Kinetics Modeling on NOx Emissions of Gas Turbine Combustors for Syngas Applications

Haoyang Liu
Department of Energy and Power Engineering, Tsinghua University
liuhaoya16@mails.tsinghua.edu.cn
China

Wenkai Qian
Department of Energy and Power Engineering, Tsinghua University
qwk17@mails.tsinghua.edu.cn
China

Min Zhu
Department of Energy and Power Engineering, Tsinghua University
zhumin@mail.tsinghua.edu.cn
China

Suhui Li*
Department of Energy and Power Engineering, Tsinghua University
lisuhui@tsinghua.edu.cn
China

ABSTRACT

This paper presents a kinetics study on NOx emissions of syngas gas turbine with RQL (rich-burn, quick-mix, lean-burn) combustion. The RQL combustor was simulated by a chemical reactor network (CRN) model using CHEMKIN-PRO program. The kinetic mechanism used in the simulation was developed by Zhang et al. (2017), dedicated to syngas fuel. NOx emissions of RQL combustion were systematically studied under representative gas turbine operation conditions, and results show that RQL combustion significantly reduces NOx emissions. Key parameters of RQL combustor, including air flow split and residence time split between rich and lean burn zones, were varied to investigate their effects on NOx emissions. Analyses show that air flow split is the key factor determining NOx formation.

Influences of mechanisms on NOx prediction in the RQL combustor were also investigated. The GRI-Mech 3.0 mechanism was chosen for comparison. The syngas mechanism developed by Zhang et al. predicts lower overall NOx emissions when the combustor outlet temperature is 1750K, and predicts higher overall NOx emissions when the outlet temperature is 1908K. In the rich-burn zone of the RQL combustor, the syngas mechanism predicts lower NOx production at 1750K, and almost the same NOx production at 1908K compared with GRI-Mech 3.0. While in the lean-burn zone of the combustor, the syngas mechanism predicts higher NOx formation at both 1750K and 1908K. Sensitivity analyses were conducted to find major reactions that influenced the NOx prediction in each mechanisms. Results show that the dominating pathways of NOx formation are not same in each mechanism. ROPs (rates of production) of these pathways were calculated to further explain the differences in predictions of each mechanism.

INTRODUCTION

Integrated gasification combined cycle (IGCC) is a promising solution for clean coal utilization by burning the coal-derived syngas in a gas turbine. Due to flashback issues of hydrogen-rich syngas flames (Hui et al. 2007), current IGCC gas turbines usually use non-premixed combustors, which lead to higher NOx emissions than lean premixed combustors. To meet the environmental regulations, alternative combustion methods need to be considered. RQL (rich-burn, quick-mix, lean-burn) combustion offers low NOx emissions while having low risk of flashback. In RQL method, air was injected into the combustor separately, and the combustor was divided into rich-burn zone (with primary air and fuel injection), quick-mix zone, and lean-burn zone (with secondary air injection). RQL combustion can avoid the high temperature of stoichiometric flame and leads to less NOx formation (Samuelsen, 2006).

RQL is widely used in both aero gas turbine and stationary gas turbine. (Pratt & Whitney used RQL in aero gas turbine (McKinney et al. 2007); Ingenito et al. (2014) conducted a numerical study on RQL combustor of a gas turbine used in aircrafts; General Electric developed RQL combustor for F-class stationary gas turbine (Feitelberg et al. 1998); Straub et al. (2005) investigated RQL stationary gas turbines combined with trapped vortex combustor.) In studies of RQL, the fuels are usually natural gas or hydrogen. Few studies focused on syngas. RQL combustor burning syngas still needs to be investigated.

