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RICE HUSK ASH-CATALYZED CO-PYROLYSIS OF EMPTY FRUIT BUNCH AND HIGH-DENSITY POLYETHYLENE FOR HYDROCARBON PRODUCTION

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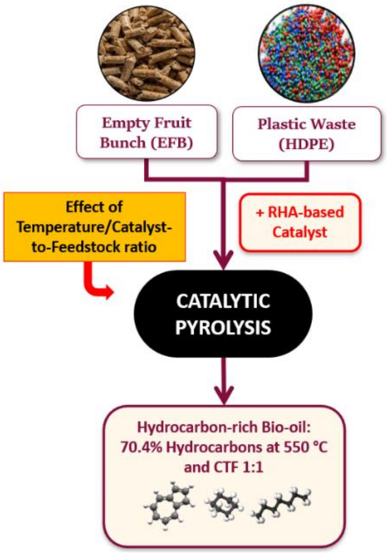
Graphical abstract



Abstract

Agricultural residues like empty fruit bunch (EFB) are valuable as it can be converted to fuel via pyrolysis, with plastic waste resources like high-density polyethylene (HDPE). Meanwhile, rice husk ash (RHA) is useful for catalyst synthesis due to its high silica content. The objective of this study is to investigate the co-pyrolysis of EFB and HDPE over RHA-based catalyst via fixed-bed reactor for hydrocarbon-rich bio-oil. Experiments were conducted where pyrolysis temperature was first varied followed by the catalyst-to-feedstock ratio (CTF). Bio-oil with the highest hydrocarbon content (70.4%) was achieved at 550 °C and a CTF of 1:1. Comparison was made with a similar run using Hydrogen exchanged Zeolite Socony Mobil-5 (HZSM-5) catalyst, where using HZSM-5 catalyst produced bio-oil containing 74.4% hydrocarbon. It was concluded that RHA is a valuable resource for catalyst synthesis and can be applied to pyrolysis for improved bio-oil quality in terms of hydrocarbon content.

Keywords: Biomass, plastic waste, catalytic pyrolysis, rice husk ash, hydrocarbons

Abstrak

Sisa pertanian seperti tandan buah kosong (EFB) amat berharga kerana ia boleh ditukar kepada minyak melalui proses pirolisis, dengan penambahan sisa plastik seperti polietilina berketumpatan tinggi (HDPE). Manakala, abu sekam padi (RHA) berguna dalam sintesis mangkin kerana kandungan silikanya yang tinggi. Objektif kajian ini adalah untuk mengkaji pirolisis bersama EFB dan HDPE dengan mangkin berasaskan RHA melalui reactor lapisan tetap untuk mendapatkan bio-minyak kaya dengan hidrokarbon. Ujikaji dilakukan dengan mengubah suhu pirolisis dahulu diikuti dengan mengubah nisbah mangkin-ke-bahan suapan (CTF). Bio-minyak dengan kandungan hidrokarbon tertinggi (70.4%) dicapai pada suhu 550 °C dan CTF 1:1. Perbandingan ujikaji dibuat dengan menggunakan mangkin 'Hydrogen exchanged Zeolite Socony Mobil-5' (HZSM-5), dimana mangkin tersebut menghasilkan bio-minyak yang mengandungi 74.4% hidrokarbon. Dapat disimpulkan bahawa RHA merupakan sumber yang berharga untuk sintesis mangkin dan boleh diaplikasikan pada pirolisis untuk memperoleh kualiti bio-minyak yang lebih baik dari segi kandungan hidrokarbon.

Kata kunci: Biojisim, sisa plastik, pirolisis bermangkin, abu sekam padi, hidrokarbon

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1.0 INTRODUCTION

The abundance and accessibility of biomass make it an attractive alternative resource for energy. Biomass can be retrieved from the agriculture sector and while agriculture allows the growth of crops for human consumption, the agricultural wastes produced alongside are often discarded. In Malaysia, the tropical weather allows for the cultivation of palm oil, with around 160 million tonnes produced yearly and consequently, around 70% of waste is generated, including empty fruit bunch (EFB) [1]. While EFB has been used as fertilizers or steam generation, plenty of EFB are disposed of in landfills or burnt, leading to air pollution [2]. Thus, EFB should be utilized for its potential to produce fuel-like chemicals [3].

Valuable compounds can be extracted from EFB using a thermochemical process, pyrolysis, where materials are thermally degraded between 300 °C and 700 °C without oxygen to produce bio-oil, char, and gas. Its ease of storage and transportation often makes bio-oil the desired product. However, although bio-oil from biomass is advantageous because of its low sulphur and nitrogen content [3], bio-oil from EFB pyrolysis alone is limited in its commercialization because of its high oxygen content and high acidity [4]. Thus, introducing materials containing high hydrogen content in biomass pyrolysis, such as plastic, can improve bio-oil quality by reducing oxygen content. While plastic waste has become a global problem because of its excessive generation and environmental pollution, it can be utilized for retrieval of valuable compounds via pyrolysis. Around 57% of plastic waste in Malaysia comes from polyethylene, including high-density polyethylene (HDPE) [5]. Therefore, HDPE can be a useful resource to improve biomass pyrolysis.

