

# Stage-pyrolysis of straw wastes: formation and control of NO<sub>x</sub> precursors

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## ABSTRACT

Source reduction or process control of fuel-N conversion into reactive NO<sub>x</sub> precursors (NH<sub>3</sub> and HCN) during pyrolysis process was fundamental and essential for clean thermal utilization of straw wastes. In this study, three typical straw wastes (bean, rice and wheat) were employed to probe formation characteristics and regulatory mechanisms of two target NO<sub>x</sub> precursors via stage pyrolysis method with the help of XPS and chemical absorption-spectrophotometry analytic techniques. Results demonstrated that consistent formation pathways of NO<sub>x</sub> precursors were elucidated by direct and indirect conversion of similar fuel-N types - amide-N/amine-N/amino-N (N-A) in straw wastes. Specifically, two NO<sub>x</sub> precursors were hardly linked with primary pyrolysis of N-A types (direct conversion) while dominantly determined by secondary reactions of subsequent nitrogen intermediates in chars and tars (indirect conversion); secondary reactions referring to hydrogenation of heterocyclic-N in chars and dehydrogenation of amine-N in tars were more responsible for NH<sub>3</sub>-N and HCN-N, respectively, leading to a maximal total yield of 45-50 wt.%. Consequently, compared to single-stage pyrolysis uniformly, two-stage pyrolysis could manipulate intensities of formation pathways at different pyrolysis stages through employing differential intermediate feedstocks for re-pyrolysis, minimizing the ratio of total yield by about 60 % with a greater effect on HCN-N yield (76-83 %) than NH<sub>3</sub>-N yield (44-50 %), which exhibited an excellent regulatory capacity on NO<sub>x</sub> precursors formation for straw wastes. These findings were favorable for developing some insights into emission control of N-containing gaseous pollutants during their thermo-chemical conversion processes.

**Keywords:** Stage pyrolysis; Straw wastes; NO<sub>x</sub> precursors; Secondary reactions; Regulatory capacity.

## 1. INTRODUCTION

Straw wastes are prominent biomass resources with a huge annual amount in the world, especially in China. Their thermo-chemical conversions to produce energy products appealing to market demand are direct potential approaches, which will alleviate some energy and environmental issues [1]. However, straw biowastes contain higher fuel-bound nitrogen (fuel-N) inevitably converted into N-containing gaseous pollutants (NGPs) by thermal-chemical conversion approaches, becoming a more significant technical challenge in relevant real industrial fields [2].

As is known, pyrolysis plays a fundamental role among these conversion technologies. Meanwhile, according to the conversion of fuel-N to NGPs [2, 3], two necessary reactive NGPs (NH<sub>3</sub> and HCN) closely interrelating with pyrolysis process are not only toxic and corrosive gases, but also typical NO<sub>x</sub> precursors. Accordingly, source reduction or process control aiming at fuel-N conversion chemistry relating to NO<sub>x</sub> precursors during pyrolysis process would be a fundamental and efficient approach to achieve NO<sub>x</sub> emission reduction.

In brief, NO<sub>x</sub> precursors were generally produced from initial decomposition of fuel-N and further conversion of subsequent char-N/tar-N, which was not only intrinsically linked with characteristics of fuel-N and its derived nitrogen intermediates, but also significantly characterized by pyrolysis conditions [4, 5]. As for straw wastes, fuel-N in them were basically in the form of various protein or protein hydrolysate types; meanwhile, their conversion into NO<sub>x</sub> precursors would be affected by the intrinsic properties of straw wastes.

Hence, quantitative information on formation pathways of NO<sub>x</sub> precursors and contributions of two target origins would be clearly ascertained.

It was reported that stage pyrolysis had advantages in the production of special pyrolytic oil and activated carbon [6, 7]. According to its typical features, this approach was capable to distinguish the role of two contributors in NO<sub>x</sub> precursor formation. In addition, it was indirectly proved that it might also have potential regulatory capability on gaseous pollutant emission. Hence, this work aims to explore decisive formation pathways of two target NO<sub>x</sub> precursors during pyrolysis of typical straw wastes, and further to reveal their regulatory mechanisms by stage-pyrolysis technique based on the effects of two target origins on their formation characteristics, and wishfully to acquire guideline on control of fuel-N conversion into final NO<sub>x</sub> during thermal utilization of straw wastes.

## 2. MATERIALS AND METHODS

### 2.1 Basic treatments & analyzes of feedstocks

Three local straw wastes (bean-BS, rice-RS and wheat-WS) in China were chosen as feedstocks, which were initially performed with basic treatments including drying, milling, sieving and re-drying to remove moisture and ensure same particle size ( $\leq 300 \mu\text{m}$ ).