Reaction mechanisms are also important in kinetics modelling of syngas RQL combustor. Sahu et al. (2014) conducted a detailed numerical study of NOx kinetics in syngas flame. Five mechanisms were compared, showing that NOx concentration predicted by each mechanisms are not same and major pathways that influence NOx prediction in these mechanisms are different. However, Sahu’s study was focused on opposed jet diffusion flame, which is far from RQL. Influences of different mechanisms on NOx prediction in RQL combustor need to be studied. And this paper analysed the influences of two reaction mechanisms, including GRI-Mech 3.0 (Gregory et al. accessed 2017) and...
REACTOR MODEL CONFIGURATION

Figure 1 shows the schematic of the CRN model for the IGCC gas turbine combustor. The model consists of a group of ideal reactors, including perfect stirred reactor (PSR), mixer and plug flow reactor (PFR). The PSR is a zero-dimensional reactor, which assumes that all reactants are perfectly mixed after entering the reactor. The mixer is a reactor that assuming no chemical reaction happens inside. The PFR is one-dimensional and assumes no axial difference but radial resolution of species, velocity, density, and temperature, etc. The rich-burn zone is simulated by a group of PSR. The quick-mix zone is simulated by a mixer. And the lean-burn zone is simulated by a PFR. All the fuel is injected into the rich-burn zone. And for the RQL combustor, the average equivalence ratio of the rich-burn zone should be always over one.

To simulate the mixing effect of fuel and air in the rich-burn zone, the equivalence ratio $\phi$ in the rich-burn zone is assumed to follow Gaussian distribution (Li et al. 2009) shown in equation (1). $\bar{\phi}$ stands for the average equivalence ratio in the rich-burn zone and $\sigma$ stands for the standard deviation. And the mixing efficiency $\eta$ is defined as equation (2).

$$f(\phi) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left[-\frac{(\phi - \bar{\phi})^2}{2\sigma^2}\right]$$  \hspace{1cm} (1)

$$\eta = \left(1 - \frac{\sigma}{\bar{\phi}}\right)$$  \hspace{1cm} (2)

The rich burn zone is separated into 9 PSRs and the equivalence ratio of the zone ranges from ($\bar{\phi} - 2\sigma$) to ($\bar{\phi} + 2\sigma$). The primary air injected into each PSR is determined by the probability distribution of the equivalence ratio within the PSR (calculated with MATLAB software). Fuel flow rates of each PSR are calculated from the air flow rates and average equivalence ratio of the PSR. The mixture of the secondary air and the products of the rich-burn zone (PSRs) continue to react in the lean-burn zone (PFR).

The syngas used in the simulation has a composition of 25.7742% H$_2$, 56.993% CO, 15.22% N$_2$, 2.0128% CO$_2$. The preheat temperatures of both air and fuel are 600K. The pressure of the combustor is 12atm. Mixing efficiency $\eta$ is set to 90%. The total residence time of the combustor is 20ms. Combustor outlet temperature, air flow split and residence time split are varied. The air flow split ratio is defined as secondary air flow rate divided by primary air flow rate.

Simulations were produced with the CHEMKIN-PRO software package. The mechanism used in the simulations was ‘SYN-Mech’. In addition, GRI-Mech 3.0 was also used for comparison to investigate the influences of different mechanisms on NOx prediction.

RESULT AND DISCUSSION

NOx emissions of RQL combustor

Figure 2 shows the NOx emissions at different combustor outlet temperature. Under RQL condition, air flow split ratio is set to 4 (20% primary air and 80% secondary air). Residence time of PSR is set to 5ms and residence time of PFR is set to 15ms. In this paper, NOx emissions are corrected to 15% O$_2$ and dry condition if not specially mentioned. The base line is made for comparison, and has an air flow split ratio of 0 (100% primary air and 0% secondary air), and same residence time split as the RQL setting. The mechanism used in the simulation is ‘SYN-Mech’. When combustor outlet temperature is above 1670K, NOx emissions of RQL are significantly reduced compared with the base line.
Meanwhile, NOx produced in PFR changes little. Thus, NOx produced in PSR zone (rich-burn zone) has major influence. Higher outlet temperature means larger equivalence ratio of the PSR zone, as shown in Figure 4. The relationship between NOx and equivalence ratio in a single PSR is shown in Figure 5 (the pressure is 12 atm, residence time is 5 ms, and preheat temperatures of both fuel and air are 600 K, the vertical axis is logarithmic). Under rich-burn condition, higher equivalence ratio means lower NOx formation. Therefore, NOx produced in rich-burn zone decrease with combustor outlet temperature. In addition, NOx produced in PSR zone is dominating, as already shown in Figure 3. Thus, NOx emissions in RQL (Figure 2) drop with temperature. And RQL combustor significantly reduces NOx emission when combustor outlet temperature is higher than 1670 K.

