



Mechanism of HCN formation from NO reduction by biomass-char in CO₂/H₂O atmosphere for oxy-fuel combustion – A combined experimental and DFT study

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ABSTRACT

The mechanism of HCN formation during NO reduction by biomass-char was studied through experiments and density functional theory (DFT) calculations. Experiments in CO₂/H₂O atmospheres showed that H₂O significantly increased HCN production, while CO₂ had minimal impact. H₂O created a “hydrogen-rich” environment essential for HCN formation, and higher temperatures and NO concentrations further promoted HCN production. In this “hydrogen-rich” atmosphere, NO concentration was the dominant factor. DFT calculations show that the HCN formation process involved several steps: adsorption of NO, H radicals, and OH radicals on the char surface; migration of H atoms in C(OH) and C(H); and the ring-opening of a six-membered structure to form a five-membered ring and HCN. The reduction of NO to HCN over char is more favored in an H₂O atmosphere than the conversion of char-N to HCN.

1. Introduction

Oxy-fuel circulating fluidized bed combustion (Oxy-CFBC) technology is a carbon capture, utilization, and storage (CCUS) method used in circulating fluidized bed (CFB) boilers for CO₂ capture during combustion (Stanger et al., 2015). Extensive experimental research on Oxy-CFBC technology has been conducted at both pilot and laboratory scales (Gómez et al., 2015; Li et al., 2017; Lupion et al., 2013; Lupion et al., 2011). Typically, NO emission (in mg/MJ) under oxy-fuel conditions are lower than those under air conditions (Duan et al., 2011; Xu et al., 2017). One reason for the lower NO emissions in oxy-fuel modes is the heterogeneous reduction between NO in the recycled flue gas and unburnt char in the dense phase of the CFB (Xu et al., 2017).

In the Oxy-CFBC reaction atmosphere, characterized by its high CO₂ concentration, the H₂O concentration can also reach up to 40 % in the wet recycle mode. When H₂O is involved in the reaction atmosphere, studies have demonstrated that char-N can be converted into N₂, NH₃, and HCN (Park et al., 2005, 2008). Park et al. (Park et al., 2005) found that at 1000 °C, the primary nitrogen products from the coal char-H₂O reaction were NH₃ and HCN, with higher H₂O concentrations increasing NH₃ proportions. McKenzie et al. (McKenzie et al., 2008) observed that at 800 °C in a 15 % H₂O atmosphere, over 70 % of char-N was converted

to NH₃ in coal-H₂O gasification, while less than 10 % was converted to HCN.

During the heterogeneous reduction of NO by char, nitrogen from NO is mostly converted to N₂. However, H₂O presence can lead to nitrogen converting to HCN. Zhao et al. (Zhao et al., 2019) observed HCN formation in coal char reducing NO in a high-temperature furnace, with HCN amounts increasing with higher water concentrations and temperatures. Lin et al. (Lin et al., 2010) found that introducing NO (8 ppm) in a 15 % H₂O atmosphere at 800 °C increased NH₃ and HCN yields in the later stages of char-H₂O gasification. They proposed that NH₃ and HCN formation involved a heterogeneous reaction mechanism where NO formed C(N) complexes on the char surface, converting to HCN or NH₃·NH₃ formation was favored by high H radical concentrations on the char surface, while lower H concentrations led to higher HCN yields.

Although experimental studies on the formation of HCN during the reduction of NO by char in an H₂O atmosphere are limited, these studies provide valuable insights: the nitrogen in the HCN may originate from both the char-N and the NO in the reaction atmosphere. Typically, the char used in NO reduction experiments is coal char or biomass char, which contains inherent nitrogen elements. Moreover, the observed concentrations of HCN in the experiments were relatively low (Zhao et al., 2019), making it difficult to distinguish the proportion of HCN derived from NO. While the homogeneous formation and oxidation

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Nomenclature			
<i>Parameter</i>		v_m	imaginary frequency of transition state (cm^{-1})
q_{HCN}	mass flow rates of HCN (g/min)	c	speed of light (m/s)
q_{Ar}	mass flow rates of Ar (g/min)	k_B	Boltzmann constant (J/K)
$\dot{q}_{\text{HCN}}$	corrected mass flow rate of HCN (g/min)	h	Plank constant ($\text{J}\cdot\text{s}$)
I_{HCN}	characteristic current intensities of HCN (A)	Q_{TS}	partial function of transition state
I_{Ar}	characteristic current intensities of Ar (A)	Q_A	partial function of reactant
t	any moment during the reaction (s)	Q_B	partial function of product
x	conversion rate of HCN	<i>Abbreviations</i>	
t_{end}	reaction time (s)	m/z	mass-to-charge ratio
k	reaction rate constant (s^{-1})	CFB	Circulating Fluidized Bed
E_a	apparent activation energy (kJ/mol)	CCUS	carbon capture, utilization, and storage
R	gas constant (J/mol/K)	DFT	density functional theory
A	pre-exponential factor (s^{-1})	IRC	Intrinsic reaction coordinate
T	reaction temperature (K)	MFB	micro-fluidized bed
$f(x)$	the differential form of the mechanism function	NTP	normal temperature and pressure
$G(x)$	The integral form of the mechanism function	OMS	on-line mass spectrometer
c_{NO}	NO concentration (vol.%)	Oxy-CFBC	Oxy-fuel circulating fluidized bed combustion
n	the fractional reaction order with respect to the NO concentration	RFG	recirculated flue gas
		TST	transition state theory

reactions of HCN during combustion are well understood (Dagaut et al., 2008), the heterogeneous mechanisms governing the conversion of NO to HCN during the reduction of NO by char in an H_2O atmosphere remain unclear, necessitating more detailed experimental and mechanistic investigations.

In this study, experiments on NO reduction were conducted using nitrogen-free cellulose char within a $\text{CO}_2/\text{H}_2\text{O}$ atmosphere in a micro fluidized bed (MFB). As cellulose char lacks nitrogen components, the nitrogen in the detected HCN originated solely from NO. An online mass spectrometer (OMS) was used for real-time HCN formation data. This study investigated the formation of HCN under various reaction atmospheres, temperatures, and NO concentrations, and calculated the kinetic parameters of HCN formation. Furthermore, quantum chemistry methods (Jiao et al., 2021; Zhang et al., 2020a) were utilized to explore the formation pathway of HCN during the reduction of NO by char in an H_2O atmosphere, elucidating the formation mechanism of HCN. This study provides new insights into the conversion processes of HCN and NO in oxy-fuel atmospheres.

2. Experimental methods

2.1. Experimental material

In this study, the char raw material used was microcrystalline cellulose. As a fundamental constituent of biomass, cellulose is composed exclusively of carbon (C), hydrogen (H), and oxygen (O) elements. This composition makes it an ideal candidate for the generation of ash-free and nitrogen-free char (Düdder et al., 2016; Wedler and Span, 2021). The pyrolysis process for the pure cellulose was carried out in a fixed bed furnace under an argon (Ar) atmosphere from room temperature to 950°C for 90 min. The resulting cellulose char had particle sizes ranging from 20 to $54\ \mu\text{m}$. The ultimate analysis of both the cellulose and

Table 1
Ultimate analysis of cellulose and cellulose char.

	Ultimate analysis (wt.%)				
	C_{ad}	H_{ad}	N_{ad}	S_{ad}	O_{ad}
Cellulose	42.4	5.9	0	0	51.7
Cellulose char	94.9	0.4	0	0	4.7

Note: ad signifies “air dry basis”.

cellulose char is presented in Table 1.

2.2. Experimental apparatus

The experimental apparatus comprises of a gas distribution system, a micro fluidized bed (MFB) reactor, and an online mass spectrometer (OMS), as depicted in Fig. 1. The MFB has an inner diameter of 20 mm; the upper part functions as the fluidized reaction zone, while the lower part as the water vaporization zone. A thermocouple is used to measure the reaction temperature in the fluidized zone. Deionized water is fed into the reactor via a peristaltic pump. The outlet of the fluidized bed connects to the OMS, which continuously collects current signal values during the reaction process. The dwell time for the online mass spectrometer is set at 32 ms. In each experiment, 3 g of quartz sand were preloaded into the reactor. The gas flow rate was set to 240 ml/min (NTP: 1 atm at 20°C), corresponding to 5.1 times the minimum fluidization velocity of the quartz sand. The MFB was heated using an electric furnace. Upon the reactor reaching the specified temperature, as indicated by the thermocouple, an electromagnetic valve was used to inject 30 mg of cellulose coke into the MFB within 6 ms. The pulse injection gas was Ar. Specific experimental conditions are detailed in Table 2.

