Catalytic Pyrolysis of Empty Fruit Bunch over Metal-modified Rice Husk Ash

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Keywords: pyrolysis, empty fruit bunch, rice husk ash, nickel, iron.
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Abstract
Rice husk ash (RHA) is gaining attention in research due to its high silica content. RHA can be used as a silica precursor for the synthesis of zeolite catalysts. Most studies focus on the synthesis of catalysts using RHA but there is a lack of study on the application of the synthesized catalysts. The purpose of this study is to synthesize zeolite catalysts using RHA as a silica source and apply the catalysts for the pyrolysis of empty fruit bunch (EFB). In addition, metals Ni and Fe, are applied for the modification of the RHA catalysts. Pyrolysis runs were conducted via a fixed bed reactor at 500 °C with a catalyst-to-feedstock ratio of 1:1. Characterization of the synthesized catalyst showed that the RHA catalyst resembles the structure of HZSM-5 and the metal modification did not disrupt the original structure of the RHA catalyst. From the experimental results, it was found that using RHA catalysts, Ni/RHA, Fe/RHA and Ni-Fe/RHA, all led to a slight decrease of bio-oil yield from 41.3 wt% to 39.8 wt%. Among the metal-modified catalysts, Ni-Fe/RHA produced the highest bio-oil yield of 40.5 wt% while using Ni/RHA produced the least bio-oil yield of 38.8 wt%. Further analysis on the chemical composition of the bio-oil oil is recommended.

1. Introduction
Pyrolysis is currently being explored due to its attractive feature that can convert biomass to useful chemicals such as hydrocarbons. Pyrolysis process convert materials via thermal decomposition at high temperatures, ranging from 300 °C to 700 °C, in the absence of oxygen [1]. This method offers an environmentally friendly approach to obtaining chemicals as it encourages the use of low-cost, renewable materials such as biomass, and more specifically agricultural residues instead of relying on fossil fuels. There are various types of agricultural residues that comes with the extensive practice of agriculture throughout the world which has the potential to be utilized instead of simply discarding them. In Southeast Asia, palm oil is one of the top agricultural industries and after processing fresh fruit bunches to obtain palm oil, 70% of it is recovered as waste, including empty fruit bunch (EFB) [2]. The large amount of EFB produced causes disposal problems and it is often simply discarded via burning, contributing to air pollution [3]. Thus, utilizing EFB in pyrolysis not only allows to obtain valuable chemicals, but it also helps to reduce pollution and offers an alternative to discarding it.

Different types of agricultural residues have been utilized in pyrolysis, including grape seeds, sugarcane bagasse, wheat straw and empty fruit bunch. Valuable chemical compounds are obtained in the form of bio-oil. Most studies report low yield of bio-oil, often less than 50 wt% [4-6]. An advantage of biomass-derived bio-oil is that it contains lower sulphur content compared to fossil fuels [7]. However, there are still limitations in the properties of bio-oil derived from biomass such as high oxygen content. Bio-oil from biomass mostly contains oxygenated compounds, including alcohols, acids, and ketones, causing it to have low heating value compared to conventional fossil fuels, which restricts its commercial use.

One of the ways to improve biomass pyrolysis is by adding catalysts in the process. The presence of catalysts allows secondary reaction of the volatilized matter to occur within the catalyst pores, which increases the bio-oil quality by further reducing oxygen content [1]. A common catalyst used in biomass pyrolysis is hydrogen-exchanged zeolite Socony mobil 5 (HZSM-5) because of its unique structure and strong acidity, which promotes the formation of hydrocarbons [8]. Catalysts can also be metal modified with nickel to promote aromatization, or iron to prevent polymerization of monocyclic aromatic hydrocarbons (MAHs) [9]. These two metals have the benefit of being cheap and widely available [10]. However, commercial catalysts like HZSM-5 are often synthesized using chemicals that can be harmful when exposed to, such as tetraethyorthosilicate (TEOS), and there is a current interest in finding alternatives that are safer. Rice husk ash (RHA) is a by-product of rice and has high silica content, around 93% [11], which makes it attractive as a potential catalyst precursor.

There have been several studies that synthesize HZSM-5 catalysts using RHA as a silica source [12-13]. However, those studies mostly focus on the catalyst synthesis and studies lack in the application of catalysts synthesized using RHA, especially for pyrolysis. This study investigates the application of catalysts synthesized using RHA on the pyrolysis of empty fruit bunch (EFB) via fixed bed reactor. In addition, nickel and iron was applied as metal-modification to the RHA catalyst to observe how metal-modified RHA catalysts affect the pyrolysis product yield.

