



Full Length Article

NO_x precursors from biomass pyrolysis: Distribution of amino acids in biomass and Tar-N during devolatilization using model compounds



Hanping Chen, Yaohui Si, Yingquan Chen*, Haiping Yang, Deming Chen, Wei Chen

State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China

HIGHLIGHTS

- 60–80% of nitrogen in biomass is existed as protein-N.
- 9 types of amino acids are recommended to be used as model amino acids.
- Cellulose promotes higher N-containing chemical selection at higher heating rate.
- Amino acids can effect N distribution and N-containing chemicals formation.
- Glutamic acid and alanine can promote more heterocyclic form.

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ABSTRACT

To elucidate the mechanism of nitrogen transformation during biomass combustion, the formation behavior of NO_x precursors during biomass devolatilization was investigated using two types of pyrolysis reactors at different heating rates (13 °C/s and 10⁴ °C/s) with model compounds (i.e., mixtures of various amino acids and cellulose/lignin). It was found that 60–80% nitrogen existed as protein-N. Cellulose promoted the formation of a greater amount of N-containing compounds at higher heating rates but resulted in the conversion of nitrogen into tar with a smaller amount of N-containing compounds at lower heating rates. Lignin promoted the transformation of nitrogen into gaseous products at lower heating rates. Higher heating rates were found to disfavor the interaction between the amino acids and lignin. However, different amino acids had different effects on the nitrogen transformation in biomass. Glutamic acid resulted in the lowest nitrogen distribution in gas and the highest distribution in tar, phenylalanine caused the conversion of a large amount of nitrogen into gaseous products, while the resulting char captured the lowest amount of nitrogen. Glutamic acid and alanine promoted the formation of N-containing heterocyclic compounds, while copyrolysis with phenylalanine afforded N-containing compounds with –NH₂ and –CN groups.

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1. Introduction

Because of the renewability and near zero emission of CO₂, biomass energy and bio-fuels have seen widespread and extensive utilization. Generally, NO_x is mostly formed as thermal NO_x during biomass combustion in a combustor [1] and biofuel combustion in engines [2]. However, the fuel-N in biomass also play an important role in NO_x formation. Although the nitrogen content in biomass is low, increased utilization of biomass can lead to increased risk of pollution by NO_x derived from combustion or gasification [3,4].

To effectively reduce this risk and develop a harmless treatment technology, in-depth understanding of the nitrogen transformation mechanism during biomass combustion or gasification is necessary [4]. The form of nitrogen in the fuels may play an important role in the nitrogen transformation from fuel-N to NO_x [3,5–7]. As opposed to other solid fuels, especially coal, the nitrogen in biomass generally exists as protein and not as the pyridinic and pyrrolic structures seen in coal [3,4]. Some types of biomass are protein rich, because they contain seeds and kitchen waste while most other types of biomass are protein poor, as they comprise leaves and stem from agriculture and forest waste [8]. Hence, in recent years, some studies focused on nitrogen conversion from nitrogen-containing model compounds (protein, amino acids, etc.) to NO_x [5,9–14]. These studies provided valuable insights into the nitrogen conversion mechanism; however, due to the complex-

* Corresponding author at: 1037 Luau Road, Wuhan, Hubei 430074, PR China.

E-mail addresses: hp.chen@163.com (H. Chen), syh850330@gmail.com (Y. Si), chenyingquan@hust.edu.cn (Y. Chen), yhping2002@163.com (H. Yang), chendm512@163.com (D. Chen), chenwei_hk@163.com (W. Chen).

ity of biomass and its conversion process, the results of these studies on model compounds may have limited validity when direct shift to biomass [15]. To elucidate the complete mechanism of nitrogen conversion, a combined study of biomass and model compounds is recommended [9,16,17].

To understand HCN formation at the molecular level, Hao et al. [10] investigated the co-pyrolysis of glycine and glucose/fructose, as the model compounds of biomass N and the major components, respectively. The results revealed that the HCN yield decreased while more N-heterocyclic compounds formed during glycine pyrolysis in the presence of glucose/fructose. Ren et al. [15,17] first investigated the co-pyrolysis of amino acids and cellulose, hemicellulose and lignin. It was found that these components could influence the yield of HCN/NH₃ and that hemicellulose inhibited N-NH₃ conversion, while lignin promoted NH₃ formation. However, Ren's work only focused on the gaseous NO_x precursor (NH₃ and HCN), while the nitrogen distribution and nitrogen form in tar and char products were ignored. In addition, the observed pyrolysis temperature was 800 °C, which was higher than the major biomass devolatilization temperature (400–600 °C), for this reason, transform from light gas-N and tar-N to NH₃/HCN could not be investigated [3,6]. Hence, it is necessary to investigate the precursor of NH₃/HCN formed during the devolatilization of biomass, especially the tar-N and the N distribution in tar and char, by the co-pyrolysis of amino acids with biomass major components.