In order to ascertain properties of straw wastes, proximate components, ultimate components, calorific values, amino acid components, organic functional groups and surface nitrogen structures were analyzed using corresponding methods and instruments, which could be found in detail in our previous study [8].

### 2.2 Stage pyrolysis experimental procedures

Stage pyrolysis experiments were conducted in a fixed bed system consisting of a gas cylinder, a horizontal pyrolyzer, a cold trap and a sampling unit, with gas flow and temperature controllers. Experiment procedures included two segments: single-stage and two-stage pyrolysis, as clearly shown in Fig. 1.

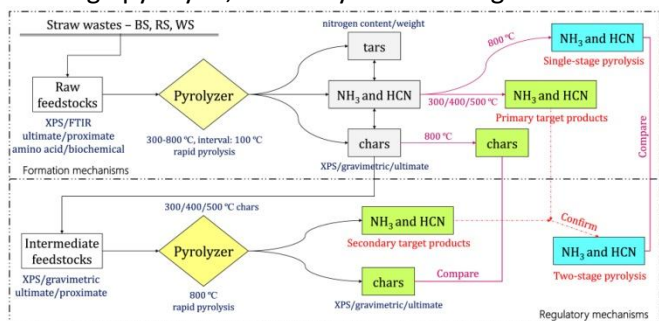


Fig. 1 Schematic of experiment procedures

Guided by experiment procedures, the experiment setup, the analytic methods and the important parameter determinations (yield of each NO<sub>x</sub> precursor-N for different stage pyrolysis, yield of each nitrogen structure in derived chars) could be referred to our previous studies [5, 9].

## 3. RESULTS AND DISCUSSION

### 3.1 Properties of raw straw wastes

Physicochemical properties of raw samples were confirmed before discussing NO<sub>x</sub> precursor formation (Fig. 2). All samples exhibited typical lignocellulosic biomass properties with a massive organic matter of 85-90 wt.% involving 40-45 % C, 5-6 % H and 37-42 % O, and an excellent calorific value of 16-17 MJ/kg.

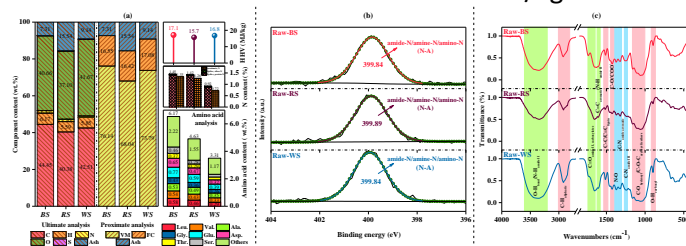


Fig. 2 Physicochemical properties of straw wastes: (a) fuel compositions; (b) N 1s XPS spectra; (c) FTIR spectra

As for N-related properties, N content by ultimate analysis basically agreed with that by Kjeldahl N analysis. XPS spectra showed a good single peak fitting by  $399.8 \pm 0.3 \text{ eV}$ , reflecting the presence of N-A types in them. Meanwhile, FTIR spectra demonstrated the significant occurrence of peptide bonds (-CO-NH). Moreover, it was revealed that total amount of amino acids was also in good agreement with Kjeldahl protein content. Multiple analyzes confirmed that straw wastes had a uniform fuel-N structure despite distinctive nitrogen content and monomers.

### 3.2 NO<sub>x</sub> precursor formed during single-stage pyrolysis

NO<sub>x</sub> precursors formed during single-stage pyrolysis was expressed as the yields of NH<sub>3</sub>-N and HCN-N derived from fuel-N. Fig. 3 presented changes of two NO<sub>x</sub> precursor-N yields with the temperature.

