Effects of water on pyridine pyrolysis: A reactive force field molecular dynamics study

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A B S T R A C T

The emission of nitrogen oxides (NOx) from coal combustion causes serious environmental problems. Fuel splitting and staging is a promising method for NOx control by combustion modification. In this process, nitrogen-containing compounds generated from pyrolysis gas play an important role in regulating NOx generation. Water from coal could potentially change reactions during the coal pyrolysis process. Adjusting the content of water in coal may be an effective way to control coal pyrolysis reactions. This work aims to investigate the effects of water on pyridine (a main nitrogen-containing compound in coal) pyrolysis via reactive force field (ReaxFF) molecular dynamics (MD) simulations. Results indicate that the addition of water during the pyridine pyrolysis process increases the number of OH radicals in the system and accelerates the consumption of pyridine at the initial stage. However, at a later stage, water inhibits the consumption of pyridine as it impedes the condensation reaction of pyridine molecules. Common and unique intermediates are identified and quantified under various water-content conditions. Results suggest that water also reduces the proportion of nitrogen atoms in the polycondensation product. Furthermore, ring opening processes of pyridine molecules are reproduced at the atomic level. The changes in reaction pathways due to the presence of water are also revealed. The new insights into the mechanisms of pyridine pyrolysis under water and water-free conditions provide a possibility to control nitrogen migration during the pyrolysis process, which is of great significance to emission reduction from coal combustion.

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Credit author statement

ZB performed the research, analysed data and wrote the manuscript draft. XZJ co-supervised the research and revised the manuscript. KHL supervised the project and finalised the manuscript.

1. Introduction

The emission of nitrogen oxides (NOx) from coal combustion causes serious environmental problems, such as photochemical smog and acid rain [1]. In recent years, a variety of technologies have been developed for coal combustion to control NOx emissions. Fuel staging or reburning is a promising method for NOx control by combustion modification. The idea of fuel reburning is to recycle the NOx formed to nitrogen during combustion. The reburning reactor includes three zones [2]: a main reaction zone, where coal combustion under fuel-lean conditions takes place and NOx is generated, a reburning zone, where reburn fuel is injected and reacts with NOx forming N2, a burnout zone, where air is added to ensure complete combustion of fuel.

Reburning fuels play a key role in NOx reduction during coal combustion. They can be divided into two categories: fossil fuels (such as natural gas, coal and oil) and pyrolysis gas. It is reported that pyrolysis gas has better performance in NOx reduction than fossil fuels [3–5]. In a fuel staging (also termed fuel splitting and staging) process, coal is decomposed to pyrolysis gas and char. Char and pyrolysis gas are primary fuel and reburning fuel respectively. Previous studies [3–5] have identified that the nitrogen-containing compounds in pyrolysis gas is important for effective NOx reduction in the fuel splitting and staging process. Water, an intrinsic component in coal, can accelerate coal pyrolysis process and greatly
alter products distribution in pyrolysis gas [6]. Therefore, adjusting the content of water in coal could be an effective way to control the N migration during coal pyrolysis, which has the potential to improve the NOx control performance during coal combustion.

Previous studies have explored chemical effects of water during coal pyrolysis by experiments and simulations. Ouyang and co-workers carried out experiments focusing on the effects of H$_2$O during char pyrolysis [7]. They proposed that H$_2$O reduced the char generation, stabilized the char structure and increased the char reaction rate. Hu and co-workers investigated the effects of H$_2$O on the pyrolysis of coal [8]. Results showed that the yield of tar increased with water content increasing during the coal pyrolysis. Liu and co-workers interrogated pyrolysis with water using a density functional theory method [9]. The computational research suggested that H$_2$O molecules inhibited the formation HCN but promoted the generation of NH$_3$. Gou and co-workers explored the effects of water vapor on the pyrolysis products of coal [6]. They found that water promoted the generation of HCN, NH$_3$, H$_2$ and CO, which can restrain the NOx formation during coal combustion [6]. Previous studies have made great contributions to understanding the pyrolysis phenomena from a wide range of perspectives, like the composition of products and reaction rate. However, there are some fundamental questions remaining unanswered. For example, the effects of water on the mechanisms of nitrogen-containing compounds pyrolysis in coal are still poorly understood. Further efforts are required to explore the atomic/molecular events therein and reveal the reaction mechanisms.