Figure 3 NOx Produced in PSR and PFR

Figure 4 Equivalence Ratios of PSR Zone

Figure 6 presents the influence of air flow split on NOx emissions of RQL combustor. The vertical axis of Figure 6 is logarithmic. The residence time of rich-burn zone is 5 ms and that of lean-burn zone is 15 ms. The outlet temperatures are 1750 K and 1908 K. The overall air flowrate and fuel flowrate are fixed under each temperature. All fuel is injected into the rich-burn area. Thus, higher air flow split ratio results in higher equivalence ratio in rich-burn area. When the rich-burn zone is near the stoichiometric condition (air split ratio of 1.5), extremely high NOx emissions appear. With higher air flow split ratio, the NOx emissions decrease instantly, due to lower flame temperature in the rich-burn zone.

Figure 5 Influence of \( \Phi \) on NOx Formation in PSR

Figure 6 Influence of Air Flow Split

Figure 7 Influence of Residence Time Split

Figure 7 shows the influence of residence time split on NOx emissions of RQL combustor. The total residence time of PSR and PFR zone is set to 20 ms, and residence time of PSR zone are varied from 1 ms to 10 ms. The combustor
outlet temperature is 1750K. NOx emissions decreases with longer residence time in PSR zone (less residence time in PFR zone). The decrease comes from the less thermal NOx production in PFR due to less residence time. However, such decrease of NOx is not significant compared with NOx produced in PSR zone and produced at the beginning of PFR. Thus, very limit amount of NOx can be reduced by increasing PSR residence time at this working condition.

**Influences of mechanisms on NOx prediction**

GRI-Mech 3.0 mechanism is chosen for comparison. To investigate the differences, model with a single PSR and PFR was used, without considering the mixing effect in the rich-burn zone. Figure 8 shows the schematic of the model. Residence time of PSR is fixed to 5ms and 15ms in PFR. Air flow split is set to 20% primary air and 80% secondary air. Two cases are studied – outlet temperature at 1908K and 1750K.

![Schematic of Model for Mech. Study](image)

Figure 8 Schematic of Model for Mech. Study

`Figure 9 NOx prediction in PFR`  
![](image)

Figure 9 shows NOx concentration in the PFR, when the outlet temperature is 1908K. Mechanisms have almost the same prediction of NOx at the very begin of the PFR at 1.64ppm. While at PFR outlet (residence time of 15ms), the predictions are different. ‘SYN-Mech’ predicts 14.8ppm, while GRI-Mech 3.0 shows 11.9ppm.

Figure 10 gives a closer look of NOx concentration at the beginning of the PFR. Both mechanisms predict a sharp increase of NOx in less than 1ms and then a linear increase at different rates. ‘SYN-Mech’ predicts both the sudden increase and the linear-increase rate higher than GRI-Mech 3.0.

Temperature, major reactions that influence NOx production and concentration of reactants are investigated to explain the differences between predictions of each mechanism. Since predictions at PFR inlet is almost same, the investigation is focused on the PFR. Figure 11 shows the change of temperature with residence time in PFR. Temperatures predicted by both mechanisms increase sharply at the beginning of PFR, and stay constant at 1908K after the initial time. Predictions of temperature are almost same of both mechanisms.

![Temperature in PFR, 1908K Outlet](image)

Figure 11 Temperature in PFR, 1908K Outlet

Considering the large amount of elementary reactions that these two mechanisms contains, major reactions that influence NOx formation need to be found to enable further investigate on concentration of reactants. Sensitivity analyses were conducted to find these major reactions, using the CHEMKIN-PRO software package. Figure 12 shows NO sensitivity on pre-exponential factor “A” of the reaction rate constant of elementary reactions, and the most sensitive 4 of each mechanisms were selected on the figure.

These reactions happen to match three pathways of the NO formation (Correa, 1993) (Li et al. 2009) (Sahu et al. 2014).