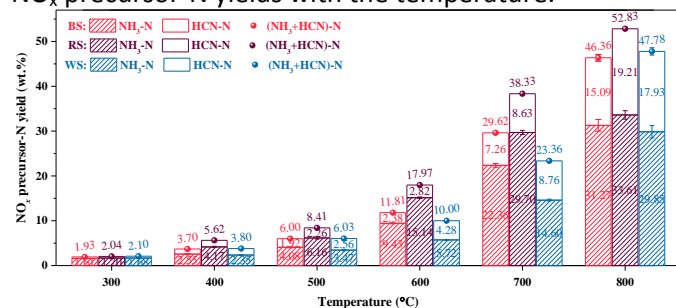
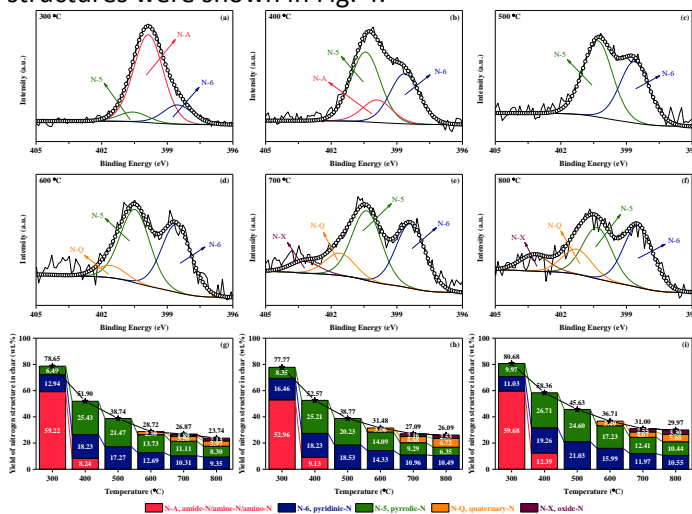


Fig. 3 Changes of each NO<sub>x</sub> precursor-N yield with the temperature during single-stage pyrolysis of straw wastes

It was clearly seen that NH<sub>3</sub>-N yield was obviously higher than HCN-N yield at any temperature for each straw wastes. Meanwhile, both of them had a constant increase in varying degrees with the temperature, characterized by pyrolytic temperature range. At low temperatures (300-500 °C), each NO<sub>x</sub> precursor-N yield showed a small ignorable level and a slow increment. Conversely, when pyrolyzing at 600-800 °C, NH<sub>3</sub>-N yield swiftly reached up to a high level resembling HCN-N yield but had a more striking increment, acquiring a maximal total yield of 45-50 wt.%. It could be concluded that two NO<sub>x</sub> precursors were barely linked with primary pyrolysis of fuel-N at low temperatures, but closely dependant on the simultaneous occurrence of devolatilisation and secondary reactions guaranteed by high temperature and fast heating rate.

### 3.3 Evolution of nitrogen structures in solid products

Targeting straw waste-derived chars at 300-800 °C during single-stage pyrolysis, characteristics of nitrogen structures were shown in Fig. 4.



**Fig. 4** N 1s spectra of BS-derived chars (a)-(f), and each nitrogen structure yield in chars for BS (g), RS (h) and WS (i)

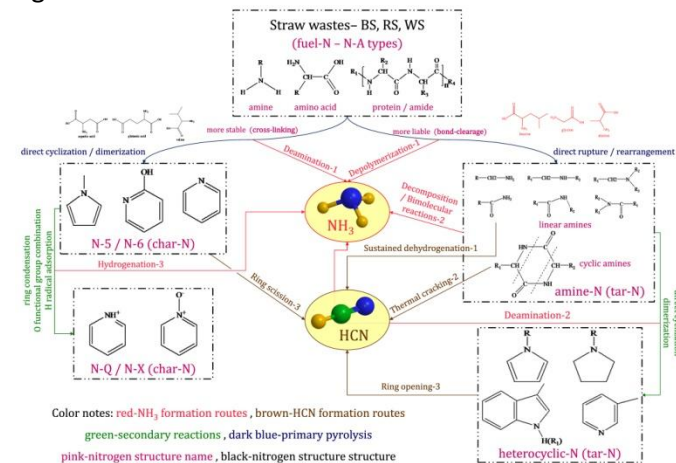
Due to the similarities of fuel-N for three samples, BS was selected to illustrate the nitrogen structures in derived chars. Five categories including N-A, N-6, N-5, N-Q and N-X were observed (Fig. 4a-f). Specifically, in low-temperatures, N-A was shrinking and vanished before 500 °C, while N-5 and N-6 were gradually enlarged, forming an interconnected structure including N-A, N-5 and N-6. In high-temperature chars, N-5 and N-6 were still remarkable, moreover N-Q and N-X were sequentially emerged with an increasing peak area, constituting a N-heterocyclic grapheme-like structure.

As for each category yield with the temperature, rapid decrease of N-A yield were observed at low temperatures, which were ascribed to the thermal

decomposition (into volatile-N) and the dimerization / cyclization (into N-5/N-6) reactions. Both N-5 and N-6 yields decreased constantly when temperature reached high, converting to a certain N-Q/N-X and NO<sub>x</sub> precursors. Hence, evolution of nitrogen structures in solid products was clearly summarized as N-A → N-5/N-6 → N-Q/N-X.

