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A sustainable thermochemical conversion of animal biomass to N-heterocycles

Yang Tang[1], Xiao Xiao[1,2], Chaojun Zhang[1], Xiaoling Wang[1,2*], Junling Guo[1,2,3,4] and Xuepin Liao[1,2,4]

Abstract

The production of high-valued organonitrogen chemicals, especially N-heterocycles, requires artificial N_2 fixation accompanied by the consumption of fossil resources. To avoid the use of these energy- and resource-intensive processes, we develop a sustainable strategy to convert nitrogen-rich animal biomass into N-heterocycles through a thermochemical conversion process (TCP) under atmospheric pressure. A high percentage of N-heterocycles (87.51%) were obtained after the TCP of bovine skin due to the abundance of nitrogen-containing amino acids (e.g., glycine, proline, and L-hydroxyproline). Animal biomass with more diverse amino acid composition (e.g., muscles) yielded higher concentrations of amines/amides and nitriles after TCP. In addition, by introducing catalysts (KOH for pyrrole and Al_2O_3 for cyclo-Gly–Pro) to TCP, the production quantities of pyrrole and cyclo-Gly–Pro increased to 30.79 mg g^{-1} and 38.88 mg g^{-1}, respectively. This approach can be used to convert the significant animal biomass waste generated annually from animal culls into valued organonitrogen chemicals while circumventing NH_3-dependent and petro-chemical-dependent synthesis routes.

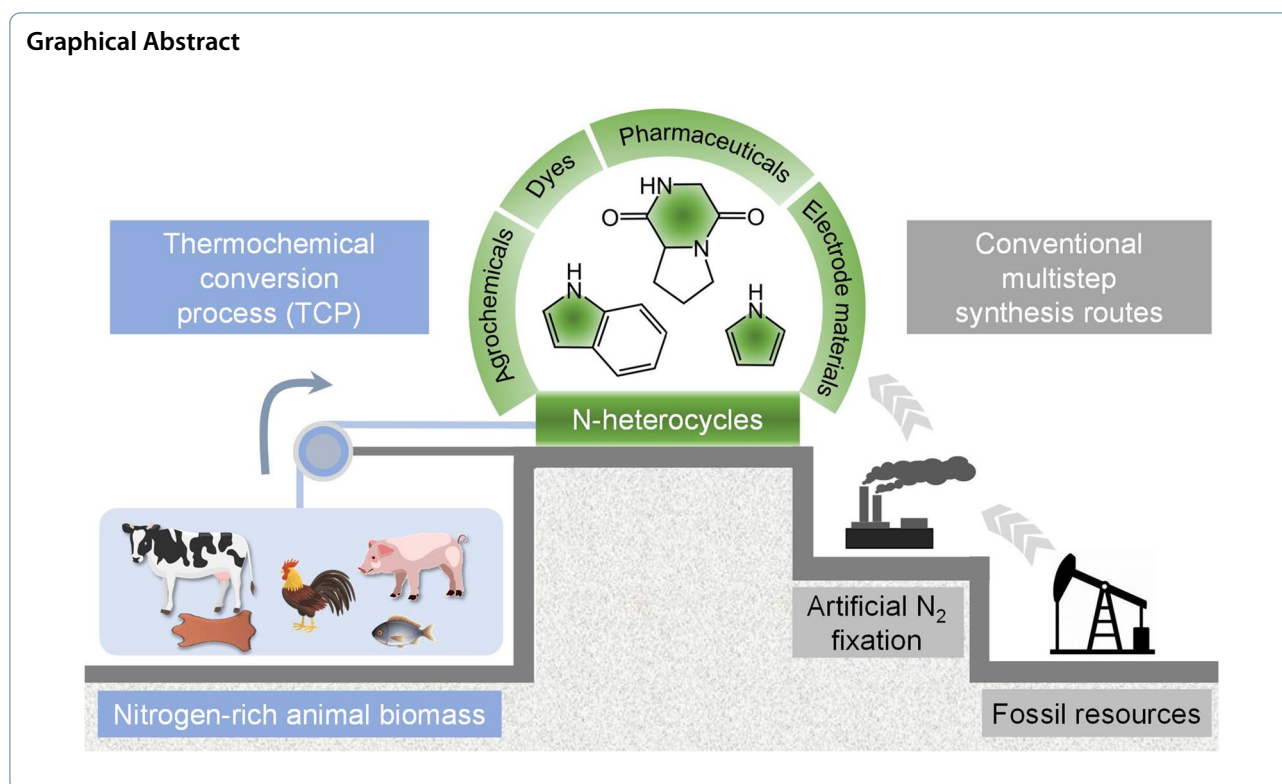**Keywords** Animal biomass, N-heterocycles, Nitrogen fixation, Nitrogenous chemicals, Thermochemical conversion

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Tang *et al. Collagen and Leather*   (2023) 5:1

Page 2 of 11

Graphical Abstract

1 Introduction

Organonitrogen chemicals are critical molecules for various industries including agriculture and medicine. N-heterocycles (such as pyrroles, pyridines, indoles, and cyclic dipeptides) are one of the most important classes of synthetic organonitrogen chemicals, accounting for more than 67% of compounds in the comprehensive medicinal chemistry database [1–3]. Currently, N-heterocycles are synthesized in an energy- and resource-intensive two-step process where first N_2 is fixed using high temperature and pressure (i.e., Haber–Bosch process), and the resultant NH_3 is then reacted with carbon sources derived from petrochemicals [4–9]. For example, the resultant NH_3 reacted with petroleum derived furan to prepare pyrroles [10]. Pyridines are often synthesized through condensation of aldehydes, ketones, or α, β-unsaturated carbonyl compounds with NH_3 or NH_3 derivatives [11]. While, the high energy barrier of the N≡N bond (941 kJ mol^{-1}) means that N_2 fixation requires significant electricity consumption (1 to 3% of the world's electricity) and fossil fuel consumption (3–5% of the world's natural gas production) [12]. Therefore, efficient routes for synthesizing N-heterocycles and other organonitrogen chemicals need to be developed to circumvent the current dependence on artificial N_2 fixation, harsh reaction conditions, fossil resources, and multiple energy-intensive synthesis steps [13–15].

