



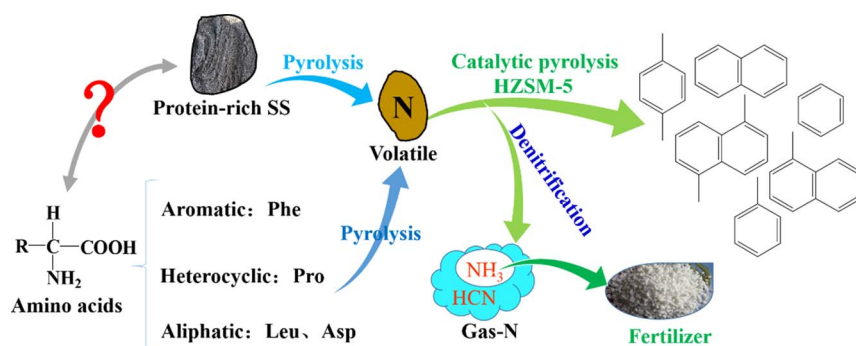
Formation of aromatics and removal of nitrogen in catalytic fast pyrolysis of sewage sludge: A study of sewage sludge and model amino acids



Fu Wei, Jing-Pei Cao*, Xiao-Yan Zhao, Jie Ren, Bo Gu, Xian-Yong Wei

Key Laboratory of Coal Processing and Efficient Utilization (Ministry of Education), China University of Mining & Technology, Xuzhou 221116, Jiangsu, China

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Sewage sludge
Amino acids
HZSM-5
Catalytic pyrolysis
Nitrogen
Aromatics

ABSTRACT

To elucidate the catalytic mechanism and nitrogen transfer behavior of sewage sludge (SS) during catalytic fast pyrolysis (CFP), product distributions and nitrogen transformation from SS and amino acids during CFP were investigated on a drop tube quartz reactor at various temperatures and HZSM-5 catalysts. Phenylalanine (Phe), proline (Pro), leucine (Leu) and aspartic acid (Asp) were employed as model compounds with different chemical structures for protein-rich SS to help analyze catalytic cracking behavior of SS. During CFP of SS, the maximum aromatics yield of 16.4% was obtained over HZSM-5 with Si/Al ratio of 25 at 500 °C, and increasing temperature promoted the conversion of nitrogen to NH₃. Amino acids with aromatic ring or saturated hydrocarbon side chain such as Phe and Leu in SS favored the formation of aromatics and NH₃. Amino acids of N-ring structure in SS promoted the formation of N-containing heterocyclic compounds, which were prone to coke on catalyst and inhibited the catalytic cracking of SS to produce more aromatics and NH₃. In addition, excessive Asp of short chain dibasic acid structure in SS was not conducive to the complete thermal decomposition of SS under the optimum pyrolysis condition. A general catalytic mechanism of SS was proposed to provide support for the resource reuse of SS.

1. Introduction

The green environmental-friendly disposal of sewage sludge (SS), the by-product of sewage treatment, has become severe challenges today [1]. Conventional disposal methods, including landfill, land

application and incineration, are difficult to meet the concept of economic and environmental [2,3]. Pyrolysis is becoming an increasingly attractive technology for its ability to stabilize various pollutants, and maximize bio-oil products for fuel use [4–6]. However, bio-oil from protein-rich SS has disadvantages of high viscosity, basicity, nitrogen

* Corresponding author.

E-mail addresses: caojingpei@cumt.edu.cn, beyondcao@hotmail.com (J.-P. Cao).

and oxygen contents, which limit its utilization as biofuel [7,8].

Catalytic fast pyrolysis (CFP) is a potential approach for reforming the properties of pyrolysis bio-oil [9,10]. Among the research on CFP reported, HZSM-5 zeolite can effectively convert pyrolysis vapors into hydrocarbon compounds, because of its prominent ability of deoxygenation, denitrogenation and shape selectivity [11–13]. Xie et al. [12] found that the optimum reaction temperature of bio-oil production was 550 °C in microwave-assisted CFP of SS over HZSM-5. Nitrogen and oxygen, the negative attributes to the quality of bio-oil, were removed under the optimal conditions. Wang et al. [14] investigated ex-situ CFP of SS using HZSM-5 and found that catalysis temperature and pyrolysis temperature played an equally important role in the formation of aromatics. Liu et al. [11] suggested that acid pretreatment of SS was conducive to the removal of volatile nitrogen and enhanced the production of aromatics in a micro-pyrolyzer. Most studies on CFP of SS always specialized in the influence of process variables on the product identification and the removal of nitrogen over HZSM-5. Due to the complex intrinsic characteristics and multi-components of protein-rich SS, in-depth study of the catalytic pyrolysis mechanism and transformation mechanism of nitrogen during SS pyrolysis are essential for the formation of aromatics and the removal of nitrogen. However, the knowledge of this part is very limited and the mechanism is unclear.