### 3.4 Formation pathways of NO<sub>x</sub> precursors

Based on the above discussions together with some previous studies [2, 4, 5, 8], formation pathways of NO<sub>x</sub> precursors from fuel-N conversion were elucidated in Fig. 5.



**Fig. 5** Possible formation pathways of NO<sub>x</sub> precursors for pyrolysis of N-A types system

Possible origins for NH<sub>3</sub> and HCN could be both attributed to three aspects. (1) NH<sub>3</sub> was produced by deamination (more stable) and depolymerization (more liable) of N-A types in fuels, bimolecular reactions, decomposition and deamination of amine-N in tars, and hydrogenation of N-5/N-6 in chars activated by H radicals; (2) HCN was originated from ring-opening of heterocyclic-N in chars/tars, constant dehydrogenation of linear amines in fuels/tars and thermal cracking of cyclic amines (indirect dehydrogenation) in tars.

Conclusively, no significant release of NO<sub>x</sub> precursors at low temperatures indicated that deamination and constant dehydrogenation reactions were difficult to occur for primary pyrolysis of N-A types in straw wastes. Two rules were revealed at high temperatures: (1) Remarkable yield of each NO<sub>x</sub> precursors was determined by joint effects of primary pyrolysis and secondary reactions; (2) Compared to HCN, the combined action on NH<sub>3</sub> was much stronger and more sensitive to the temperature.

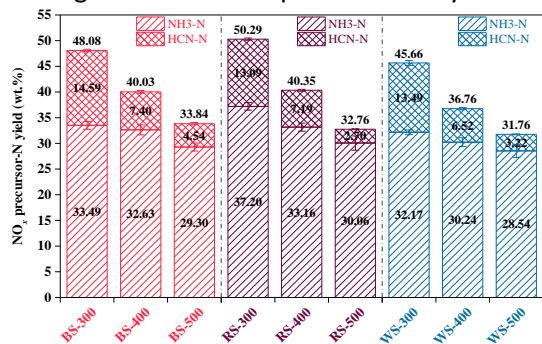
### 3.5 NO<sub>x</sub> precursors formed from re-pyrolysis process

When re-pyrolyzing intermediate feedstocks at 800 °C (second procedure of two-stage pyrolysis), two



$\text{NO}_x$  precursors produced from this procedure for straw wastes were shown in Fig. 6.

During re-pyrolysis process, with intermediate feedstocks switching from 300 to 500 °C, both  $\text{NH}_3\text{-N}$  and  $\text{HCN-N}$  yields were shrinking in varying extent. Specifically, each intermediate feedstock had a close remarkable  $\text{NH}_3\text{-N}$  yield in spite of a slight drop, which was even higher than raw feedstock. On the contrary,  $\text{HCN-N}$  yield was observed to sharply decrease, mainly contributing to dramatic drop on the total yield.



**Fig. 6 Comparisons of  $\text{NO}_x$  precursors from re-pyrolysis of intermediate feedstocks at 800 °C for straw wastes**

A close remarkable  $\text{NH}_3\text{-N}$  yield could demonstrate that hydrogenation of heterocyclic-N in chars predominated the formation of  $\text{NH}_3$ . And a slight drop for intermediate feedstocks with devolatilisation process might be ascribed to gradual shrink of H radicals amount and N-A fraction. Meanwhile, dramatic drop of  $\text{HCN-N}$  yield could prove that  $\text{HCN}$  formation was more dependent on dehydrogenation reactions of amine-N in tars.

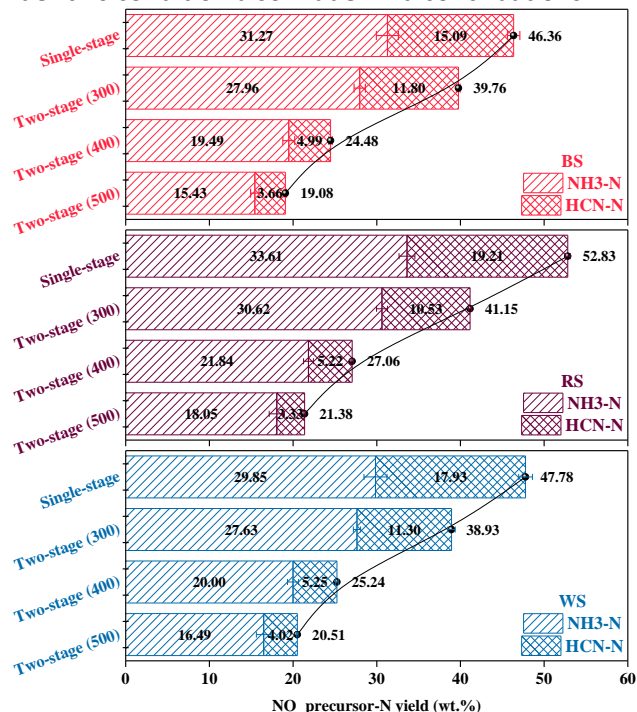
### 3.6 Regulation of $\text{NO}_x$ precursors by stage-pyrolysis

Depending on above results obtained, each  $\text{NO}_x$  precursor-N yield from stage-pyrolysis of straw wastes at 800 °C were compared in Fig. 7.

