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Catalytic upgrading of sugarcane bagasse pyrolysis vapours over rare earth metal (Ce) loaded HZSM-5: Effect of catalyst to biomass ratio on the organic compounds in pyrolysis oil☆

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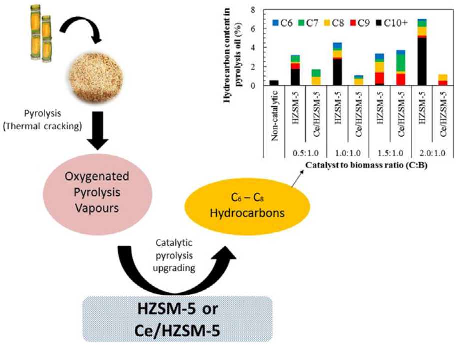
HIGHLIGHTS

- Catalytic upgrading of biomass-derived oxygenated pyrolysis vapours over cerium loaded HZSM-5 catalyst.
- Catalyst to biomass ratio of 2.0:1.0 showed the highest yield of pyrolysis oil over Ce/HZSM-5 catalyst.
- Catalyst to biomass ratio of 1.5:1.0 has attained the highest C_6–C_8 hydrocarbons in pyrolysis oil.
- Ce/HZSM-5 catalyst had massively lowered the coke yield than HZSM-5 catalyst.
- Ce/HZSM-5 catalyst inhibits the secondary cracking of hydrocarbons in pyrolysis oil.

GRAPHICAL ABSTRACT



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ABSTRACT

The main objective of the current work is to investigate the influence of catalyst to biomass ratio (by weight%) on the catalytic upgrading of sugarcane bagasse derived pyrolysis vapours over cerium (Ce) loaded Hydrogen exchanged Zeolite Socony Mobil-5 (HZSM-5) catalyst via in-situ fixed bed reactor. The temperature of pyrolysis was kept at 500 °C for all investigated samples. The HZSM-5 catalyst was used as a support with 1 wt% of Ce as promoter loaded via incipient wetness impregnation method. The biomass sample was fixed at 2 g, while the catalyst mass loading was loaded according to the catalyst to biomass ratio which are 0.5:1.0, 1.0:1.0, 1.5:1.0, and 2.0:1.0. For comparison, the non-catalytic and biomass catalytic over HZSM-5 catalyst was also pyrolyzed at the same operating conditions. The results show that the yields of pyrolysis oil and coke were significantly influenced by the use of Ce/HZSM-5 catalyst at various catalyst to biomass ratio than the catalytic pyrolysis over HZSM-5, in which generate higher pyrolysis oil yield (58.0–68.0 wt%) and lower coke yield (2.9–4.1%). The increasing loading of mass in Ce/HZSM-5 catalyst has additional effect with respect to C_6–C_8 hydrocarbon contents in pyrolysis oil than the catalytic samples over the HZSM-5 catalyst. Among the tested catalyst to biomass ratio, the catalyst to biomass ratio of 1.5:1 has demonstrated to be the potential candidates in the catalytic upgrading of sugarcane bagasse derived oxygenated pyrolysis vapours into higher content of C_6–C_8

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hydrocarbons (2.45%) in pyrolysis oil with lower coke yield (3.2%) over Ce/HZSM-5 catalyst. The bi-functional Ce/HZSM-5 catalyst was more effective in suppressing the coke formation in comparison to HZSM-5 catalyst at all investigated catalyst to biomass ratios and this was attributed to the synergistic effect of Ce on HZSM-5 support.

1. Introduction

Biomass is considered as a promising eco-friendly alternative source of renewable energy in the context of current energy scenarios [1,2]. The utilization of biomass has attracted more attention due to the environmental considerations and increasing demand for energy worldwide [3]. The processes for conversion of biomass into renewable energy are generally divided into two broad categories such as thermochemical (combustion, gasification, and pyrolysis) and biological (fermentation and anaerobic digestion) processes [4]. From the literature, it gives the impression that conventional gasification technology converts biomass into a higher yield of incondensable gas products such as carbon monoxide (CO), carbon dioxide (CO_2), and hydrogen (H_2) [1–4]. However, in the gasification process, the formation of phenol compounds limits the conversion efficiency and causes fouling on the surface of the reactor. In the meantime, combustion of biomass with oxidizing atmospheres produces high amount of solid char products that can be used as commercial fertilizers [5,6]. Consequently, the combustion of biomass also releases pollutants (SO_x and NO_x). On the other hand, the biological technique has advantages in terms of lower energy consumption and less environmental damage [7]. However, biological technique is a slow process and notably hard to scale up due to large amount of sterile area required for production and that biomasses are consumed by the microorganisms during fermentation or anaerobic digestion [8]. Among the conversion technologies, pyrolysis is the most promising thermochemical conversion techniques for large-scale exploitation of biomass material and production of liquid fuel [5].

