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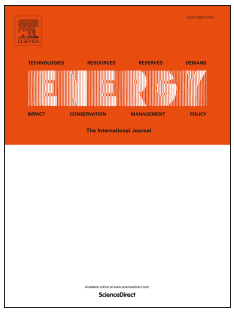

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Promotion of the vapors from biomass vacuum pyrolysis for biofuels under Non-thermal Plasma Synergistic Catalysis (NPSC) system

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Abstract: Non-thermal Plasma Synergistic Catalysis (NPSC) was firstly proposed and employed in the upgrading of biomass pyrolysis vapors for preparation of biofuels. The effects of the three-way catalysis (non-thermal plasma, HZSM-5 body and modified components) on the bio-oil upgrading performance and catalyst stability were comprehensively investigated. Bio-oil yields continued to decrease, but the physicochemical properties were further improved. The contents and compositions of hydrocarbons in bio-oil were increased and improved to varying degrees. The introduction of non-thermal plasma technology enhanced performance of cracking and deoxygenation for whole catalytic process. Besides, anti-coking performance of Zn/HZSM-5 was enhanced to a certain extent, but the multiple interactions significantly improved the cracking performance when Ti species introduced, increased the coke content, and an "isomorphism" phenomenon for two kinds of coke was emerged. In general, obtained biofuels still belonged to the hydrogen-deficient fuel, lower $(H/C)_{eff}$ of the vapors limited substantial improvement of the fuel grade.

Keywords: Biomass; Upgrading; Biofuel; NPSC; Modified HZSM-5

1. Introduction

Bio-oil as a primary fuel, there are obvious shortcomings in the physical and chemical properties, including high oxygen content, strong corrosive, high dynamic viscosity, low calorific value, instability, etc. [1]. Therefore, the improvement of bio-oil fuel grade is a key to realize its alternative to petroleum fuels. The introduction of zeolite catalysts, especially for HZSM-5, in the process of biomass pyrolysis is a research hotspot [2-3]. But the technical means of relying solely on the zeolite catalyst to improve the bio-oil is more traditional, especially for the extremely complex bio-oil. Although it can improve the quality of bio-oil to a certain extent, it is difficult to achieve a qualitative leap, and the stability of the zeolite catalyst is poor, easy to coking deactivation. Williams et al. [4] earlier employed the HZSM-5 to study the bio-oil upgrading, the properties of the bio-oil were improved with the formation of coke on the catalyst, and PAHs were obviously increased after catalysis. Zhang et al. [5] studied fast catalytic pyrolysis of corncob in a fluidized bed reactor by using HZSM-5. The results showed that the yield of bio-oil decreased with the decrease of oxygen content, the content of aromatic hydrocarbons increased obviously, the fuel grade was increased, but HZSM-5 was prone to coking, and the upgrading performance was quickly lost. In the previous study, we also carried out in-situ catalytic upgrading to prepare refined bio-oil by employing HZSM-5, and obtained similar results [6]. In order to further improve the catalytic selectivity and stability of HZSM-5, we continued to conduct the study on the P, Zn and Ti modification of HZSM-5, and achieved some progress in the field of bio-oil upgrading [7]. Overall, the traditional catalysis means had been difficult to effectively improve the efficiency of the entire upgrading process.

"Plasma" was first proposed by Langmuir in 1927 [8], refers a gas discharge region composed of electrons, ions, free radicals, excited particles and other high activity species, showing the overall electrical neutrality, also known as the fourth state of matter in the universe (99% substances are plasma) [9]. The plasma can be divided into equilibrium plasma and non-equilibrium plasma according to the different thermodynamic equilibrium states. The electron temperature and the ion temperature are almost equal in the equilibrium plasma system, the thermodynamic equilibrium

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