Along with the ardent desire to transform the chemical industry into a greener and more sustainable manner, it will be significant to explore alternative routes to access organonitrogen chemicals from renewable sources. Recently, plant biomass (e.g., cellulose, hemicelluloses, and lignin) becomes one of the strategies to synthesize high-valued organonitrogen chemicals from renewable resources without the need for carbon from fossil resources [16–18]. However, extrinsic nitrogen source is still required due to the relative absence of nitrogen in plant tissue (0.3 to 5 wt.% of dry weight) [19, 20]. For instance, after being impregnated with 10% urea, wood chips could transform into pyrolysis oil with large content of organonitrogen chemicals [21]. Ammonia can also react with the cracked bonds (C–C, C–O, C=O, C–H and/or O–H) of cellulose during the thermal treatment to obtain a large number of diverse nitrogen-containing compounds [22]. Moreover, with the help of ammonia, furfural (a platform chemicals from hemicellulose) could be a substrate for the production of N-heterocycles through a single-step decarbonylation-amination reaction in a catalytic system [7]. Generally, the key chemistry of the above strategies is based on the transformation of oxygen-containing groups of these starting materials into

nitrogen-containing molecules with the involvement of ammonia or its derivatives derived from artificial N_2 fixation. Therefore, the need of fossil resources, harsh reaction conditions, and multiple energy-intensive synthesis steps still significantly hampered the further development of these plant biomass-based production of organonitrogen chemicals.

Nitrogen-rich biomass resource utilization can expand the boundaries of biorefinery and product diversity. The natural nitrogen cycle in the ecosystem begins with N_2 fixation (e.g., diazotrophs), after which nitrogen migrates up the food chain and finally accumulates mainly in the form of amino acids (Fig. 1a) [23–27]. Therefore, animal biomass often contains higher nitrogen (>12 wt.% of

dry weight) (Additional file 1: Fig. S1) than that of plant biomass, and this abundant nitrogen is primarily in the form of proteins. This accumulation of nitrogen in animals potentially offers a route towards the one-step conversion of biomass into organonitrogen chemicals. Currently, no previous studies have been reported focusing on the potential use of animal biomass in synthesizing high-valued organonitrogen chemicals. Composed of amino acids, animal tissues require relatively less energy to decompose compared with chitin, or other nitrogen-rich biomass, which needs complex or harmful pre-treatments to break down the recalcitrant structures due to the high crystallization and widespread hydrogen-bond networks [28, 29]. Moreover, from a sustainable and
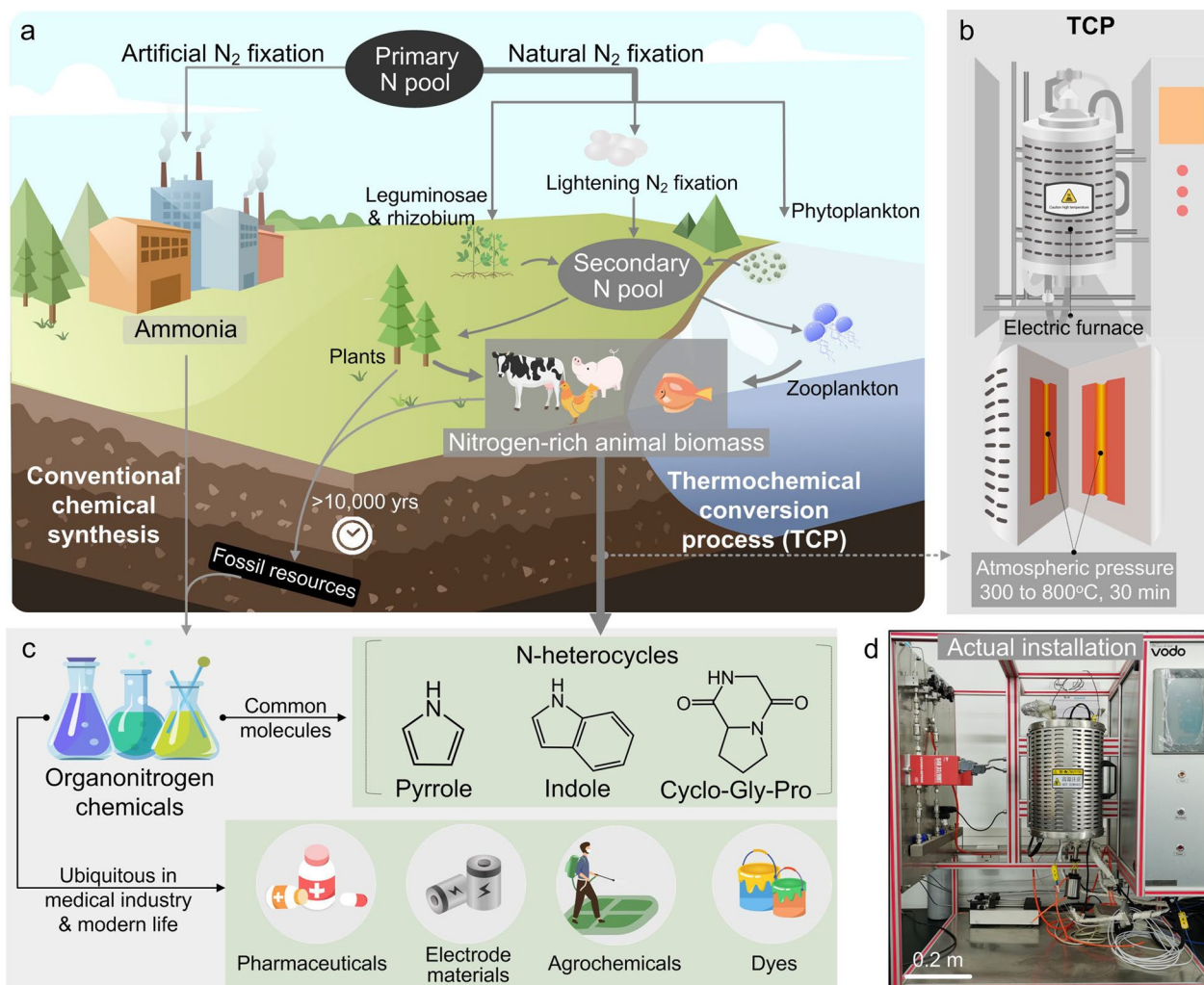