Moreover, catalysts also improve bio-oil quality by promoting certain chemical reactions during pyrolysis. For example, hydrogen exchanged Zeolite Socony Mobil-5 (HZSM-5) can produce bio-oil with higher hydrocarbon content by promoting aromatization and deoxygenation reactions. However, since synthesizing HZSM-5 catalysts can be expensive and involve harmful chemicals, such as tetraethylorthosilicate (TEOS), research has been exploring alternative resources for catalyst synthesis [6]. Using catalysts sourced from renewable biomass resources for thermochemical processes currently is appealing to researchers due to its low cost and ready availability [7, 8]. Rice husks, a by-product of the production of rice, is an attractive agricultural waste as it can be converted to rice husk ash (RHA) rich in silica (around 94%) [9]. Interestingly, silica is a main component of the HZSM-5 framework; thus, RHA can replace synthetic silica precursors for catalyst synthesis.

In our previous work, a catalyst with a HZSM-5 framework was successfully synthesized using RHA as the silica precursor. The study showed that from X-ray diffraction (XRD), the characteristic peaks of a HZSM-5 catalyst were seen for the RHA-based catalyst, and from Fourier Transform Infrared spectroscopy (FTIR), the vibration bands of the RHA-based catalyst were similar to that of conventional HZSM-5 catalyst [10]. While our previous work studied the thermogravimetry and kinetics of the process, the product yield analysis, especially the resulting bio-oil of the catalytic co-pyrolysis has not yet been explored [10, 11].

Since there are limited studies on the application of the catalysts synthesized using RHA in thermochemical processes, this study expands on our previous study, where the synthesized RHA-based catalyst is applied to the catalytic co-pyrolysis of EFB and HDPE via fixed-bed reactor and the resulting bio-oil is analysed for its composition. This research explored the utilization of various low-cost waste materials not only for renewable energy feedstock (EFB and HDPE), but also for catalyst synthesis (RHA), supporting the Sustainable Development Goal (SDG) 7 for affordable and clean energy.

2.0 METHODOLOGY

Empty fruit bunch (EFB) was used as the biomass feedstock, while high-density polyethylene (HDPE) was used as the plastic feedstock. The preparation of these two materials can be referred to in our previous work [11]. Both EFB and HDPE were prepared into particle sizes of 0.5mm.

Rice husks were converted to rice husk ash (RHA) and then used as the silica source in catalyst synthesis, where the final synthesized catalyst was labelled 'RHA-based catalyst', following our recent work [10]. HZSM-5 was prepared as a benchmark from ZSM-5 in ammonium form.

Pyrolysis runs were conducted using a fixed-bed reactor connected to a nitrogen gas tank upstream and a condenser system downstream as shown in Figure 1. Approximately 2 g of EFB and 2 g of HDPE were used. The reactor was heated at a rate of 20 °C/min. EFB-to-HDPE ratio was fixed at 1:1. From the inlet of the tube, EFB and HDPE were placed, followed by RHA-based catalyst. Nitrogen flow was fixed at 100 mL/min and the pyrolysis runs were conducted at 1 atm. The first set of experiments varied pyrolysis temperatures at 400 °C, 450 °C, 500 °C, 550 °C and 600 °C, and labelled BP-RT400, BP-RT450, BP-RT500, BP-RT550 and BP-RT600 respectively, while fixing CTF at 1:1 to observe and choose at which temperature bio-oil contained the highest hydrocarbon content. The first run was conducted twice and the error percentage was applied to the rest of the runs. The second set of experiments varied the CTF at 0:1, 0.5:1, 1:1, 1.5:1 and 2:1 and labelled BP-RC0, BP-RC0.5, BP-RC1, BP-RC1.5 and BP-RC2 respectively while keeping the pyrolysis temperature fixed at the temperature chosen from the previous set. Bio-oil was collected from condensed pyrolysis vapours in the condenser system. Any non-condensable gas flowed into a gas bag. Biomass feedstock that remained in the crucible boat was collected as char, while plastic feedstock that remained was collected as wax. Bio-oil, char and wax were weighed accordingly whereas non-condensable gas was calculated by difference. The bio-oil collected was analysed using gas chromatography-mass spectrometry (GC/MS) (Agilent, G3171A), where the detailed procedure is referred to our previous work [12] to determine its organic composition.