2.3. HCN quantitative analysis methods

In an OMS, the relationship between the characteristic current value of HCN and its volume flow rate can be quantitatively described using the equivalent characteristic spectrum method (Xia and Wei, 2015). The relationship is mathematically represented by the following equation:

$$\frac{q_{\text{HCN}}}{q_{\text{Ar}}} = r \frac{M_{\text{HCN}} I_{\text{HCN}}}{M_{\text{Ar}} I_{\text{Ar}}} \quad (1)$$

where q_{HCN} and q_{Ar} are the mass flow rates of HCN and the carrier gas Ar, respectively, in g/min. r is the relative sensitivity coefficient between Ar and HCN. M_{HCN} and M_{Ar} refer to the relative molecular masses of the gas molecules of HCN and Ar, respectively. I_{HCN} and I_{Ar} are the characteristic current intensities of HCN and the carrier gas Ar, respectively, in A. The characteristic currents of HCN and Ar can be obtained at $m/z = 27$ and 40, respectively. Since pure HCN gas is highly toxic and difficult to obtain for calibration, the relative sensitivity coefficient r between HCN and Ar cannot be determined using conventional calibration

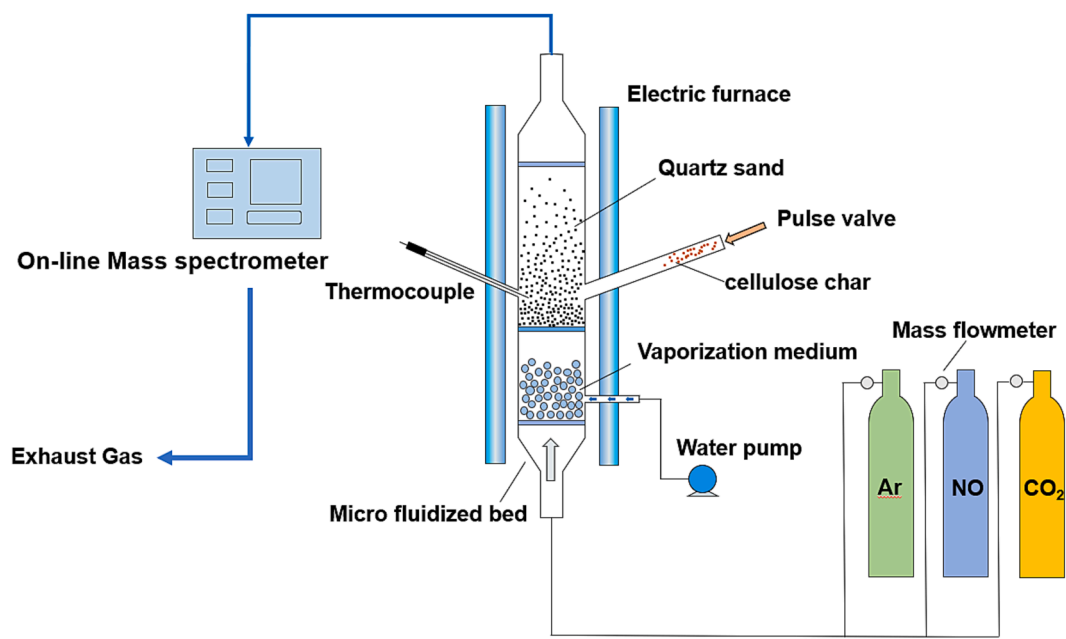


Fig. 1. Schematic diagram of the experimental system.

Table 2

Experimental conditions Parameters.

Condition	CO ₂ concentration (%)	H ₂ O concentration (%)	CO ₂ flow rate ^a (g/min)	H ₂ O flow rate ^a (g/min)	NO ^b (ppm)	Temperature (°C)
1	40	0	0.176	0	500	900
2	40	10	0.176	0.018	500	900
3	40	20	0.176	0.036	500	900
4	40	30	0.176	0.054	500	900
5	0	20	0	0.036	500	900
6	20	20	0.088	0.036	500	900
7	60	20	0.264	0.036	500	900
8	40	20	0.176	0.036	500	850
9	40	20	0.176	0.036	500	875
10	40	20	0.176	0.036	500	925
11	40	20	0.176	0.036	200	900
12	40	20	0.176	0.036	800	900
13	0	20	0	0.036	500	850
14	0	20	0	0.036	500	875
15	0	20	0	0.036	500	925
16	0	20	0	0.036	200	900
17	0	20	0	0.036	800	900

Note: ^a Volumetric flow rate at NTP (20°C, 1 atm); ^b Ar as balance gas.

methods. To quantitatively analyze HCN formation, the parameter $\dot{q}_{\text{HCN}}$ was used to represent the generation of HCN during the reaction:

$$\dot{q}_{\text{HCN}} = \frac{\dot{q}_{\text{HCN}}}{r} = q_{\text{Ar}} \frac{M_{\text{HCN}} I_{\text{HCN}}}{M_{\text{Ar}} I_{\text{Ar}}} \quad (2)$$

In the mass spectrometry analysis, the relative sensitivity r between HCN and Ar remains constant. A linear relationship between the modified mass flow rate ($\dot{q}_{\text{HCN}}$) and the actual mass flow rate ($\dot{q}_{\text{HCN}}$) is established, as depicted in Eq. (2). It is important to note that $\dot{q}_{\text{HCN}}$ does not represent the true mass flow rate of HCN. However, it reliably mirrors the variation trends of HCN flow, proving essential for capturing dynamic changes under different reaction conditions.

The conversion rate of HCN can be expressed as:

$$x = \frac{\int_0^t \dot{q}_{\text{HCN}} dt}{\int_0^{t_{\text{end}}} \dot{q}_{\text{HCN}} dt} \quad (3)$$

where t is any moment during the reaction, and t_{end} is the moment when the reaction ends. The reaction between cellulose and NO to produce

HCN is a gas–solid reaction, and its kinetic expression can be represented as:

$$\frac{dx}{dt} = k \cdot f(x) = A e^{-E_a/RT} f(x) c_{\text{NO}}^n \quad (4)$$

Where k is the reaction rate constant, and $f(x)$ is the differential form of the reaction mechanism function. A , E_a , R , and T represent the pre-exponential factor (s^{-1}), apparent activation energy (kJ/mol), gas constant, and reaction temperature (K), respectively. c_{NO} denotes the NO concentration (vol.%); n is the fractional reaction order with respect to the NO concentration.

The reaction mechanism function can be determined through model fitting methods. The integral form of the mechanism function $G(x)$ is expressed as Eq. (5) (Zha et al., 2022):

$$G(x) = \int_0^x \frac{dx}{f(x)} = kt \quad (5)$$

From Eq. (5), it is evident that $G(x)$ and time t have a linear relationship in an isothermal reaction, where the slope of the line

corresponds to the reaction rate constant. The reaction mechanism function is determined by fitting $G(x)$ and t and selecting the linearity of the fitted line with the highest value. Furthermore, the reaction order and activation energy can be determined by fitting $\ln k$ with $\ln c_{\text{NO}}$ and $\ln k$ with $1/T$, as shown in Eq. (6).

$$\ln k = -\frac{E_a}{RT} + \ln A + n \ln c_{\text{NO}} \quad (6)$$

3. Density functional theory (DFT) calculations

3.1. Biomass-char model

In the study of nitrogen transformation during char combustion, a zigzag configuration with seven benzene rings has been widely used as a representative carbonaceous matrix (Chen et al., 2022a; Xu et al., 2023; Yue et al., 2022). The carbon atoms at the top of the model are unsaturated to simulate active sites on the char surface, while the remaining carbon atoms are saturated, representing inactive sites. The zigzag-shaped char with seven benzene rings effectively explains experimental phenomena and elucidates the reaction pathways of nitrogen transformation. Yue et al. (Yue et al., 2022) employed the zigzag-shaped char model with seven benzene rings to investigate nitrogen transformation pathways in an oxy-steam atmosphere. They discovered that hydroxyl radicals (OH) in the H_2O atmosphere facilitated the $\text{HCN} \rightarrow \text{NH}_2 \rightarrow \text{NO}$ process, resulting in increased NO emissions. This mechanism explains the phenomenon observed in their fixed-bed experiments, where NO emissions were higher in an oxy-steam atmosphere compared to an air atmosphere. Chen et al. (Chen et al., 2022a) used quantum chemical methods to elucidate the phenomenon of NH_3 promoting char reduction of NO. They explored the heterogeneous reduction mechanism of NO in the presence of NH and NH_2 radicals using a zigzag configuration with seven benzene rings, highlighting that the formation of OH on the char surface is a critical step in promoting NH reduction of NO. The heterogeneous reduction rate of NH-NO is seven times that of the homogeneous NH_3 -NO reduction reaction and twenty times that of the NH_2 -NO heterogeneous reaction rate. This study employs a zigzag-shaped char similar to that used by Yue et al. (Yue et al., 2022) and Chen et al. (Chen et al., 2022a) to explore the HCN pathway in an H_2O atmosphere. Since the cellulose char used in this study does not contain alkali metal elements, the biomass char model employed in this paper does not consider their effects. The impact of alkali metal-modified char will be addressed in future research. The optimized char structure is shown in Fig. 2.