Zeldovich (thermal) pathway:

\[
N + NO = N_2 + O
\]  
(3)

\[
N_2O + O = 2NO
\]  
(4)

\[
NH + NO = N_2O + H
\]  
(5)
NNH pathway:

\[ \text{NNH} + O = \text{NH} + \text{NO} \]  

Figure 12 NO Sensitivity in PFR, 1908K

Figure 13 gives a closer look of NO sensitivity at the beginning of the PFR. NO sensitivities of all these pathways increase sharply, at the beginning. After the initial increase, both mechanisms predict that NO sensitivity of N\(_2\)O pathway and NNH pathway decrease, and NO sensitivity of thermal pathway increases. The most sensitive pathway initially is N\(_2\)O pathway in both mechanisms. NNH pathway is the least sensitive among major pathways in ‘SYN-Mech’, yet in GRI-Mech 3.0 it is much more sensitive at the beginning. NO sensitivity of NNH pathway and N\(_2\)O pathway reduce with residence time, while sensitivity of thermal pathway continually increases. Within 0.75ms, NNH pathway and N\(_2\)O pathway have the largest influence. When residence time increases, thermal pathway becomes the dominating one.

Figure 14 and 15 shows the concentration of reactants of the major pathways in PFR. The results are NOT corrected to 15%\(O_2\) and dry condition. The vertical axis of Figure 14 is logarithmic. All the reactant drops to low concentration after entering PFR, followed by a peak, then fall back to constant values. For O, N\(_2\)O and H, the constant values are same in both mechanism, and ‘SYN-Mech’ predicts higher peak (shown in Figure 14). For NNH, GRI-Mech predicts higher peak, and the constant value are not same, 8.3E-6ppm in ‘SYN-Mech’ and 1.3E-5ppm in GRI-Mech 3.0 (shown in Figure 15).

To further investigate the contribution to NO formation of each pathway, rate of production (ROP) has been calculated. Figure 16 and Figure 17 present ROP with residence time lower than 1ms, matching the temperature increasing range. In the sharp temperature-increase zone inside PFR, both mechanism consider N\(_2\)O pathway having the highest ROP of NO. NNH pathway is considered more important in GRI-Mech 3.0 than in ‘SYN-Mech’. ROP of N\(_2\)O pathway of ‘SYN-Mech’ is much higher than in GRI-Mech 3.0. Thus, ‘SYN-Mech’ predicts higher NO concentration at the beginning of PFR.

Figure 18 shows ROP after 1ms in PFR. ROP of each pathway is almost constant due to the constant temperature
and concentration of reactants. Thermal pathway dominates in both mechanisms, followed by N$_2$O pathway. ‘SYN-Mech’ predicts a higher ROP of thermal pathway, and a lower ROP of N$_2$O pathway, compared with GRI-Mech 3.0. The total ROP of these major pathways is higher in ‘SYN-Mech’. Therefore, ‘SYN-Mech’ predicts a higher increasing rate of NO when the temperature becomes constant.

Figure 16 ROP within 1ms of GRI-Mech 3.0, 1908K

![Figure 16](image)

**Figure 16 ROP within 1ms of GRI-Mech 3.0, 1908K**

Figure 17 ROP within 1ms of ‘SYN-Mech’, 1908K.

![Figure 17](image)

**Figure 17 ROP within 1ms of ‘SYN-Mech’, 1908K.**

Combining Figure 16 to 18, both higher prediction of NO within sharp temperature-increase zone and constant temperature zone contribute to the higher NOx prediction of ‘SYN-Mech’ when outlet temperature is 1908K.

The 1750K case is another story, in which mechanisms have different predictions in both PSR (PFR inlet) and PFR, as shown in Figure 19. Figure 19a) is corrected to 15% O$_2$ and dry condition while Figure 19b) is corrected to ONLY dry condition. ‘SYN-Mech’ predicts lower overall NOx emission, different from the 1908K case. In in Figure 19a), the NOx drop at PFR beginning is caused by the 15% O$_2$ correction, as O$_2$ concentration changes rapidly when O$_2$ reacts with extra fuel from PSR zone at the beginning. Figure 19b) shows that both mechanisms predict a sharp NOx increase at the beginning of PFR followed by a linear increase. ‘SYN-Mech’ predicts both higher initial increase and linear-increase speed, but a lower NOx concentration at PFR inlet. To explain these, sensitivity analyses have been conducted concerning both PSR and PFR, and major reactions contributed to NO production have been selected. ROP of these reactions are then calculated.