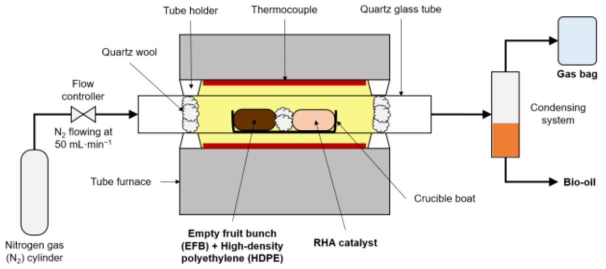

Figure 1 Schematic diagram of pyrolysis setup via fixed-bed reactor

3.0 RESULTS AND DISCUSSION

3.1 Effect of Pyrolysis Temperature on Pyrolysis Product Yield and Bio-oil Organic Composition

Figure 2 shows the product yield distribution (wt%) obtained when pyrolysis temperature was varied at 400 °C, 450 °C, 500 °C, 550 °C and 600 °C for the catalytic co-pyrolysis of EFB and HDPE over RHA-based catalyst.

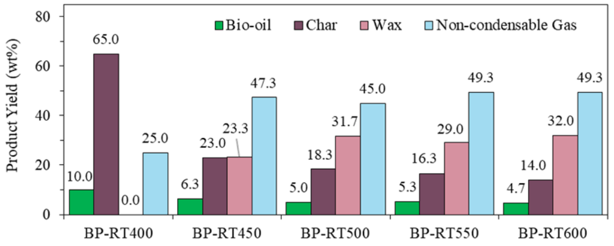

Figure 2 Product yield distribution for catalytic co-pyrolysis of EFB and HDPE over RHA-based catalysts with varying pyrolysis temperature at CTF of 1:1

The error percentage of the runs was within 0.1 wt% (not visible in figures). Bio-oil yield of 10.0 wt% was highest at 400 °C (BP-RT400). However, char was seen to be significantly high (65.0 wt%) at P-RT400, among other runs. This was because HDPE did not fully degrade, and thus remained in the boat with the EFB char since its degradation temperature is approximately 430 °C [13]. As the temperature increased from 450 °C to 600 °C, char yield decreased from 65.0 wt% and wax was present (refer to Figure 2), indicating that HDPE fully degraded during the process. Within 450 °C and 600 °C, with the presence of HDPE, bio-oil yield reduced, ranging from 4.7 wt% to 6.3 wt%, which aligned with a previous study by Brachi, Migliaccio [14], where the co-pyrolysis of a biomass and plastic feedstock with catalyst can reduce bio-oil yield when compared with catalytic pyrolysis of biomass alone. Char yield decreased from 23.0 wt% to 14.0 wt% as temperature increased from 450 °C to 600 °C due to increased thermal cracking [15]. Furthermore, increasing pyrolysis temperature from 450 °C to 600 °C overall increased the non-condensable gas yield from 25.0 wt% to yields ranging from 47.3 wt% to 49.3 wt% from the contribution of the fully degraded HDPE.

Wax is an intermediate formed from the pyrolysis of plastics and can be cracked into gases that eventually condense into bio-oil [16]. However, in some cases, the waxes may not undergo further cracking, leading to wax remaining as the final product. From Figure 2, wax yield increased from 23.3 wt% to 31.7 wt% as temperature increased from 450 °C to 500 °C, then decreased to 29.0 wt% at 550 °C. This pattern was unforeseen but similar to a study by Li, Mašek [17], where at 550 °C and higher, HDPE wax was easier to crack into gases. However, wax yield increased to 32.0 wt% at 600 °C. This could be due to the competition between the cracking of the two feedstocks during the pyrolysis process where EFB at 600 °C was more prone than the wax to degrading further and cracking into gases, as seen from the lowest char yield of 14.0 wt%.

The chemical composition of the bio-oil was further analysed via GC/MS to observe the impact of pyrolysis temperature change. The compounds were identified and categorized into hydrocarbons, phenols, acids, alcohols, esters, furans, and ketones. Figure 3 shows the relative contents of the categorized organic compounds.

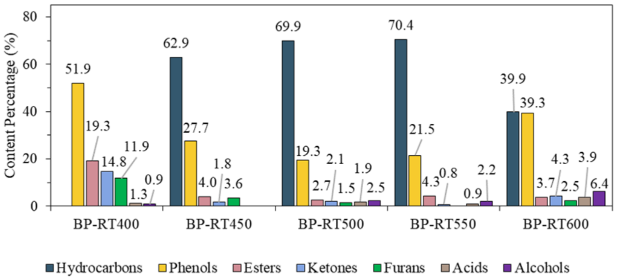

Figure 3 Relative contents of organic compounds in bio-oil from catalytic co-pyrolysis of EFB and HDPE over RHA-based catalyst with varying pyrolysis temperature at CTF of 1:1

Overall, from Figure 3, increasing pyrolysis temperature led to a decrease of oxygenated compounds when compared with BP-RT400. As discussed previously, at 400 °C, HDPE did not fully degrade and impacted its contribution in decomposing EFB, thus, no hydrocarbons were present. At 450 °C and higher, hydrocarbons appeared, confirming the contribution of HDPE in decomposing EFB. As temperature increased from 450 °C to 550 °C, hydrocarbon content increased from 62.91% at 450 °C, reaching a maximum of 70.37% at 550 °C and decreased to 39.9 wt% at 600 °C. The high temperature of 600 °C could encourage secondary reactions of the pyrolysis vapours on the catalyst surface, deactivating the catalyst and further inhibiting the formation of hydrocarbons [18].