3.2. Calculation methods

All quantum chemical calculations were based on DFT. Geometry optimizations were performed using the B3LYP/6-31G(d) method. The B3LYP/6-31G(d) method has been widely applied to the NO reduction

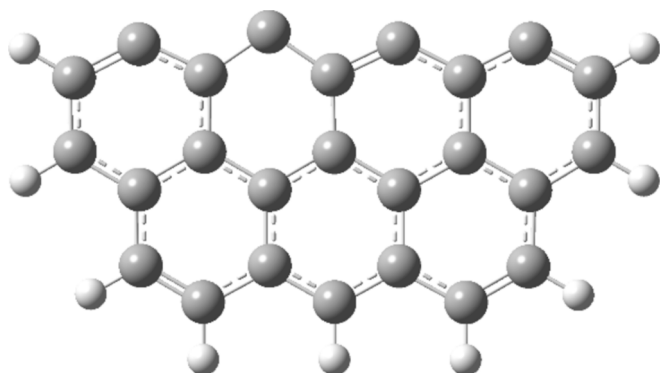


Fig. 2. The biomass-char model with zigzag edge.

reaction by char, showing good agreement with experimental observations (Espinal et al., 2005; Oyarzún et al., 2016; Zhang et al., 2020b). The D3 method was introduced to characterize the London dispersion interaction (Zhang et al., 2020a). Frequency calculations were conducted at this computational level to ensure that reactants, intermediates, and products in all reaction pathways had no imaginary frequencies, while transition states had exactly one imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were performed on the transition state structures to confirm the correct reaction pathways. The M06-2X/def2-TZVP method was used to calculate the energies of the structures along the reaction pathways (Chen et al., 2022b; Chen et al., 2022c). All quantum chemical calculations were carried out using the Gaussian 09 D01 package. Thermodynamic data calculations were performed using the Thermo program (Lu and Chen, 2021), with zero-point energy corrections applied.

Based on transition state theory (TST), kinetic calculations were performed using the rate-determining step in the reaction pathway. The formula is as follows:

$$k = \Gamma \frac{k_B T}{h} \frac{Q_{\text{TS}}}{Q_A \cdot Q_B} \exp\left(\frac{-E_c}{RT}\right) \quad (7)$$

where Γ is the quantum tunneling correction factor; k_B is the Boltzmann constant, J/K; T is the reaction temperature, K; h is the Planck constant, J.s; Q_{TS} , Q_A , and Q_B are the partition functions of the transition state (TS), reactant, and product, respectively; R is the universal gas constant, J/mol/K; E_c is the energy barrier of the reaction step, kJ/mol.

The calculation formula for Γ is as follows

$$\Gamma = 1 + \left(\frac{1}{24}\right) \times \left(\frac{h \nu_m c}{k_B T}\right)^2 \quad (8)$$

where ν_m is the imaginary frequency value of the transition state structure, cm^{-1} ; and c is the speed of light, m/s. After calculating the reaction rate constant, the activation energy and pre-exponential factor can be obtained using the linear least squares fitting method:

$$k(T) = A \times \exp\left(\frac{-E_a}{RT}\right) \quad (9)$$

where A is the pre-exponential factor, s^{-1} ; and E_a is the activation energy, kJ/mol.

4. Results and discussion

4.1. HCN emission in $\text{CO}_2/\text{H}_2\text{O}$ atmosphere

Fig. 3 illustrates the formation of HCN under various reaction atmospheres, with experiments conducted at a temperature of 900°C and a NO concentration of 500 ppm. As depicted in Fig. 3A, in a 40 % CO_2 atmosphere, the HCN production is relatively low, with a peak q_{HCN} of only 0.03 g/min. The introduction of H_2O into the atmosphere leads to a significant increase in HCN production. In a 40 % CO_2 + 10 % H_2O atmosphere, the peak q_{HCN} increases to 0.21 g/min, which is 7.15 times greater than that in the 40 % CO_2 atmosphere. Further increases in H_2O concentration continue to enhance the peak HCN flow rate, although the increments are smaller compared to the initial increase from 0 % to 10 % H_2O . As cellulose char does not contain nitrogen, the nitrogen in the produced HCN originates from NO. These experimental results indicate that the addition of H_2O in the reaction atmosphere facilitates the conversion of NO to HCN during its reduction by char, providing a hydrogen source for HCN formation. Fig. 3B presents the variation of HCN with different CO_2 concentrations in a 20 % H_2O atmosphere. This figure shows that increasing CO_2 concentration from 0 to 60 % slightly enhances the peak HCN flow rate, which remains between 0.17 and 0.24 g/min. Fig. 3A and 3B demonstrate that H_2O is the predominant factor influencing HCN production in a CO_2 + H_2O atmosphere, with just 10 % H_2O significantly boosting HCN formation. The key to HCN

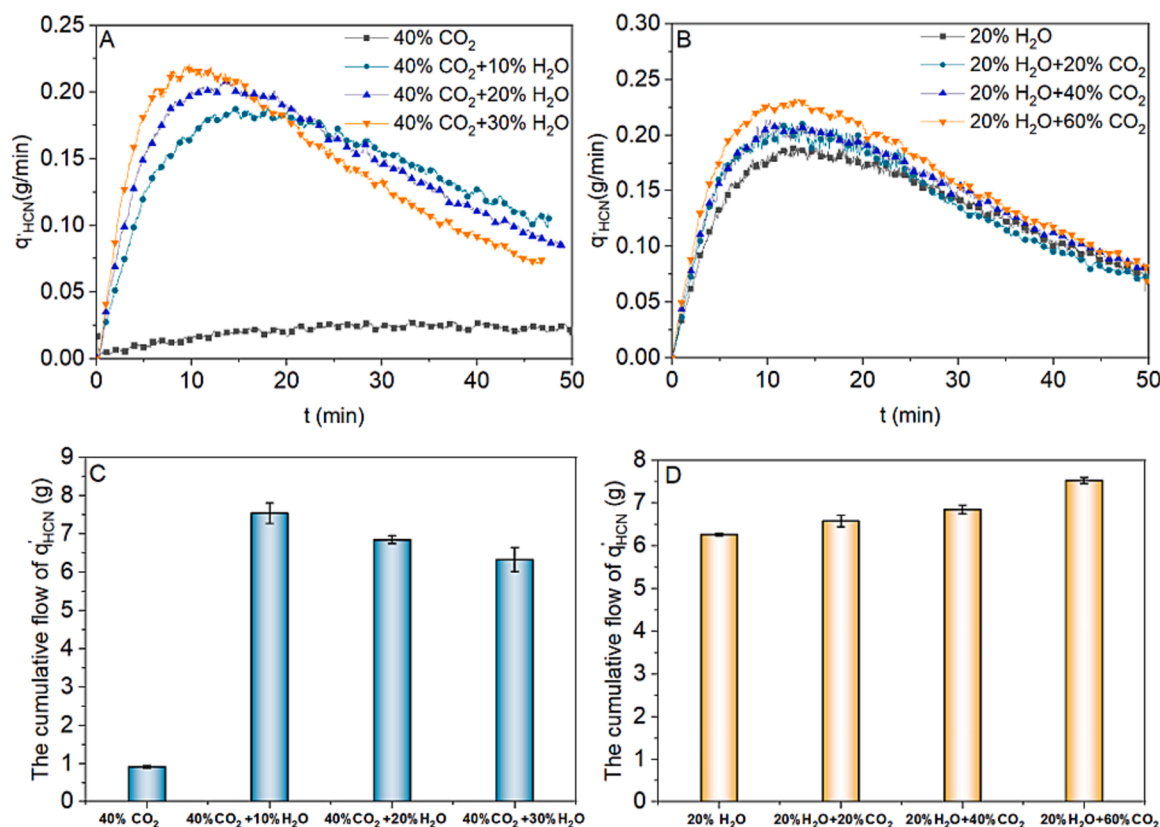


Fig. 3. Effect of reaction atmosphere on the formation of HCN (A: effect of H_2O concentration; B: effect of CO_2 concentration; C: the cumulative flow of HCN under different H_2O concentrations within 45 min; D: the cumulative flow of HCN under different CO_2 concentrations within 45 min).

formation lies in the availability of sufficient hydrogen in the reaction atmosphere (Orikasa et al., 2002). The H_2O concentration (10 %) is notably higher—200 times—than the NO concentration (500 ppm). NO, once adsorbed onto the char surface, forms C(N) in a 'rich-hydrogen' atmosphere, resulting in a significant increase in HCN production with the addition of just 10 % H_2O compared to a no- H_2O atmosphere.