2. Materials and Method
2.1 Feedstock and catalyst preparation
The feedstock, EFB, was obtained from a local biomass company in Selangor, Malaysia. EFB was dried, ground and sieved into particle sizes of 0.5 mm. For catalyst preparation, RHA, used as a silica source, was prepared by pyrolyzing...
rice husks under a N\textsubscript{2} atmosphere at 900 °C at 20 °C/min for 1 hour in a muffle furnace and combusted in static air in a muffle furnace at 900 °C for 1 hour. RHA was then mixed with sodium aluminate, tetrapropylammonium bromide (TPABr) and sodium carbonate decahydrate with a molar composition of 30 SiO\textsubscript{2}·Al\textsubscript{2}O\textsubscript{3}·3.75 TPABr·9 Na\textsubscript{2}CO\textsubscript{3}·10H\textsubscript{2}O in a beaker for 5 minutes. The mixture was then transferred into a Teflon-lined autoclave reactor and heated at 145 °C for 72 hours in an air-circulating oven. After the reaction, the sample was washed with deionized (DI) water, filtered and dried in the oven at 110 °C overnight to remove the DI water. The catalyst sample was then calcined in a muffle furnace at 600 °C for 4 hours (ramp rate of 5°C/min). The synthesized catalyst was labelled as ‘RHA catalyst’, indicating that RHA was used in the synthesis of the zeolite.

The impregnation of metals Ni and Fe onto RHA was conducted via incipient wetness impregnation (IWI) method. For the preparation of 5 wt% Ni onto RHA, nickel (II) nitrate hexahydrate, Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O (purity = 97%) was added to RHA in a beaker. Next, 80 mL of deionized water was added into the beaker. The mixture was then mixed on a magnetic stir plate for 4 hours at 80 °C. After mixing, the catalyst mixture was filtered using a Buchner funnel and dried overnight in an air-circulating oven at 110 °C. The dried catalyst sample was then calcined in a muffle furnace at 600 °C for 4 hours. The synthesized catalyst was labelled as ‘Ni/RHA’. The procedure was repeated with the impregnation of 5 wt% Fe onto using iron (III) nitrate nonahydrate, Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O (purity = 99%) labelled as ‘Fe/RHA’ and the impregnation of 2.5 wt% Ni and 2.5 wt% Fe onto RHA, labelled as ‘Ni-Fe/RHA’.

2.2 Catalyst characterization

Several characterization methods were conducted to investigate the physicochemical properties of the synthesized catalysts. The phase analysis of synthesized catalysts was conducted via X-ray diffraction (XRD) (Rigaku SmartLab X-ray diffractometer, Japan). The synthesized catalyst samples were irradiated at a tube voltage of 40 kV and tube current of 30 mA with a CuK\textalpha{} radiation with a wavelength (\lambda{}) of 0.15405 nm. Sample scanning was performed over a 2\theta{} range from 3° to 60° with a scanning rate of 5°C/min. The surface morphology of the synthesized catalysts was investigated using field emission scanning electron microscopy (FESEM) analysis (Hitachi SU8020 UHR Cold-Emission, Japan). Each catalyst sample was placed on the carbon stub followed by a high-resolution coater to be coated with platinum/palladium (Pt/Pd). The accelerating voltage was set between 2 kV to 5 kV and the working distance was set to 9.7 – 10.3 mm in a vacuum condition with a magnification of 10,000. The characterization of the vibration bands of the synthesized catalysts was analysed via Fourier transform infrared spectroscopy (FTIR, Shimadzu IRTracer-100, Japan). Each spectrum was collected between the range of 400 to 4000 cm\textsuperscript{-1} with a resolution of 4 cm\textsuperscript{-1}.

2.3 Experimental setup

Pyrolysis runs were conducted, with EFB as the feedstock, in a fixed bed reactor with a catalyst-to-feedstock ratio of 1:1 and a pyrolysis temperature of 500 °C. The five pyrolysis runs that were conducted for this study were non-catalytic pyrolysis of EFB, and catalytic pyrolysis of EFB over RHA, Ni/RHA, Fe/RHA, and Ni-Fe/RHA respectively. The detailed procedure can be referred to in our previous work in Balasundram et al (2017) [14].

3. Results and Discussion

3.1 Catalyst characterization

The phase analysis via XRD for all four synthesized catalysts is as shown in Figure 1. In Figure 1(a), peaks are observed at the 2\theta{} position ranges of between 8.0° and 9.0°, between 13.0° and 17° and between 21° and 23°. The peaks seen in the XRD pattern are also narrow, indicating that the structure is crystalline. In other previous studies, these peak ranges represent the characteristic peaks of HZSM-5 [13]. This implies that the method used in this study to synthesize HZSM-5 with RHA as a silica source has been successfully conducted. In the following Figures 1(b), 1(c) and 1(d), NiO and Fe\textsubscript{2}O\textsubscript{3} species was expected to be observed around 37° and 63°, according to a study conducted by Cheng et al. (2017), but this was not seen [15]. This could be due to very low amounts of metal loaded onto the catalyst used in this study, which was 5 wt% while the study conducted by Cheng et al. (2017) loaded at least 10 wt% of metals onto the HZSM-5 catalyst. On the other hand, in our previous work using a different type of metal with a 6 wt% loading amount, a similar observation was seen where the presence of metal in the catalyst did not appear in the resulting XRD pattern due to low amount of metal loading [16]. However, for the metal-loaded catalysts, this did indicate that the metal oxides, NiO and Fe\textsubscript{2}O\textsubscript{3} were highly dispersed on the catalyst surface because no amorphous phase due to aggregation of particles were observed on the XRD pattern. In addition, the HZSM-5 structure is seen for all catalysts, indicating that the impregnation of metals on the catalyst did not destroy the original structure of the catalysts.
Figure 1. XRD pattern for (a) RHA catalyst, (b) Ni/RHA, (c) Fe/RHA and (d) Ni-Fe/RHA

