



# Catalytic pyrolysis of amino acids: Comparison of aliphatic amino acid and cyclic amino acid



Guangyi Liu<sup>a,b</sup>, Mark M. Wright<sup>c,\*</sup>, Qingliang Zhao<sup>a,d,\*</sup>, Robert C. Brown<sup>b,c</sup>, Kaige Wang<sup>b,c</sup>, Yuan Xue<sup>b,c</sup>

<sup>a</sup>School of Municipal & Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

<sup>b</sup>Bioeconomy Institute, Iowa State University, Ames, IA 50011, United States

<sup>c</sup>Department of Mechanical Engineering, Iowa State University, Ames, IA 50011, United States

<sup>d</sup>State Key Laboratory of Urban Water Resources and Environments (SKLUWRE), School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China

## ARTICLE INFO

### Article history:

Received 3 November 2015

Accepted 11 January 2016

Available online 23 January 2016

### Keywords:

Leucine

Proline

Catalytic pyrolysis

Hydrocarbon

Nitrogen

Deoxygenation

## ABSTRACT

Catalytic pyrolysis (CP) of protein-rich biomass such as microalgae is a promising approach to biofuel production. CP of amino acids can help understand the cracking of protein-rich biomass in the presence of zeolite catalysts. In this study, as representatives of aliphatic amino acid and cyclic amino acid, respectively, leucine and proline were pyrolyzed with ZSM-5 catalyst in a Tandem micro-furnace reactor coupled with a MS/FID/TCD. At 650 °C, leucine produced more hydrocarbons (aromatic hydrocarbons of 29.6%, olefins of 34.9% and alkanes of 8.1%) than proline (aromatic hydrocarbons of 25.3%, olefins of 14.0% and alkanes of 5.5%) because its relatively simpler amino structure readily detached as ammonia during CP. However, with an N-cyclic structure, proline produced large quantities of nitrogen-containing heterocyclic compounds that favored coke formation in CP. Accordingly, 28.2% of the nitrogen in proline was retained in the solid residue while most of the nitrogen in leucine was converted into ammonia leaving only 4.3% in the solid residue. In addition, though decarboxylation to carbon dioxide was favored in non-catalytic pyrolysis of leucine and proline, decarbonylation to carbon monoxide became the primary deoxygenation pathway in CP. These results indicate that the chemical structures of amino acids have significant effects on product distributions during CP and N-cyclic amino acid is less favored in CP for production of hydrocarbons and ammonia.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Pyrolysis has been considered as a promising method for producing bio-fuels and bio-chemicals to replace fossil fuels [1]. Most work to date has focused on lignocellulosic biomass as feedstock [2,3]. More recently, protein-rich biomass such as microalgae and other species have been investigated as feedstocks because of their potential for high biomass productivity compared to terrestrial plants [4].

Pyrolysis of biomass yields a viscous liquid known as bio-oil [1]. Bio-oil from protein-rich biomass has high heating value, desirable pH and low total acid number [5–7]. However, it contains many oxygenates [8], which contributes to its instability in storage and

makes it incompatible with commercial infrastructure designed for hydrocarbons [9]. On the other hand, the high nitrogen content of protein-rich biomass compromises the usefulness of the resulting oil as fuel [10,11] due to environmental concerns such as photochemical smog and acid rain [12].

Much research [13–15] has emerged focusing on catalytic pyrolysis to improve the quality of pyrolysis products of protein-rich biomass. Among the catalysts reported, ZSM-5 is relatively inexpensive and robust and is often employed in catalytic pyrolysis studies for hydrotreating and deoxygenation. Thangalazhy-Gopakumar et al. [16] conducted catalytic pyrolysis of *Chlorella vulgaris* with ZSM-5 catalyst and confirmed that the negative attributes of algae bio-oil such as high content of oxygen and nitrogen could be removed by reacting the biomass in the presence of catalyst. Wang et al. [17] employed ZSM-5 catalyst to convert dried distillers grains with solubles (DDGS) in a Tandem microscale reactor system and reported significant yields of hydrocarbons (56.8 C %) and conversion of nitrogen in the biomass to ammonia (45.1 N %). Although these studies reveal that ZSM-5 catalyst is

\* Corresponding authors at: School of Municipal & Environmental Engineering, Harbin Institute of Technology, Harbin 150090, China. Tel.: +86 451 86283017; fax: +86 451 86282100 (Q. Zhao). Tel.: +1 515 294 0913; fax: +1 515 294 8993 (M.M. Wright).

E-mail addresses: [markmw@iastate.edu](mailto:markmw@iastate.edu) (M.M. Wright), [qlzhao@hit.edu.cn](mailto:qlzhao@hit.edu.cn) (Q. Zhao).