Among the different oxygenated compounds, phenols were highest in all the runs. This indicated that EFB preferred the formation of phenols in pyrolysis, consistent with a previous study by Francis Prashanth, Midhun Kumar [19]. From Figure 3, as temperature increased from 400 °C to 600 °C, the relative content of phenols decreased from 52.87% (BP-RT400) to a range between 19.35% and 39.28%. This decrease could be due to further conversion of phenols to hydrocarbons via aromatization and deoxygenation reactions on the catalyst surface with a temperature increase [18].

Other oxygenated compounds reduced with increasing pyrolysis temperature include esters, furans, and ketones, which is advantageous as these compounds can contribute to the reduction of the bio-oil calorific value. Esters reduced from a relative content of 19.28% at 400 °C to a minimum of 2.73% at 500 °C. Furans, present at 11.86% at 400 °C, was eliminated at 550 °C. Ketones, initially present at a relative content of 14.82%, reduced to a minimum of 0.77% at 550 °C. The reduction of esters, furans, and ketones, at higher temperatures (> 400 °C) was likely due to the synergistic effect of the cracking of HDPE with the degradation of EFB and the impact of high temperatures allowing secondary cracking and deoxygenation of the pyrolysis vapours on the RHA-based catalyst surface. These results were consistent with previous literature where catalyst presence and high temperatures contribute to the reduction of oxygenated compounds via aromatization, decarboxylation and decarbonylation [18]. Acids and alcohols show varying patterns of decrease and increase in relative content with increasing pyrolysis temperature via deoxygenation from the presence of the RHA-based catalyst. Thus, while oxygenated compounds were impacted at varying degrees, overall, oxygenated compounds were reduced, with minimum oxygenated compounds achieved at the pyrolysis temperature of 550 °C.

Figure 4 shows the breakdown of hydrocarbons present in the bio-oil, categorized by the number of carbon atoms.

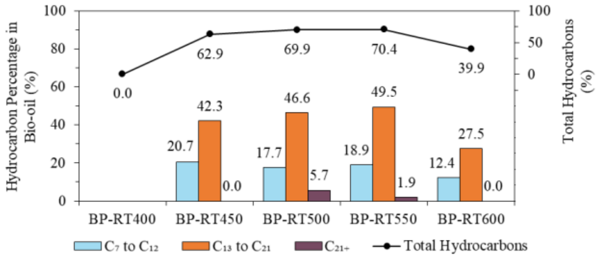

Figure 4 Hydrocarbon breakdown for bio-oil obtained from catalytic co-pyrolysis of EFB and HDPE over RHA-based catalyst with varying pyrolysis temperature at CTF of 1:1

A wide spectrum of hydrocarbons was expected due to the random scission that occurs contributed by the pyrolysis of HDPE [20]. To identify the yield of valuable products for this study, the hydrocarbons were distributed into categories of C_7 to C_{12}, which includes hydrocarbons in the gasoline and diesel range, C_{13} to C_{20}, which includes hydrocarbons in the diesel range and C_{21+}, which includes heavy hydrocarbons [21, 22].

As pyrolysis temperature increased from 450 °C to 500 °C, C_{13} to C_{20} and C_{21+} hydrocarbons increased, to 46.6% and 5.7% respectively. At 550 °C, C_7 to C_{12} and C_{13} to C_{20} hydrocarbons increased to 18.9% and 49.5% respectively while C_{21+} hydrocarbons decreased to 1.9%. Finally, at 600 °C, total hydrocarbon content reduced to 39.9% and C_{21+} hydrocarbons were not identified in the bio-oil composition. This indicated that with RHA-based catalyst at high temperatures above 500 °C, larger hydrocarbons can be cracked. Similarly, Shen, Zhao [23] observed the reduction of heavy hydrocarbons from the increase of pyrolysis temperature with the presence of catalyst. Meanwhile, at 450 °C, C_{21+} hydrocarbons were absent due to the relatively low temperature that did not favour the thermal polymerization of hydrocarbons from the pyrolysis vapours [24].

Overall, 550 °C was the best temperature determined among other investigated temperatures for the co-pyrolysis of EFB and HDPE over RHA-based catalyst based on the highest hydrocarbon content achieved with minimal heavy hydrocarbon content. This parameter was used for the next experiment investigating the impact of CTF for the catalytic co-pyrolysis run.