In order to gain insight into the mechanism of CFP of SS, comparison with suitable nitrogen-containing model compounds is extremely essential. Unlike the complexity of protein and its conversion process, amino acids, the basic unit of protein, can be effectively used to understand pyrolysis mechanism of protein-rich SS. Considerable effort has been devoted to the pyrolysis of amino acids, which mainly focused on thermal decomposition mechanism [15,16]. The formation and transfer mechanisms of nitrogen-containing compounds from amino acids has also been extensively studied [17,18]. These studies revealed that the molecular construction of amino acids had a great impact on the pyrolysis process. In catalytic amino acids processes, the difference in reaction pathways of amino acids with different structures and properties can predict the product distributions in CFP of SS. However, research on CFP of amino acid over HZSM-5 is limited. A comprehensive understanding of CFP of amino acids can provide theoretical basis for catalytic mechanism of SS, especially the transformation mechanism of nitrogen.

Herein, four different structures of amino acids, phenylalanine (Phe), proline (Pro), leucine (Leu) and aspartic acid (Asp), were selected for CFP. We compared distributions of carbon and the fate of nitrogen in CFP of SS and amino acids over HZSM-5. The possible mechanism of SS catalytic pyrolysis was also proposed in this paper.

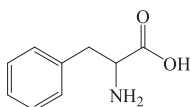
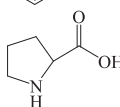
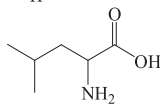
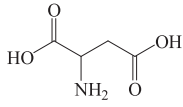
2. Experimental

2.1. Materials

The SS sample was collected from sewage management center in Xuzhou Guozhen, China. Phe and Pro were representatives of aromatic amino acids and cyclic amino acids, respectively. Leu and Asp represent aliphatic amino acids of different chain lengths. The selected amino acids (purity: 98% or more) were commercially available samples without further purification. The SS and amino acid samples were dried for 24 h at 105 and 80 °C, respectively, then compressed and pulverized to a particle size of 0.4–1.0 mm before use. The proximate and ultimate analyses of SS were obtained from our previous work [19]. Characteristics of amino acids are listed in Table 1.

Three commercial HZSM-5 catalysts used in this study were obtained from the Catalyst Plant of Nankai University, China with the SiO₂/Al₂O₃ ratio of 25, 50, and 80 (HZSM-5(25), HZSM-5(50), and HZSM-5(80)). The catalysts were sieved to 0.4–1.0 mm and activated in air at 550 °C for 5 h prior to experiments.

Table 1
Characteristics of amino acids.

Amino acids	Molecular formula	Chemical structure	Purity
Phe	C ₉ H ₁₁ NO ₂		≥ 98%
Pro	C ₅ H ₉ NO ₂		≥ 99%
Leu	C ₆ H ₁₃ NO ₂		≥ 99%
Asp	C ₄ H ₇ NO ₄		≥ 99%

2.2. CFP experiments

CFP experiments were conducted in a drop tube quartz reactor in the specified temperature range of 400–700 °C under high-purity Ar atmosphere as reported previously [20]. The catalyst bed height was 1.5 cm and the gas resident time was 1 s. About 1.5 g samples were gradually fed into the preheated reactor at a constant rate of 0.1 g/min. The pyrolysis vapors transported through the catalyst bed was collected in methanol-containing tar trap cooled with condensing device (−20 °C). The non-condensable gases were collected in a gas bag. For NH₃ and HCN collection, separate experiments were conducted using deionized water instead of methanol with the same steps as described above. The NH₃ and HCN were quantified by a BANTE 931 ion meter as reported [19]. The carbon containing gases were analyzed using a Shimadzu GC-2014 gas chromatograph. The tar was qualitatively analyzed by Agilent 7890/5797 GC-MS and quantitatively analyzed by Shimadzu GC-2014 GC-FID. The detailed instrument information, the system and GC settings can be found in a previous paper [20,21]. Carbon in char and coke deposited on catalyst were quantitatively analyzed by an Elementar vario MACRO cube CHNS elemental determinator. All experiments and measurements were repeated at least twice to ensure the reliability of experimental data and the mean was used for experimental analysis.

3. Results and discussion

3.1. CFP of SS

As presented in Fig. 1, HZSM-5 catalyst and reaction temperatures intensely affected the carbon distributions during SS pyrolysis. Compared with CFP, the carbon balance in non-catalytic pyrolysis (NCFP) of SS was worse as a result of the generation of various aliphatics, organonitrogen and organooxygen species [7,19]. With the addition of HZSM-5, a large number of aromatics were produced, accompanied by the elimination of organonitrogen and organooxygen species. Only trace amounts of phenols were detected because of strong Brønsted acid sites of HZSM-5. The results indicated that HZSM-5 had remarkable activity for denitrogenation, deoxygenation and cyclization-aromatization as has been previously reported [22]. The carbon yield of aromatics obtained over HZSM-5(25) was 16.4% at 500 °C, which was higher than that of 12.7% and 10.2% obtained by HZSM-5(50) and HZSM-5(80), respectively. This should be due to the decreasing amounts of acid sites in HZSM-5, indicating that the concentration of acid sites in the zeolite framework is a key factor for the acquisition of aromatics [23]. The HZSM-5 catalyst with low Si/Al ratio promoted the

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