Fig. 3C and 3D depict the cumulative production of q_{HCN} within 45 min under varying atmospheres. Fig. 3C indicates that the cumulative HCN production significantly increases when H_2O is added to the reaction atmosphere. Specifically, in a 40 % CO_2 + 10 % H_2O atmosphere, the HCN production reaches 7.54 g, which is 8.2 times greater than that in the 40 % CO_2 atmosphere. However, increasing the H_2O concentration from 10 % to 30 % results in a declining trend in HCN production. Compared to the 40 % CO_2 + 10 % H_2O atmosphere, the HCN production in the 40 % CO_2 + 30 % H_2O atmosphere decreases by 16 %. Furthermore, as illustrated in Fig. 3A, at the 45-minute mark, the HCN flow rate in the 40 % CO_2 + 30 % H_2O atmosphere is lower than that in the 40 % CO_2 + 10 % H_2O atmosphere, suggesting that the total HCN production in the entire reaction period is reduced in the higher H_2O concentration environment. This reduction may be attributed to the increased occupation of active sites on the char surface by H_2O molecules, thereby enhancing the char- H_2O gasification reaction and reducing the availability of active sites for HCN formation. Fig. 3D compares of total HCN production under different CO_2 concentrations in an H_2O atmosphere. As the CO_2 concentration increases, the HCN production slightly increases, remaining between 6.08 and 7.43 g. In a 20 % H_2O atmosphere, the HCN production is 6.26 g, while in a 20 % H_2O + 40 % CO_2 atmosphere, the HCN production increases to 6.84 g, a modest 9.27 % increase despite a 40 % increase in CO_2 concentration. This indicates that H_2O molecules have a more pronounced effect on occupying the active sites on the char surface compared to CO_2 molecules (Chen et al., 2016; Wang and Bell, 2017), making H_2O the primary factor

influencing HCN production relative to CO_2 .

4.2. Effect of operating parameters on HCN formation

Fig. 4 shows the production of HCN at different temperatures within a 40 % CO_2 + 20 % H_2O atmosphere and a 20 % H_2O atmosphere. Fig. 4A and Fig. 4B demonstrate a positive correlation between temperature and the peak q_{HCN} value. The time of peak q_{HCN} occurs earlier as the temperature rises. Specifically, as the temperature rises from 850 °C to 925 °C, the peak q_{HCN} in the 40 % CO_2 + 20 % H_2O atmosphere increases from 0.10 g/min to 0.24 g/min, representing an approximate doubling. Similarly, in the 20 % H_2O atmosphere, the peak q_{HCN} increases from 0.13 g/min to 0.22 g/min, marking a 74 % increase. Additionally, Fig. 4A and Fig. 4B reveal that with increasing temperatures, the q_{HCN} flow rate at 45 min exhibits a gradual decline, with more pronounced decreases at higher temperatures, indicating a shortened reaction time for HCN production due to temperature elevation. The percentage of residual char relative to the initial char after 45 min in a 20 % H_2O atmosphere at different temperatures is presented in Table S1. As the temperature increases, the proportion of residual char decreases, indicating that higher temperatures promote the conversion of char. Table 3 display HCN production in both atmospheres, highlighting that HCN output within the first 45 min also increases with temperature. At 925 °C in a 20 % H_2O atmosphere, HCN production reaches 6.93 g, approximately 50 % higher than that observed at 850 °C. This suggests that higher temperatures facilitate the conversion of NO to HCN during NO reduction by char.

Orikasa et al. (Orikasa et al., 2002) reported formation of HCN in reactions between phenol/formaldehyde resin char and NO. Their experiments were conducted in a fixed-bed reactor at temperatures ranging from 850 °C to 1100 °C, without the presence of oxygen and H_2O in the reaction atmosphere. They observed that elevated

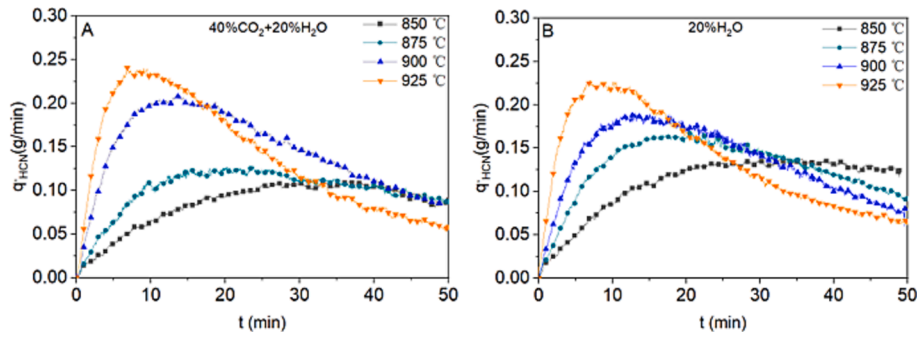


Fig. 4. Effect of reaction temperature on the formation of HCN (A: HCN flow rate at 40 %CO₂ + 20 %H₂O atmosphere; B: HCN flow rate at 20 %H₂O atmosphere).

Table 3

HCN generation under different temperatures within 45 min.

Temperature (°C)	HCN ^a (g)	
	40 %CO ₂ + 20 %H ₂ O	20 %H ₂ O
850	3.57	4.61
875	4.60	5.64
900	6.85	6.26
925	6.99	6.39

temperatures promoted HCN formation, with the hydrogen content in the reaction atmosphere being the main factor influencing the formation rate. They proposed that the key to HCN formation is the availability of sufficient hydrogen in the reaction atmosphere. The reaction mechanism for HCN formation involves the initial reaction of NO with char to form a C(N) complex:



Subsequently, the hydrogen sources for HCN include H₂, H radicals, and H atoms on the char surface. The C(N) complex reacts with these hydrogen sources to form HCN:



As the temperature increases, the desorption rate of C(O) accelerates, enhancing the release rates of gaseous products such as CO and CO₂, and freeing more active sites on the char surface, thereby accelerating the formation of C(N). Furthermore, in an H₂O atmosphere, high temperatures significantly promote the formation of H₂ (R4) and H radicals (R5–R7) in the reaction atmosphere (Sun et al., 2017), increasing the reactant concentration for reaction R2. On the other hand, the desorption rate of C(H, N) accelerates at high temperatures, increasing the HCN production rate.



Fig. 5 depicts the production of HCN at 900 °C under different varying NO concentrations in a 40 % CO₂ + 20 % H₂O atmosphere and a 20 % H₂O atmosphere. Fig. 5A and 5B illustrate that as the NO concentration increases, there is a significant escalation in the peak q_{HCN} values. Specifically, when the NO concentration rises from 200 ppm to 800 ppm, the peak q_{HCN} in the 40 % CO₂ + 20 % H₂O atmosphere increases from 0.11 g/min to 0.36 g/min, and in the 20 % H₂O atmosphere, it increases from 0.08 g/min to 0.27 g/min. Additionally, Table 4 demonstrate that the total HCN production also markedly increases with higher NO concentrations. In the 40 % CO₂ + 20 % H₂O atmosphere, when the NO concentration is maintained at 800 ppm, the HCN production is 11.64 g, which is approximately three times the HCN production at 200 ppm NO.

As the NO concentration increases, a greater proportion of NO molecules occupy the active sites on the char surface, leading to an increased rate of HCN production per unit time. As detailed in section 4.1, the presence of H₂O in the reaction atmosphere is crucial, as the hydrogen in the HCN formed from the reaction between char and NO

Table 4

HCN generation under different NO concentration within 45 min.