Figure 2(a), 2(b), 2(c) and 2(d) shows the FESEM images of RHA catalyst, Ni/RHA, Fe/RHA and Ni-Fe/RHA. In Figure 2(a), it can be seen that the RHA catalyst has structure that is rectangular and showing high crystallinity, which is an agreement to XRD peaks seen in Figure 1(a). The structure is also in agreement to what was obtained by Zhang et al. (2019), which uses the same method of catalyst synthesis [13]. For Ni/RHA in Figure 2(b), deposits can be seen appearing on the RHA catalyst, resulting in a coarser catalyst surface. This is due to the NiO species depositing on the surface, which is similar to the observations made by Chen et al. (2016) [17]. Fe/RHA also had deposits of Fe₃O₄ particles observed on the catalyst surface, shown in Figure 2(c). In Figure 2(d), the inclusion of both NiO and Fe₃O₄ species, resulted in a layering that covers the RHA catalyst surface.

Figure 2. FESEM images of (a) RHA catalyst, (b) Ni/RHA, (c) Fe/RHA and (d) Ni-Fe/RHA

The characterization of the vibration bands for the synthesized catalysts is shown in Figure 3. It was pointed out by Zhang et al. (2019), the characteristic double 5-ring of HZSM-5 is represented by the vibration bands around 540 cm⁻¹ and 1220 cm⁻¹ and these bands can be observed for the RHA catalyst in Figure 3(a) [13]. The presence of Si(Al)O₄ asymmetric stretching is observed around 795 cm⁻¹ and 1060 cm⁻¹ in Figure 3(a), indicating the presence of silica from RHA, which is also a part of the zeolite framework for HZSM-5. For the metal-modified RHA catalysts, in Figure 3(b), 3(c) and 3(d), there was no shift in the absorption bands, suggesting that the presence of metals did not cause any significant modification of the original RHA catalyst structure.
3.2 Catalytic pyrolysis of EFB

The mass yield of the pyrolysis products of the non-catalytic and catalytic pyrolysis of EFB can be seen in Figure 4. From Figure 4, it can be seen that overall, the addition of catalysts to the pyrolysis of EFB led to a decrease in bio-oil yield. However, the addition of metals on the RHA catalysts resulted in either a decrease or an increase in bio-oil yield when compared to using RHA alone. Using Ni/RHA resulted in a decrease of bio-oil yield from 38.8 wt% to 35.6 wt%, while using Fe/RHA resulted in a slight decrease of bio-oil yield from 38.8 wt% to 37.9 wt%. This could be due to the higher cracking performance of Ni compared to Fe, leading to an increase of gas yield, which was also observed and reported by Persson et al. (2019) when Ni and Fe were individually applied to HZSM-5 [9]. However, when both Ni and Fe were added to the RHA catalyst, an increase of bio-oil yield from 38.8 wt% to 40.5 wt% was observed. Although the bio-oil obtained from catalytic pyrolysis runs were less than that of non-catalytic run, the chemical composition of the bio-oil is not yet known. Biomass pyrolysis is known to have high oxygen content in the bio-oil and thus, further analysis, such as via gas chromatography/mass spectrometry (GC/MS), should be conducted to discover the effect of RHA catalyst and metal-modified RHA catalyst on chemical composition of the bio-oil.

Figure 4. Mass yield from non-catalytic and catalytic pyrolysis runs (catalyst-to-feedstock = 1:1, 500 °C)

4. Conclusion

In conclusion, RHA has the potential to be a suitable catalyst for pyrolysis with added benefits of being a low-cost resource and being widely available. RHA also can be modified with metals to fine tune its catalytic functionality for pyrolysis. The addition of metals onto RHA catalyst did not disrupt the original catalyst structure according to the XRD and FTIR results. From the pyrolysis results, for the metal-modified RHA catalysts, it was seen that bio-oil yield of 40.5 wt% was highest when Ni-Fe/RHA was used while bio-oil yield of 35.6 wt% was the least when Ni/RHA was used. Since slightly lower bio-oil yield was observed for the catalytic runs compared to the non-catalytic runs, further research should be focused on the analysis of the bio-oil via GC/MS to determine how metal-modified RHA improves the bio-oil quality in terms of the chemical composition.

Acknowledgement

A special thanks to Universiti Teknologi Malaysia (UTM) for the financial support to carry out this research project under the Research University Grant - UTM ER (Vot number: Q.K130000.3843.19J46).
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