The current experimental techniques are unable to accurately detect the temporal evolution of the distributions of intermediates and products. Atomistic-scale computational techniques, like reactive molecular dynamics that can capture atomistic behaviors of constitutive atoms/molecules [10], lend the possibility to reveal the detailed reaction mechanisms and obtain intermediate structures [11,12] that cannot be obtained by current measurement methods. Among the existing atomistic methods, the ReaxFF MD is a promising method to simulate complex chemical reactions with reasonable computational cost and high accuracy. Recently, ReaxFF MD simulations have been applied to pyrolysis of coal [13–19] and chemical reactions of nitrogen-containing compounds [20,21]. However, due to the complexity and uncertainty of coal molecular structures, low content of nitrogen, and the influence of other radicals or functional groups [22], it is difficult to build a complete coal molecular model to investigate nitrogen properties during coal pyrolysis. Alternatively, nitrogen-containing compounds in coal such as pyridine [23,24] are used as a surrogate for coal.

In this study, a series of ReaxFF MD simulations are conducted to investigate the effects of water on pyridine pyrolysis. Firstly, effects of water on the pyridine pyrolysis rate and intermediates are studied. Secondly, ring-opening reactions and proportion of polycarbonation products are explored during pyrolysis. Finally, reaction mechanisms of principal products like H$_2$, CO, HCN and NH$_3$ are compared between conditions with and without water addition.

2. Methods

2.1. ReaxFF MD

The ReaxFF is a force field MD method that lies in between quantum chemical simulation and classical molecular dynamics simulation, which was originally developed by van Duin and co-workers [25] to study the kinetics of chemical reactions. ReaxFF employs a bond-order formalism in conjunction with polarizable charge descriptions to determine both reactive and non-reactive interactions between atoms [26]. Energy contributions to the ReaxFF potential are shown in Equation (1):

$$E_{\text{System}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{angle}} + E_{\text{tors}} + E_{\text{vdWaals}} + E_{\text{Coulomb}} + E_{\text{Specific}}$$

where the terms are total energy, bond energy, penalty energy, valence angle energy, torsion angle energy, van der Waals energy, Coulomb energy and specific energy, respectively. Further details of ReaxFF are shown in Ref. [26].

2.2. Case set-ups

The initial parameters of the simulated systems are shown in Table 1. In each case, the computational domain is a periodic box. System 1 contains 20 pyridine molecules only. In systems 2 to 8, there are 20–500H$_2$O molecules added to investigate the effects of water on pyridine pyrolysis. Fig. 1 shows the model configurations for pyridine pyrolysis without and with water. $z$ is the ratio of the number of water molecules, n (H$_2$O), to the number of pyridine molecules, n (C$_7$H$_5$N), as shown in Equation (2). The density of each system is kept the same at 0.3 g/cm$^3$ by varying the size of the computational box.

$$z = \frac{n(H_2O)}{n(C_7H_5N)}$$

2.3. Simulation details

In this paper, the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) was used to carry out ReaxFF MD simulations of pyridine pyrolysis. The reactive force field of the C/H/O/N system was chosen, whose parameters are trained with quantum chemistry calculations and have been carefully validated [27,28]. The time step was 0.1 fs and the bond order cutoff value was 0.3. The NVT ensemble [29] was selected for all simulations. Due to excessive computational cost, MD typically adopts higher temperatures than in the experiments in order to accelerate simulations. This approach has been verified to reproduce reaction mechanisms observed in experiments [30–32].

