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Investigation of Calcium Oxide–Impregnated Zeolite Catalyst Toward Catalytic Pyrolysis of Oil Palm Empty Fruit Bunch: Bio-oil Yields, Characterizations, and Kinetic Study

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Abstract

This work investigated the in situ catalytic pyrolysis of oil palm empty fruit bunch using CaO-impregnated zeolite (CaO/HZSM-5) catalyst. An optimum point was obtained via central composite rotatable design at reaction temperature of 567.10 °C, catalyst loading of 3.22 wt%, and CaO loading of 1.25 wt%, with an expected bio-oil yield of 35.31 wt%. Validation runs' experimental yield was 37.59 ± 1.74 wt%, indicating reliability of the condition. The impregnated catalyst was characterized, and CaO was observed to be successfully impregnated onto HZSM-5 with minor degradation on the catalyst structures. The bio-oil produced through catalytic pyrolysis had increased 16.102 wt% water content, and also lower acid content by 8.02%, and higher aromatic content by 18.86% as compared with non-catalytic pyrolysis, possibly contributed by the combined catalytic effect of CaO/HZSM-5 catalyst via deoxygenation and neutralization reactions. Kinetic study using Coats-Redfern method indicated the decrement of activation energy and frequency factor by 2.14% and 49.17%, respectively, at reaction order of three with addition of CaO/HZSM-5 catalyst. Similar reductions in activation energies in presence of CaO/HZSM-5 catalyst was observed in model-free methods, and the activation energies gradually increased with process conversion due to differences in valorization temperatures of hemicellulose (300 °C), cellulose (340 and 390 °C), and lignin (> 400 °C).

Keywords Central composite rotatable design · Response surface methodology · Wet incipient impregnation · In situ catalytic pyrolysis · CaO/HZSM-5

Introduction

Pyrolysis is a thermochemical biomass conversion technology defined as thermal decomposition of biomass feedstocks to obtain typically three products: biochar, bio-oil, and non-condensable gases at elevated temperatures in atmosphere without oxygen [1–3]. Among different types of pyrolysis, fast pyrolysis is identified to involve fast heating rate and short residence period, producing substantial amount of liquid bio-oil [1, 4]. This bio-oil cannot be directly used as drop-in fuel, attributable to poor qualities of bio-oil derived via non-catalytic pyrolysis, e.g., high viscosity and acidity, instability, and low calorific value [5]. To overcome this challenge, some techniques had been explored such as co-pyrolysis and catalytic pyrolysis. In the most recent, co-pyrolysis of oil palm trunk with polypropylene had been studied and obtained a bio-oil yield of 16.17 wt% with higher hydrocarbon content in presence of polypropylene [6]. To further enhance the quality of the bio-oil, catalysts such as nickel-based solid acid catalysts can be used, which enhance the removal of oxygenated compounds and production of hydrocarbons [7].

A variety of catalysts have been investigated in the attempt to improve bio-oil yields and quality. For example, oxygenated compounds affect the calorific value of bio-oil, which may be reduced by deoxygenating with zeolite catalysts [8]. In a screening study by Du et al. [9], it is found that ZSM-5 zeolite showed the largest yield for aromatic compounds from catalytic pyrolysis of microalgae. This may be contributed by the shape selectivity of ZSM-5 where the pore size of 5.5–5.6 Å promotes the formation of aromatic and olefin compounds, while keeping the large coke molecules outside of the pores [10]. However, the small pore

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