₂ and HNO₃ with time. The concentration of NO is seen to decrease with time to produce NO₂ and within first 10s the NO₂ is seen to increase but HNO₃ is still produced slowly because of the input exhaust gases is containing NO₂ and react with OH to form HNO₃.

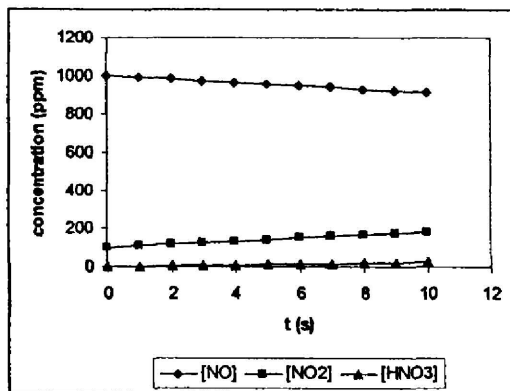


Figure 1: The conversion in the time scales of 10s

From Fig.2 it is seen that after 10s the concentration of NO is started decrease very fast. Meanwhile the NO₂ also is continued to increase and it showed that rate of NO consumption equal to rate of NO₂ production. NO₂ will be consumed with OH to form NO₃. So the HNO₃ is increasing aggressively within time period 100s.

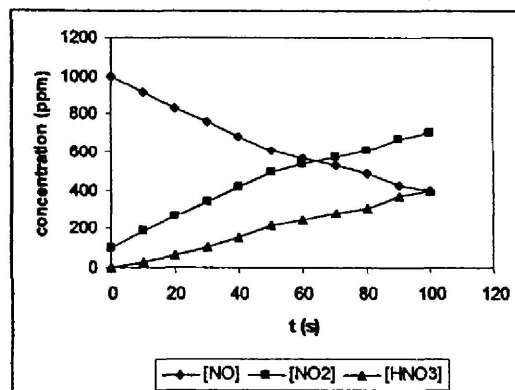


Figure 2: The conversions in the time scales of 100s

Fig.3 shows that the NO became negligible at 500s. It means that NO were completely oxidized by ozone. Hence there are no NO₂ production and NO₂ is began to be constant at approximately at 600s. The HNO₃ stop to be produced at 300s. the percentage of NO removal by ozone oxidation was 95%. It seem to be desirable but it required a large amount of ozone concentration.

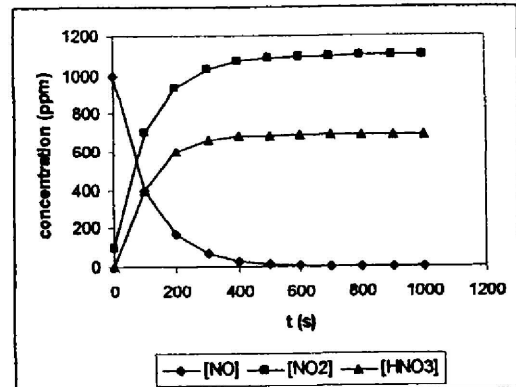


Figure 3: The conversions in the time scales of 1000s

As shown in Table 3, it determined that the removal of NO due to ozone oxidation occurs largely through the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ and $\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$. Although at high concentration of O₃ and it also determined that higher residence time do not imply higher high NO removal.

Table 3: Majority of reaction occur in the oxidizing of NO_x at 500K.

Reactions	Dominant	Normal	Slow
$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$			√
$\text{NO} + \text{OH} + \text{M} \rightarrow \text{HNO}_2 + \text{M}$		√	
$\text{HNO}_2 + \text{OH} \rightarrow \text{NO}_2 + \text{H}_2\text{O}$			√
$\text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	√		
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$			√
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	√		
$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$		√	
$\text{OH} + \text{O}_3 \rightarrow \text{HO}_2 + \text{O}_2$		√	
$\text{O} + \text{OH} \rightarrow \text{H} + \text{O}_2$			√
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$			√
$\text{OH} + \text{HO}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2$			√
$\text{O} + \text{HO}_2 \rightarrow \text{OH} + \text{O}_2$			√
$\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$		√	
$\text{H} + \text{O}_3 \rightarrow \text{HO} + \text{O}_2$			√

ACKNOWLEDGEMENTS.

ACKNOWLEDGEMENTS

The researchers wish to acknowledge:

- 1. The USM for awarding the short term grant which enabled the program of research to be carried out and make presentations at seminars leading to publications.**
- 2. The Deans and Deputy Deans of Research and Academic for their devotion and advice during the tenure and completion of this research.**
- 3. To the colleagues for all the valuable advice, support and discussions related to this research.**
- 4. To all the technical staff and office staff of the School of Chemical Engineering of the USM for their co-operation during the conduct of the research program.**