Compared to single-stage pyrolysis, total  $\text{NO}_x$  precursor-N yield for two-stage pyrolysis became lower, and had a constant drop when sequentially selecting intermediate feedstocks (300-500 °C). Specifically, from single-stage to two-stage pyrolysis, both  $\text{NH}_3\text{-N}$  and  $\text{HCN-N}$  yields exhibited drastic decrements, reaching maximal levels of 13.4-15.8 wt.% (taking up 45-50 %) and 11.4-15.9 wt.% (occupying 76-83 %), respectively.

Based on single-stage pyrolysis (see section 3.2), primary pyrolysis of fuel-N at low temperatures had little impact on NGPs production. Based on re-pyrolysis of intermediate feedstocks (see section 3.5),  $\text{NH}_3$  and  $\text{HCN}$  at high temperatures were more dependent on secondary reactions of char-N (hydrogenation of heterocyclic-N) and tar-N (dehydrogenation of amine-

N), respectively. Meanwhile, primary pyrolysis of fuel-N under this condition also made mild contributions.



**Fig. 7 Comparisons of two  $\text{NO}_x$  precursors produced from stage-pyrolysis process of three straw wastes**

Accordingly, two-stage pyrolysis led to a partial or full separation of devolatilisation and secondary reactions. For one thing, no significant  $\text{NO}_x$  precursors were released during initial pyrolysis of raw feedstocks due to their little relationships with primary pyrolysis of fuel-N; for another, secondary reactions to produce  $\text{NO}_x$  precursors would be inhibited more significantly for re-pyrolysis of intermediate feedstocks ranging from 300 to 500 °C, causing an obvious drop on both  $\text{NH}_3\text{-N}$  and  $\text{HCN-N}$  yields in varying degrees. Consequently, by summarizing two processes, it was inevitable that each  $\text{NO}_x$  precursor yield for two-stage pyrolysis had a varying decrement determined by selection of intermediate feedstocks.

In summary, for straw waste pyrolysis, it was uniformly concluded that stage pyrolysis was beneficial for manipulating  $\text{NO}_x$  precursor formation. Specific speaking, formation of  $\text{NO}_x$  precursors were hardly associated with primary pyrolysis of fuel-N, but strongly influenced by secondary reactions of char-N and tar-N. Moreover, predominant secondary reactions exhibited their specific preferential pathways towards two  $\text{NO}_x$  precursors. Consequently, intensities of formation pathways in relation to primary pyrolysis and secondary reactions could be well regulated by two-stage pyrolysis via selecting targeted intermediate feedstocks for re-

pyrolysis. Compared to single-stage pyrolysis under a suitable thermal utilization temperature, two-stage pyrolysis was capable of minimizing the ratio of total yield by 57-60 % for three samples.

#### 4. CONCLUSIONS

Stage-pyrolysis of straw wastes were used to quantitatively explore decisive formation pathways and feasible regulatory approaches of two NO<sub>x</sub> precursors (NH<sub>3</sub> and HCN). Fuel-N in straw wastes were similarly bound in N-A types, resulting in consistent formation characteristics and pathways of NO<sub>x</sub> precursors via direct and indirect conversions during their pyrolysis. For single-stage pyrolysis, formation of NH<sub>3</sub> and HCN were both scarcely linked with primary pyrolysis of N-A types, while predominantly ascribed to preferential secondary reactions of subsequent nitrogen intermediates in chars and tars, respectively. Consequently, the total yield at high temperatures reached up to a range of 45-50 wt.%. Compared to single-stage pyrolysis, two-stage one under same conditions was able to minimize the ratio of total yield by 57-60 % with a more significant effect on HCN-N yield (76-83 %) than NH<sub>3</sub>-N yield (45-50 %) by regulating intensities of formation routes at different pyrolysis stages. It was therefore concluded that stage pyrolysis had the potential capacity on inhibiting conversion of fuel-N into NO<sub>x</sub> precursors for straw wastes.

#### ACKNOWLEDGEMENT

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