3.2 Effect of Catalyst-to-feedstock Ratio on Pyrolysis Product Yield and Bio-oil Organic Composition

Figure 5 shows the product yield distribution (wt%) when CTF was varied at 0:1, 0.5:1, 1:1, 1.5:1 and 2:1 for the catalytic co-pyrolysis of EFB and HDPE over RHA-based catalysts at 550 °C. When compared with the non-catalytic run (BP-RC0), the catalytic runs showed an increase in bio-oil yield, ranging from 5.0 wt% (BP-RC0.5) to 9.0 wt% (BP-RC2 and BP-RC1.5). When compared with the non-catalytic run, there was minimal increase (0 to 0.3 wt%) in the bio-oil yield at CTF of 0.5:1 (BP-RC0.5) and 1:1 (BP-RC1), and a significant increase (4.0 wt%) observed at CTF of 1.5:1 (BP-RC1.5) and 2:1 (BP-RC2). This indicated that the increase of RHA-based catalyst loading encouraged the production of bio-oil yield where primary pyrolysis vapours that was able to react within the catalyst pores to form condensable secondary pyrolysis vapours [25].

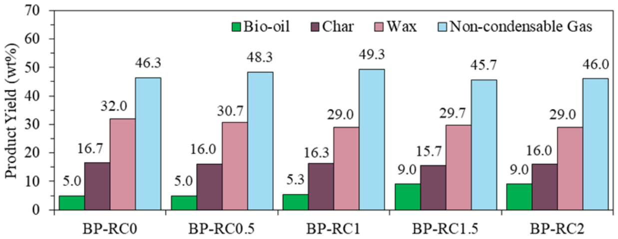

Figure 5 Product yield distribution for catalytic co-pyrolysis of EFB and HDPE over RHA-based catalysts with varying CTF at 550 °C

As catalyst loading increased from CTF of 0.5:1 to 2:1, the char yield fluctuated but overall, was lower than that of the non-catalytic run. Char yield for the catalytic runs ranged between 15.7 wt% (BP-RC1.5) and 16.3 wt% (BP-RC1). The slight decrease in char yield was consistent with findings reported by Hassan, Lim [26] where catalyst loading did not significantly affect the char yield, rather, catalyst loading would affect the production of bio-oil and non-condensable gas. The fluctuating char yield that occurred from the increase of catalyst loading in this study could be due to repolymerization of the pyrolysis vapours [27].

Wax yield decreased from 32.0 wt% (BP-RC0), to the lowest yield of 29.0 wt%, achieved by BP-CR1 and BP-CR2. This can be clarified based on a study by Colantonio, Cafiero [20], where the cracking of wax occurs internally in the catalyst and thus, if the amount of catalyst increases, more available sites allowed the waxes to further crack, leading to the decrease of wax yield.

For the non-condensable gas, the non-catalytic run had a yield of 46.3 wt% while the catalytic runs had yields ranging between 46.0 wt% (BP-RC2) and 49.3 wt% (BP-RC1). At a lower catalyst loading (CTF of 0.5:1 and 1:1), the limited amount of catalyst could only crack the primary pyrolysis vapours into non-condensable gas, indicated by the higher amount of non-condensable gas yield of BP-RC0.5 (48.3 wt%) and BP-RC1 (49.3 wt%). However, at higher catalyst loading (CTF of 1.5:1 and 2:1), the extra amount of catalyst compared to the feedstock allowed further cracking of not only the pyrolysis vapours but also wax, increasing the yield of bio-oil compared to non-condensable gas. The cracking of wax allowed the formation of pyrolysis vapours, rather than more non-condensable gas, that can condense into bio-oil [16].

Figure 6 shows the categories of organic components identified via GC/MS. With the varying amounts of catalyst, the same categories that were identified previously in Section 3.1 were also identified here. From Figure 6, hydrocarbon was the largest component in all runs with yields ranging between 59.0% and 70.4% in the presence of RHA-based catalyst. Without RHA-based catalyst, 63.3% hydrocarbon was obtained, indicating that HDPE helped the formation of hydrocarbon compounds as EFB degraded. However, as CTF increased to 0.5:1, hydrocarbon yield decreased to 59.0%, due to limited amount of catalyst compared to the feedstock, where the primary pyrolysis vapours would react continuously at the same acid sites leading to the deactivation of the catalyst, inhibiting the formation of hydrocarbons [28]. As CTF increased to 1:1, a maximum hydrocarbon yield of 70.4% was obtained, indicating that a CTF of 1:1 was ideal for the catalytic co-pyrolysis of EFB and HDPE.

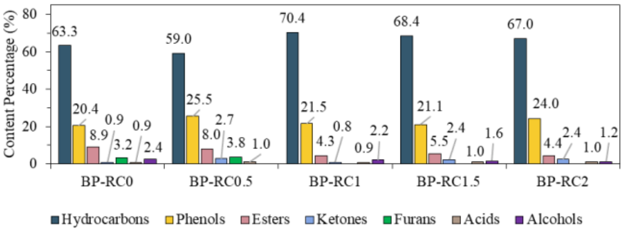

Figure 6 Relative contents of organic compounds contained in bio-oil of catalytic co-pyrolysis of EFB and HDPE over RHA-based catalysts with varying CTF at 550 °C

As CTF further increased to 1.5:1 and 2:1, the hydrocarbon yields decreased to 68.4% and 67.0% respectively. This occurrence was also observed in a previous study by Fan, Chen [29], where as more active sites of the catalyst were available, more oxygenates of the pyrolysis vapours, instead of the hydrocarbons, were further cracked into lighter oxygenates, leading to the increase of oxygenated compounds instead of hydrocarbons.