Fig. 1 Comparison between the conventional two-step route and the one-step animal biomass-dependent TCP route to generate N-heterocycles. **a** Schematic illustration of organonitrogen synthesis using TCP compared with the traditional chemical synthesis based on artificial N_2 fixation and fossil resources conversion (based on the Haber–Bosch process). **b** Schematic of the internal structure of the TCP device with the controlled temperature from 300 to 800 °C under atmospheric pressure. **c** Molecular structures and industrial applications of representative obtained N-heterocycles. **d** Optical photographic image of the installation of an actual TCP device

Tang *et al. Collagen and Leather*   (2023) 5:1

Page 4 of 11

ethical perspective, the number of the top five species of livestock is ever expanding and has reached 2.77×10^{10} in 2017 globally [30], and about 1.11×10^9 animal carcasses need to be disposed annually due to the general mortality of livestock (3–5%), not to mention carcasses related to culls. This large number of waste animal biomass threatens public health safety and can cause severe environmental problems without proper and prompt disposal.

Herein, we develop a viable one-step strategy to produce N-heterocycles from animal biomass obtainable from culls or processing plants (i.e., bovine skin, bovine muscle, chicken muscle, porcine muscle, and fish muscle) using thermochemical conversion process (referred to as TCP) under atmospheric pressure. Compared with the traditional chemical synthesis involved in artificial N_2 fixation and refinement of fossil resources, TCP presents as a more convenient and straightforward way to obtain N-heterocycles (Fig. 1b–d), during which the organic intermediates of nitrogen-rich animal biomass are largely decomposed and restructured during the thermochemical process (Additional file 1: Figs. S2–6). Our results show that the bio-oil produced from bovine skin after TCP has a high content of N-heterocycles (87.51% in all nitrogenous products), while other types of animal biomass result in a more uniform distribution of N-heterocycles, amines/amides, and nitriles. Mechanistic studies provide insight into the formation mechanisms of different N-heterocycles and how the presence and concentration of these compounds after TCP correlate with the distribution of amino acids in the different biomass sources. For example, cyclo-Gly–Pro could be easily generated after the dehydration condensation of glycine (Gly) and proline (Pro) in bovine skin. These findings demonstrate that the conventional two-step synthesis routes currently used for synthesizing organonitrogen chemicals can be completely circumvented through the further development of this sustainable, one-step thermochemical conversion strategy of animal biomass.

2 Experimental
2.1 Pre-treatment of animal biomass
The bovine skin powder was prepared from bovine skin according to the standard procedures of traditional leather industry [31]. In brief, the bovine skin was cleaned, un-haired, limed, splitted, and delimed to remove non-collagen components. Then the skin was soaked in an aqueous solution of acetic acid (16.0 g L^{-1}) for 1.5 h and washed by high-purity Milli-Q water for three times to remove mineral substances. After the pH was adjusted about 4.8 with acetic acid-sodium acetate buffer solution, the bovine skin was dehydrated by absolute ethyl alcohol, dried in vacuum.

The other four types of animal biomass (bovine muscle, chicken muscle, fish, and porcine muscle) were first cut into debris, and then demineralized by stirring in an equal mass EDTA-Na$_4$ solution (2 wt.%) for 24 h. After washed for three times by high-purity Milli-Q water, the collections were dried in a freeze dryer. Finally, the dried samples were degreased with petroleum ether through Soxhlet Extraction Method, and further dried in room temperature overnight. The use of degreaser is to remove the fat in the animal biomass to avoid the effect of fat in our experiment to study the conversion of animal protein to N-containing chemicals. In practical application scenario, there is no need of use of degreaser to remove the fat which can be processed with protein for nitrogenous chemical production. Finally, the animal biomass was ground and sieved, and the sifted (20 mesh, < 0.85 mm) biomass powder was obtained.

2.2 The bench-top units of TCP
A bench-top continuous flow reactor consisted of a quartz tube reactor heated by a furnace, and a condensation tube bathed in ice water was set up for the thermochemical conversion process (TCP, Fig. 2a). Firstly, the furnace chamber was heated to the preset temperature (300–800 °C) and the N_2 flow was injected for 20 min with the rate of 50 mL min^{-1} to ensure that the inner air was discharged completely. Then, quartz tube reactor loaded with 3.0 g pre-treated animal biomass powder (bovine skin, bovine muscle, chicken muscle, porcine muscle, fish, or a mixture of Gly, Pro, and Hyp) was put into the furnace chamber with the preset temperature. In the thermochemical conversion process, the bovine skin biomass was mixed with catalysts uniformly and added into the reactor (mass ratio of catalyst/feedstock = 1:1) before reaction.

2.3 Collection of the products in three phases
When the reaction began, the animal biomass powder was heated up rapidly and the volatile evolved out quickly. During TCP, the bio-oil was trapped in the ice-water mixture condensing unit. The bio-char was remained in quartz tube reactor. The bio-gas was collected via the bubbling system where H$_2$SO$_4$ (0.1 mol L^{-1}) and NaOH (0.2 mol L^{-1}) solutions were used for NH$_3$ and HCN collection, respectively. The following mixed tail gas was collected by gas collecting bag, which was then tested by gas chromatography (GC) to further obtained the content (vol %) of each composition in the mixed gas.