NO concentration (ppm)	HCN (g)	
	40 %CO ₂ + 20 %H ₂ O	20 %H ₂ O
200	3.60	2.68
500	6.85	6.26
800	11.64	8.13

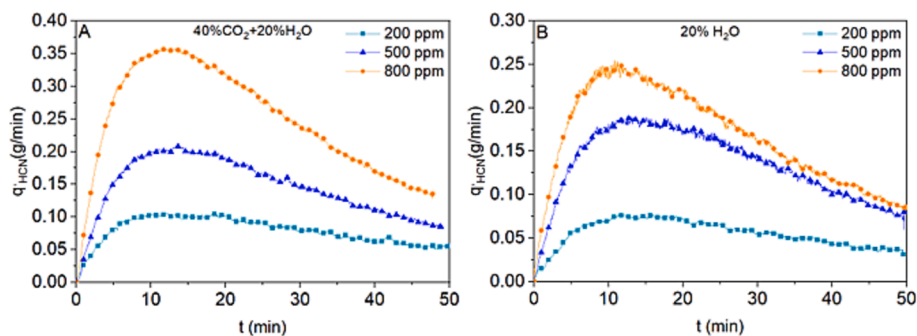


Fig. 5. Effect of NO concentrations on the formation of HCN (A: HCN flow rate at 40 %CO₂ + 20 %H₂O atmosphere; B: HCN flow rate at 20 %H₂O atmosphere; C: the cumulative flow of HCN under 40 %CO₂ + 20 %H₂O atmosphere within 45 min; D: the cumulative flow of HCN under 20 %H₂O atmosphere within 45 min).

predominantly originates from the hydrogen in H₂O. When the H₂O concentration ranges between 10–30 %, H₂, H radicals, and OH radicals are all potential hydrogen donors for HCN production. Considering the NO concentration is in the ppm range, significantly lower than the H₂O concentration (10–30 %), the reaction atmosphere is inherently “hydrogen-rich.” Thus, the concentration of NO, which provides the nitrogen for HCN, becomes the critical factor in determining the volume of HCN produced. As the NO concentration increases, the reaction described as R1 is enhanced, leading to an accelerated formation of the C(N) complex. This elevation in C(N) formation favors the subsequent synthesis of C(H, N) and accelerates the production rate of HCN.

4.3. Formation pathways of HCN in an H₂O atmosphere

The experiments in section 4.1 and 4.2 demonstrate that the presence of H₂O in the reaction atmosphere facilitates the conversion of NO to HCN during the reduction of NO by char, while CO₂ shows no substantial impact on HCN formation. In the heterogeneous formation of HCN, the source of nitrogen is NO, hydrogen is derived from the H₂O in the reaction atmosphere, and carbon comes from char. In this section, quantum chemistry calculations will be employed to investigate the heterogeneous formation pathways of HCN.

4.3.1. Adsorption of reactants

Fig. 6 illustrates the adsorption process of NO molecules, H atoms, and OH radicals on the char surface. NO molecules are easily adsorbed in a parallel manner on the carbon substrate surface (Zhang et al., 2014; Zhang et al., 2020b). Two primary adsorption configurations, R0 and R1, are identified. In R0, the NO molecule adsorbs onto C1 and C3 atoms, while in R1, adsorption occurs onto C3 and C5 atoms. Findings from Section 3.1 indicate that the introduction of H₂O into the atmosphere enhances HCN formation, suggesting that hydrogen in HCN likely originates from H or OH radicals. Upon adsorption of NO molecules, configurations R0 and R1 change with H and OH radicals adsorption, labeled as IM0-1, IM0-1a (OH near N1), IM0-2, IM0-2a (H near N1) for R0, and IM0-3, IM0-3a (OH near N1), IM0-4, IM0-4a (H near N1) for R1. Each adsorption process is exothermic, with the adsorption energy calculated using the following formula:

$$E_{\text{ads}} = E_{\text{gas} + \text{model}} - E_{\text{gas}} - E_{\text{model}} \quad (11)$$

where E_{ads} is the adsorption energy, $E_{\text{gas} + \text{model}}$ is the energy of the adsorption configuration, E_{gas} is the energy of the NO molecule, H radical, and OH radical, and E_{model} is the energy of R. The calculated adsorption energies under 900 °C are shown in Fig. 8, indicating that the adsorption processes forming configurations IM0-1, IM0-2, IM0-3, and IM0-4 are highly exothermic and represent stable adsorption configurations.

4.3.2. Reaction pathways

The pathway for HCN formation from IM0-1 involves several key transitions (Fig. 7). Geometrical structures of stagnation points in pathway 1–3 were shown in Fig.S1. Initially, IM0-1 overcomes a 98.5 kJ/mol energy barrier to form IM1, absorbing 38.2 kJ/mol. H₂ atom migration breaks the H₂-O₂ bond and forms an NH group. Subsequently, rotation of the H₂ atom around the N1-C3 bond changes the dihedral angle, reducing $\angle\text{C4-C3-N1}$ and increasing O1-N1 separation, requiring a 184.7 kJ/mol barrier and absorbing 137.5 kJ/mol. The IM2 to TS2 transition lengthens the C3-C4 bond, leading to ring opening and N1-C4 bond formation, crossing a 143.1 kJ/mol barrier. The TS2 to IM3 transition stabilizes a seven-membered ring, absorbing 88.3 kJ/mol. Transition from IM4 to IM5 involves structural changes, including a dihedral angle shift and forming a C-C covalent bond. HCN desorption from IM5 requires a 193.0 kJ/mol barrier and releases 120.2 kJ/mol, weakening the C2-C3 and N1-C4 bonds until they sever. Post-HCN desorption, the char surface forms a carbonyl structure at C1 and C5.

Pathway 2 begins with transferring the H₂ atom from O₂ to C₄, forming a C-H bond, requiring a 324.4 kJ/mol energy barrier and absorbing 94.6 kJ/mol to form IM8. Transitioning from IM8 to IM9 involves overcoming a 224.1 kJ/mol barrier and absorbing 124.2 kJ/mol, leading to a ring-opening reaction. Significant dihedral angle rotations weaken and break the C₄-C₅ bond, forming a C(CN) structure. The IM9 to IM10 transition involves rotations around the C₂-C₈ and C₄-C₉ bonds, forming a new C-C bond and transforming a six-membered ring into a five-membered ring, releasing 78.6 kJ/mol. The H₂ atom then moves towards C₃, forming a C(N, H) structure.

Pathway 3 shares initial steps with Pathway 2, where the transition from IM0-1 to IM8 involves the transfer of the H₂ atom, requiring a 257.8 kJ/mol barrier and absorbing 256.0 kJ/mol. The subsequent stage, from IM8 to IM12, involves transferring the H₂ atom from C₄ to C₃, with the same energy requirements. During the IM12 to IM13 transition, dihedral angles shift, leading to the breaking of the C₃-C₄ bond and a ring-opening reaction, requiring a 78.3 kJ/mol barrier and absorbing 53.2 kJ/mol. IM13 then overcomes a 53.8 kJ/mol barrier and releases 14.3 kJ/mol to form IM14. The dihedral angle rotates, shortening the C₂-C₄ distance and forming a five-membered ring. The C₂-C₃ bond length increases, indicating bond breakage. Finally, transitioning from IM14 to P1 and releasing HCN requires a 136.1 kJ/mol barrier and releases 276.3 kJ/mol.

The pathway for HCN formation from IM0-2 involves several steps (Fig. 8). Geometrical structures of stagnation points in pathway 4 and 5 were shown in Fig.S2. In Pathway 4, initially, the H₁ atom migrates from C₅ to C₄, overcoming a 329.9 kJ/mol barrier and absorbing 316.6 kJ/mol to form IM16. The H₁ atom then moves to C₃, increasing the C₃-C₄ bond length, causing bond cleavage and ring opening. This step requires a 183.0 kJ/mol barrier and absorbs 17.2 kJ/mol. Transitioning from IM17 to IM18 involves a 307.6 kJ/mol barrier and releases 20.9 kJ/mol, with N₁ and O₁ atoms separating and the C₂-C₃ bond breaking, leading

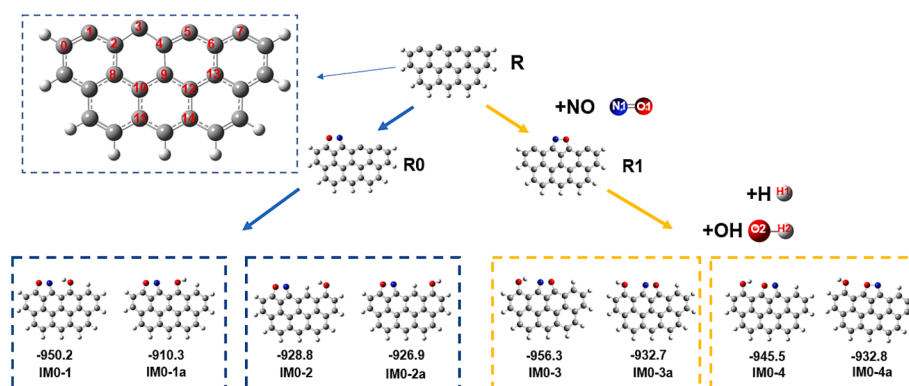


Fig. 6. Adsorption configuration and energy of NO, H, and OH on char surface.