For oxygenated compounds, phenols, again, were the largest component across all runs, ranging from 20.4% (BP-RC0) to 25.5% (BP-RC0.5). From Mukarakate, McBrayer [30], although phenols can be formed without catalyst, phenols can also be formed via interactions with hydrocarbon intermediates within catalyst pores, increasing phenols yield whenever catalyst is present.

The relative content of other oxygenated compounds such as acids, esters and ketones fluctuated as CTF increased from 0:1 to 2:1. For acids, relative content fluctuated within 0.87% (BP-RC1) and 1.04% (BP-RC1.5) for the catalytic runs, while the non-catalytic run had a relative content of 0.89%. Similarly, for ketones, relative content also fluctuated, ranging from 0.77% (BP-RC1) to 2.75% (BP-RC0.5). For esters, although relative content overall decreased from 8.93% with the presence of catalyst, increasing catalyst loading resulted in the fluctuation of relative content within the range of 4.30% (BP-RC1) to 8.00% (BP-RC0.5). However, it was seen that a CTF of 1:1 achieved the minimum relative content (4.30%) of esters.

Meanwhile, alcohols were eliminated at a CTF of 0.5:1, but appeared when CTF was increased from 1:1 to 2:1. The elimination of alcohols at the CTF of 0.5:1 could be due to the limited availability of active sites of the RHA-based catalyst inhibiting the formation of alcohols [26]. As CTF increased from 1:1 to 2:1, alcohols formed between 1.19% (BP-RC2) and 2.17% (BP-RC1). A sufficient catalyst allowed the formation of alcohols from the cracking of lignocellulosic components of EFB in the catalyst pores [26]. Another possible reaction is between a hydroxy radical and a vinyl group forming alcohols based on a study by Zhao, Yang [31]. Finally, for furans, its relative content increased from 3.18% to 3.79% when CTF increased from 0:1 to 0.5:1. As CTF further increased from 1:1 to 2:1, furans were eliminated. Furans, usually formed from cellulose and hemicellulose, may react with alkenes formed from HDPE to form hydrocarbons via Diels-Alder reactions in catalyst pores, and the increasing availability of active sites from the increased RHA-based catalyst loading favoured such reactions, leading to the elimination of furans [18].

Figure 7 shows the hydrocarbon breakdown in the bio-oil when CTF was varied. A similar categorization of hydrocarbons in Section 3.1 was made for this section. Overall, the majority of hydrocarbons present in the bio-oil were between C_{13} to C_{20}, ranging from 47.7% (BP-RC1.5) to 55.7% (BP-RC0). Meanwhile, C_7 to C_{12} hydrocarbons ranged from 5.4% (BP-RC0) to 18.9% (BP-RC1) and C_{21+} hydrocarbons ranged from 0.0% (BP-RC0.5 and BP-RC2) to 2.7% (BP-RC1.5).

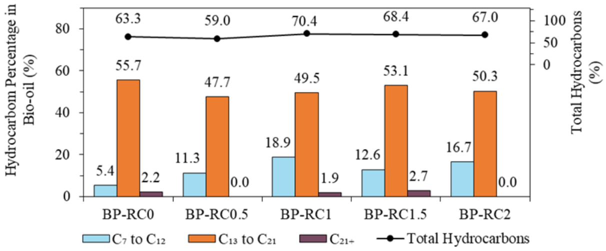

Figure 7 Hydrocarbon breakdown for bio-oil obtained from catalytic co-pyrolysis of EFB and HDPE over RHA-based catalyst with varying CTF at 550 °C

When compared with the non-catalytic run, more C_7 to C_{12} hydrocarbons formed with the presence of catalyst while C_{13} to C_{20} hydrocarbons reduced, indicating that the RHA-based catalyst could crack the pyrolysis vapours into shorter hydrocarbons useful for gasoline or diesel. C_7 to C_{12} hydrocarbons was highest at 18.9% when CTF was 1:1. Meanwhile, although a CTF of 0.5:1 and 2:1 showed 0.0% heavy hydrocarbons (C_{21+}) were present, the bio-oils of the two runs show less percentage of C_7 to C_{12} hydrocarbons, compared to when CTF was 1:1. This indicated that a CTF of 1:1 not only produced the highest amount of total hydrocarbons (70.4%), it also produced the highest amount of shorter hydrocarbons in the gasoline and diesel range. Moreover, a low CTF ratio such as 1:1 is beneficial as cost of catalyst preparation can be expensive [32]. Therefore, from this study, a pyrolysis temperature of 550 °C and a CTF of 1:1 produced bio-oil derived from the catalytic co-pyrolysis of EFB and HDPE over RHA-based catalysts with the highest percentage of hydrocarbons. The following subsection compares the usage of RHA-based catalyst with HZSM-5 catalyst for catalytic co-pyrolysis of EFB and HDPE and non-catalytic individual and co-pyrolysis runs at the chosen parameters, a pyrolysis temperature of 550 °C and a CTF of 1:1.