3 Results and discussion
Bio-oil, bio-gas, and bio-char can be produced by the TCP (Fig. 2a), and each contains different types of nitrogenous compounds. The corresponding nitrogen
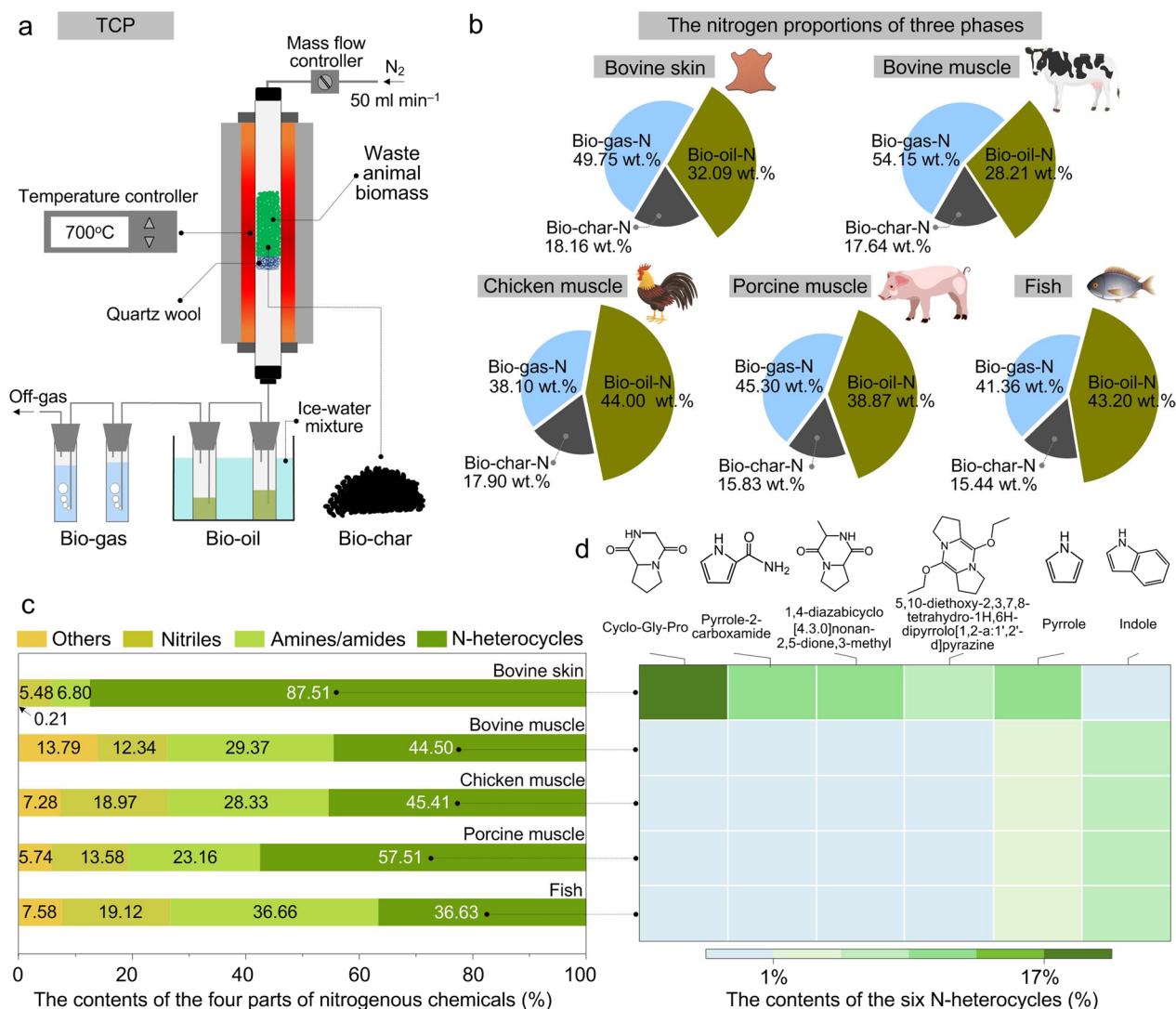
Fig. 2 Analysis of the nitrogenous compounds derived from different animal biomass via TCP. **a** Schematic illustration of the fixed bed nitrogen-rich thermochemical conversion and collection system of TCP at 700 °C under atmospheric pressure for 30 min. **b** Nitrogen proportions of three phases products (bio-gas-N, bio-oil-N, and bio-char-N) in total nitrogen of different animal biomass. **c** The contents of the four parts of nitrogenous compounds (N-heterocycles, amines/amides, nitriles, and others) in all the nitrogenous compounds of bio-oil. **d** The contents of the six N-heterocycle products in all the nitrogenous compounds of bio-oil

proportions of the produced bio-oil in total nitrogen (nitrogen in the raw animal biomass) varies from 28.21 to 44.00 wt.% among the five types of animal biomass (Fig. 2b and Additional file 1: Fig. S7–9), and these nitrogenous products can be primarily identified as four categories: N-heterocycles, amines/amides, nitriles, and others (other nitrogenous compounds) (Additional file 1: Table S1). Notably, the content of N-heterocycles in all the nitrogenous compounds of bio-oil from bovine skin reaches 87.51% (Fig. 2c), while nitrogenous products in bio-oil from other types of animal biomass distributes more equally between N-heterocycles (36.63–57.51%), amines/amides (23.16–36.66%), and

nitriles (12.34–19.12%). The obtained N-heterocycles are mainly present as cyclo-Gly–Pro, pyrrole, indole, pyrrole-2-carboxamide, 1,4-diazabicyclo[4.3.0]nonan-2,5-dione,3-methyl, and 5,10-diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1′,2′-d]pyrazine (Fig. 2d). For bovine skin, cyclo-Gly–Pro is the dominant N-heterocycle (22.72% of all the nitrogenous compounds), while pyrrole-2-carboxamide and pyrrole account for 11.24% and 9.81%, respectively. Indole is the dominant N-heterocycle (6.46–9.51%) for the other four types of animal biomass (bovine muscle, chicken muscle, porcine muscle, and fish). Bio-gas is also produced in large quantities after TCP, and a large proportion of nitrogen

Tang *et al. Collagen and Leather*   (2023) 5:1

Page 6 of 11

is present in the bio-gas as HCN and NH$_3$ (Additional file 1: Fig. S10). Bio-char can be also collected, albeit in lower quantities, and the nitrogen in bio-char is mainly present as pyridinic-N, pyrrolic-N, and quaternary-N (Additional file 1: Figs. S11–17).

