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## Review Article

# Insights into pyrolysis and catalytic co-pyrolysis upgrading of biomass and waste rubber seed oil to promote the formation of aromatics hydrocarbon

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## ABSTRACT

To solve the problem of low aromatic hydrocarbon yield and selectivity in biomass catalytic pyrolysis, we used added oxygen-containing hydrogen supplier of rubber seed oil (RSO) with a higher hydrogen-to-carbon ratio to investigate the thermal decomposition behaviors, kinetic and production distribution of biomass, cellulose and RSO with the weight ratio of 1:2 using thermogravimetric analyzer (TGA) for kinetic analysis and fixed bed reactor with the feed composition of 1.2 g: 0.4 mL/min (Biomass to RSO) for product distribution in non-catalytic and catalytic co-pyrolysis over a HZSM-5 catalyst. The results show that there was a positive synergistic interaction between biomass and RSO according to the difference in weight loss, which could decrease the formation of solid coke at the end of experiment. The addition of the HZSM-5 catalyst can markedly increase the reaction activity, accelerate the reaction rate, and the reaction  $E_a$ , leading to a substantial increase in the conversion rate; furthermore, the residual carbon content will decrease, and the activations of Cellulose + RSO + Catalyst and Biomass + RSO + Catalyst are only 50.80 kJ/mol and 62.36 kJ/mol, respectively. The kinetic analysis showed that adding a catalyst did not change the decomposition mechanism. Co-pyrolysis of biomass and RSO could effectively improve the yield and selectivity of aromatics, when the pyrolysis temperature and catalytic temperature were 550 °C and 500 °C, respectively, the mass space velocity of RSO was 0.4 mL/min, the reaction time was 30min, the yields of benzene, toluene, xylene and ethyl benzene (BTXE) were up to 78.77%, and the selectivity of benzene, toluene and xylene was much better. Finally, the coke yield was substantially lower.

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## Introduction

With the depletion of fossil energy and increasingly serious environmental pollution, it is important to find renewable and clean fuels to replace traditional fossil energy [1–5]. Biomass is a renewable energy that can be converted into solid, gas and liquid fuels at the same time; it is one of the best new energy sources to potentially replace fossil energy. Therefore, in line with the major strategic needs of China, biomass can fundamentally ease the oil shortage in China and protect the energy security of the country. At present, high quality liquid fuels and high value-added chemicals obtained from biomass have attracted widespread attention [6]. Among the many biomass high-value utilization technologies, catalytic fast pyrolysis (CFP) for the preparation of high-value liquid fuels and chemicals has good prospects for development [7–10]. During the CFP process, organic vapor products flow through certain catalysts for further cracking and upgrading, which form high quality upgraded bio-oil products, such as aromatic hydrocarbons and olefins [11–13]. However, some problems exist with biomass. It has been reported that the low aromatics yield and the high coke formation derived from CFP are attributed to hydrogen deficiencies and the oxygen-enriched biomass essence [14–16]. Thus, these problems present difficulties with the efficient transformation and utilization of biomass; however, the selection of a suitable hydrogen source can effectively solve these problems. Zhang et al. [17] concluded that the low H/C molar ratio in biomass (0–0.3) is responsible for coke formation and its effective conversion to advanced biofuels. To improve the H/C of biomass, it is reasonable that the catalytic fast co-pyrolysis of biomass with various other samples possessing high H/C will contribute to enhancing the carbon efficiency and minimizing the coke yield. In our previous work, a series of hydrogen rich materials

such as hydrogen gas, HDPE, LDPE, PP, PS, PET, food waste and saturated alcohol were used in co-CFP experiments as hydrogen source, the latter of which has H/C atom ratio of around 2.0 and contains no oxygen, but it was observed that the aromatics yield significantly increased compared to the use of non-catalytic products [18].

Compared to other hydrogen-rich sources such as plastic (H/C<sub>eff</sub> = 2) and saturated alcohol (H/C<sub>eff</sub> = 2), the hydrogen to carbon effective ratio of vegetable oil was approximately 1.5; however, it is slightly lower than that of plastics and saturated alcohols, most of all, which contained the oxygen; due to its wide range of sources and low cost, the conversion conditions are similar to those of biomass, which can be theoretically co-catalyze with biomass to provide a hydrogen source for biomass [19]. At present, at the Kingston Plant, vegetable oil production was very large in Yunnan Province, China.

Rubber seed oil is the main woody oil plant in China. The oil content of rubber seed kernels is approximately 40–50%, and it can produce 200 thousand tons of rubber seed oil every year. However, most of the rubber seed oil is waste and cannot be used, so it is important to use an appropriate technology to convert these to high value-added fuels to make these wastes profitable while decreasing environmental pollution. The oil can be used directly for high value-added fuels thought out conversation and as a hydrogen supplier. Therefore, the co-catalytic pyrolysis of biomass and RSO provide an effective and efficient way to promote the total H/C ratio of feedstock samples, which overcome the low heating value of the liquid products derived from the catalytic pyrolysis while upgrading of biomass alone.

To the best of our knowledge, research on the co-catalytic pyrolysis of biomass and vegetable oil using as oxygen-containing hydrogen supplier over HZSM-5 catalyst with TGA is limited. Simultaneously, the influences of various reaction conditions on the synergetic effects between biomass

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