3.3 Comparison of RHA-based Catalyst with HZSM-5 Catalyst and Individual Pyrolysis

The chosen parameters based on varying the pyrolysis temperature and the CTF for the co-pyrolysis of EFB and HDPE over RHA-based catalyst were 550 °C and 1:1 respectively. These parameters were then applied to a similar co-pyrolysis run using HZSM-5 catalyst (labelled as 'EFB + HDPE, HZSM-5 Catalyst') to observe how the two catalysts compare. Moreover, results of the non-catalytic individual runs of EFB (labelled as 'EFB') and HDPE (labelled as 'HDPE') and the non-catalytic co-pyrolysis run (labelled as 'EFB + HDPE') conducted at 550 °C were included for additional comparison. Figure 8 shows the comparison of product yield distribution for the five runs.

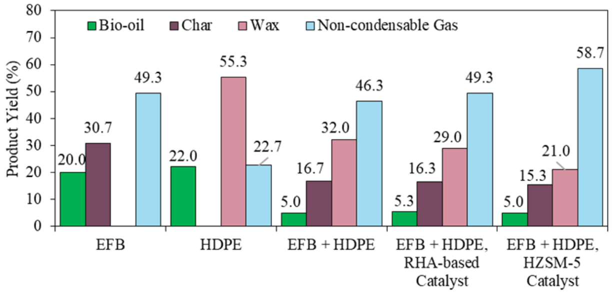

Figure 8 Comparison of product yield from individual pyrolysis, non-catalytic and catalytic co-pyrolysis of EFB and HDPE at 550 °C and CTF of 1:1

From Figure 8, for the individual runs, without any influence of catalyst at 550 °C, EFB produced 20.0 wt% bio-oil, with 30.7 wt% char. Meanwhile, HDPE produced 22.0 wt% bio-oil and instead of char, 55.3 % wax was produced. The mixing of these two feedstocks resulted in 5.0 wt% bio-oil yield. For the catalytic runs, since the RHA-based catalyst possesses an almost similar framework to the HZSM-5 catalyst as discussed in our previous work [10], they were expected to have similar catalytic performance. However, it can be seen from the product yield distribution that using the RHA-based catalyst produced a slightly higher bio-oil yield (5.3 wt%) compared to that of the HZSM-5 catalyst (5.0 wt%). Moreover, with RHA-based catalyst, solid products, such as char and wax, both had higher yields at 16.3 wt% and 29.0 wt% respectively, than that of HZSM-5 catalyst (15.3 wt% and 21.0 wt%, respectively). Generally, catalysts in pyrolysis are used to crack pyrolysis vapours, either into lighter compounds in pyrolysis oil or as non-condensable gas [4]. As seen from the lower solid products yield (i.e., the char and wax yield) and the higher non-condensable gas yield

(58.7 wt%) for the catalytic run over the HZSM-5 catalyst, the HZSM-5 catalyst had better cracking ability of the pyrolysis vapours into gases than the RHA-based catalyst.

Figure 9 shows the comparison between the organic composition of bio-oil collected from the various runs via GC/MS analysis. From individual pyrolysis, EFB contained mainly oxygenated compounds, with phenols having the highest relative content of 49.02%. Lignocellulose of EFB, especially lignin, can degrade to form phenols due to its phenolic components [33]. Meanwhile, HDPE readily forms hydrocarbons, where 94.17% hydrocarbons were present with minimal amounts of oxygenated compounds. The oxygenated compounds found in bio-oil of HDPE could be due to additives [34], since recycled HDPE was used in this study instead of virgin HDPE. As HDPE was added into EFB, hydrocarbons increased to a relative content of 63.27%. This showed that HDPE played a significant role in improving the hydrocarbon content of the bio-oil. In addition, oxygenated compounds in the bio-oil overall decreased from the co-pyrolysis process, where alcohols reduced from 11.68% to 2.44%, esters reduced from 16.24% to 8.93%, furans reduced from 19.77% to 3.18% and ketones reduced from 10.50% to 0.85%.

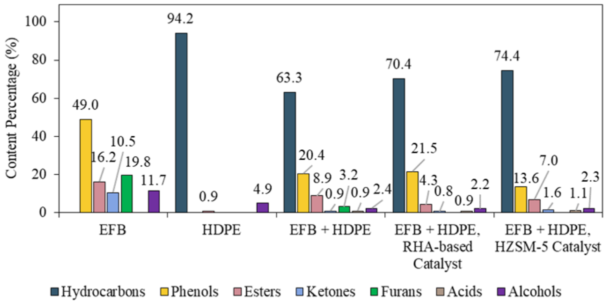

Figure 9 Comparison of relative content of organic compound contained in bio-oil of individual pyrolysis, non-catalytic and catalytic co-pyrolysis of EFB and HDPE at 550 °C and CTF of 1:1

