Renewable Energy 139 (2019) 730–738

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

In-depth experimental study of pyrolysis characteristics of raw and cooking treated shrimp shell samples

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ARTICLE INFO

Article history:
Received 30 October 2018
Received in revised form
20 February 2019
Accepted 21 February 2019
Available online 26 February 2019

Keywords:
Shrimp shells
Pyrolysis
Secondary reactions
Cooking treatment
Interactions

ABSTRACT

Shrimp shells discharged in large quantities causes serious environmental pollution. Pyrolysis is a promising method to achieve the resource utilization of discarded shrimp shells as renewable energy. However, the distribution and the characteristics of pyrolysis products are strongly determined by the volatile-char interactions. On the other hand, cooking treatment changes the properties of shrimp shells, making the pyrolysis process more complicated. The focus of this study is to explore the pyrolysis mechanism of both raw and cooked shrimp shells by observing the interactions among volatiles as well as the reactions between volatiles and char. The results showed that char accounted for 60–70 wt% in the pyrolysis products, tar occupied about 20 wt%, and the rest was gases. In the volatile-char interactions, H radicals combined with the special sites to promote the volatilization of the N-containing components and aromatic compounds. Interestingly, a large amount of carbon was stabilized in $CaCO_3$, which was tightly doped with organic carbon in char. Meanwhile, the secondary reactions among volatiles caused the cyclization and dehydrogenation of the N-containing compounds. After cooking treatment, the partial structures of organics became more easily cracked, and more H radicals went deep into the carbon matrix to generate more volatiles.

1. Introduction

Crayfish are crustaceans with exoskeletons containing approximately 30–40 wt% protein, 30–50 wt% mineral salts, 20–30 wt% chitin and other compounds such as pigments and lipids [1]. Huge quantities of crayfish are cultured and cooked especially in central China such as Hubei, Hunan and Anhui provinces. In 2017, the total production of crayfish in China was 11.30 million tons (the year-on-year growth rate was 25.65%), and the shrimp shells waste (including raw and cooked shrimp shells) accounts for 50–70 wt% of the original weight [2,3]. The disorderly disposal of shrimp shells will cause foul odor, water and soil pollution. Therefore, many researchers tried to exploit the shrimp shells to extract chitin and convert it into high-value organic components such as chitosan by using chemical or biological methods [4–6]. However, the inorganic composition in the shrimp shells was mainly discharged, and a large amount of wastewater was generated by using these methods.

In recent years, it was proposed to realize the resource utilization of discarded shrimp shells through the pyrolysis technology. At medium-low temperatures, the shrimp shells were fully utilized through the decomposition of macromolecular components into carbon materials, tar and pyrolysis gases. In particular, carbon materials from shrimp shells were widely used to generate high-valued products. Zhang et al. [7] used shrimp-shell derived N-doped carbon nanodots as precursors to develop Co/CoO nanoparticles immobilized on Co-N-doped carbon. Based on the self-template of $CaCO_3$ in the pyrolytic carbon of shrimp shells, Gao et al. [8] prepared nitrogen-decorated hierarchical porous carbon with electrochemical performance. During the pyrolysis of the shrimp cuticle, plenty of volatiles were produced [9]. These volatiles contained useful derivatives such as acetamide, pyridine and pyrrole, which could be applied to the organic synthesis and

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https://doi.org/10.1016/j.renene.2019.02.119
0960-1481/