The amino acids differed among various types of biomass; more than 10 types of amino acids were found to be present in each biomass [4,9,18,19]. Hansson et al. [9] provided the amino acid composition of whey protein and scots pine, and detected 18 species of amino acids. Ren et al. [18] analyzed the amino acids composition of three types of agriculture biomass, rice straw, wheat straw and corn cob, using a high performance liquid chromatograph and demonstrated that 18 amino acids existed in the three biomass sample, with the major components being glycine, glutamic acid, aspartic acid, leucine, phenylalanine and proline. However, reports on the amino acids composition in biomass are rare. This limited literature information on the amino acids composition in biomass might influence the appropriate screening of model amino acids to represent various types of biomass.

In this study, we investigated the amino acids in 15 types of biomass, including 10 types of agro biomass, 4 types of woody biomass, and 1 energy crop, in order to extend determine the information of amino acids composition in biomass. Meanwhile, to determine the amount of nitrogen present as protein-N in biomass, the total nitrogen content estimated by ultimate analysis and the nitrogen content in protein, as determined by the Kjeldahl method, were compared. Based on the results, several kinds of amino acids were selected as representative compounds and model nitrogen-containing compounds and co-pyrolysis between these amino acids and cellulose/lignin was carried out. Detailed information on tar-N may be useful to further understand the fuel-N conversion mechanism during biomass combustion or gasification.

2. Material and method

2.1. Material preparation

15 types of biomass were collected from the surrounding area of Wuhan City, Hubei Province, including 10 types of agro biomass (*Triticum* straw, *Zea mays* stalk, *Zea mays* cob, *Gossypium* stalk, *Oryza sativa* straw, *Oryza sativa* husk, *Arachis hypogaea* hull, *Brassica napus* stalk, *Nicotiana* stem, and *Glycine max* stalk), 4 types of woody biomass (*Pinus massoniana* wood, *Salix babylonica* wood,

Cinnamomum camphora wood, and *Cunninghamia lanceolata* sawdust) and an energy crop (*Arundo donax*). The biomass major components, cellulose and lignin, were purchased from Sigma Chemical Co. Cellulose is a white powder with an average particle size of 20 µm, while lignin is a brown powder and alkali lignin. The ultimate analysis indicated that the nitrogen contents in cellulose and lignin were almost negligible; hence, in the subsequent co-pyrolysis experiment, the nitrogen compounds in the products may be considered to be derived only from the amino acids.

The selected model amino acids (purity: 99% or more) were purchased from Sinopharm Chemical Reagent Co. In the co-pyrolysis experiment, a mixture of selected amino acid with cellulose or lignin was used. The nitrogen content in the mixture was varied as 0.5 wt%, 1 wt%, 1.5 wt% and 2 wt%. The weight of the amino acid was calculated from the objective nitrogen content in the mixture and the nitrogen content in the amino acid. Detailed information about the blend proportions of the amino acids and lignin/cellulose is provided in Table 1. Before the pyrolysis experiment, the sample blend was dried for about 24 h at 80 °C in a vacuum drying oven, in order to avoid the influence of water on pyrolysis.

2.2. The analysis on protein-N content and amino acids composition in biomass

The nitrogen content in protein was analyzed by the Kjeldahl method using a Kjeltac Auto Analyzer (SKD-3000, Shanghai Peiyou Analytical Instruments CO., LTD, China). First, 3 g of biomass was digested using concentrated sulfuric acid and about 30 ml of the digestion solution was transferred to the analyzer to obtain the protein-N content.

Amino acids compositions were detected using an L8800 automated amino acid analyzer (Hitachi High-Technologies, Tokyo, Japan). The protein in the samples was hydrolyzed into the corresponding amino acids and an independent adsorption process for these amino acids was carried out under low pH conditions using cation exchange resin. Then, though different elution programs, different amino acids were eluted at different stages. Subsequently, the eluted amino acids were allowed to react with ninhydrin with heating, and the generated violet material was used to determine the specific amino acid species under 570 nm and 440 nm light detection by a spectrophotometer. Meanwhile, the amino acids were quantified by the external standard method. The operation conditions for the instrument have been reported elsewhere [20]. A 4.6 mm × 60 mm of #2622 resin column was used. The temperature of the analysis column and the reaction column was 50 °C and 135 °C, respectively. The flow rates of the buffer and the chromogenic agent were 0.4 mL min⁻¹ and 0.35 mL min⁻¹, respectively. In each trail the injection volume was 20 µL of hydrolysate. Analysis of each sample were repeated twice and the relative error of result was below 10%.

2.3. Pyrolysis procedure and analysis of products

Two types of pyrolysis experiments were carried out. The experiment at a relatively lower heating rate pyrolysis was carried out on the lab scale using a fixed bed pyrolysis reactor. This system comprised the following: (1) the reactor, a tiltable quartz tube (height: 180 mm, internal diameter: 20 mm); (2) the temperature control system, which concluded a thermocouple, a heating coil ring and a digital temperature indicator; and (3) the liquid condensation system. Before pyrolysis, a sandwich structure between the sample and a quartz fiber was constructed in the reactor, and about 1.5 g of the sample was used in each trail. A flow of preheated argon (99.9999%, 100 ml/min) was used to provide a reductive atmosphere in the reactor. When pyrolyzing the samples, the reac-

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