Figure 19 NOx prediction in PFR, 1750K

**Figure 19 NOx prediction in PFR, 1750K**

Corrected to a) 15% O$_2$, Dry; b) Dry

![Figure 19](image)

**Figure 19 NOx prediction in PFR, 1750K**

Figure 20 shows the most sensitive reactions in PSR. The major ones are thermal pathway, N$_2$O pathway and NNH pathway. In the prediction of ‘SYN-Mech’, thermal pathway dominates. However, in prediction of GRI-Mech 3.0, NNH pathway dominates. ROP of these major reactions is shown in Figure 21. Both mechanisms predict similar ROPs of

Figure 20 NO Sensitivity in PSR, 1750K

**Figure 20 NO Sensitivity in PSR, 1750K**

![Figure 20](image)

**Figure 20 NO Sensitivity in PSR, 1750K**
thermal pathway and N\textsubscript{2}O pathway. But GRI-Mech 3.0 predicts a much higher ROP of NNH pathway. The total ROP predicted by GRI-Mech 3.0 is higher, leading to higher NO\textsubscript{x} concentration in PSR.

Figure 21 ROP in PSR, 1750K

Figure 22 shows the most sensitive reactions in PFR. The N\textsubscript{2}O pathway is dominating, and ‘SYN-Mech’ predicts higher NO sensitivity on N\textsubscript{2}O pathway, compared with GRI-Mech 3.0.

Figure 22 NO Sensitivity in PFR, 1750K

CONCLUSIONS

Chemical reactor network (CRN) model is used to investigate NO\textsubscript{x} emission in RQL combustor. With fixed air flow split, RQL combustor significantly reduces NO\textsubscript{x} emissions at high temperature. Influences of air flow split and residence time split are also investigated, with fixed outlet temperature. The air flow split is the key parameter - NO\textsubscript{x} emissions drop significantly when less primary air is injected to rich-burn zone.

Influences of reaction mechanisms on NO\textsubscript{x} prediction are studied:

(1) In the 1908K case, ‘SYN-Mech’ predicts 24% higher overall NO\textsubscript{x} emissions compared with GRI-Mech 3.0. ‘SYN-Mech’ predicts similar NO\textsubscript{x} production in PSR and higher NO\textsubscript{x} production in PFR. In PFR, ‘SYN-Mech’ predicts higher ROP of N\textsubscript{2}O pathway at the beginning and then higher ROP of thermal pathway after temperature reached the constant 1908K, compared with GRI-Mech 3.0.

(2) In the 1750K case, ‘SYN-Mech’ predicts 4% lower overall NO\textsubscript{x} emissions compared with GRI-Mech 3.0.
‘SYN-Mech’ predicts lower NOx production in PSR and higher NOx production in PFR. In PSR, both mechanisms predict similar ROPs of thermal and N2O pathway. However, ‘SYN-Mech’ predicts much lower ROP of NNH pathway, leading to lower NOx prediction in PSR. Situation in PFR is same with the 1908K case.

**NOMENCLATURE**

ϕ  equivalence ratio  
σ  standard deviation  
η  mixing efficiency  
A  pre-exponential factor of the reaction rate constant

**ABBREVIATION**

CRN chemical reactor network  
IGCC integrated gasification combined cycle  
PFR plug flow reactor  
PSR perfect stirred reactor  
ROP rate of production  
RQL rich burn quick mix lean burn

**ACKNOWLEDGMENTS**

The authors thank the financial support of NSFC (Grant #51776105) and the Thousand Young Talents project of China.

**REFERENCES**


Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song, William C. Gardiner, Jr., Vitali V. Lissianski, and Zhiwei Qin [http://www.me.berkeley.edu/gri_mech/], accessed 2017