The amino acid contents of the different types of animal biomass correlate with the specific organonitrogen chemicals produced during TCP, which gives mechanistic insight into the transformations of nitrogen during the conversion process (Fig. 3a and Additional file 1: Table S2). For example, bovine skin has a high content of

glycine (Gly, 18.45 wt.%), proline (Pro, 23.90 wt.%), and L-hydroxyproline (Hyp, 11.87 wt.%), which together contribute to the formation of N-heterocycles (87.51%).

To confirm that these three amino acids are the main drivers of N-heterocycles formation, TCP was performed on a mixture of just Gly, Pro, and Hyp, which yielded the same three main N-heterocycle products as bovine skin (i.e., pyrrole, 5,10-diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1',2'-d]pyrazine, and cyclo-Gly–Pro) (Fig. 3b and Additional file 1: Table S3). Specifically, cyclo-Gly–Pro is a conjugate of Gly and Pro/Hyp (Fig. 3c)
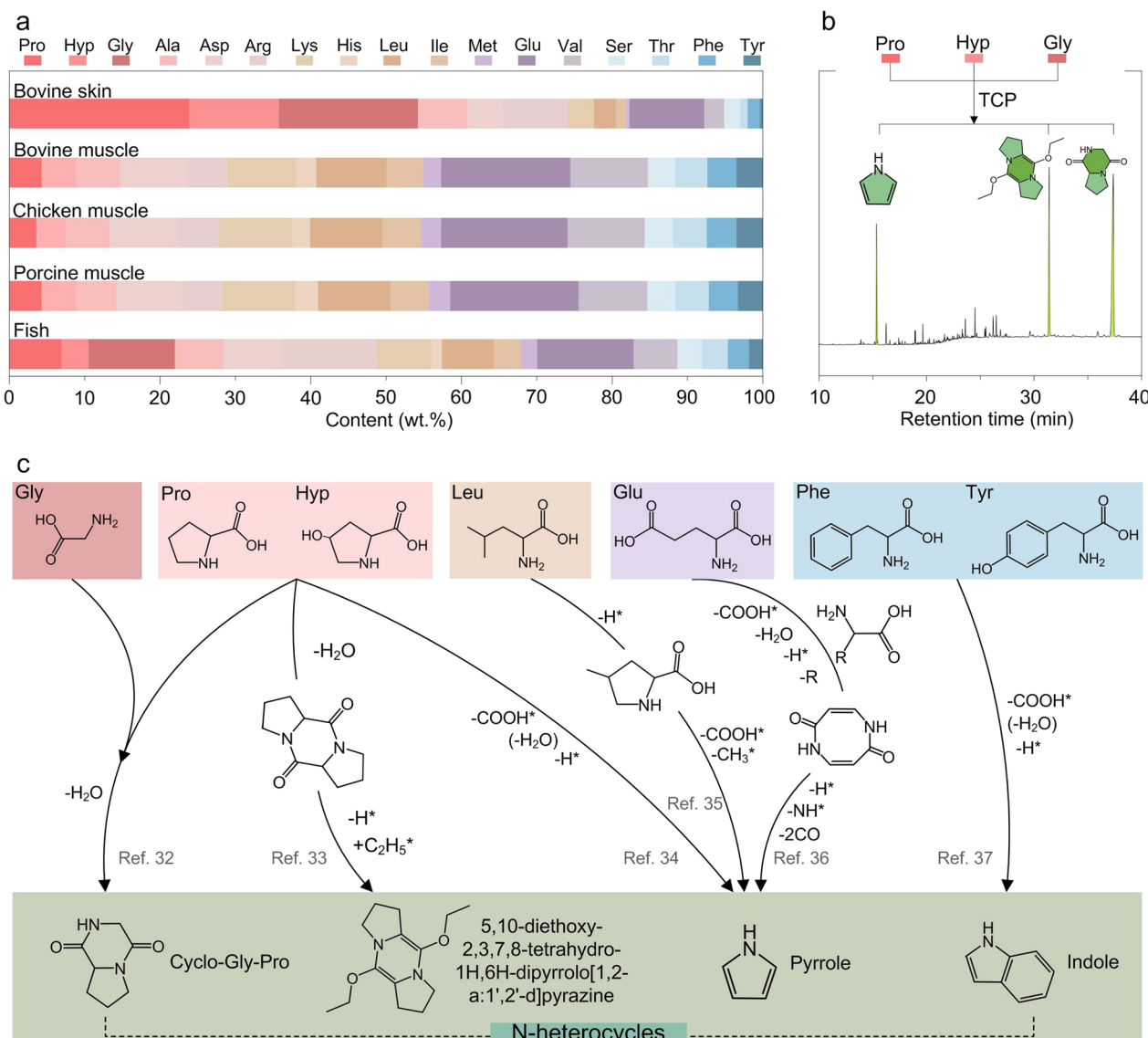

Fig. 3 Nitrogen transformation from the animal biomass into main N-heterocycles. **a** The contents of the amino acids in the animal biomass. **b** GC–MS spectrum of the products in bio-oil after TCP of the mixture of glycine, proline, and L-hydroxyproline. **c** Proposed mechanism of nitrogen transformation from amino acids into the N-heterocycles

[32], while 5,10-diethoxy-2,3,7,8-tetrahydro-1H,6H-dipyrrolo[1,2-a:1,2'-d]pyrazine forms through the dimerization between Pro or Hyp [33], and pyrrole forms from Pro or Hyp degradation through H* release and the loss of COOH*, or further loss of H_2O [34].