Before “production” simulations, energy minimization and system equilibration were carried out. The temperature was kept constant at 1000 K for 50 ps After that, the temperature of each system is increased to a final temperature of 3000 K with a heating rate of 100 K/ps and then kept constant. The total simulation time is 1000 ps Three replicates with different initial positions of reactants were simulated for every case. The simulation was complemented via REAXC package on the platform of Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).

2.4. Post-processing

The reaction pathways are obtained by Chemical Trajectory Analyzer (ChemTraYzer) scripts [33]. The dynamic trajectories were visualised using VMD [34]. Unless otherwise indicated, the data used in the figures of this study are the average results of the three replicate simulations. Error bars in all figures are Standard Error (SE) of three replicates.
3. Results and discussions

3.1. Validation of simulations

The validation of the ReaxFF MD simulations is achieved by comparing intermediate products obtained from this study with those from previous studies. The key intermediate species are HCN, CN, NH3, H2 and C2H2, which agrees with previous work [30].

The mechanisms of pyridine pyrolysis and chemical effects of water during pyridine pyrolysis are analyzed in the following sections.

3.2. Effects of water on pyridine consumption rate

Fig. 2a and b shows the time evolutions of C5H5N with $\alpha$ value ranging from 0 to 25 at 3000 K. At the initial stage up to 600 ps, at least 90% of C5H5N molecules are consumed in all cases. To study the water influence on consumption rate of pyridine, the consumption number of pyridine at different stages was calculated as shown in Fig. 2c. It is clear that water promotes pyridine consumption rate during the first 200 ps. A similar phenomenon was also observed in previous studies that water can promote reactions during ethanol and methane oxidation and pyrolysis char [7,31,35].

Under water-free conditions, pyridine molecules are consumed by reactions:

\[
\begin{align*}
C_5H_5N + H &\rightarrow C_5H_4N \quad \text{(R1)} \\
C_5H_5N &\rightarrow C_5H_4N + H \quad \text{(R2)} \\
C_5H_5N + H &\rightarrow C_5H_4N + H_2 \quad \text{(R3)}
\end{align*}
\]

However, OH radicals are generated with water addition during pyridine pyrolysis by reactions:

\[
\begin{align*}
H_2O &\rightarrow OH + H \quad \text{(R4)} \\
H_2O + H &\rightarrow OH + H_2 \quad \text{(R5)}
\end{align*}
\]

And new reactions are found during pyridine pyrolysis with water as follows:

\[
\begin{align*}
C_5H_5N + OH &\rightarrow H_2O + C_5H_4N \quad \text{(R6)} \\
C_5H_5N + OH &\rightarrow C_5H_6NO \quad \text{(R7)}
\end{align*}
\]

The addition of water during the pyridine pyrolysis process brings OH radicals in the system and accelerates the consumption of pyridine. More details about the effects of water on intermediates are shown in Table 2, which will be discussed in Section 3.3. However, as the pyrolysis goes on, water presents obvious inhibitory effects on the consumption of pyridine. To explain this phenomenon, we investigated the effects of water on poly-condensation compounds in Section 3.4.

3.3. Effects of water on intermediates

Fig. 3a and b describe time evolution of the total species number for $\alpha$ ranging from 0 to 25. In general, the species number during pyrolysis increases to a peak value and then decreases in both cases. And the species number in this case with water is significantly higher than that without water during pyridine pyrolysis. This implies H2O molecules take part in various intermediate reactions.

Table 1
Initial parameters of the simulated systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Number of C5H5N molecules</th>
<th>Number of H2O molecules</th>
<th>$\alpha$</th>
<th>Density (g/cm^3)</th>
<th>Box size(Å)</th>
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<td>20</td>
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</tbody>
</table>

Fig. 1. Initial configurations for pyridine pyrolysis. (a) $\alpha = 0$ (b) $\alpha = 1$. 
and generate additional intermediates during the pyrolysis process. This result is also confirmed by results in Section 3.2 that water molecules produce OH radicals during pyridine pyrolysis, which promote the consumption of pyridine. Besides, when the value of $\alpha$ is higher than 5, the number of species in the system remains more or less the same even with $\alpha$ increasing.