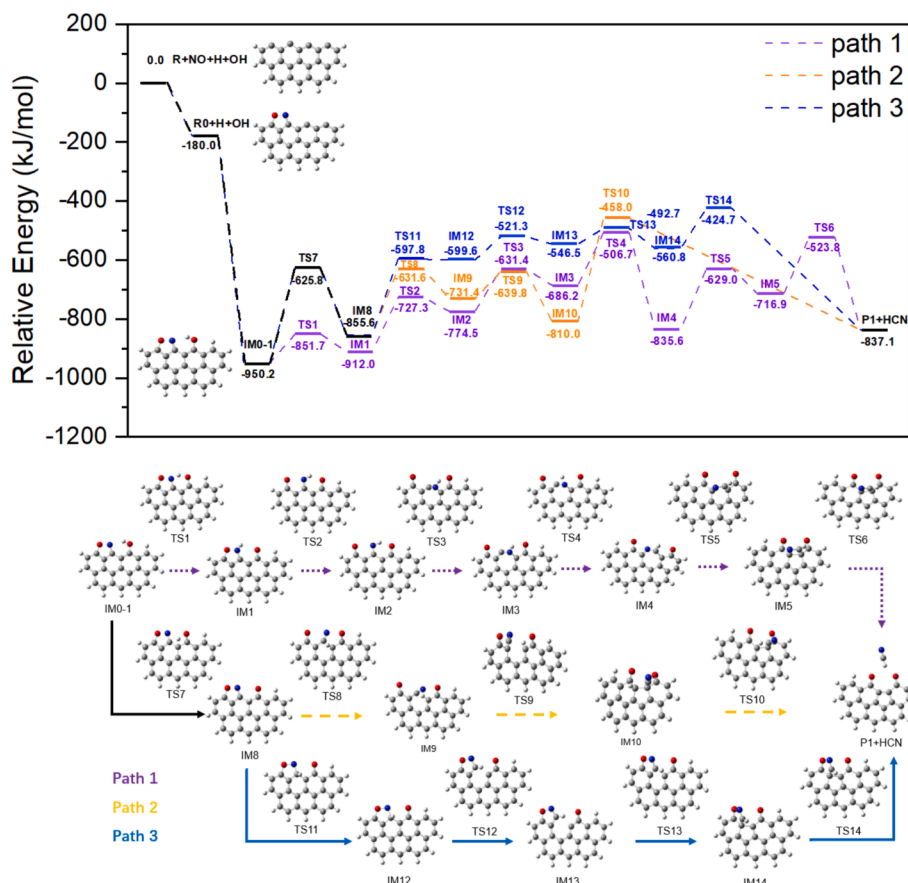


Fig. 7. Energy and configuration profiles for HCN generation of path 1–3.

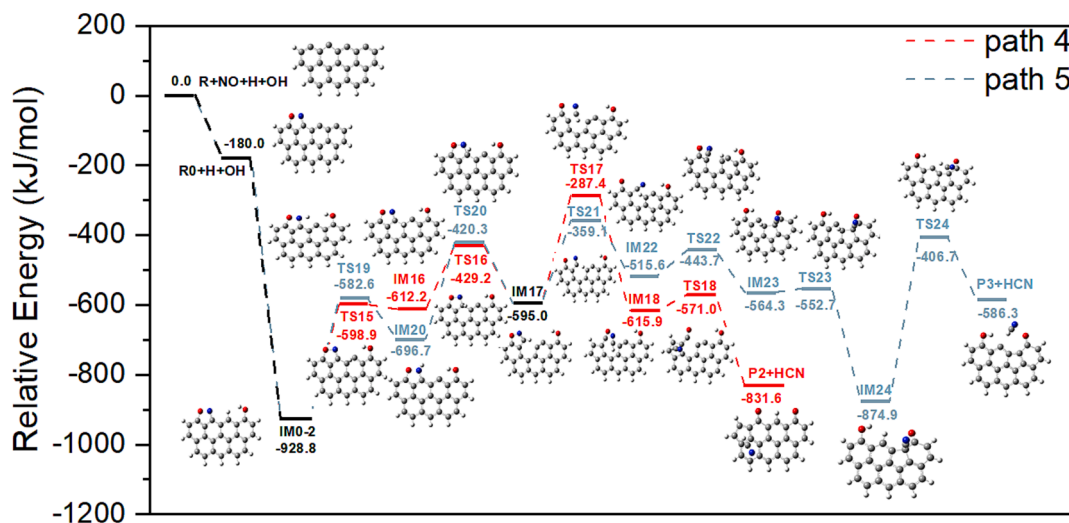


Fig. 8. Energy and configuration profiles for HCN generation of path 4,5.

to HCN desorption. Concurrently, C0 and C2 form a five-membered ring. IM18 then overcomes a 44.97 kJ/mol barrier and releases 215.67 kJ/mol to form P2 and HCN. The final step involves forming a stable C-C bond, reconstructing the six-membered ring.

Pathway 5 begins with the H1 atom migrating from C5 to N1, decreasing the distance from 2.82 Å to 1.01 Å, overcoming a 346.3 kJ/mol barrier and absorbing 232.1 kJ/mol. Next, H1 migrates from N1 to C3, forming a C-H bond with a 276.4 kJ/mol barrier and absorbing 101.7 kJ/mol. IM17 transitions to IM22 by overcoming a 236.0 kJ/mol

barrier and absorbing 79.4 kJ/mol, with H1 migrating from C3 to C4 and significant dihedral angle changes. Transitioning from IM22 to IM23 requires a 71.9 kJ/mol barrier and releases 48.7 kJ/mol, with C3 and C5 forming a stable C-C bond. In IM23, H1 migrates from C4 to C5, forming IM24, requiring an 11.6 kJ/mol barrier and releasing 310.6 kJ/mol. Finally, in IM24, the H atom on C5 reacts with the -CN structure on C2 to form HCN, involving a 468.1 kJ/mol barrier and absorbing 288.6 kJ/mol.

Pathways 6 and 7 for HCN formation from IM0-3 are shown in Fig. 9.

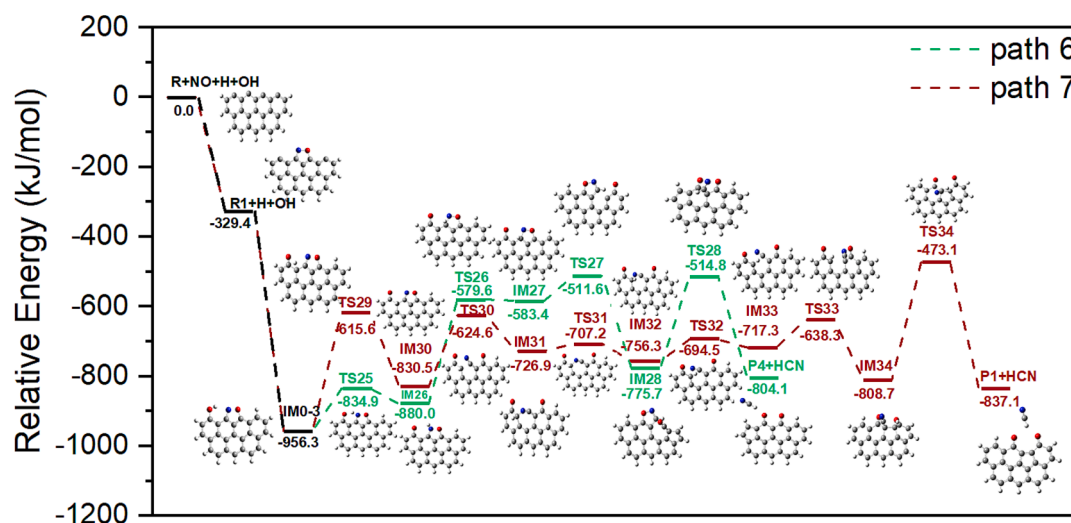


Fig. 9. Energy and configuration profiles for HCN generation of path 6,7.

Geometrical structures of stagnation points in pathway 6 and 7 were shown in Fig.S3. Pathway 6 begins with H2 atom migration, requiring a 121.4 kJ/mol barrier and absorbing 76.2 kJ/mol. The H2 atom approaches N1, forming an NH group. In the transition from IM26 to IM27, H2 migrates to C3, reducing the H2-C3 distance from 2.10 Å to 1.14 Å, with a 300.4 kJ/mol barrier, absorbing 296.7 kJ/mol. IM27 undergoes a ring-opening reaction to form IM28, involving dihedral angle shifts and C2-C3 bond elongation until it breaks, forming a five-membered ring. This requires a 71.8 kJ/mol barrier and releases 192.3 kJ/mol. Subsequently, IM28 overcomes a 260.8 kJ/mol barrier to reach TS28, where C1 and C3 move closer, and N1 and O1 separate. The final step involves HCN desorption from TS28 to P4, with a 260.8 kJ/mol barrier.