For the other types of animal biomass, leucine (Leu) (6.93–9.65 wt.%) and glutamic (Glu) (12.80–17.16 wt.%) are the dominant amino acids. Leu is pyrolyzed into pyrrole by releasing H* followed by the loss of COOH* and its side-chain [35]. Pyrrole could also potentially be produced by the reaction of Glu with any amino acids through the loss of H_2O and any side groups to form an 8-membered ring followed by decarbonylation and deamination [36]. Additionally, the muscle and fish animal biomass have higher contents of tyrosine (Tyr) (1.86 to 3.52 wt.%) and phenylalanine (Phe) (2.80 to 3.95 wt.%) than bovine skin (0.41 and 1.63 wt.%), which lead to the formation of indole through the dehydrogenation, decarboxylation, and dehydration reactions of Tyr and Phe [37]. Collectively, these results indicate that the transformation of nitrogen is closely related to the specific amino acids composition of the animal biomass source.

The temperature used for TCP determines the nitrogen proportion of three phases products in total nitrogen of bovine skin. The bio-gas-N proportion increases from 13.64 to 53.80 wt.% with the increasing temperature (< 600 °C) then remain almost unchanged at higher temperature (> 600 °C). And the bio-oil-N proportion increases from 1.72 to 33.03 wt.% with the increasing temperature, while the corresponding bio-char-N proportion reduces from 84.64 to 18.63 wt.% (Fig. 4a and Additional file 1: Fig. S18–21). The content of N-heterocycles in all the nitrogenous compounds of bio-oil is 26.43% and the content of amines/amides is 60.74% at 300 °C (Fig. 4b and Additional file 1: Table S4), but when the temperature of TCP is increased to 700 °C, the content of N-heterocycles dramatically increases to 87.51%.

Moreover, among the obtained N-heterocycle products, the contents of cyclo-Gly–Pro and pyrrole increase with rising temperature (Fig. 4c). These above results suggest that the nitrogen of proteins in bovine skin can just be cracked into bio-gas and a few bio-oil compounds (amines/amides, nitriles, and N-heterocycles) due to the weak deamination and dehydration at low temperatures (300 to 500 °C) of TCP (Fig. 4d). Another portion of nitrogen from proteins migrates into the bio-char as pyridinic-N and pyrrolic-N at low temperatures (Additional file 1: Fig. S22–24). While, at high temperatures (500 to 800 °C), the bio-oil nitrogen is mainly incorporated as N-heterocycles (Fig. 4b) owing to the vigorous cracking reactions and cyclization reactions of the amino acid fragments. Meanwhile, the amines/amides will further decompose into N-heterocycles through the deamination

reaction. Moreover, the pyridinic-N in bio-char can also transform into quaternary-N by ring condensation reactions, and further decompose into N-heterocycles [36]. Finally, bio-gas can release from the cracking of bio-oil or bio-char, so that the proportion of bio-gas-N accumulates at higher temperatures.

Among all the N-heterocycles derived from bovine skin, pyrrole and cyclo-Gly–Pro are two major N-heterocycles. Pyrroles have the advantages of high biological activity and low toxicity, which were widely used as important platform chemicals in the agrochemical, pharmaceutical, and dye industries [38]. Cyclo-Gly–Pro, a type of cyclic dipeptide, is reported to demonstrate physiological activities such as anti-amnesic effects and neuroprotective actions [39, 40]. To enhance the generation of these two valuable N-heterocycles, different types of catalysts (solid acid catalyst, metal oxides, metals, and alkalis) were introduced to TCP. The contents of N-heterocycles in all nitrogenous compounds of bio-oil slightly increased when solid acid catalyst, metal oxides, and metals were introduced. Inversely, alkalis ($Ca(OH)_2$ and KOH) decreased the contents of N-heterocycles in all nitrogenous compounds of bio-oil from 87.51% to 72.78% and 74.31%, respectively (Fig. 5a).