To further clarify the influence of water molecules on intermediates during pyridine pyrolysis, the intermediates are compared among cases under water-free and water conditions as shown in Table 2. H2, NH3, CN, HCN, C4H2, C4H3 and C4H4 are shared among all cases. CO, CHNO, CH2NO, C2H2O and C2H3O are found in cases with water addition. CNO, CHO, CHO2 and C2HO2 are observed for $\alpha$ over 2. CO2 is produced in $\alpha = 4$ cases. C4H3O is spotted in cases with $\alpha = 5$. C3H4O and C4H4O are detected when $\alpha$ is 10 or 25. C2O2 occurs in $\alpha = 3, 4, 5$ and 25 cases. C3H2O and C3H3O are found in $\alpha = 4, 5, 25$ and $\alpha = 5, 25$ cases, respectively.

### 3.4. Effects of water on polycondensation compounds

During coal pyrolysis, there are both decomposition and polycondensation reactions. The pyrolysis products are char (C40), tar (C5–C40) and gas (C0–C5) in descending order according to the number of C atoms [13]. In this part, water influence on decomposition and polycondensation reactions is explored during pyridine pyrolysis.

Fig. 4a–c presents the proportion of C, N and H elements in C5 during pyridine pyrolysis. With the increase of water molecules in system, the percentages of C, N and H in C5 decrease greatly. When $\alpha$ is 25, few C5 compounds are formed during pyridine pyrolysis. This phenomenon is in agreement with previous experimental studies [7,8]. Results show that water molecules greatly inhibit polycondensation reactions and modify pathways to char, tar and gas, which is of great significance to control nitrogen migration during coal pyrolysis. In addition, according to the products analysis of pyridine in the water-free condition, the polycondensation reaction mainly occurs after 200 ps. This provides an explanation for the finding in Section 3.2 that water exerts obvious inhibitory effects on the consumption of pyridine after 200 ps. Fig. 4d shows snapshots of C5 with the increasing $\alpha$. As the value of $\alpha$ ranges from 0 to 10, the number of C atoms contained in the polycondensation product is significantly reduced (from C21 to
3.5. Effects of water on ring-opening reactions

According to previous studies [8,9], pyridine molecules undergo ring opening reactions firstly during pyrolysis. Fig. 5a illustrates snapshots of ring-opening reactions during pyridine pyrolysis at all cases. Four types of ring-opening pathways were detected by MD during pyridine pyrolysis. Type A happens when o-C5H5N reacts with H atom forming o-C5H4N firstly. Then o-C5H4N opens the ring to form a chain C5H6N. Type B occurs when C5H2N directly opens the ring to generate chain C5H3N. Type C is the case when pyridine molecules lose an H atom and then undergoes a ring-opening reaction, which is in agreement with previous studies [31,36–38]. Type D occurs when C5H2N reacts with OH radicals in the system to form an oxygen-containing intermediate and then ring-opening reaction occurs. As it happens, the H atom on the C atom adjacent to N atom is transferred to the N in all types. After that, chain intermediates (C5) are pyrolyzed and HCN, CN, C4H4 and C4H3 are generated. The effects of water on key species will be discussed in detail in Section 3.6.

Fig. 5b shows the proportion of each type under different α values. As the content of water molecules in the system increases, the proportion of pyridine molecules to open rings through type A and type B decreases. Besides, the percentage of type C increases to the peak point at α = 10 and then decreases with increasing value of α. Ring-opening reactions of type D only occurs when the water content in the system is high. In pyridine pyrolysis without water addition, pyridine molecules convert to C5H2N and C5H4N through R1 to R3. The water addition brings about OH radical by reactions R4 and R5. And the OH radical promotes the generation of C5H4N by R6. Thus, water suppresses the ring-opening reactions via type A and type B and promotes type C of ring-opening reactions. However, when the value of α increases to 4, there are pathways to generate oxygen-containing intermediates (C5H6NO, C5H5NO, C5H4NO and C5H3NO). Those are:

\[
\begin{align*}
C_5H_2N + OH & \rightarrow C_5H_4NO \quad (R7) \\
C_5H_2N + H_2O & \rightarrow C_5H_4NO + H \quad (R8) \\
C_5H_2N + H_2O & \rightarrow C_5H_3NO + H \quad (R9) \\
C_5H_4NO + HO & \rightarrow C_5H_3NO + H_2O + C_4H_4NO \quad (R10) \\
C_5H_4NO & \rightarrow C_5H_3NO + H \quad (R11)
\end{align*}
\]

Results indicate that H2O accelerates the consumption of C5H4N and promotes the production of oxygen-containing intermediates. That is the reason why high concentration of water has an inhibitory effect on type C and type D only occurs in systems with high water concentration.

3.6. Effects of water on products H2, CO, HCN and NH3

Pyridine molecules undergo ring-opening reactions and then pyrolyze to produce the main intermediates HCN, CN, C4H4 and C4H3, which is in agreement with previous results [31,36–38]. In this part, we explore the effects of water on those radicals as well as principal products H2, CO and NH3 during pyridine pyrolysis.

Fig. 6 presents the effects of H2O on the generation of H2, CO, HCN and NH3. As the number of H2O molecules increases, the yield of H2, CO and NH3 shows an upward trend, which is in good agreement with a previous study in Ref. [6]. However, water influence on HCN is more complicated. When the value of α is in the range of 0–3, the yield of HCN remains the same. As α increases, a parabolic profile is observed which peaks at α = 10. According to the findings in Section 3.4, water reduces the content of C, H and N in C5+, which accounts for the increasing trend of H2, CO and NH3. To understand the trend of HCN, the influence of water on transfer pathways of main intermediates was interrogated as shown in Fig. 7a and b.

In pyridine pyrolysis under water-free conditions, H2 mainly comes from H in the pyrolysis process, that is

\[
H + H \rightarrow H_2 \quad (R14)
\]

Water during the pyrolysis process adds a new pathway to H2 by R5. Fig. 6a describes effects of H2O on transfer pathways of nitrogen-containing intermediates. As pyrolysis goes on, HCN and CN will convert to NH3 in all cases [30]. And the transfer pathway is HCN → CNH → NH → NH2 → NH3 [39]. However, due to the conversion of HCN and CN to N2 occurring at high temperatures [30], N2 is not observed in our simulations. New pathways HCN →
CH$_2$NO and CH$_2$NO → CHNO are generated with water addition during pyridine pyrolysis by reactions:

\[
\text{HCN} + \text{OH} \rightarrow \text{CH}_2\text{NO} \quad \text{(R15)}
\]

\[
\text{CH}_2\text{NO} \rightarrow \text{CHNO} + \text{H} \quad \text{(R16)}
\]

When \( \alpha \) is greater than 2, R17 to R20 are found during the pyrolysis process as shown below:

\[
\text{CN} + \text{OH} \rightarrow \text{CHNO} \quad \text{(R17)}
\]

\[
\text{CN} + \text{H}_2\text{O} \rightarrow \text{CHNO} + \text{H} \quad \text{(R18)}
\]

\[
\text{CHNO} \rightarrow \text{CNO} + \text{H} \quad \text{(R19)}
\]

\[
\text{CH}_2\text{NO} \rightarrow \text{NH}_2 + \text{CO} \quad \text{(R20)}
\]

Besides, R21 takes place in the range of \( \alpha = 4-25 \) as follows:

\[
\text{CHNO} \rightarrow \text{CO} + \text{NH} \quad \text{(R21)}
\]