In Pathway 7, the IM0-3 to IM30 transition involves H2 atom migration from O2 to C2, requiring a 340.6 kJ/mol barrier and absorbing 125.8 kJ/mol. In the IM30 to IM31 transition, the C2-C3 bond breaks, and the N1 and C2 atoms form an N-C bond, transforming the six-membered ring into a seven-membered ring, with a 205.9 kJ/mol barrier and absorbing 103.6 kJ/mol. The subsequent IM31 to IM32 transition involves significant dihedral angle rotation and a slight increase in the C2-N1 bond length, requiring a 19.7 kJ/mol barrier and releasing 29.5 kJ/mol. During the IM32 to IM33 transition, the C2-N1 bond breaks, and the C4 atom connects to C3-H2, forming a C(CH)

structure, requiring a 61.8 kJ/mol barrier and absorbing 39.0 kJ/mol. The IM33 to IM34 transition involves a 79.1 kJ/mol barrier and releases 91.4 kJ/mol. Finally, IM34 desorbs HCN, requiring a 335.6 kJ/mol barrier and releasing 28.4 kJ/mol, breaking the C2-H2 bond and migrating the H2 atom to C3, with the C3-C4 bond breaking.

Pathway 8 for HCN formation from IM0-4 is shown in Fig. 10, illustrating configurations and energy distributions. Geometrical structures of stagnation points in pathway 8 were shown in Fig.S4. The pathway starts with the H1 atom migrating from C7 to C5 in IM0-4, following two routes, 8a and 8b, forming IM37. Route 8a passes through transition states TS35 and TS36, with energy barriers of 387.2 kJ/mol and 153.3 kJ/mol, respectively. Route 8b involves TS36 and TS37, with barriers of 385.3 kJ/mol and 268.4 kJ/mol, respectively. Both migration pathways break the six-membered ring at the C5-C6 position, increasing the distance between C5 and C6 from 1.47 Å to 2.82 Å. IM37 then undergoes HCN desorption, forming P6, overcoming a 296.0 kJ/mol barrier and releasing 39.6 kJ/mol. During this process, C4 and C6 atoms draw closer from 3.12 Å to 1.45 Å, forming a new five-membered ring. Additionally, N1 and O1 atoms separate, and the C4-C5 bond weakens until it breaks, resulting in HCN desorption from the char surface.

From pathways 1 to 8, it can be observed that the first step in the

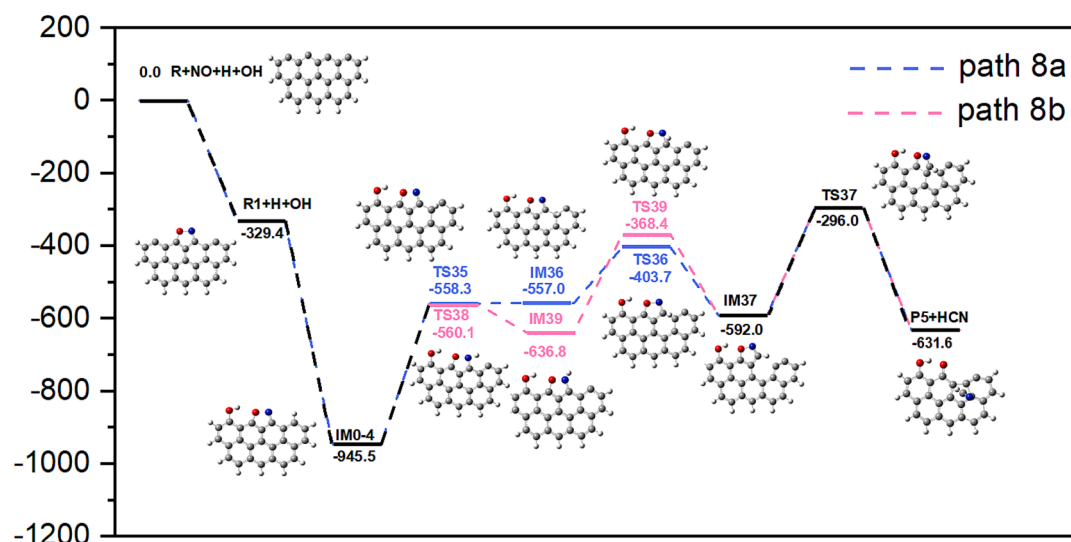


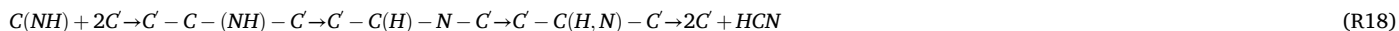
Fig. 10. Energy and configuration profiles for HCN generation of path 8.

formation of HCN involves the transfer of a hydrogen atom. The hydrogen atom can originate from either C(N) or C(OH). Given the abundance of free hydrogen radicals in the H₂O environment, additional sources of hydrogen may include NO adsorbed on the char surface, leading to the formation of C(NH) via hydrogen adsorption, or free hydrogen radicals directly participating in the reaction. The mechanisms of these processes are further explored in pathways 9 and 10, as illustrated in Fig. 11. Geometrical structures of stagnation points in pathway 9 and 10 were shown in Fig.S5. In pathway 9, the hydrogen atom in the C(NH) group is transferred to a carbon atom adjacent to the nitrogen atom. This is followed by a ring-opening reaction in the char structure, which subsequently rearranges to form a new five-membered ring, leading to the release of the HCN molecule. In pathway 10, the ring-opening reaction first generates C(CN) and C(H) structures. The system then re-forms the five-membered ring, during which the hydrogen atom from C(H) is transferred to the C(CN) structure, resulting in the formation of an HCN molecule that subsequently detaches from the char surface.

4.3.3. HCN formation mechanism

Orikasa et al. (Orikasa et al., 2002) proposed a mechanism for the formation of C(N) + $\frac{1}{2}$ H₂/H/C(H) → C(H, N) → HCN, but they did not discuss the structure of C(H, N). In this study, the reaction pathway for HCN was determined using quantum chemical methods. DFT studies indicate that HCN formation can proceed via two pathways: C(N, H) → HCN and C'(CN) + C'(H) → 2C'() + HCN. The detailed reaction mechanisms are as follows:

(1) Adsorption of reactants on the char surface: The initial step involves the adsorption of NO molecules, H radicals, and OH radicals at active sites on the char surface, leading to the formation of C(N), C(O), C(H), C(OH) and C(NH) structures as outlined in reactions R8 to R11:



(2) Migration of H atoms: The H atoms in the newly formed C(H) and C(OH) structures undergo migration, which varies across different pathways:

In pathways 1, 5, 6, 8b and 9, the H atom migrates to the N atom, forming an NH group (R12)–(R14). Subsequently, in pathways 5, 6, 8b and 9, the H atom continues to migrate to the C atom connected to the N atom, forming a C(N, H) structure (R14):



In pathway 2, the H atom in C(OH) migrates to an internal carbon atom (C'), following after a ring-opening reaction to form C(H) (R15).



pathways 3, 4, 7, and 8a involve a two-step migration of the H atom to a C atom connected to an N atom, forming a C(N, H) structure ((R16) and (17):



(3) Ring-Opening and Formation of HCN: the processes of six-membered ring-opening and subsequent formation of five-membered rings, along with HCN, exhibit variability across different pathways.:

In pathway 1, the formed C(NH) integrates into the six-membered ring structure, transitioning to a seven-membered ring. The H atom connected to the N atom migrates to the adjacent C atom, bringing the C2 and C5 atoms of the seven-membered ring closer to form a five-membered ring, and subsequently, HCN is formed ((R18):

In pathways 2, 7 and 10, ring-opening reactions occur during H atom migration, forming C'(CN) (19). In pathway 5, the H atom in the formed C(H, N) structure migrates, forming C'(CN) and C'(H) ((R19).