Additionally, the catalysts promoted the generation of pyrroles (pyrrole and its alkyl derivates) or cyclo-Gly–Pro (Fig. 5b), which was determined by the types of catalysts. The content of pyrroles in all nitrogenous compounds of bio-oil was increased from 27.43% to 45.18% by acidic ZSM-5 catalyst, which could promote the dehydration reaction and pyrroles polymerization reaction [38]. Metal oxides (Fe_2O_3 and Al_2O_3) and metals (Ni and Pd) increased the content of cyclo-Gly–Pro in all nitrogenous compounds of bio-oil from 14.29% to 25%~33.57%. The solid acid catalyst, metal oxides, and metal catalysts (especially ZSM-5 and Al_2O_3) provide an acid environment, which improved the cracking reaction of protein and promoted more organic compounds to decompose into small molecules. Thus, more cyclo-Gly–Pro could derive from the condensation of light N-containing chemicals (acetamide, propylamine, and hydroxyethylamine) as well as the dimerization of Gly and Pro/Hyp [41–43]. On the other hand, the alkalis ($Ca(OH)_2$ and KOH) increased the basicity of the pyrolysis environment and promoted the decarboxylation process, which resulted in the content increase of the pyrrole and its alkyl derivatives generating mainly from the decarboxylation process of Pro and Hyp [44, 45]. Meanwhile, the loss of carboxy inhibited the dimerization of Gly and Pro/Hyp and caused the decrease of the content of cyclo-Gly–Pro. Simultaneously, the contents of pyrroles and amines/amides (ring-opening product) increased (Fig. 5a and b). Furthermore, the production quantities of pyrrole and
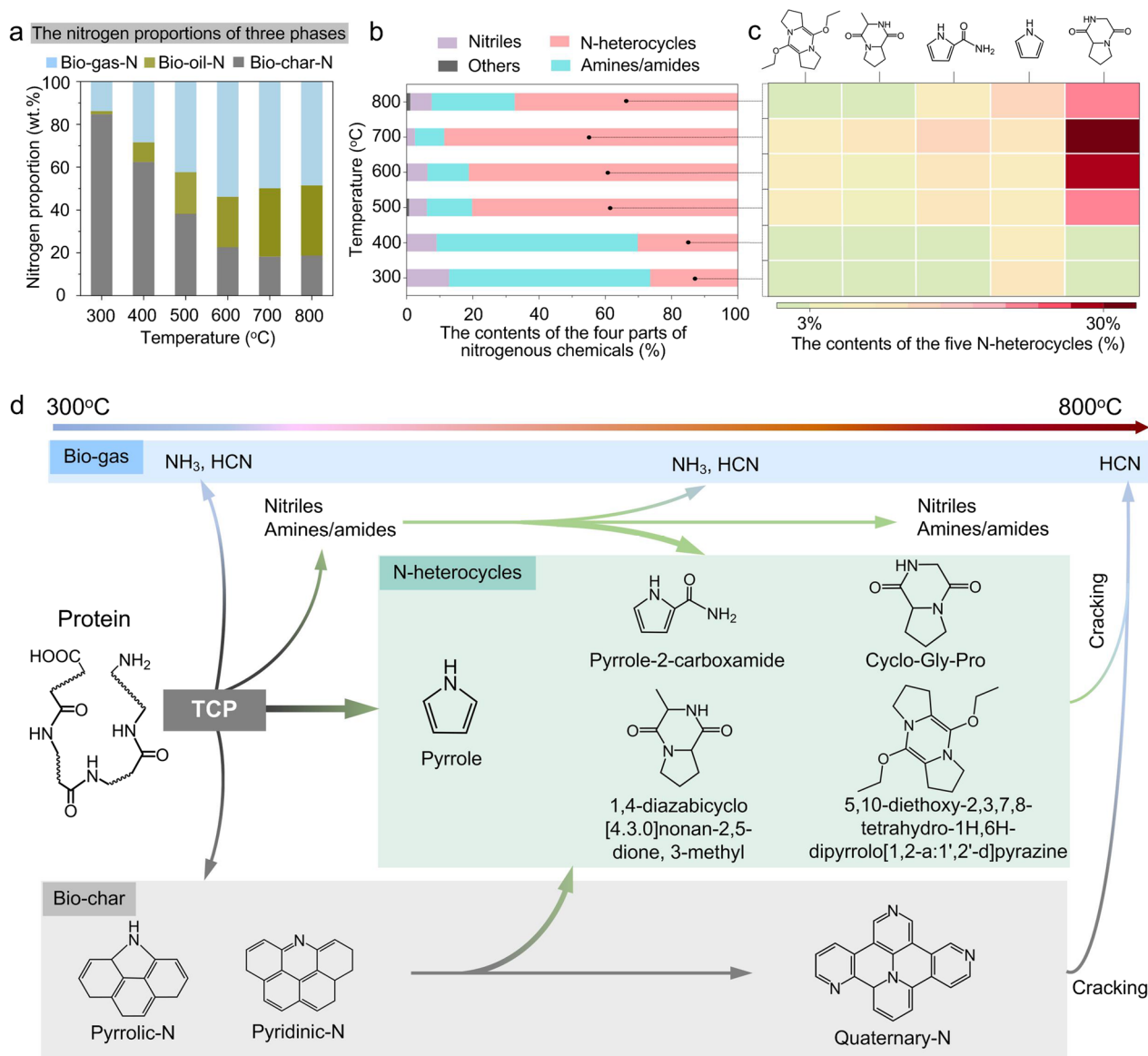
Fig. 4 Nitrogen transformation from bovine skin at different TCP temperatures. **a** Nitrogen proportions of three phases products (bio-gas-N, bio-oil-N, and bio-char-N) in total nitrogen. **b** The contents of the four parts of nitrogenous compounds (N-heterocycles, amines/amides, nitriles, and others) in all the nitrogenous compounds of bio-oil. **c** The contents of the five N-heterocycle products in all the nitrogenous compounds of bio-oil. **d** Proposed mechanism of nitrogen migration from bovine skin into N-heterocycles

cyclo-Gly–Pro were determined by constructing calibration curves of their standards (Additional file 1: Fig. S25). The production quantities of pyrrole and cyclo-Gly–Pro were increased to 30.79 mg g^{-1} and 38.88 mg g^{-1} by introducing KOH and Al$_2$O$_3$ catalysts into TCP, respectively (Fig. 5c). The production quantities of the object products were highly consistence with the contents in the bio-oil.

The release of HCN and NH$_3$ could also confirm the change of N-heterocycles contents (Fig. 5d). Obviously, these catalysts increased the N content of NH$_3$ which