effective in removing oxygen and nitrogen from the products of pyrolysis, it is difficult to describe the underlying mechanisms due to the complex composition of biomass. Researchers employed corn protein [17], egg white [18], soybean protein [19] as model compounds of protein to investigate the pyrolysis process of protein-rich biomass but the results were not consistent. This is because protein has a very complex structure, and its amino acid composition varies greatly from one biomass species to another which plays a significant role in product distributions during protein pyrolysis [20]. Therefore, an investigation of the amino acids pyrolysis process is needed to help understand the cracking of protein-rich biomass [21]. Pyrolysis of amino acids has been widely reported in the last several decades. Haidar et al. [22] pyrolyzed leucine and proline to investigate gas emissions. They found that leucine yielded relatively high carbon monoxide while proline yielded negligible carbon monoxide but large amounts of carbon dioxide through decarboxylation. Li et al. [23] investigated the thermal behavior of leucine and observed large amount of primary amine compounds while Sharma [24] conducted pyrolysis of proline and obtained large amounts of nitrogen-containing heterocyclic compounds including pyrrole, indole and pyridine etc. These reports demonstrated that chemical structures can significantly affect the pyrolysis process of amino acids. However, to our knowledge, limited work has focused on catalytic pyrolysis of amino acids. In order to better understand the influence of chemical structures on catalytic pyrolysis of amino acids, we employed leucine and proline, in this paper, as representatives of aliphatic amino acid and cyclic amino acid, respectively. They were pyrolyzed in a Tandem micro-furnace reactor coupled with MS/FID/TCD. Yields of aromatic hydrocarbons, olefins and alkanes from leucine and proline were investigated. Removal of oxygen and nitrogen in catalytic and non-catalytic pyrolysis were comparatively examined.

## 2. Materials and methods

### 2.1. Materials

Leucine and proline were selected as representatives of aliphatic amino acids and cyclic amino acids, respectively. They were purchased from Sigma–Aldrich Co, USA with a purity of 99%. Characteristics of leucine and proline are shown in Table 1. Effective hydrogen index (EHI) was calculated as  $(H - 2O - 3N)/C$ , where H, O, N and C are the number of moles of hydrogen, oxygen, nitrogen and carbon in amino acid [25].

ZSM-5 (CBV2314) with a silica to alumina ratio of 23 was purchased from Zeolyst, USA. The received catalyst was calcined in a muffle furnace at 550 °C for 5 h. The calcined catalyst was mixed with amino acid at a catalyst-to-amino acid weight ratio of 20:1 until the mixture was homogeneous. Both catalyst and catalyst/amino acid mixtures were stored in sealed glass vials in a

desiccator to minimize moisture adsorption prior to the pyrolysis experiments.

### 2.2. Catalytic pyrolysis experiments

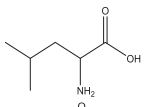
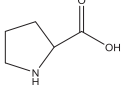
Catalytic pyrolysis experiments were conducted in a tandem micro-furnace pyrolyzer (Rx-3050 TR, Frontier Laboratories, Japan). The micro-furnace was temperature controlled within the range of 40–900 °C with an interface heater operating at temperatures of 100–400 °C that prevents undesired temperature drops of the pyrolysis vapors as they exit the furnace.

For a typical run, approximately 5 mg of catalyst/amino acid mixture was pyrolyzed in the first furnace at the desired temperature while the temperature of the second furnace and the interface were held at 320 °C to prevent product condensation. The products were analyzed by a gas chromatograph (GC, 7890A, Agilent Technologies, USA) installed with a three-way splitter that directed the gas stream to three GC columns. The GC oven temperature was programmed for a 3-min hold at 40 °C then increased at a 10 °C/min rate to 250 °C and finally held constant for 6 min. The injector temperature was 250 °C and the total helium flow passing through the reactor was 90 ml/min. Two identical capillary columns, Phenomenex ZB 1701 (60 m, 0.250 mm and 0.250 μm film thickness) were used to analyze the condensable volatiles: one was connected to a mass spectrometer (MS) (5975C, Agilent Technologies, USA) for compound identification, and the other one was connected to a flame ionization detector (FID) for product quantification. After molecular identification of peaks with MS, standard samples dissolved in methanol at 5 different level points were prepared to calibrate FID for products quantification [14]. A Porous Layer Open Tubular (PLOT) column (60 m, 0.320 mm) (GS-GasPro, Agilent, USA) was connected to a thermal conductivity detector (TCD) for measurement of non-condensable gas (NCG) products including CO, CO<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>8</sub>, C<sub>4</sub>H<sub>8</sub> and C<sub>4</sub>H<sub>10</sub>. A standard gas mixture (Praxair, USA) was used to calibrate the yield of NCG. Carbon and nitrogen content in the solid residue was quantified with an elemental analyzer (vario MICRO cube, Elementar, USA).

For nitrogen-containing gas collection, the micro-furnace pyrolyzer was detached from the GC and connected through a tar trap to a NaOH (0.1 mol/L) solution for HCN, or H<sub>2</sub>SO<sub>4</sub> (0.1 mol/L) solution for NH<sub>3</sub>, respectively [19]. After collection, NH<sub>4</sub><sup>+</sup> and CN<sup>-</sup> were analyzed by DR 3900 Benchtop Spectrophotometer (HACH, USA).

All product yields were reported as molar carbon/oxygen/nitrogen yield, which was defined as the molar ratio of carbon/oxygen/nitrogen in a specific product to total moles of carbon/oxygen/nitrogen in the feedstock. Selectivity for aromatic hydrocarbons/olefins/alkanes in this study was defined as the molar ratio of carbon in a specific aromatic hydrocarbon/olefin/alkane to total moles of carbon in aromatic hydrocarbons/olefins/alkanes products. All measurements were performed in duplicate to mitigate the impacts of experimental error.

**Table 1**  
Characteristics of leucine and proline.

Name	Chemical structure	Molecular formula	Effective hydrogen index
Leucine		C <sub>6</sub> H <sub>13</sub> NO <sub>2</sub>	1.0
Proline		C <sub>5</sub> H <sub>9</sub> NO <sub>2</sub>	0.4

Download English Version:

<https://daneshyari.com/en/article/763512>

Download Persian Version:

<https://daneshyari.com/article/763512>

[Daneshyari.com](https://daneshyari.com)