Generally, biomass pyrolysis is defined as thermal degradation of biomass under inert atmosphere at moderate reaction temperature range (400–600 °C) that could generate pyrolysis oil (60–70 wt%) as the major product [6]. Consequently, the generated raw pyrolysis oil has several drawbacks such as high viscosity, thermal instability, high corrosiveness and low heating value due to high content of oxygenated compounds such as anhydrosugars, furans, acids, ester, ether, ketones, aldehydes, alcohols, and phenols in pyrolysis oil [4]. Despite these drawbacks, generated raw pyrolysis oils also have some promising properties, such as less toxicity, good lubricity and greater biodegradation than the petroleum fuels [1]. Thus, raw pyrolysis oil shall be further upgraded in order to improve its physicochemical properties and extend its applications.

Various catalytic upgrading technologies are available as upgrading method of oxygenated pyrolysis vapours such as hydrogenation (HYD), hydrodeoxygenation (HDO), steam reforming, and catalytic pyrolysis into renewable chemicals (hydrocarbons) [1–4]. The selection of suitable upgrading technique solely depends on the cost of the system, the selectivity of liquid products, high hydrocarbon yields, lower oxygenated compounds, and lower coke formation. For example, HYD process requires a specific condition, such as high pressure (10–20 MPa), elevated temperature ($>$ 400 °C) and requires hydrogen atmosphere as well as an efficient catalyst to generate low oxygenated pyrolysis oils [3,4]. Similarly, during HDO reaction, a large amount of pressurized hydrogen (H_2) gas is required to improve the pyrolysis oil, but directly increased the cost of the operating system [5]. Moreover, the HDO process require complicated equipment, superior techniques, costing high, and halted by deactivation of catalyst and reactor clogging [6]. Meanwhile, steam reforming is also a catalytic cracking technology employed to upgrade pyrolysis oil derived from biomass pyrolysis and simultaneously upgrading it to produce renewable and clear hydrogen gaseous [1]. Consequently, is unsuitable to be employed in steam reforming for pyrolysis oil due to its tendency to decompose thermally and carbon deposition (coking) on the surface of the catalyst. Thus, upgrading the pyrolysis vapour via steam reforming is a feasible but novel technology, cost effective as well steady and fully developed reactor systems that are still needed to be developed in the future.

Hence, among the aforementioned upgrading technologies of oxygenated pyrolysis vapours, the catalytic upgrading of pyrolysis vapours seems to be a more promising method for upgrading oxygenates in pyrolysis vapours to improve its physicochemical properties of pyrolysis oil and extend its applications [7–9]. Moreover, this technology has numerous advantageous over other upgrading technologies such as operating at atmospheric pressure, single-step conversion and low-cost system. Finally, the upgraded pyrolysis vapours through catalytic upgrading can generate hydrocarbons that have the following applications: (1) combustion fuel, (2) used for power generation, (3) production of resins and chemicals, (4) used as transportation fuel and could be used as gasoline enhancers in the petrochemical industry [5–8]. However, it is crucial to select the suitable catalyst for catalytic upgrading pyrolysis vapours.

Recently, most of the literatures have reported that the HZSM-5 catalyst is the most promising zeolite type catalyst in achieving higher hydrocarbons contents in biomass-derived pyrolysis oil [9,10]. The Hydrogen exchanged Zeolite Socony Mobil-5 (HZSM-5) is a zeolite type catalyst in a protonic form. Generally, HZSM-5 has pore system of zigzag 10-ring channels (5.1 × 5.5 Å) intersecting straight with another 10-ring channels (5.3 × 5.6 Å) that are perpendicular to each other. Good architecture of HZSM-5 is advantageous in terms of enabling easy diffusion of most oxygenates to reach the active acid sites along pore passage.

Recently Mochizuki et al. [11] has investigated the influence of pore size of zeolite catalysts on catalytic pyrolysis of Jatropha husk via pyrolysis-gas chromatography/mass spectrometry (pyrolyzer-GC/MS) system. The zeolite catalysts are zeolite beta (H-β) and HZSM-5, in which has average pore sizes of 4.2 Å and 5.5 Å respectively. They reported that the contents of hydrocarbons were higher for HZSM-5 at 46.2% than H-β at only 12.3%. The HZSM-5 showed lowest oxygenates (3.7%) contents in pyrolysis oil compared to H-β (20.5%) and non-catalytic sample (26.6%). They claimed that oxygenates are larger than the pore diameter of H-β catalyst that unable to diffuse into the pores. Fortunately, oxygenates are small enough to diffuse through the pore mouth of HZSM-5 zeolite and reached the active acid sites.

Moreover, HZSM-5 catalyst consists of two types of treasured acid sites such as Brønsted and Lewis acid sites, in which involved in acid-catalysed reactions [4]. In general, the Brønsted acid sites are associated with $-$OH groups and developed with thermal treatment. In addition, Brønsted acid sites are more likely to involve in the catalytic pyrolysis of biomass due to the nature of the various intermediate reactions involved [12]. The introduction of acid sites in catalyst enhances the cracking and abscission of C$-$O and C$-$C bonds connected in the biomass structure via dehydration, decarboxylation, aromatization, isomerization, cracking, dealkylation and oligomerization [13]. Additionally, the presence of acid sites in catalyst plays a key role in the formation of both hydrocarbons and coke [5]. Therefore, the catalyst should be designed at suitable acidity in order to achieve higher hydrocarbon yields, while reducing the possibility of further polymerization of hydrocarbons into coke materials. The formation of coke is the results of the production of heavy compounds, which are deposited on the surface of catalyst that changes the catalytic activity of