Combining the findings from Fig. 6c and d, it is clear that the influence of OH radicals on HCN dominates when the value of \( \alpha \) is 0, 1 and 25. Thus, water shows an inhibitory effect on the yield of HCN in those cases. And due to the promotional effects on pyridine pyrolysis, water enhances HCN production over \( \alpha = 2-10 \). Besides, OH radicals add new pathways of NH and NH$_2$, which are important precursors to NH$_3$. H$_2$O also enhances the conversion of NH$_2$ to NH$_3$ via reaction:

\[
\text{H}_2\text{O} + \text{NH}_2 \rightarrow \text{NH}_3 + \text{HO} \quad \text{(R22)}
\]

Therefore, the yield of NH$_3$ is promoted with water addition during pyridine pyrolysis.

Fig. 7b describes water influence on migration pathways of main nitrogen-free intermediates during pyridine pyrolysis. In all cases, C$_4$H$_4$ and C$_4$H$_3$ were major initial nitrogen-free species during pyridine pyrolysis [30]. And C$_2$H$_2$ and C$_2$H are mainly produced by thermal decomposition of C$_4$H$_4$ and C$_4$H$_3$. C$_2$H$_2$ is formed by the loss of one H atom from C$_4$H$_3$. In pyridine pyrolysis with water addition, OH reacts with main intermediates (C$_4$H$_3$, C$_4$H$_2$, C$_2$H$_2$ and C$_2$H) to form CO. However, there are huge differences in transfer pathways to generating CO at various \( \alpha \) values. When the H$_2$O content in the system is low (the value of \( \alpha \) in the range 1–4), OH radicals mainly react with C$_2$ compounds to generate oxygen-containing intermediates by reactions:

\[
\text{C}_2\text{H} + \text{OH} \rightarrow \text{C}_2\text{H}_2\text{O} \quad \text{(R23)}
\]

\[
\text{C}_2\text{H}_2 + \text{OH} \rightarrow \text{C}_2\text{H}_3\text{O} \quad \text{(R24)}
\]

And C$_2$H$_2$O, C$_2$H$_3$O and CHO are key precursors forming CO for \( \alpha \) ranging from 1 to 4. When the range of \( \alpha \) is 2–25, CO will convert to CHO$_2$ through R25:

\[
\text{CO} + \text{OH} \rightarrow \text{CHO}_2 \quad \text{(R25)}
\]
And CO₂ is generated by decomposition of CHO₂ through R26 with \( \alpha = 4\text{--}25 \).

\[
\text{CHO}_2 \rightarrow \text{CO}_2 + \text{H} \quad \text{(R26)}
\]

When the value of \( \alpha \) is 5--25, OH radicals will react with C₃&C₄ compounds via reactions:

\[
\begin{align*}
\text{C}_3\text{H}_3 + \text{OH} & \rightarrow \text{C}_3\text{H}_4\text{O} \quad \text{(R27)} \\
\text{C}_4\text{H}_2 + \text{OH} & \rightarrow \text{C}_4\text{H}_3\text{O} \quad \text{(R28)} \\
\text{C}_4\text{H}_3 + \text{OH} & \rightarrow \text{C}_4\text{H}_4\text{O} \quad \text{(R29)}
\end{align*}
\]

And C₄H₂O, C₃H₂O, C₃H₂O, C₂H₂O and C₂O₂ are key intermediates to form CO. In addition, the pathway HCN \( \rightarrow \text{CH}_2\text{NO} \rightarrow \text{CO} \) is broadly shared in water addition cases.

4. Discussion

In the present study, ReaxFF MD simulations were conducted to understand the influence of water on nitrogen-containing compounds (pyridine) in coal pyrolysis. We have uncovered new intermediates and reaction pathways that were not reported in previous studies [6,9]. Besides, the effects of water molecules on the consumption rate of pyridine and ring opening processes of pyridine molecules are also revealed at the atomic level. Based on the aforementioned analysis, we have demonstrated that the modification of pyrolysis by water addition can be applied to improve NOx control performance in the fuel splitting and staging process.