indicated a promotion of the deamination and dehydration, and decreased the N content of HCN. The limitation of the release of HCN might be attributed to the increase of the main N-heterocycles (pyrroles or cyclo-Gly–Pro), which demonstrated an enhanced condensation and suppressed degradation of these N-heterocycles. In addition, due to the remarkable transformation from N-heterocycles to amines/amides by Ca(OH)$_2$ or KOH, the source of HCN decreased thus inhibiting the generation of HCN. These results demonstrated that the catalysts were conducive to controlling the emissions of
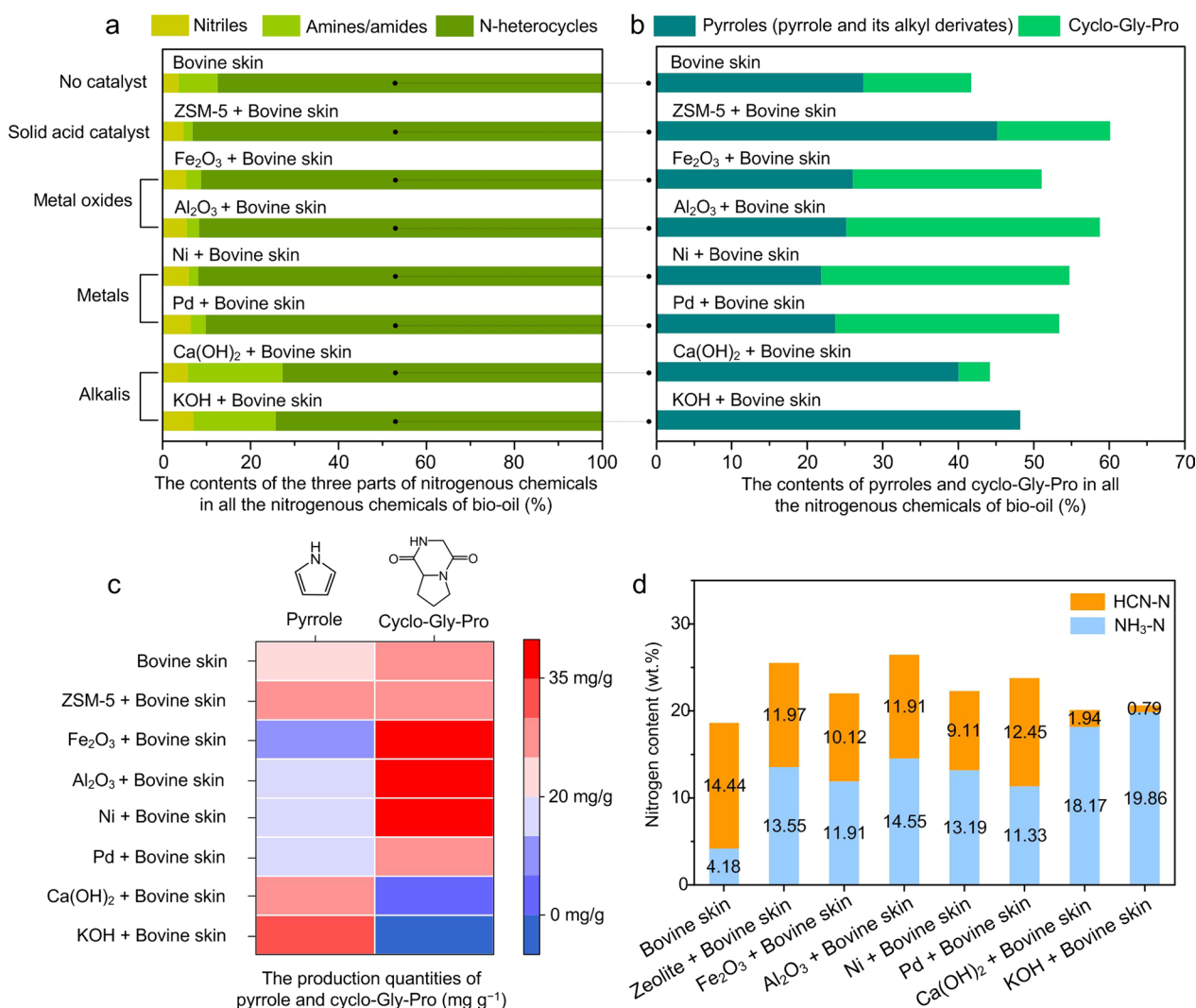
Tang *et al. Collagen and Leather*   (2023) 5:1

Page 9 of 11

Fig. 5 Nitrogen transformation from bovine skin through TCP at 700 °C with different catalysts. **a** The contents of the nitrogenous compounds (N-heterocycles, amines/amides, and nitriles) in all the nitrogenous compounds of bio-oil. **b** The contents of the pyrroles (pyrrole and its alkyl derivates) and cyclo-Gly-Pro in all the nitrogenous compounds of bio-oil. **c** The actual production quantities of pyrrole and cyclo-Gly–Pro derived from bovine skin (mg g^{-1}). **d** The nitrogen contents of HCN-N and NH_3-N in total nitrogen derived from bovine skin after TCP at 700 °C

the valuable nitrogenous tail gases (especially HCN and NH_3). Besides, the composition and content of other tail gases were measured and the low heating values (LHV) of the mixed gases varied from 10.01 to 15.78 MJ Nm^{-3} (Additional file 1: Fig. S26 and 27), which mean that these tail gas might be potential gas fuels after appropriate post-treatments of the valuable gases [46].

4 Conclusions

In summary, we propose a new method for producing high-value N-heterocycles from animal biomass through a sustainable thermochemical conversion process (named as TCP). In this research, the generation of nitrogenous products and the transformation mechanism of different animal biomass were comparatively investigated. Specifically, high content of N-heterocycles (87.51%) was obtained from bovine skin. Furthermore, the production quantities of pyrrole and cyclo-Gly–Pro (main N-heterocycle) could be increased to 30.79 mg g^{-1} and 38.88 mg g^{-1} by introducing KOH and Al_2O_3 catalysts into TCP, respectively. From a fundamental perspective, TCP provides a facial and one-step strategy for access to organonitrogen chemicals that are normally dependent on artificial N_2 fixation via harsh reaction conditions, non-renewable carbon sources (fossil resources), and multistep synthesis routes.

Tang *et al. Collagen and Leather*   (2023) 5:1

Page 10 of 11

Abbreviations

TCP	Thermochemical conversion process
Gly	Glycine
Pro	Proline
Leu	Leucine
Glu	Glutamic
Tyr	Tyrosine
Phe	Phenylalanine
LHV	Low heating value

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s42825-022-00109-z.

Additional file 1. Supporting Information.

Availability of data and materials

All data from this study are presented in the paper and the supporting information.

Declaration

Competing interests

The authors declare that they have no competing interests.

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Tang *et al. Collagen and Leather*   *(2023) 5:1*

Page 11 of 11

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