For the catalytic runs, regarding hydrocarbons, RHA-based catalysts achieved a similar relative content (70.4%) to the HZSM-5 catalyst (74.4%). This indicated that the efficiency of the RHA-based catalyst was almost near to HZSM-5 catalyst in cracking pyrolysis vapours into hydrocarbons. Moreover, RHA-based catalyst reduced more oxygenated compounds in the bio-oil compared to the HZSM-5 catalyst, except for phenols. From Figure 9, the relative content of acids (0.9%), alcohols (2.2%), esters (4.3%) and ketones (0.8%) when using the RHA-based catalyst were all lower than that of when HZSM-5 catalyst was used (acids = 1.1%, alcohols = 2.3%, esters = 7.0%, and ketones = 1.6%). Meanwhile, the relative content of phenols when using RHA-based catalyst (21.5%) was higher than when using HZSM-5 catalyst (13.6%). This indicated that using RHA-based catalyst favoured the formation of phenols among other oxygenated compounds than the HZSM-5 catalyst. It was also interesting to note that no furans were present in either catalytic runs, indicating that furans were converted into other compounds with the presence of either the RHA-based catalyst or the HZSM-5 catalyst.

Figure 10 shows the comparison of the hydrocarbons obtained in the bio-oil between the five different runs. The hydrocarbons were categorized similarly to the previous sections. Bio-oil derived from EFB did not contain any hydrocarbons and thus, no further discussion regarding its hydrocarbon breakdown was made. From the hydrocarbons contained in bio-oil derived from HDPE, 83.9% were of C_7 to C_{20} hydrocarbons with the remaining 10.3% being C_{21+} hydrocarbons. With the mixing of feedstock (EFB+HDPE), C_{21+} hydrocarbons were reduced to 2.2% compared to HDPE alone (10.3%).

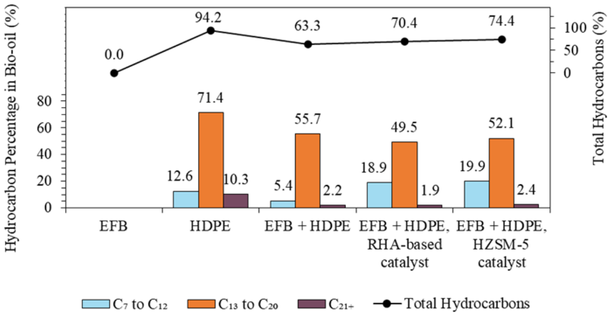

Figure 10 Hydrocarbon breakdown for the bio-oil obtained from individual pyrolysis, non-catalytic and catalytic co-pyrolysis of EFB and HDPE at 550 °C and CTF of 1:1

Moreover, from Figure 10, for the RHA-based catalyst, 18.9% of the hydrocarbons were of C_7 to C_{12}, 49.5% were of C_{13} to C_{20} and 1.9% were of C_{21+}, which were all less than that when the HZSM-5 catalyst was used (C_7 to C_{12} = 19.9%, C_{13} to C_{20} = 52.1%, C_{21+} = 2.4%). For C_{21+}, using RHA-based catalyst allowed the cracking of more heavy hydrocarbons compared to the HZSM-5 catalyst. This could be explained by the larger average pore diameter of the RHA-based catalyst (4.06 nm) compared to the HZSM-5 catalyst (3.87 nm), as shown in our previous study [10], allowing larger molecules to enter and react in the catalyst pores [32].

Therefore, using RHA-based catalyst in the co-pyrolysis of EFB and HDPE produced a slightly higher bio-oil yield when compared to HZSM-5 catalyst. Moreover, in terms of the organic composition of bio-oil, hydrocarbon content in the bio-oil produced with the presence of the RHA-based catalyst was similar to that of when using HZSM-5 catalyst. Therefore, RHA-based catalyst has almost similar catalytic performance to HZSM-5 catalyst. However, the organic composition of gasoline is around 91.6% hydrocarbons (inclusive of alkanes, alkenes and aromatics), and thus, further studies will need to be conducted to further refine and reduce oxygen content in the bio-oil.

4.0 CONCLUSION

RHA-based catalyst was applied to the catalytic co-pyrolysis of EFB and HDPE via fixed-bed reactor where pyrolysis temperature and catalyst-to-feedstock ratio (CTF) were varied respectively. Both sets of experiments showed the highest hydrocarbon content (70.4 wt%) achieved at 550 °C and a CTF of 1:1, which were chosen as the best parameters in this study. A comparison was made between the RHA-based catalyst and the commercial HZSM-5 catalyst using the chosen parameters. It was found that the catalytic performance of RHA-based catalyst was similar to that of HZSM-5, where the former produced 5.3 wt% bio-oil yield while the latter produced a bio-oil yield of 5.0 wt% with 74.4% hydrocarbon. For future work, the obtained bio-oil can be further upgraded through secondary processes such as liquid-liquid extraction to further remove the undesired components, such as acids. Moreover, the spent RHA-based catalyst can be analysed to investigate its reusability in subsequent pyrolysis runs.

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Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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