In the fuel splitting and staging process, the released nitrogen-containing species from large N-containing compounds are beneficial for NOx reduction as it can reduce nitrogen oxides selectively [4,5,40]. However, Greul et al. also proposed that small N-

![Fig. 5. Schematic diagram of pyridine ring-opening reactions and the influence of \( \alpha \) on the types of ring-opening reactions. (a) Snapshots of four different types of pyridine ring-opening. (b) Percentages of each type under varying \( \alpha \).]
containing species in pyrolysis gas will react with O\(_2\) to form NO\(_x\), causing negative impact on NO\(_x\) control [40]. Hence, controlling the proportion of large N-containing compounds in the pyrolysis gas and the pyrolysis process of N-containing compounds is important to reduce NO\(_x\) emissions. The current results suggest that the addition of water molecules would modify the reaction pathways in the pyrolysis process of N-containing compounds, thus achieving maximum NO\(_x\) reduction.

Though nitrogen-containing compounds show better NO\(_x\) reduction performance than nitrogen-free compounds, nitrogen-free radicals can also convert NO\(_x\) to N\(_2\). According to previous studies [41,42], the possibility of non-hydrocarbon fuels, such as H\(_2\) and CO, to reduce NO to N\(_2\) is low compared with the hydrocarbon radicals in the reburning process. According to the present research, the addition of water can promote conversion of hydrocarbon compounds to small C-containing radicals, which is beneficial for NO\(_x\) control. On the other hand, high water concentration will convert hydrocarbon compounds into CO, CO\(_2\) and H\(_2\), alleviating NO\(_x\) reduction in the reburning process. Thus, a proper water content in the process of reburning is required if water is used to regulate NO generation.

In general, the regulating effects of water on pyridine pyrolysis is monotonic. This behaviour is beneficial for control of the pyrolysis process. However, there are also non-monotonic behaviors with respect to water content in intermediate species (C\(_2\)O\(_2\), C\(_3\)H\(_2\)O and C\(_3\)H\(_3\)O) and consumption rates of pyridine pyrolysis. For intermediate species C\(_2\)O\(_2\), C\(_3\)H\(_2\)O and C\(_3\)H\(_3\)O, when the value of \(\alpha\) is lower than 10, the process is controlled by the condensation reaction of species (CO reacts with CO, C\(_2\)H\(_2\) and C\(_3\)H\(_3\), respectively). It is found that the yields of C\(_2\)O\(_2\), C\(_3\)H\(_2\)O and C\(_3\)H\(_3\)O are low, and their roles in the conversion of NO\(_x\) to N\(_2\) are insignificant [41,42]. Thus, their effects on NO\(_x\) control can be neglected. The non-monotonic relationship between water content and pyridine consumption rates suggest that different strategies for NO\(_x\) control are required as the reaction evolves at different stages.

5. Conclusions

In this study, pyridine pyrolysis without and with water were investigated via ReaxFF-MD simulations. The effects of the added water with different proportions on pyridine pyrolysis reactions were investigated in detail. It is found that the addition of water during the pyridine pyrolysis process facilitates the generation of OH radicals and accelerates the consumption of pyridine at the initial stage of pyrolysis. By contrasts, as water greatly inhibits the condensation reaction of pyridine molecules, water exerts inhibitory effects on the consumption of pyridine as pyrolysis goes on. Furthermore, water has significant influence on the total number of species during the pyridine pyrolysis and intermediates are identified and quantified under various conditions. In addition, water also reduces the N content in the polycondensation product (C\(_5^+\)). This research provides new insights into atomic-level mechanisms...
of pyridine pyrolysis under water and water-free conditions, and has implications on control of N migration during the pyrolysis process and the emission of nitrogenous pollutants from coal pyrolysis and combustion.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Fig. 7. Effects of H2O on transfer pathways. (a) nitrogen-containing, (b) nitrogen-free intermediates. The numerical values in the figure are values of $a$. The species in the yellow box are the starting intermediates. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

References

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