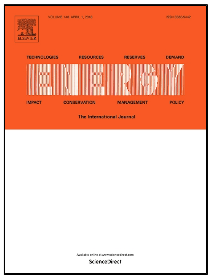

Catalytic Effects of Ion-Exchangeable K^+ and Ca^{2+} on Rice Husk Pyrolysis Behavior and its Gas–Liquid–Solid Product Properties

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Abstract: The effects of ion-exchangeable K^+ and Ca^{2+} on rice husk pyrolysis, with a focus on the yields and properties of the gas–liquid–solid products, and their pyrolysis kinetic characteristics, were investigated by thermogravimetry/Fourier-transform infrared spectroscopy in a laboratory-scale fixed-bed reactor. The results indicated that the pyrolysis gas and char yields increased, and the tar yield decreased, with increasing concentrations of K^+/Ca^{2+} in the rice husks. Compared with that of 340 °C for H-form rice husks, the maximum weight loss temperature decreased by more than 25 °C for the 2.0 wt% K-loaded sample, and increased to 360 °C for the 0.2 wt% Ca-loaded one. K^+ (2.0 wt%) lowered the first-order activation energy by 18 kJ/mol, and Ca^{2+} (<0.1 wt%) was more reactive in pyrolysis. The K^+/Ca^{2+} ratio affected the amounts of pyrolysis gases, but not the species, and their presence increased the amount of aromatic C=C structures and surface C=O groups in the biochar. Catalysis with K^+/Ca^{2+} transformed heavy pyrolysis tar compounds into small-molecule ones.

Keywords: Catalyzed pyrolysis; Rice husk; Potassium; Calcium; Gas–liquid–solid products; Kinetic analysis

1. Introduction

Renewable resources and advanced energy utilization techniques are needed to ensure a sustainable energy future and to deal with increasing depletion of fossil fuels and serious environmental problems [1, 2]. Biomass has great potential as a low-sulfur, low-nitrogen, and carbon-neutral renewable clean energy source, and is also of interest as a feedstock for manufacturing synthetic fuels and chemicals [3]. Global annual rice production is nearly 571 million tonnes and about 140 million tonnes of rice husk waste are available for biomass energy production [4]; 96% of rice husk waste is generated in developing countries [5]. Advanced techniques for rice husk use, e.g., CO_2/steam/air gasification and advanced complete combustion, need to be developed [1, 6-8]. In the first step in biomass thermal conversion, pyrolysis is performed to degrade the feedstock, without an external oxidizing agent, to volatiles (mainly H_2, CO, CO_2, CH_4, H_2O, and tar) and biochar [9-12]. A detailed and profound understanding of the pyrolysis characteristics of rice husks is important for the comprehensive use of biomass energy.

Biomass resources such as rice husks contain a certain amount of inorganic metal species, which are associated with functional groups in the biomass or are present as inorganic salts [13]. The presence of inorganic species can influence the pyrolysis behavior of biomass and the distribution of pyrolysis products [14]. Alkali and alkaline-earth metal (AAEM) species are the predominant (>85%) inherent metal species in biomass samples [15]. Comprehensive studies have been performed to examine the pyrolysis behavior of biomass under catalysis with