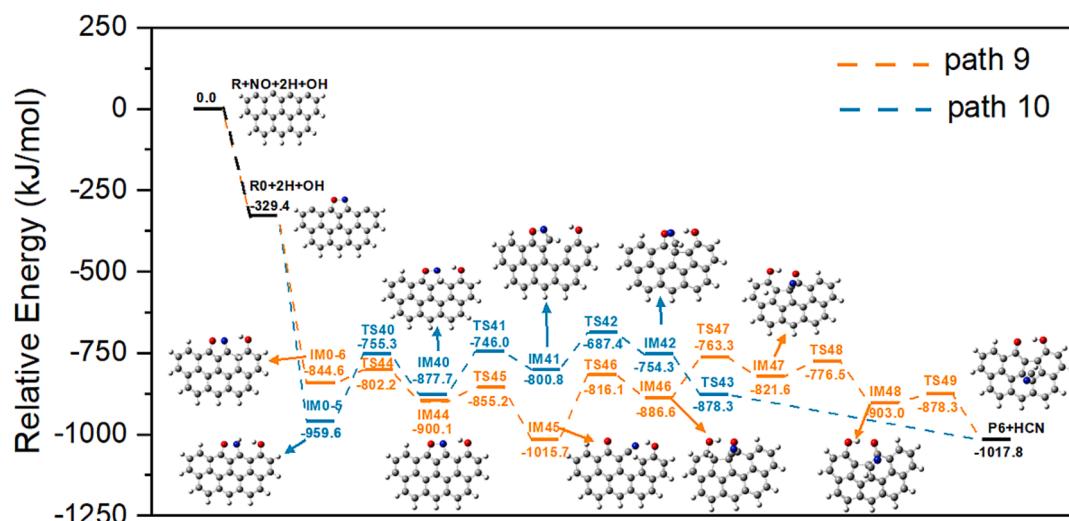


Fig. 11. Energy and configuration profiles for HCN generation of path 9,10.

Subsequently, $C'(CN)$ reacts with $C'(H)$ to form HCN ((R21):



In pathways 3, 4, 6, 8 and 9, the H atom migrates to the C atom connected to the N atom, forming a $C(N, H)$ structure. Subsequently, the formed $C(H, N)$ structure increases the distance to the adjacent C atoms, forming HCN (22):



4.4. Kinetics analysis

As discussed in section 4.1, when the reaction atmosphere is “hydrogen-rich” the H_2O concentration does not significantly affect HCN production. Consequently, a 20 % H_2O atmosphere was selected for the calculation of kinetic parameter. Considering the relatively slow HCN formation rate at an NO concentration of 500 ppm, a 1 % NO concentration was employed to facilitate complete HCN conversion within a shorter timeframe. To ensure the reaction was under kinetic control and minimize the impact of gas diffusion, the HCN conversion rates at different gas flow rates were compared, as shown in Fig. S6. Fig. S6 illustrates that as the gas flow rate exceeds 360 ml/min (NTP), the increase in HCN conversion rate becomes negligible.

Kinetic parameters for HCN formation were determined using a gas flow rate of 360 ml/min at NTP. A model-fitting method was employed, utilizing typical mechanistic functions cited from the existing literature (Liu et al., 2017; Zha et al., 2022). At 900 °C and an NO concentration of 1 %, the fitting plots of the mechanistic functions $G_6(x)$, $G_{18}(x)$, and $G_{19}(x)$ exhibit the highest linearity, as shown in Fig. S7. The fittings of these three mechanistic functions against time at different NO concentrations are shown in Fig. S8A-C, and the fitting curves at different temperatures are shown in Fig. S8D-E. Notably, Fig.S8 indicates that the mechanistic function $G_6(x) = [-\ln(1-x)]^{2/3}$ accurately describes the HCN formation process during the reduction of NO by char. Furthermore, the reaction order with respect to NO concentration and the activation energy were determined by linear fitting of $\ln[k(T)]$ versus $\ln c_{NO}$ and $\ln[k(T)]$ versus $1000/T$, with the respective fitting curves displayed in Fig. 12. As a result, the analysis confirmed that HCN formation is a fractional-order reaction with respect to NO concentration, exhibiting a reaction order of 0.51, and an activation energy of 186.67 kJ/mol. The equation for the reaction rate constant is articulated in (10).

$$k = 2.52 \times 10^8 \times \exp\left(-\frac{22453}{T}\right) \times c_{NO}^{0.51} \quad (10)$$

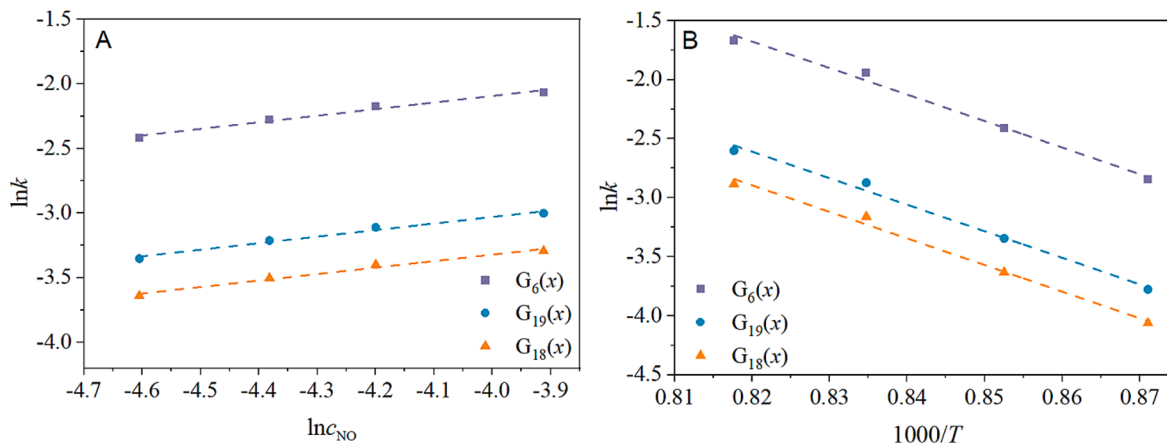


Fig. 12. The linear fitting of $\ln[k(T)]$ and $\ln c_{NO}$ (A) and $1000/T$ (B).

Table 5

Energy barriers of different path.

path	Energy barriers (kJ/mol)
1	443.5
2	492.2
3	525.5
4	641.4
5	569.8
6	444.6
7	483.1
8	649.5
9	272.2
10	254.4

The energy barriers for paths 1–10 are presented in Table 5. From Table 5, the energy barriers for paths 9 and 10 range between 250–280 kJ/mol, which are significantly lower than those of the other paths. This suggests that, during the reduction of NO by char in an H_2O atmosphere, the hydrogen source in the formation of HCN is more likely to be free hydrogen radicals present in the reaction environment rather than hydrogen originating from $C(H)$ or $C(OH)$ groups formed through adsorption. The nitrogen contained within the biomass char can also be converted into HCN. Table 3 compares the highest energy barriers involved in HCN formation in this study with those reported by Zhang et al. (Zhang et al., 2020a) (472.29 kJ/mol) through DFT analysis. The comparison reveals that the energy barrier for the NO-to-HCN conversion is significantly lower than that for the conversion of char(N) to HCN. Furthermore, the findings of Lin et al. [16], which showed a substantial increase in HCN production during the char- H_2O gasification reaction upon the addition of NO. This observation underscores the role of NO as a facilitator in the HCN formation process, suggesting a more favorable pathway for HCN synthesis in the NO to HCN compared to the char(N)-to-HCN under H_2O atmospheres.

5. Conclusion

This study focused on the formation of HCN during the reduction of NO by biomass-char in CO_2/H_2O atmospheres. Nitrogen-free cellulose char was utilized to ensure that the nitrogen in HCN originated exclusively from NO. DFT methods were applied to elucidate the pathways of HCN formation, leading to several key conclusions:

The presence of H_2O in the reaction atmosphere creates a “hydrogen-rich” environment that significantly enhances HCN formation. In contrast, CO_2 shows minimal influence on HCN production. Moreover, the rate of HCN formation increases with increasing temperatures and NO concentrations. The formation process of HCN was accurately described by the kinetic model function $G_6(x) = [-\ln(1-x)]^{2/3}$. The reaction follows a fractional order with respect to NO concentration,

characterized by a reaction order of 0.51 and an activation energy of 186.67 kJ/mol.

The HCN formation pathway involves initial adsorption of NO, H radicals, and OH radicals at active sites, followed by migration of H atoms to carbon atoms connected to the N atom. This migration facilitates the opening and subsequent reforming of a six-membered ring structure into a five-membered ring, culminating in HCN production. The heterogeneous mechanisms for HCN formation in an H₂O atmosphere include $C(NH) + 2C \rightarrow 2C' + HCN$, $C'(CN) + C(H) \rightarrow 2C' + HCN$, and $C(N,H) \rightarrow HCN$.

Experimental results and DFT calculations consistently demonstrate that the energy barriers for converting NO to HCN during the reduction process is significantly lower than that for converting char-N to HCN. The conversion of NO to HCN in NO reduction over char is more likely to occur in an H₂O atmosphere compared to the conversion of char N to HCN.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ces.2024.121090>.

Data availability

Data will be made available on request.

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